### 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

# **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

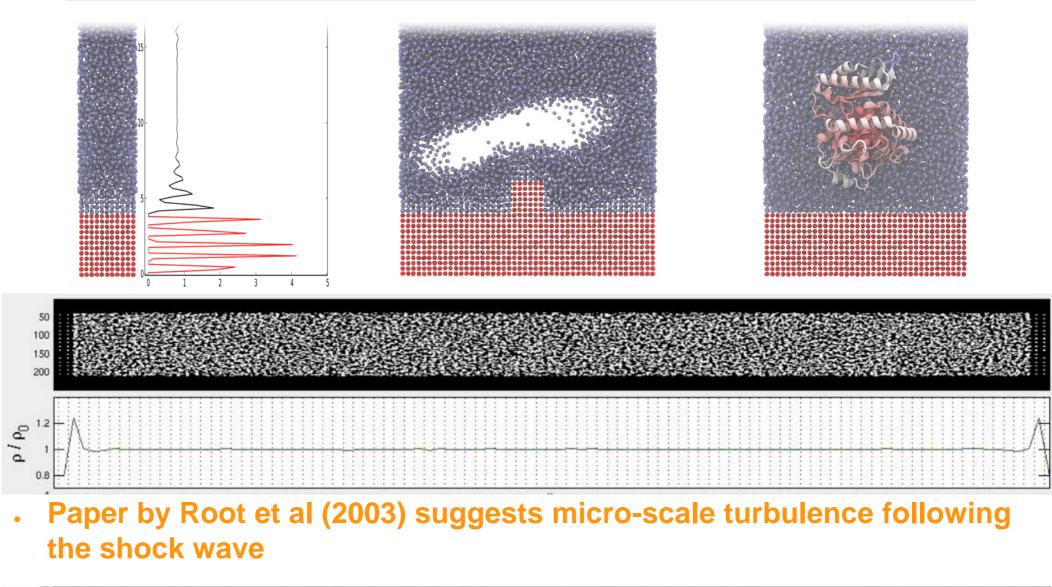


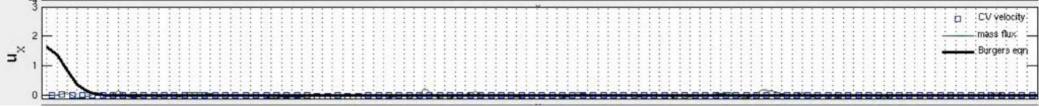
# **Motivation**

#### • 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?



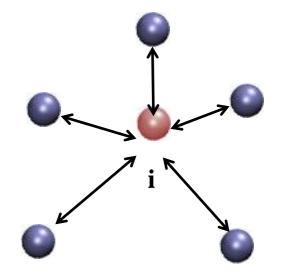


# **Molecular Dynamics**

#### . Discrete molecules in continuous space

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

$$egin{aligned} \dot{m{r}}_i &
ightarrow \dot{m{r}}_i \ \dot{m{r}}_i &
ightarrow m{r}_i(t) \end{aligned}$$

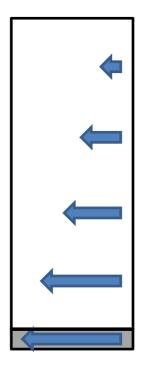


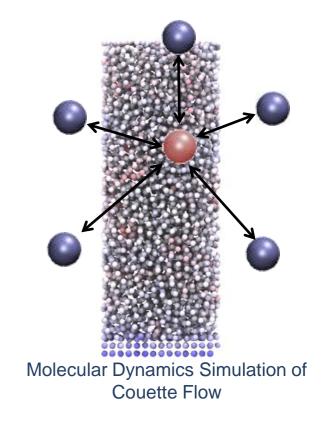
### . Acceleration obtained from forces

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

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

# **Molecular Dynamics**





# **Molecular Dynamics**

- 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



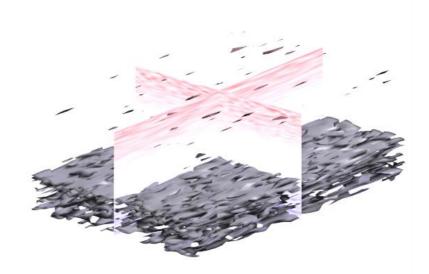
# **Continuum Field Equations**

- . 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)

$$rac{\partial}{\partial t}
hooldsymbol{u}+oldsymbol{
abla}\cdot
hooldsymbol{u}=oldsymbol{
abla}\cdotoldsymbol{\Pi}$$



Direct Numerical Simulation of Turbulent Couette Flow

# **Solving the Continuum Equations**

. The Navier-Stokes Equation

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

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

. Finite Difference Method

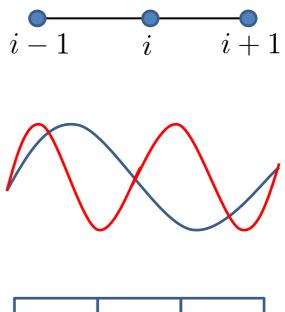
$$\frac{\partial u_i}{\partial x} \approx \frac{u_{i+1} - u_{i-1}}{\Delta x}$$

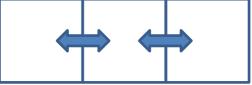
. Spectral Methods

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

. Finite Volume Method

$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{u} dV = -\oint_{S} \rho \boldsymbol{u} \boldsymbol{u} \cdot d\mathbf{S} - \oint_{S} \boldsymbol{\Pi} \cdot d\boldsymbol{S}$$





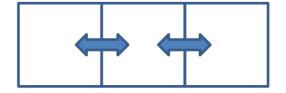
## **The Finite Volume Form**

. The integrated Navier-Stokes equation over a control volume

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

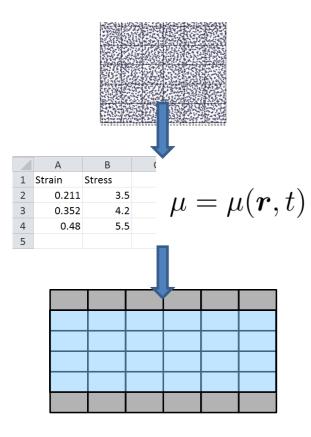
- A reformulation of the equations of motion in terms of changes inside volumes and surface fluxes
- Exactly conservative what goes out comes in
- . Most commonly used CFD discretisation technique
  - Splits the domain into a range of contiguous volumes and any shape of volume can be used
  - Better 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**





#### Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

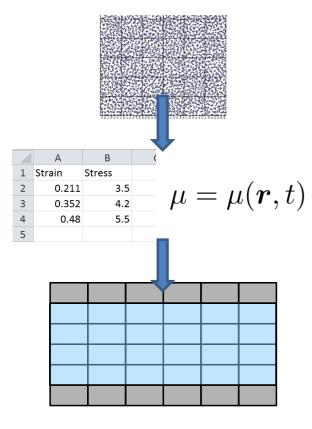
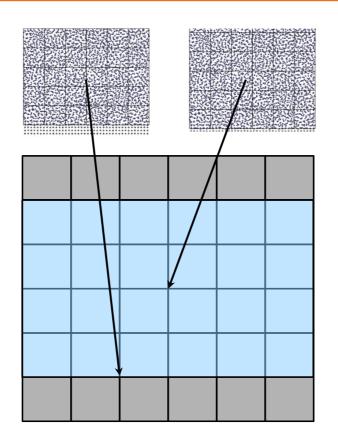


Table Lookup or Coefficients

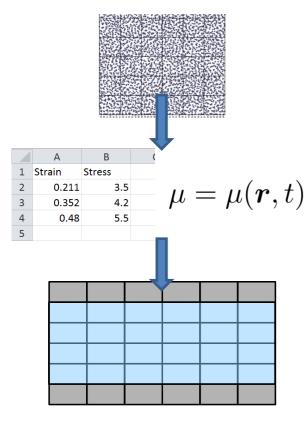
MD parameter study stored in table and CFD uses data



### **Embedded Models**

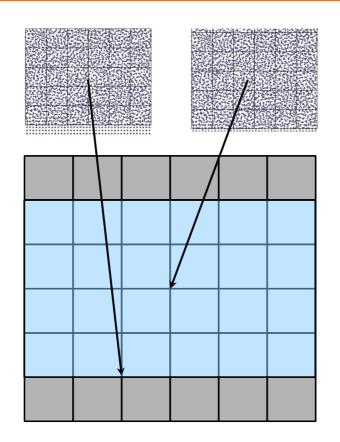
MD – embedded in a CFD simulation

Used for Non-Newtonian effects Ren (2007), E et al (2003), Borg et al (2013)



### Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

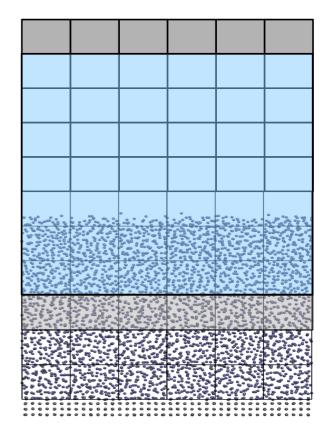


### **Embedded Models**

MD – embedded in a CFD simulation

Used for Non-Newtonian effects

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

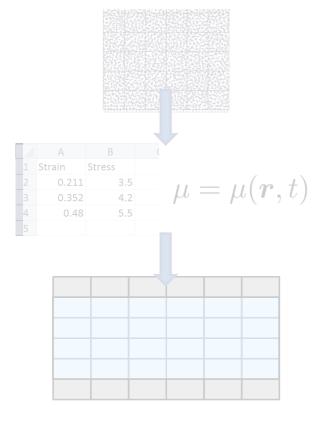


### **Domain Decomposition**

MD –CFD linked along an interface with overlap

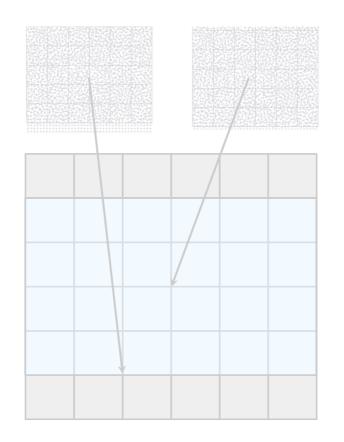
# Used for wall textures and local features e.g. contact line

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



### Table Lookup

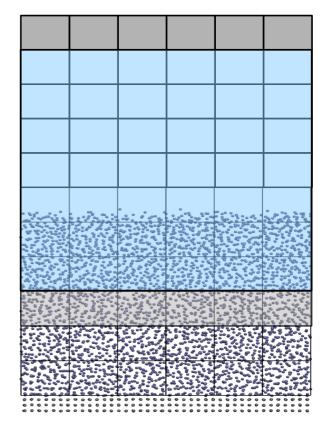
MD parameter study stored in table and CFD uses data Simplest approach



### **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

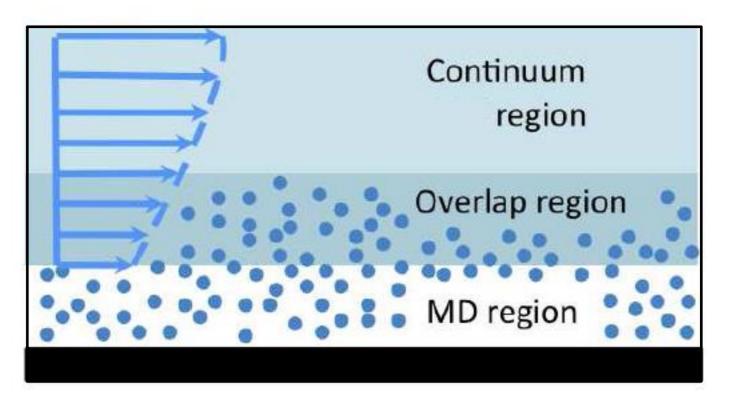
# Used for wall textures and local features e.g. contact line

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

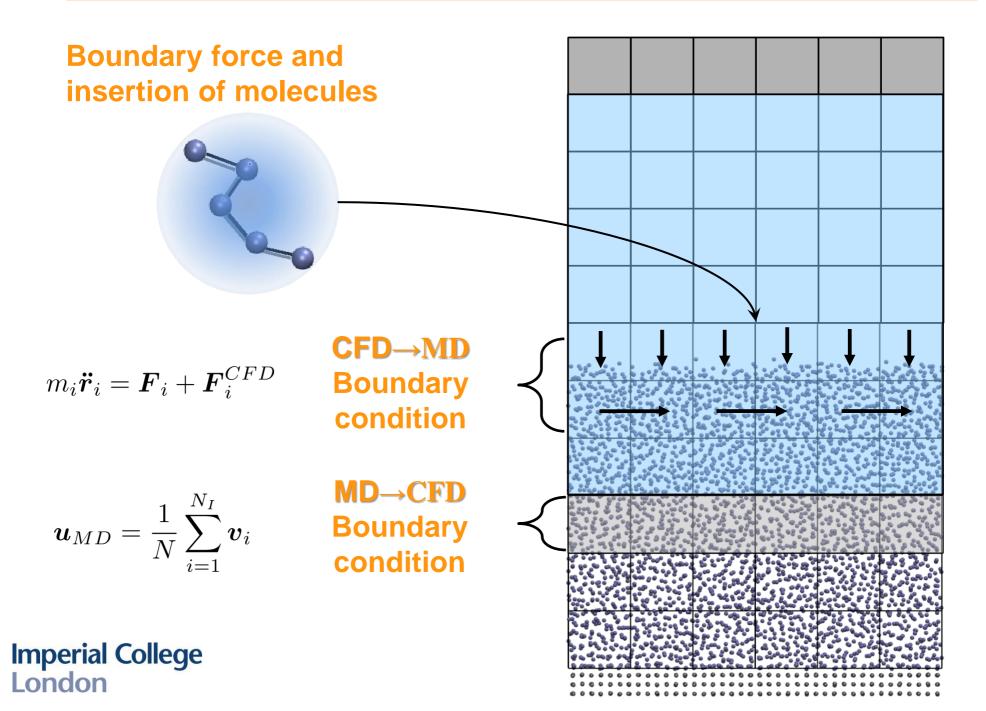
## **Domain Decomposition**

### . Connect the two descriptions of matter

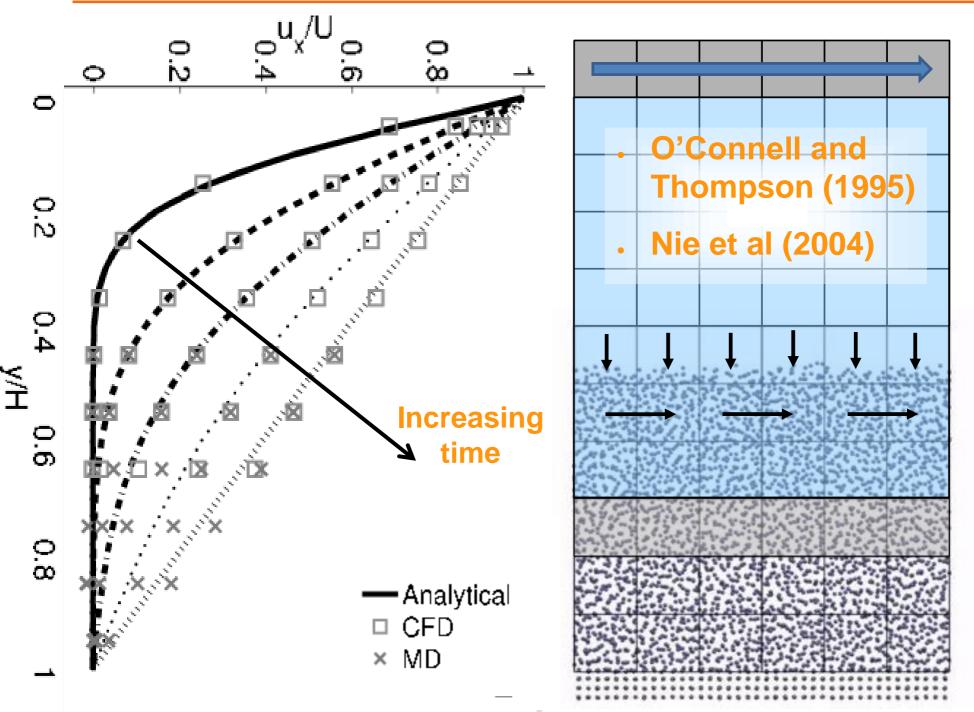
- . Continuum only region majority of the spatial domain
- Overlap of arbitrary size for purely numerical reasons
- Molecular only region required where molecular effects are important



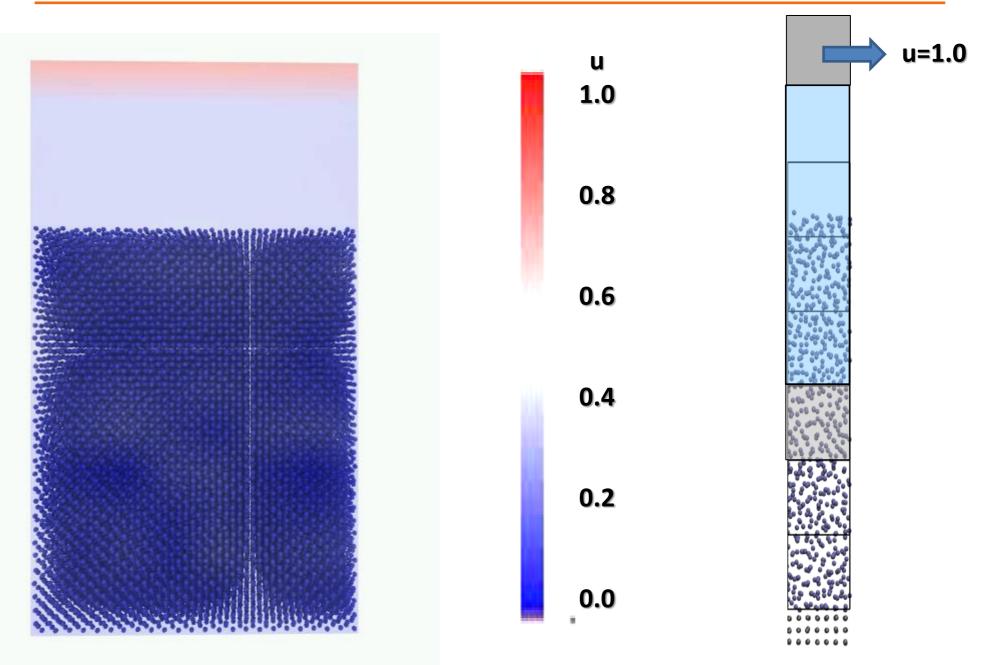
# **Coupling Challenges**



## **Coupling Results – Couette Flow**



## **Coupling Results – Couette Flow**



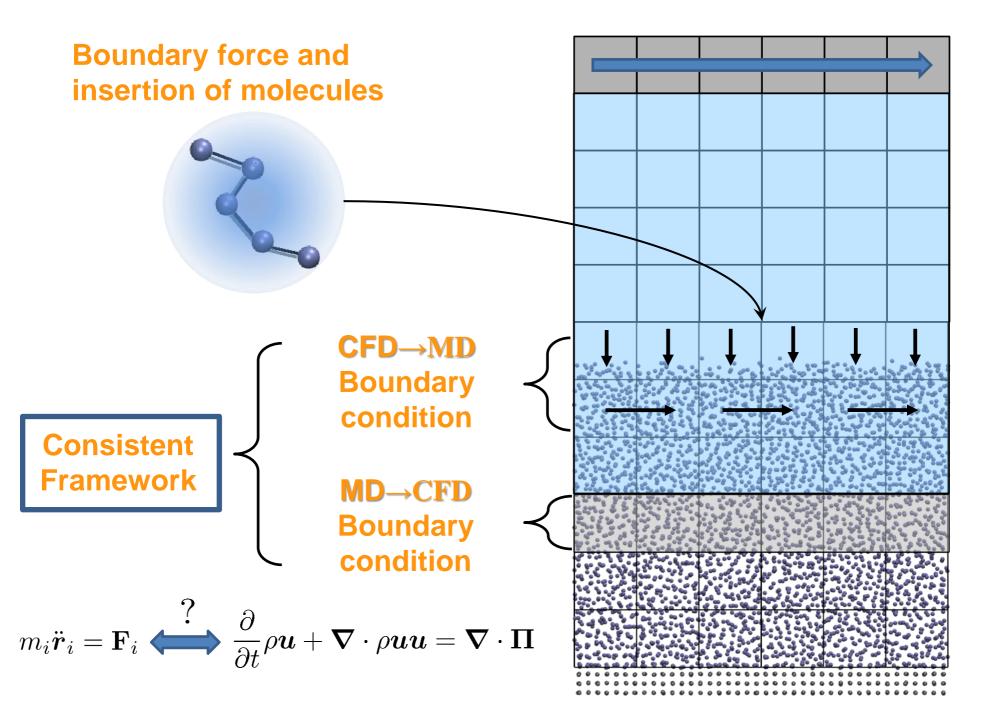
# **Notable Coupling Literature**

• 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**



#### **Imperial College** London

(2.3) for the probability distribution in Gross phase space and then perious repealed laterations. Since \* This work was supported by the L.S. ONR under Oxtract Ninatr 244 with the California Indirect of TweInstands J. G. Kirkwood, J. Chun. Phys. 14, 30 (1946)

current density is the arm of the forminar unger par-and a quarketure involving the potential of inter-noicentar force and the density and current density and the content of the density and current density and the content of the density of currents are the second more that the activity and current activity in the configuration space of a pair of molecular. The re-sults were resolved to show the fact activity of acthe contiguration space of a pair of non-enders. The re-sults were previously stated in the first article of this arties, when this definition was promited. To obtain explicit expressions for the pair probability density and revealability expressions denotes are sensed to To obtain explicit expressions for the pair probability density and probability current density one would in principle need to police the Linuville equation [Eq. (2.3)] for the grobability distribution in Gives phase over a data then readous constant terministic Since

THIS paper will be concerned with a derivation of the equations of hydrodynamics from the minireacting aperiositica assumption. Another, generalization of the well-known Fokker-Planck equi-His paper will be concered with a derivation of the espations of hydrodynamics frem the cipies of the classical statistical mechanics. In pargeneralization of the well-known rocker-rance coun-tion of stochastic theory, has been derived by Kjrk-100 of stochastic theory, has been derived by Kit-wood by introducing the concepts of time smoothing, ciples of the classical statistical mechanics, in par-ticular, the equation of continuity, the equador of motion, and the equation of energy transport will be wood ny introducing use concepts as true smoothing and a triction constant. This latter equation has been notion, and the equation of energy transport will be derived. By so doing, the stress tensor and heat current derived and be an energy of the stress tensor and tenso derived. If so doing, the stress tensor and boll current density can be expressed in terms of molecular variables. The stress service consists of a location of the location density can be expressed in terms of molecular variables. The stress tensor consists of a kinetic part (which excurs in the kinetic fueror) of gaugi and another term (dominant for a liquid) which will be expressed as a modering involving the constraint of intermetation trommant for a neuron will be expressed as a quadrature involving the potential of intermulecular force and the second of ratio of evolution of the last quadrature involving the potential of intermalecular force and the tensity of pairs of molecules. The hert force and the uensity of pairs of molecules. The best current density is the sum of the ismiliar kinetic part

approximately by the probability distribution function in the phase space of a rair of molecules. One such equa-tion has been derived by Born and Green' using a rescalined "superposition" assumption. Another, a superposition of the next process pathware built.

have been made to obtain a closed equation satisfied approximately by the probability distribution function

The equations of hydrolynamics—conticulty equation, equation of easier, and repeations of energy tradpert- are derive with beam and the classics arounder the standard repeation in the familiar for the system tensor with beam derively in terms of underived querality, upon the standard repeation terms of under the system of the standard repeation of the system of this program is untenable for a liquid, various attempts une program se untenance sor a numa, vanous autorana have been unde to obtain a closed equation satisfied

The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics\* THE INCREAT OF CREMICAL PHYSICS J. H. IRVING AND JUNY G. EUROWOOD Gates and Crelline Jahrmieries of Chemistry No. 1343, Passdene, California (Resoluted Konsender 31, 1963).

to the A. Iondamental. However, this band could be an upper-stage band corresponding to S19 cm<sup>-1</sup>. The interpretation of the faint sharp hand at 769.4 cm<sup>-1</sup> as an upper-stage band, 778+v<sup>-1</sup>-v<sub>-1</sub> scame more plauible than its interpretation as the B<sub>1</sub> combination, 2104-558 cm<sup>-1</sup>. The faint sharp Racean hand at \$25 C. F. Hammer and E. L Gu Pont de Nenours and Company for the samples; to Doctors Isabella and Icome Karle for electron differential data; and to Dr. V. Buden and the Network Buseney of Counderle for Jerome Karle lot electron diffraction dats; and in Dr. E. K. Phyler and the National Bureau of Standards for plausible than its interpretation as the H w consummation, 2104-558 cm<sup>-1</sup>. The faint sharp Raman band at \$28.5 methods been been been under the unmanifold processing band lata in the long wave-kngth region. 210+558 cm<sup>-1</sup>. The faint sharp Raman band at 835. cm<sup>-1</sup> has been interpreted as an upper-stage band. 2X a07 + v<sub>0</sub> − v<sub>0</sub>, rabter than as the R<sub>2</sub>, difference band 1540-510 cm<sup>-1</sup>, because the corresponding sum band VULUME 15. NUMBER 6

175.9 cm<sup>-1</sup>. The band at 809.7 cm<sup>-1</sup> has been interpreted 17: 9 cm<sup>-4</sup>. The band at 300.7 cm<sup>-1</sup> has been interpreted as 22×394, the rather large difference between calculated and decoursed forements being standard to the communic is  $3X_334$ , the rather large difference between calculated and observed incomency being a scriber, to the "proximity to the  $A_2$  (undermand). However, this hand could be an unstationer band commenceding to Stutement The writers wish to express their inceptedness to Dr. The writers wan to express their incediedness to Dr. C. F. Hanmer and E. L can point de Nemours and

TRANSPORT PROCESSES

has not been observed. If the preferred interpretations this hot been ouserved, it the preferren interpretations are correct, the group of Raman hands, 769, 778, 819, and 829 cm<sup>2</sup>, are related to each other in much the same and 8.50 cm<sup>-1</sup>, are related to each other in much the same manner as similar groups in the spectra of CO<sub>2</sub> and CS<sub>2</sub>.

817

JUNE. 1950

and a triction constant. Loss after equation has occar applied to obtain an expression for the stress tensor

applied to obtain an expression for the stress innor-linear in gradierts of third velocity and, thereby, ex-

linear in granteris of fluid velocity and, incessivy, ex-pressions (in terms of molerular variables) (or co-efficients of abeat and volume viscosity.) The same

encorns or snow and volume viscosity. Ine same equation generalized to annumine superstance,

equasions generations to acumunitaria empenations in the temperature (radient, leads to acumunitaria emperature (radient, leads to acumunitaria e acumunitaria

atter uneariang in the temperature grausers, sens to an explicit expression for the hear current and thereby

an explicit cupression for the next current and memory to an expression for the coefficient of themal com-

ducibyly. We shall assume, for purposes of malle-natical simplicity, a single component, single place duid content conductor of molecular uplich interact

CallCal simplicity, a single component, angle page fuld system consisting ul nolecules which interact under central forces only. It is not difficult to generalize the treatment to a multicule common to emulticule

the trained accessive contrast or initiation

M. USAMMAN, M. S. Creen, Proc. Roy, Suc. A188, 10 (1996). N. Boost and M. S. Creen, Proc. Roy, Suc. A188, 103 (1987). N. Elbarosod, Standards, and Tarsen, J. Chem. The strain relation of the strain strains a more preside composation of up the relation total disciplination function.

pressure for the cochostic of method cor-

 $S(x_n)f(x,y)dy = f(x,y)?$ The probability distribution function (relative den-as the expectation value of the dynamical variable sity of representative points in phase space) we denote  $d' \int \mathcal{E}_{R}$ Die C where U is the potential energy of the entire system. Any cynamical variable,  $\alpha(\mathbf{k}_1, \cdots, \mathbf{k}_r; \mathbf{k}_1, \cdots, \mathbf{k}_r)$ , bas an expectation value given at time / by

Irving and Kirkwood (1950)

satisfying the normalize tion condition mentum space of the still molecule. ; Charges 1 according to the well-known Liouville equation  $\frac{df}{dt} = \sum_{k=0}^{N} \left[ -\frac{p_k}{m_k} \nabla \mathbf{R}_k f + \nabla \mathbf{R}_k U \cdot \nabla \mathbf{P}_k f \right]$ 

 $\langle \alpha_{i,j} \rangle = \int \cdots \int \alpha \langle \mathbf{R}_{l_{1}} \cdots \langle \mathbf{p}_{l_{l}} \cdots \rangle / \langle \mathbf{R}_{n} \cdots \langle \mathbf{p}_{u} \cdots \langle l \rangle$ 

If the array We thus denote he (a; j) the expectation value of a that the kth in induct of a and j taken over the search; the inner  $\langle a(\mathbf{R}_{i}, \mathbf{v})_{i} \rangle \rangle^{n}$ . Frowding a does not decend on time emblecity, the

· FRAT)

+ (a; Ve, U. Von) /. (2.4)

Providing a cose not depend on time explositly, the rate of change of the expectation value of a is given by

 $\frac{\partial}{\partial t}(\alpha_i, f) = \left(\alpha_i, \frac{\partial f}{\partial t}\right) = \sum_{k=1}^{N} \left[ \left(\alpha_i, \frac{\mathbf{p}_k}{\mathbf{m}_k}\right) - \frac{\mathbf{p}_k}{\mathbf{m}_k} \right]$ 

ANO

Eps. 1.

CAULA

10-015=0

Thus, (2.4) becomes

 $B_{3'}$  Green's theorem applied in the space of  $R_{4}$ 

providing the integrated part vanishes; i.e., providing the system is bounded or f falls off sufficiently applied as R. . . . . I. I. Kenning simo up, f is independent of applied

the gystem x bounded or f tails of sufficiently tags as  $R_{k} \rightarrow \infty$ . Likewise, since  $\nabla R_k f$  is independent of mentum n, and since f is in or satisfies as a second

is  $K_{k} \to \infty$ . Likewise, since  $V_{k+1}$  is unependent meature  $p_{k}$  and since f falls off rapidly is period.

of Green's theorem in the momentum space of g

 $(\alpha; \nabla R_k U \cdot \nabla p_k f) = -\langle \nabla R_k U \cdot \nabla p_k \alpha; f \rangle$ 

 $\rho(\mathbf{r},t) =$ 

(a; - Pi Part) - (Pe

 $\int \cdots \int f d\mathbf{R}_{t} \cdots d\mathbf{R}_{t} d\mathbf{p}_{t} \cdots d\mathbf{p}_{t'} = 1$ where  $d\mathbf{R}_{4}$  stands for a volume element  $\pi$  the con-summation more and  $d_{2n}$  is volume element in the more where  $d\mathbf{R}_{t}$  stands for a volume element in the con-figuration space and  $d\mathbf{p}_{t}$  a volume element in the mo-mentum space of the 4th molecule, stands in the mo-security of the society of the standard in the security of the sec

(2.1)

561-10

The r

it is at

(2.5)

, (2.4) becomes  $\frac{\partial}{\partial t} (a; f) = \sum_{i=1}^{n} \left( \sum_{m_{e_{i}}}^{p_{e_{i}}} \nabla_{R_{i}a} - \nabla_{R_{i}} \nabla_{R_{i}a} \right) (2.7) \qquad \begin{array}{c} Consecucity, (p_{i}f)(R_{i} - t), f) \text{ is the } p_{i}(a_{i}, f) = 1 \\ mean momentum by the from the product of this is the product of the interval is the consecutive product of the interval inte$ 

N

Sol The TRACE VEGUE POR

 $\cdots \int \delta(\mathbf{R}_{b}-t) f(\mathbf{R}_{t_{1}}\cdots ;p_{t_{t}}\cdots ;t) d\mathbf{R}_{t}\cdots d_{t_{t_{t}}}$ 

others are ;

 $\langle m_i \delta \left( \boldsymbol{r} - \boldsymbol{r}_i \right); f$ 

The total roass density at r due to all audecules is thus

 $P(z; t) = \sum_{k=1}^{N} m_k(\delta(\mathbf{R}_k - t));$ 

 $\int P_{i}\partial(R_{k}-r)/(R_{i_{1}}\cdots ; p_{i}\cdots ; i)dR_{i_{1}}\cdots dp_{i_{r}}$ 

id the locations of the

 $\int \cdots \int \delta(\mathbf{R}_{1} - \mathbf{r}) f(\mathbf{R}_{1}, \cdots, \mathbf{p}_{1}, \cdots, \mathbf{j}) d\mathbf{R}_{1} \cdots d\mathbf{p}_{N}$ 

at the eth molecule to the momentum per unit values (mass current decas(y), "The local momentum decasity

apple and I link Brought = MX Jong.

(3.1)

HENM

We shall use (2.7) to derive the equations of hydro- ${}^{Avnomize}$ 

III. STATISTICAL MICHANICAL EXPRESSIONS FOR DENSITIES

The equations of hydrodynamics (1.1), (1.2), and (1.4) are concerned with densitive in ecdancy 3-space, e.g., mass density, momentum density, and energy density. We shall now express these as the expectation values of hydramical variables over an ensemble baving distribution function f. instruction for the probability per unit volume that the kth molecules be as  $R_{\rm e}$  is  $\int \cdots \int f(\mathbf{R}_1, \cdots, \mathbf{p}_l, \cdots, \mathbf{i}) d\mathbf{R}_1 \cdots$  $(\mathbf{R}_1, \dots, \mathbf{R}_n, \dots, \mathbf{d}_{n-1})$  where the integration is over all position vectors are  $\mathcal{A}_{n-1}$  of  $\mathcal{B}_{n-1}$  and over all momental vectors. Introducing that the kth molecule be at t at time t is

Steral-fins da +

81

In (Re + Solt)

23

# **Selecting Functions**

### . The Dirac delta selects molecules at a point

- Infinitely high, infinitely thin peak
- Equivalent to the continuum differential formulation at a point

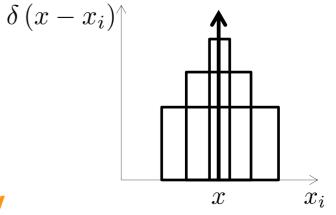
$$\rho(\mathbf{r},t) = \sum_{i=1}^{N} m_i \delta\left(\mathbf{r} - \mathbf{r}_i\right)$$

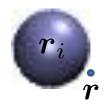


- . Other difficulties with the Dirac delta function
- . Relaxed weighting functions
  - By Hardy(1981), Todd, Hansen and Daivis (2008), Hoover/Lucy (2009), Murdoch (2010)

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

Imperial College London





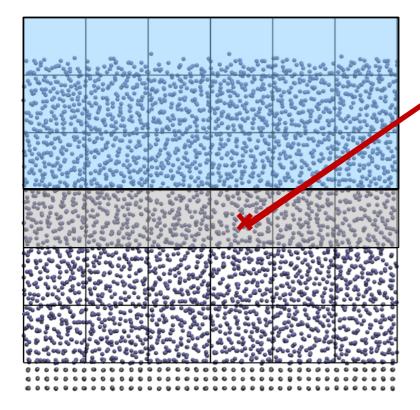
x

 $x_i$ 

 $\Delta (x - x_i)$ 

## **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

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

• 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

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

. Momentum

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

• Energy

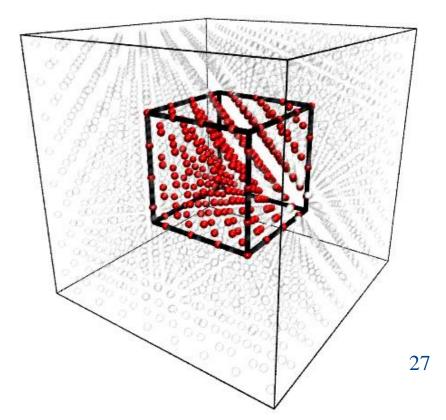
$$\rho \mathcal{E} = \sum_{i=1}^{N} e_i \delta \left( \boldsymbol{r} - \boldsymbol{r}_i \right) \qquad \qquad \int_{V} \rho \mathcal{E} dV = \sum_{i=1}^{N} e_i \int_{V} \delta \left( \boldsymbol{r} - \boldsymbol{r}_i \right) dV$$

## **Control Volume Function**

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

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

$$= [H(x^{+} - x_{i}) - H(x^{-} - x_{i})]$$
  
 
$$\times [H(y^{+} - y_{i}) - H(y^{-} - y_{i})]$$
  
 
$$\times [H(z^{+} - z_{i}) - H(z^{-} - z_{i})]$$



## **Derivatives yields the Surface Fluxes**

. Taking the Derivative of the CV function

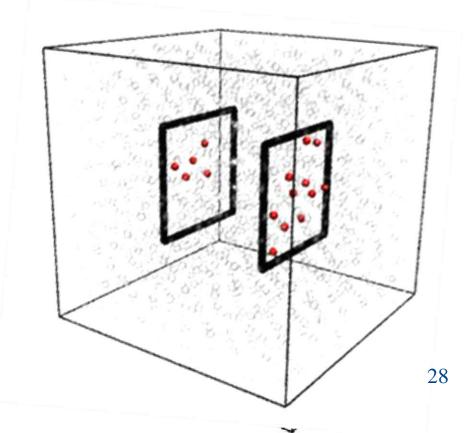
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \\ \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \\ \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

• Surface fluxes over the top and bottom surface

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

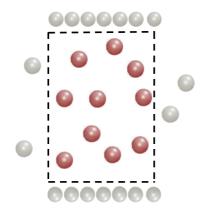
. Vector form defines six surfaces

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



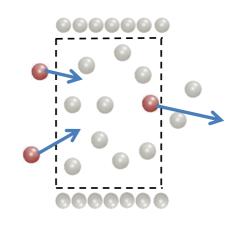
## **Control Volume Functional**

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



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

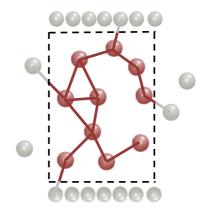
. Its derivative gives the fluxes over the surface



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

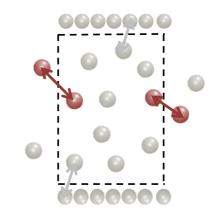
# **Control Volume Functional - Forces**

 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)



$$dS_{xij} \equiv \int_{0}^{1} \frac{\partial \vartheta_s}{\partial x} ds$$

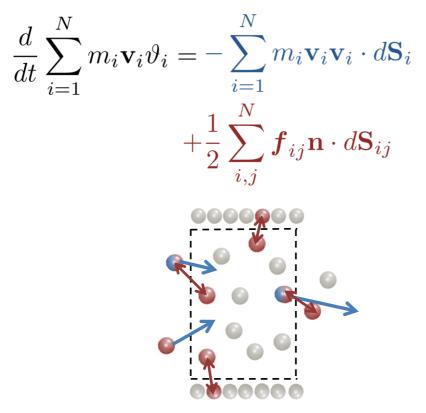
## **The Control Volume Equations**

### . Using the CV functional, the following equations are derived

Mass Conservation

$$\frac{d}{dt}\sum_{i=1}^{N}m_{i}\vartheta_{i} = -\sum_{i=1}^{N}m_{i}\mathbf{v}_{i} \cdot d\boldsymbol{S}_{i}$$

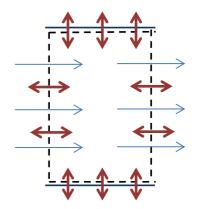
Momentum Balance



$$\frac{\partial}{\partial t} \int_{V} \rho dV = -\oint_{S} \rho \boldsymbol{u} \cdot d\mathbf{S}$$

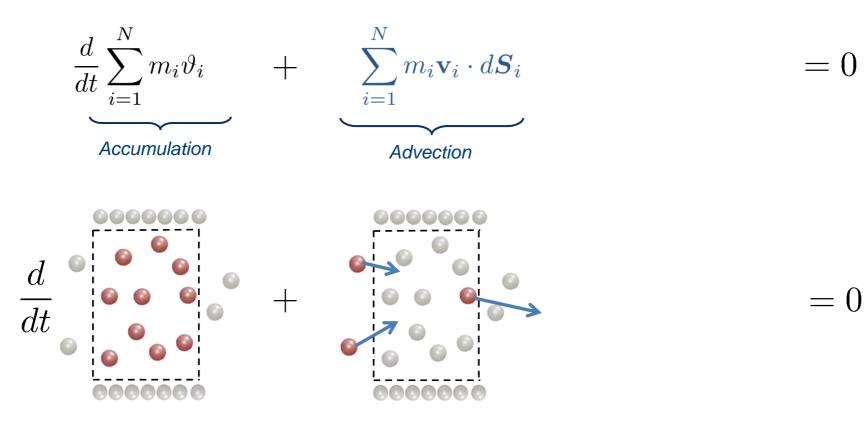
$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{u} dV = -\oint_{S} \rho \boldsymbol{u} \boldsymbol{u} \cdot d\mathbf{S}$$

$$-\oint_{S} \mathbf{\Pi} \cdot d\mathbf{S}$$



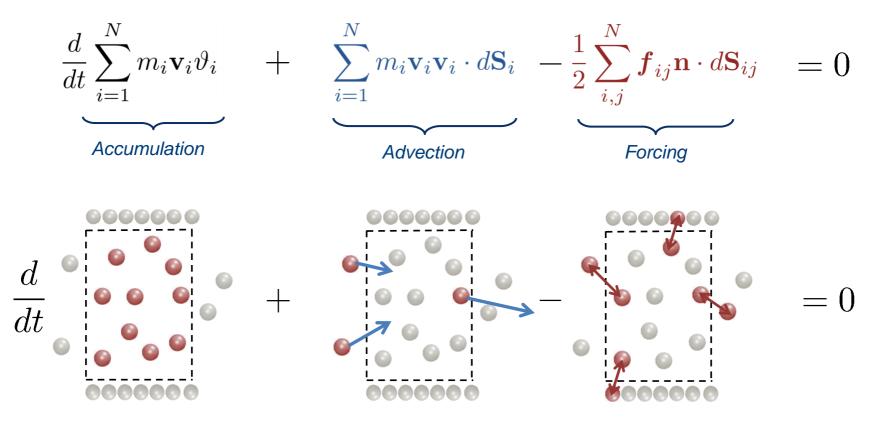
### **Exact Conservation**

. Mass Conservation



### **Exact Conservation**

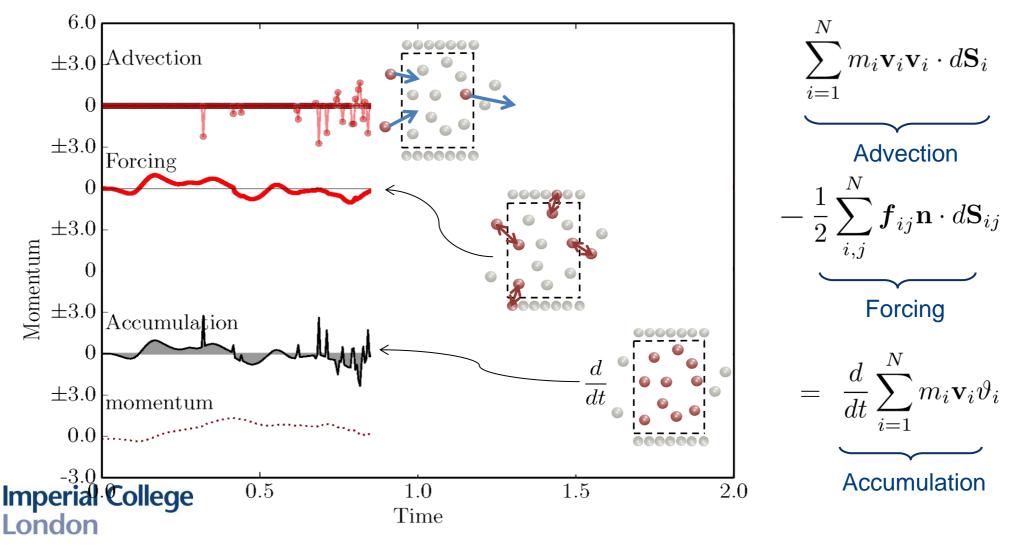
#### . Momentum Balance



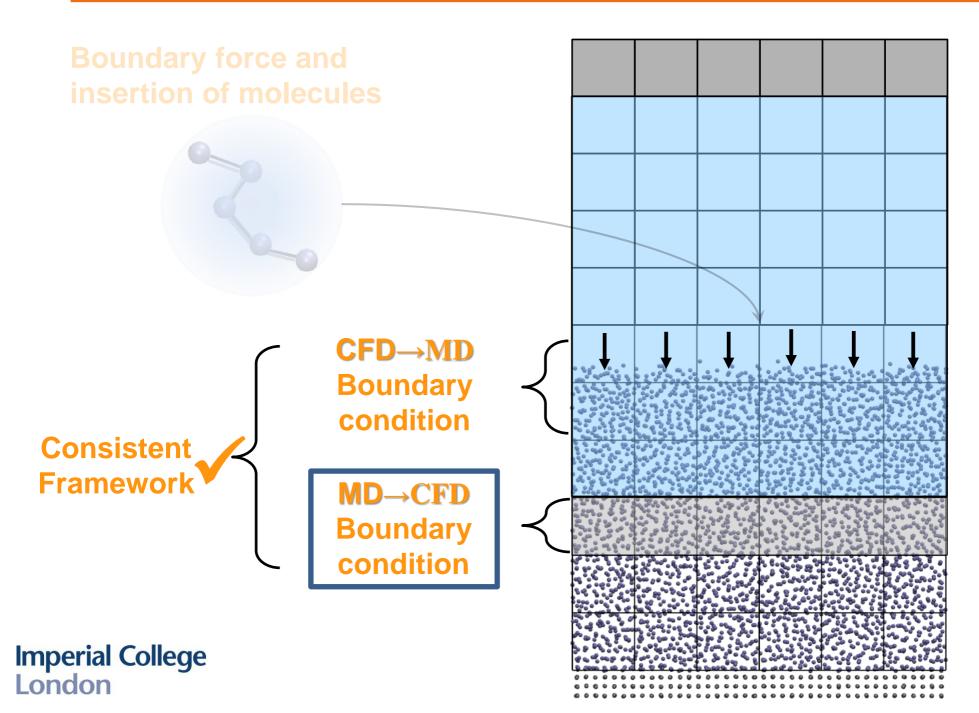
## **Exact Conservation**

### . Results from any arbitrary volume

- Accumulation = Forcing + Advection
- Momentum evolution is the integral of accumulation



# **Coupling Using the Control Volume**



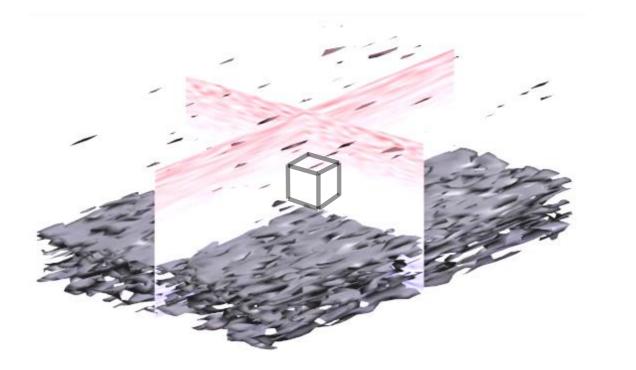
# **Coupling Using the Control Volume**

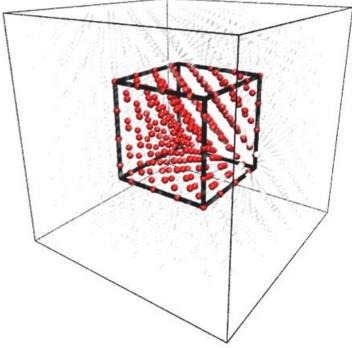
- . We now have an equivalent description in both regions
  - . Momentum or stresses inside an arbitrary control volume in both domains

$$\int_{V} \rho u dV = \sum_{i=1}^{N} m_{i} \boldsymbol{v}_{i} \vartheta_{i}$$
$$\oint_{S} \boldsymbol{\Pi} \cdot d\boldsymbol{S} = \sum_{i=1}^{N} m_{i} \boldsymbol{v}_{i} \boldsymbol{v}_{i} \cdot d\boldsymbol{S}_{i} + \frac{1}{4} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \boldsymbol{n} \cdot d\boldsymbol{S}_{ij}$$

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

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

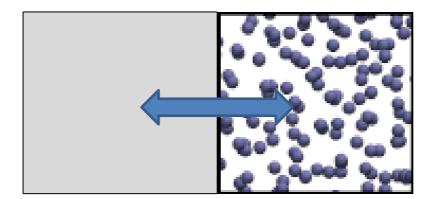




## **Consistent Formulation**

#### . We now have an equivalent description in both regions

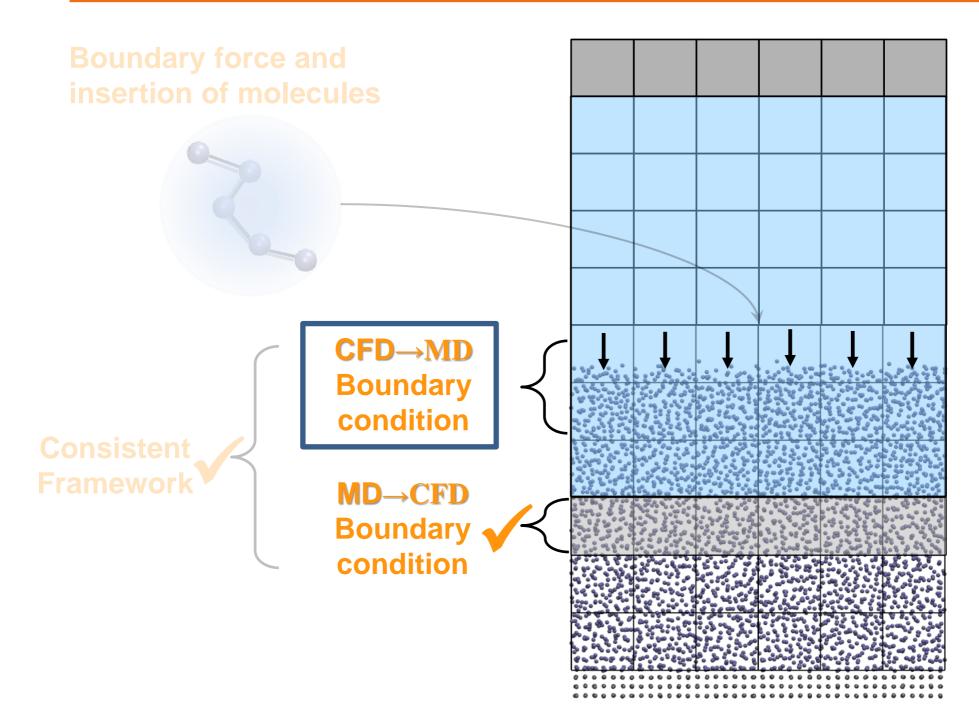
- Flux out of one system can be supplied as a flux into the other using method of planes stresses (Todd et al, 1995) in the MD and surfaces fluxes in the CFD
- Potential to develop a coupled system which is exactly conservative



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



# **Coupling Using the 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 <u>localised</u> 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

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

### . Gauss Principle of Least Constraint Applied

• Resulting constrained equations are differential e.g. the evolution of momentum is matched to the continuum

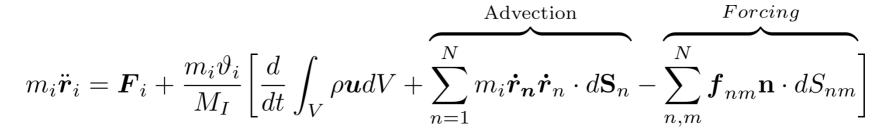
$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i \vartheta_i}{M_I} \left[ \frac{d}{dt} \int_V \rho \boldsymbol{u} dV - \frac{d}{dt} \sum_{n=1}^N m_i \dot{\boldsymbol{r}}_i \vartheta_i \right]$$

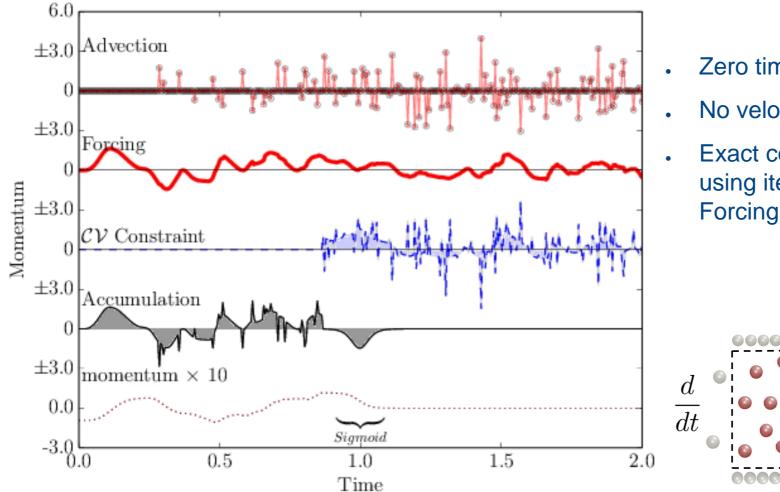
 Surface fluxes and force *exactly* cancel the molecular terms and replace them with the coupled continuum values

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

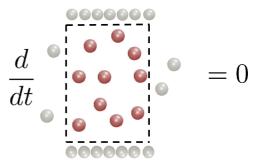
- An Iterative Implementation of the Constraint is Required
  - Similar to SHAKE but iterating to cancel effects of momentum flux instead of bond length
  - Momentum control must be exact for a local differential constraint to be applied with no drift

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

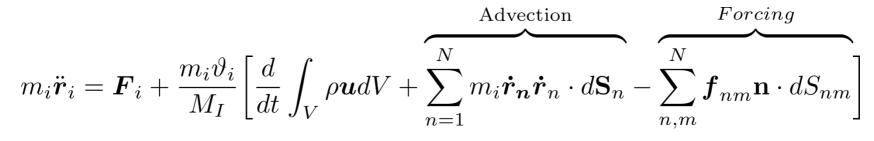


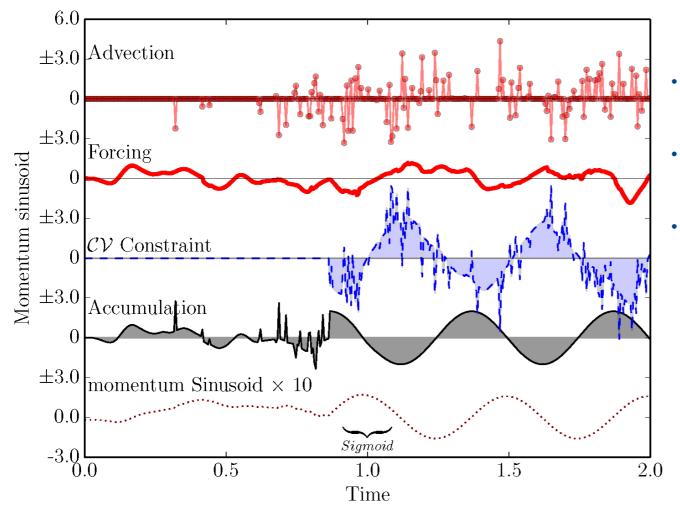


- Zero time evolution applied
- No velocity evolution results
- Exact control of momentum using iteration to cancel both Forcing and Advection

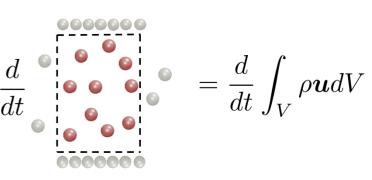


. Provides a method of controlling a volume's velocity and stress





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



. Provides a method of controlling a volume's velocity and stress

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

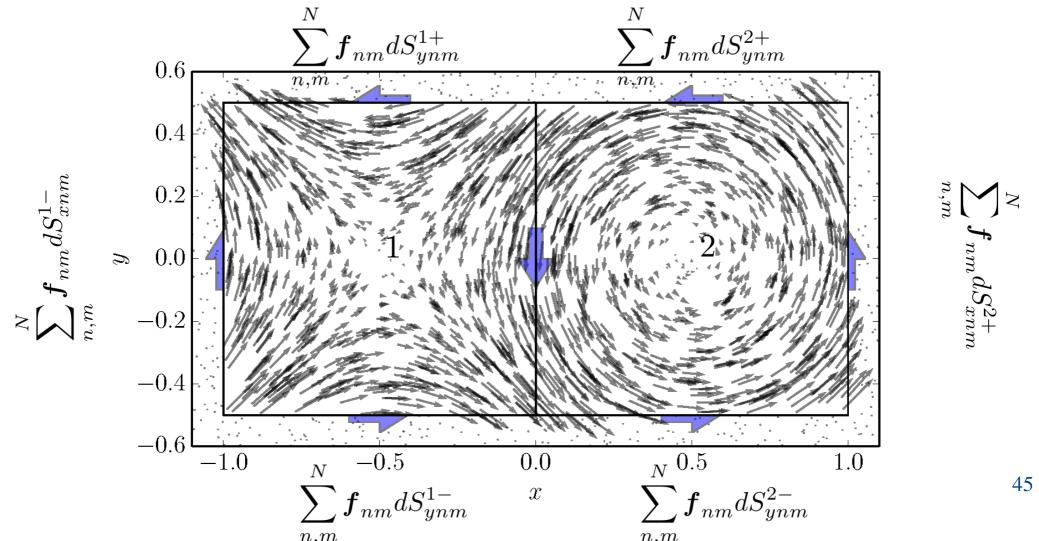
• Forcing applies an arbitrary 18 component 3D stress field

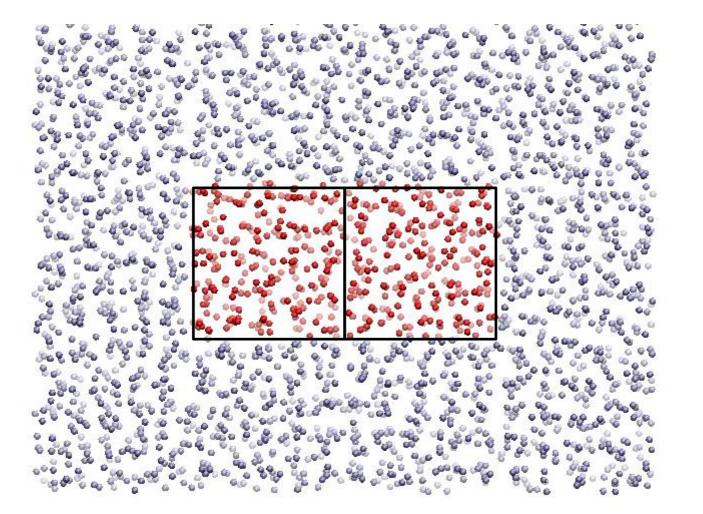


Provides a method of controlling a volume's velocity and stress

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

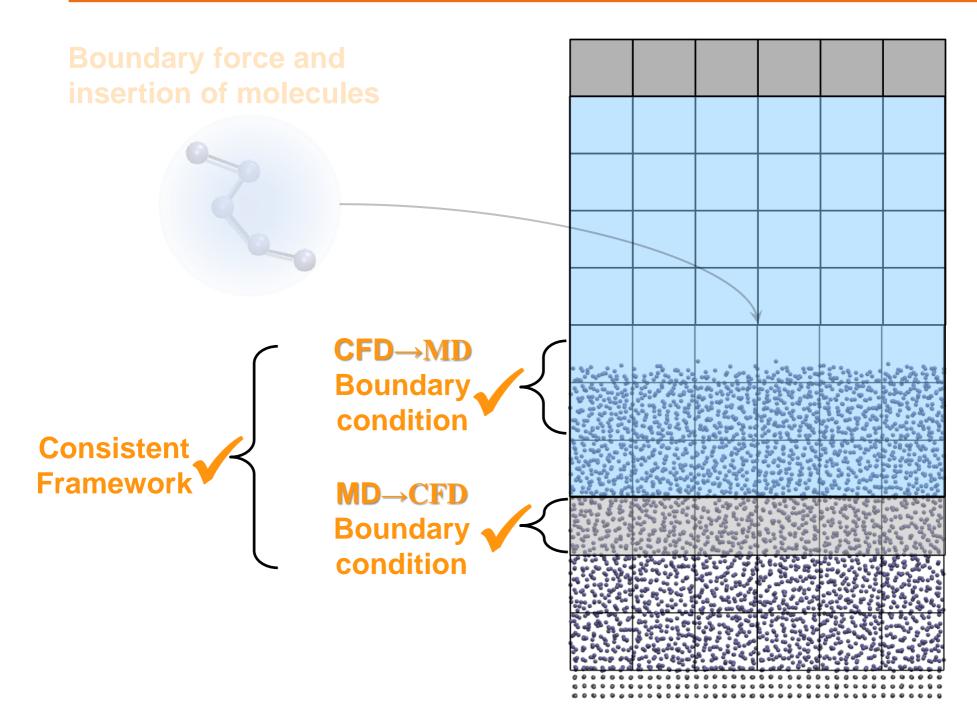
. Forcing applies an arbitrary 18 component 3D stress field





×

# **Coupling Using the Control Volume**



## **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

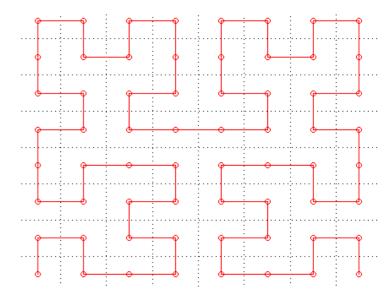
### But first, some computational development

# **Coupled Simulation**



# **MD Computing – Serial optimisations**

- All pairs simulation uses local cell and neighbour lists
  - N<sup>2</sup> 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,XMMO
  - MOVSD XMMO,XMM2
  - ANDPD XMMD,XMM1

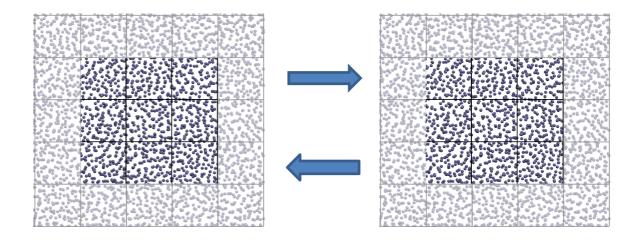


#CHECK INPUT LESS THAN 0.0;

- #SAVE 1.0 INTO XMMO
- **#AND 1.0** WITH ALL ZEROS/ONES

# **MD Computing – Parallel optimisations**

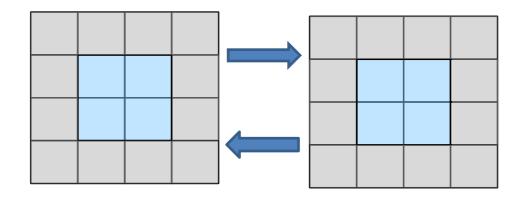
- Localisations lends itself to parallel computing using MPI
  - Spatial decomposition employed
  - . Halo cells (ghost molecules) are used to link adjacent regions



- Halo exchange of variable amounts of data
  - MPI\_Send, MPI\_Probe and MPI\_Recv employed

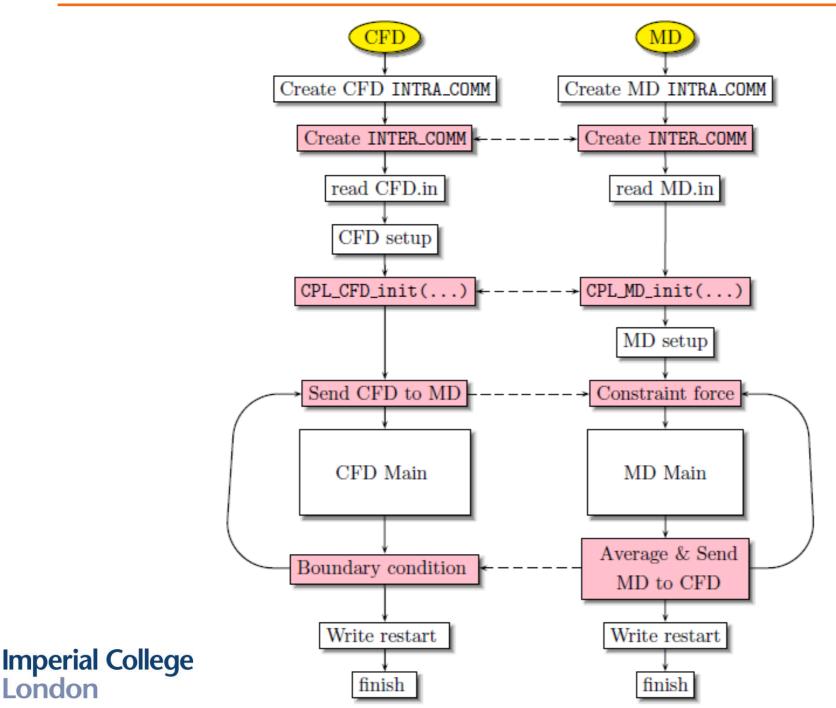
# **Computational Fluid Dynamics**

- 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**



London

53

### **CPL\_LIBRARY** Overview

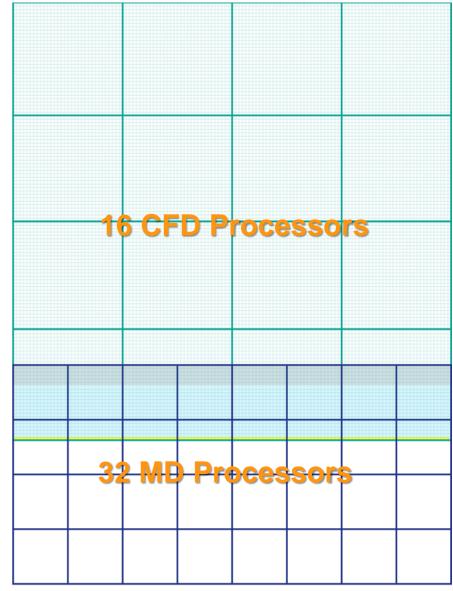
### Based on the MPI module

- 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

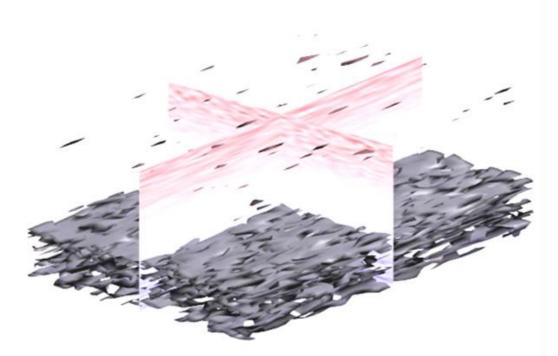


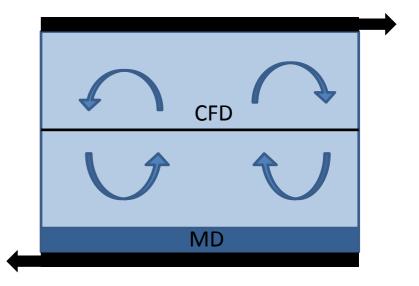


## **Turbulent Flow**

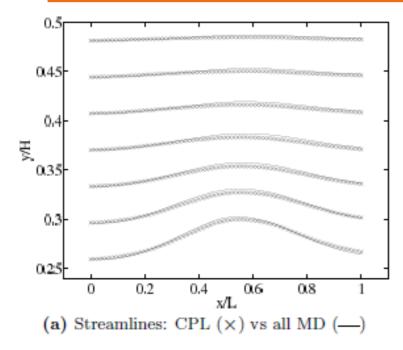
### • Turbulent Flow in a channel

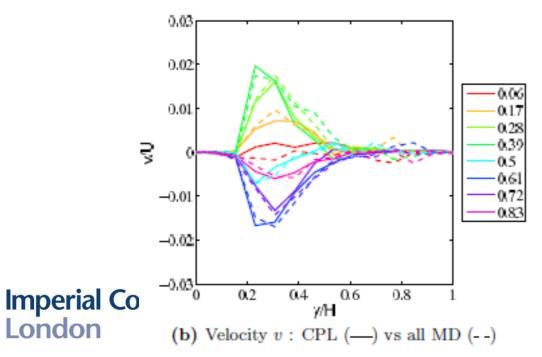
- CFD used for the majority of the domain
- MD solves the near wall region which is known to have a major effect on the dynamics of the system

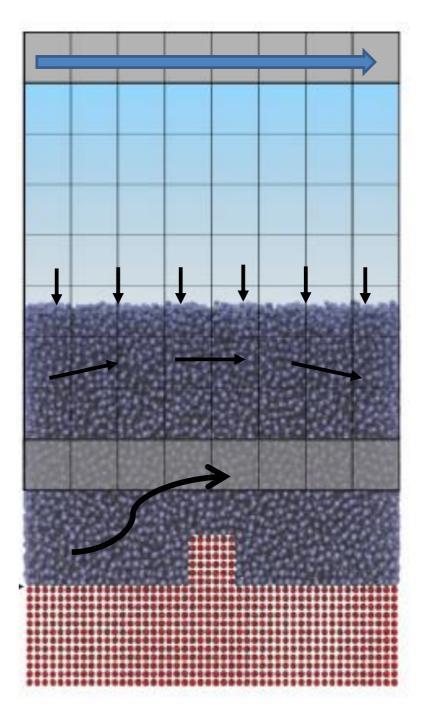




## **Couette Flow with Wall Roughness**

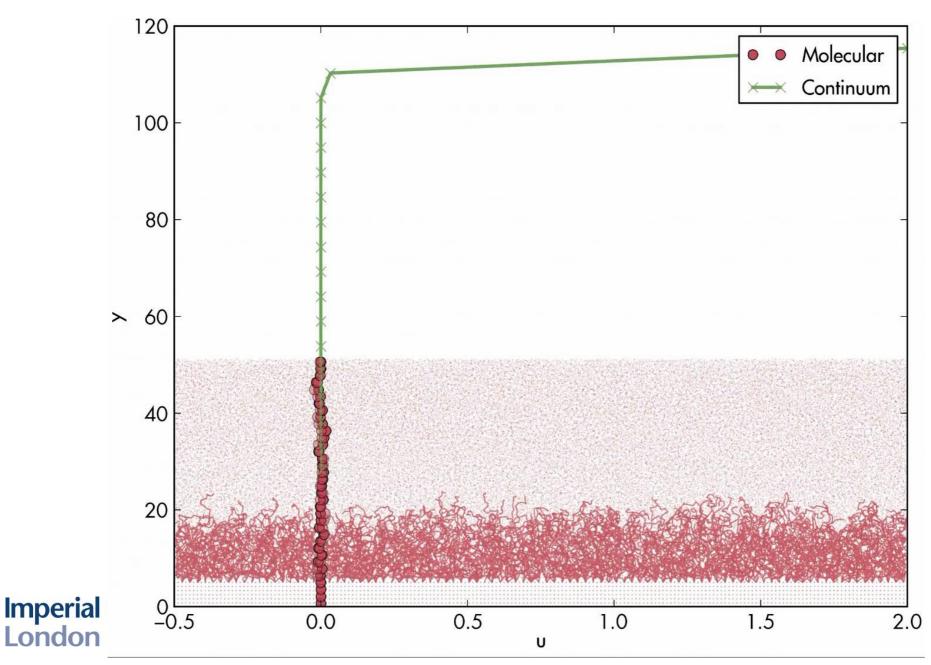






### **Polymer Brushes**

### • Simulation run by David Trevelyan



57

# **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 (<u>https://code.google.com/p/cpl-library/</u>)
- 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:**

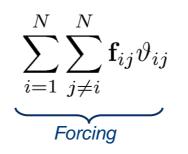
- Professor David Heyes
- Dr Daniele Dini
- Dr Tamer Zaki
- . Mr David Trevelyan
- Dr Lucian Anton (NAG)

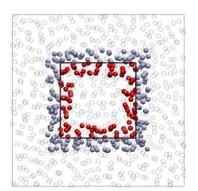
### **Extra Material**

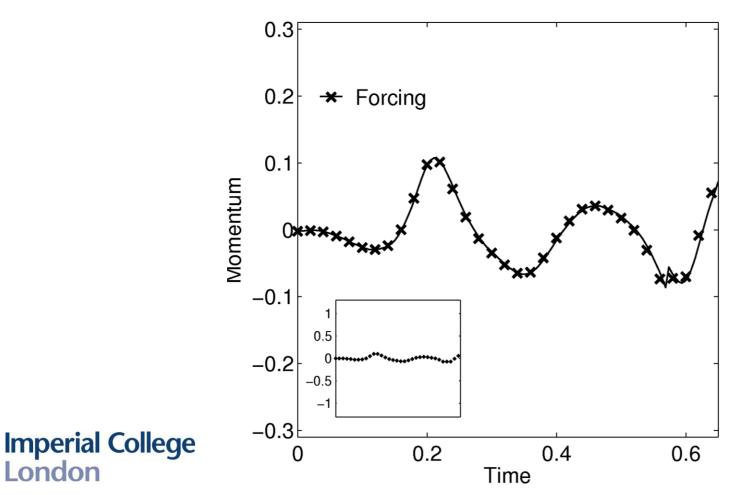


### **Testing Momentum Balance**

. Momentum Balance





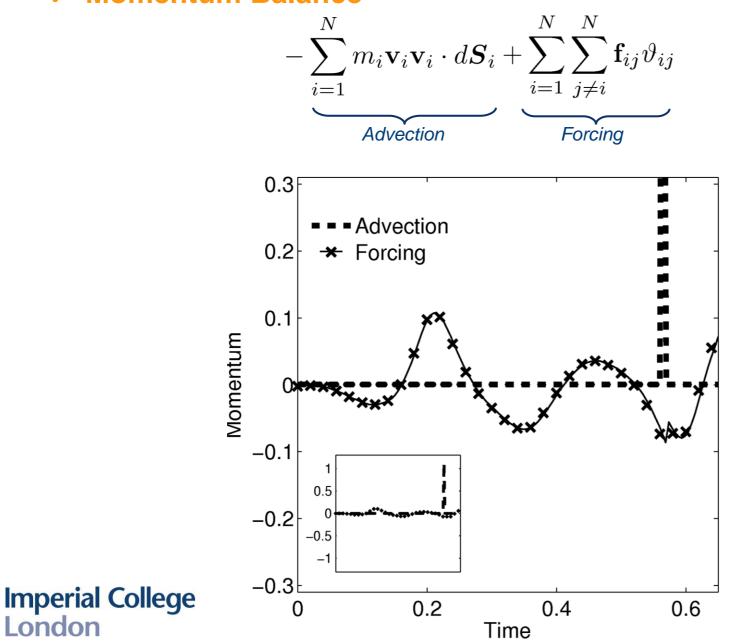


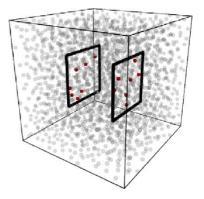
61

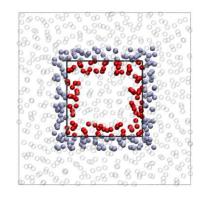
## **Testing Momentum Balance**

#### **Momentum Balance**

London

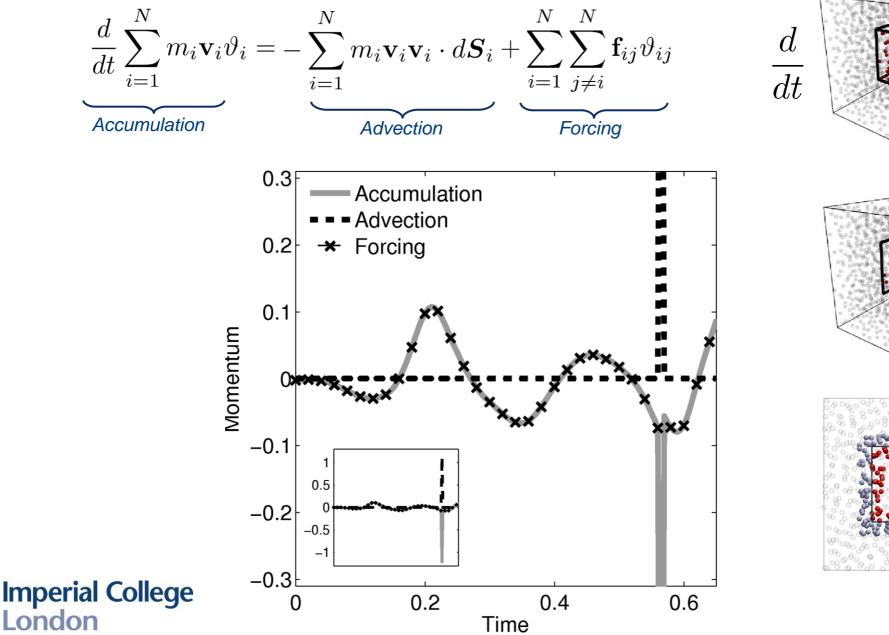


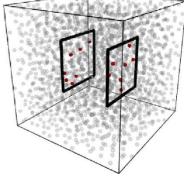


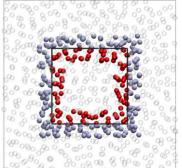


## **Testing Momentum Balance**

#### . Momentum Balance







63

# **Control Volume Function (revisited)**

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

$$\vartheta_i \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i) \, dV$$
  
=  $\begin{bmatrix} H(x^+ - x_i) - H(x^- - x_i) \end{bmatrix}$   
×  $\begin{bmatrix} H(y^+ - y_i) - H(y^- - y_i) \end{bmatrix}$   
×  $\begin{bmatrix} H(z^+ - z_i) - H(z^- - z_i) \end{bmatrix}$ 

• Replace molecular position with equation for a line

$$m{r}_i 
ightarrow m{r}_i - s m{r}_{ij}$$



#### 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)

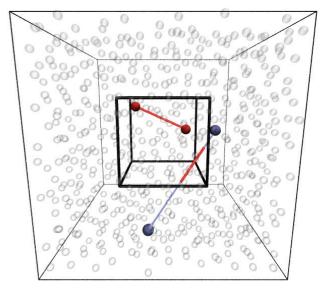
# **Control Volume Function (revisited)**

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

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

. 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

$$\frac{\partial \vartheta_s}{\partial x} \equiv \left[ \delta(x^+ - x_i + sx_{ij}) - \delta(x^- - x_i + sx_{ij}) \right] \\ \times \left[ H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij}) \right] \\ \times \left[ H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij}) \right]$$

66

• Surface fluxes over the top and bottom surface

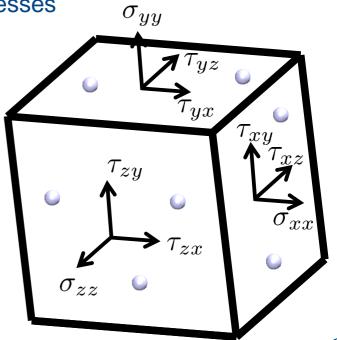
$$dS_{xij} \equiv \int_{0}^{1} \frac{\partial \vartheta_s}{\partial x} ds = dS_{xij}^{+} - dS_{xij}^{-}$$

Imperial College  
London
$$dS_{xij}^{+} = \frac{1}{2} \underbrace{\left[sgn(x^{+} - x_{i}) - sgn(x^{+} - x_{j})\right]}_{MOP} S_{xij}$$

# **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

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

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

$$\frac{\partial}{\partial t} \int_{V} \rho dV = -\oint_{S} \rho \boldsymbol{u} \cdot d\mathbf{S}$$

Lagrangian mass conservation

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

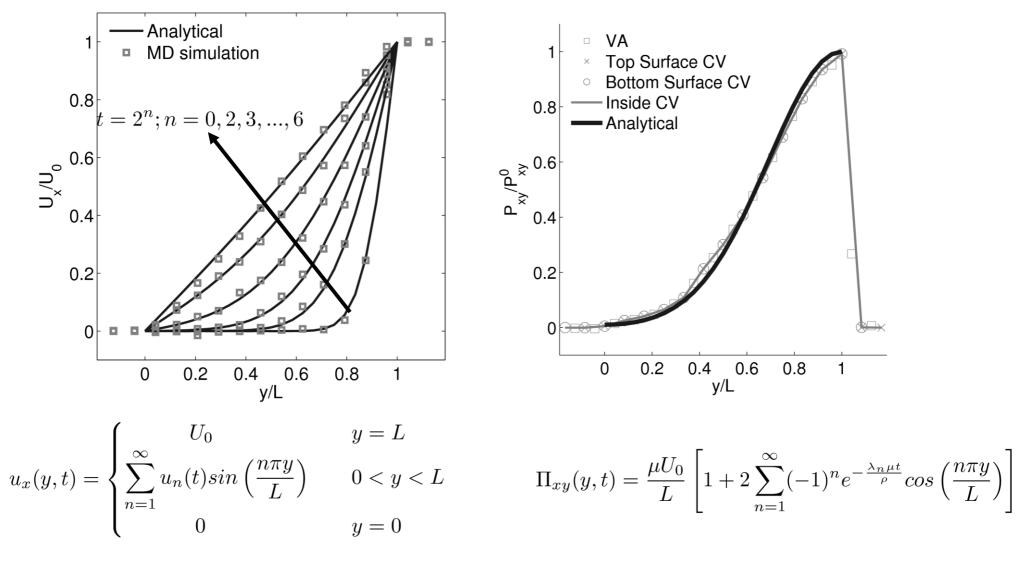
 $\overline{\boldsymbol{u}} \cdot d\boldsymbol{S}_i = \frac{d\boldsymbol{r}}{dt} \cdot \frac{d\vartheta_i}{d\boldsymbol{r}}$ 

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

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

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

## **Continuum Analytical Couette Flow**



Where,  $\lambda_n = \left(\frac{n\pi}{L}\right)^2$  and  $u_n(t) = \frac{2U_0(-1)^n}{n\pi} \left(e^{-\frac{\lambda_n \mu t}{\rho}} - 1\right)$ **Imperial College**London
69

# **Unsteady Couette Flow**

y

### Continuum Analytical

• Simplify the momentum balance (Navier-Stokes) equation

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

• Solve the 1D unsteady diffusion equation.

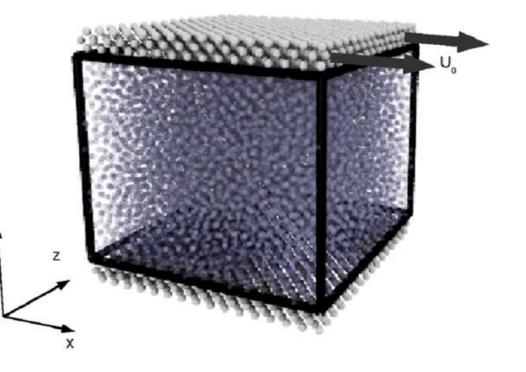
$$\frac{\partial u_x}{\partial t} = \frac{\mu}{\rho} \frac{\partial^2 u_x}{\partial y^2}$$

• 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

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

#### Imperial College London

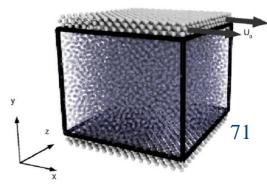
- Molecular Dynamics
  - Discrete form of the Momentum balance equation

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

• Simplifies for a single control volume

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

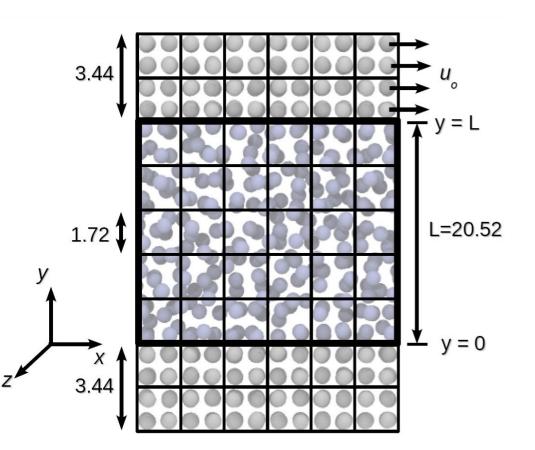
• Fixed bottom wall, sliding top wall with both thermostatted

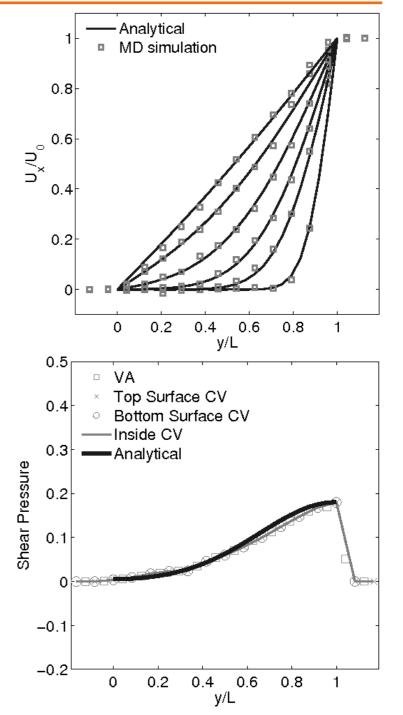


## **Unsteady Couette Flow**

### . Simulation setup

- . Starting Couette flow
- · Wall thermostat: Nosé-Hoover
- Averages are computed over 1000 time steps and 8 realizations

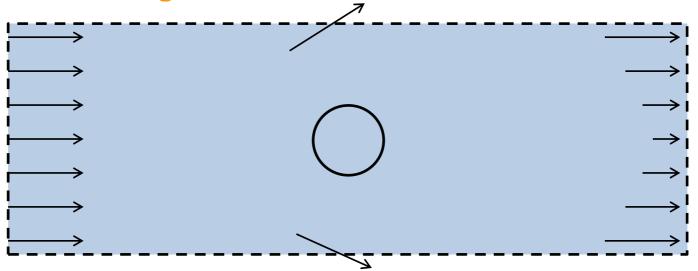




72

### 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

