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# Linking the Continuous and the Discrete

## Coupling Molecular Dynamics to Continuum Fluid Mechanics

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# Outline

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## • Introduction

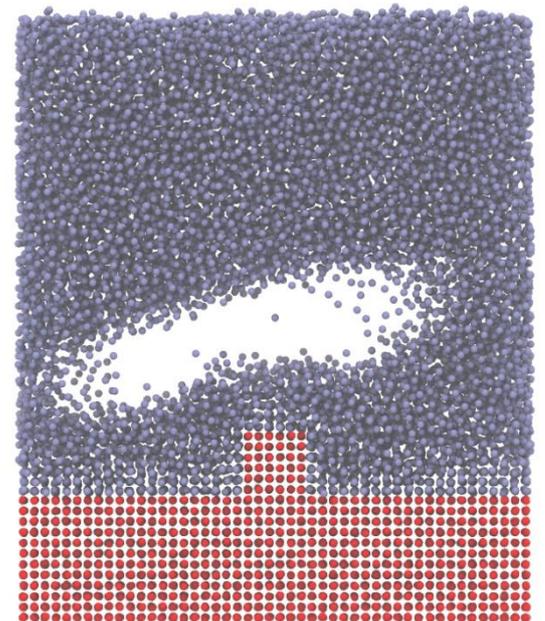
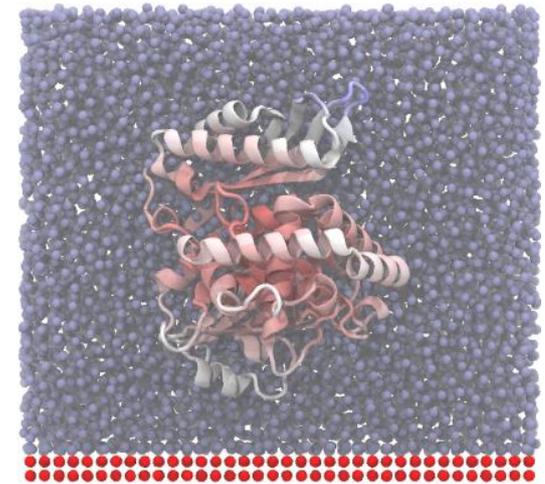
- Motivation for coupling
- Molecular dynamics (MD)
- Computational fluid dynamics (CFD)

## • Mathematical Formulation for Coupling

- Irving and Kirkwood (1950)
- The control volume function
- Coupling using Hamilton's principle

## • Computational Developments

- The molecular dynamics solver
- The computational fluid dynamics solver
- The CPL\_Library (open source)



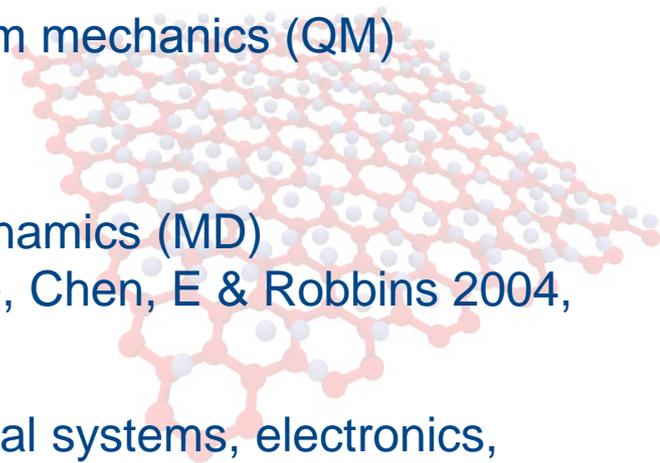
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# Introduction

# Motivation

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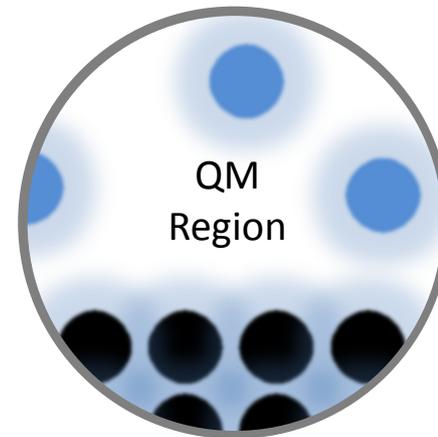
- **Modern engineering problems require sub-continuum models**
  - Quantum mechanics is limited to very small systems
  - Even Molecular dynamics is still prohibitively expensive
  - Multi-scale coupling overcomes these limitations by linking to cheaper methods
  - Quantum mechanics  $\leftrightarrow$  Molecular dynamics (MD) (Karplus, Levitt and Warshel)
- **Multi-scale coupling has been employed since the 1970's (Curtin & Miller 2003) in solid mechanics modelling (e.g. for crack tips)**
  - Essential to fully capture both the complicated detail in the crack and the impact on the wider system
  - Continuum  $\leftrightarrow$  Molecular mechanics (MM)  $\leftrightarrow$  Quantum mechanics (QM)
- **Classical coupling for fluids is less mature**
  - Computational fluid dynamics (CFD)  $\leftrightarrow$  Molecular dynamics (MD) (O'Connell & Thompson 1995, Flekkøy et al 2000, Nie, Chen, E & Robbins 2004, Delgado-Buscalioni & Coveney, 2004)
  - Important for e.g. flow over carbon allotropes, biological systems, electronics, chemical reactions and combustion



# Motivation

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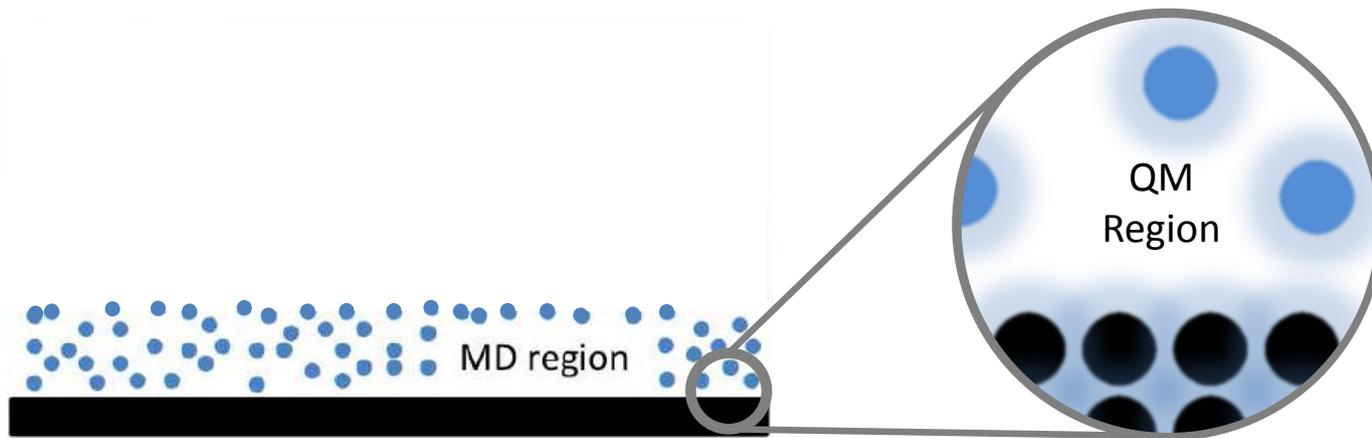
- **Long term goal is to seamlessly link various scales of modelling**
  - Fine/coarse graining as required based on the problem of interest
  - Dynamic resource allocation and load balancing on multi-core architectures



# Motivation

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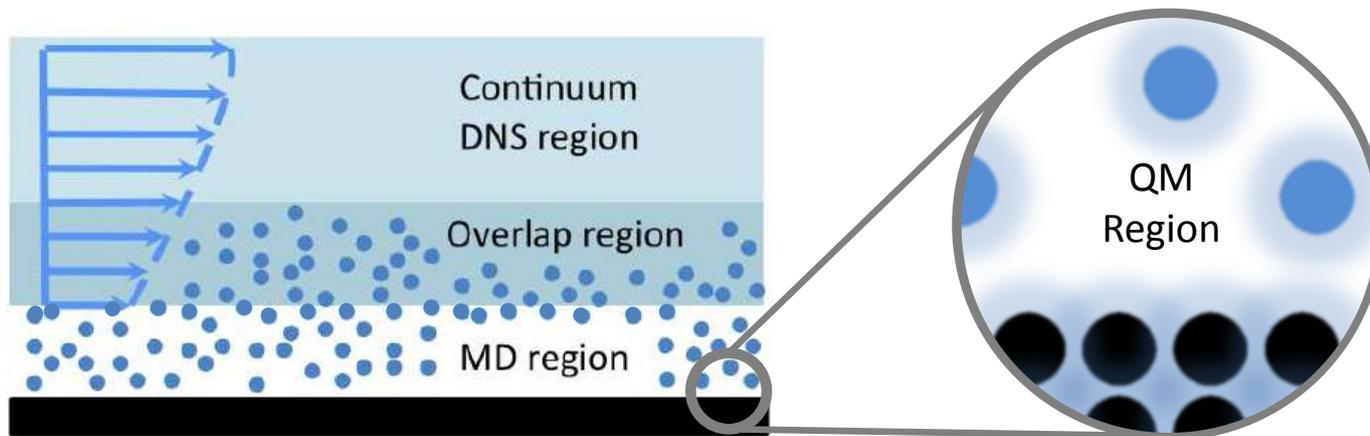
- **Long term goal is to seamlessly link various scales of modelling**
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# Motivation

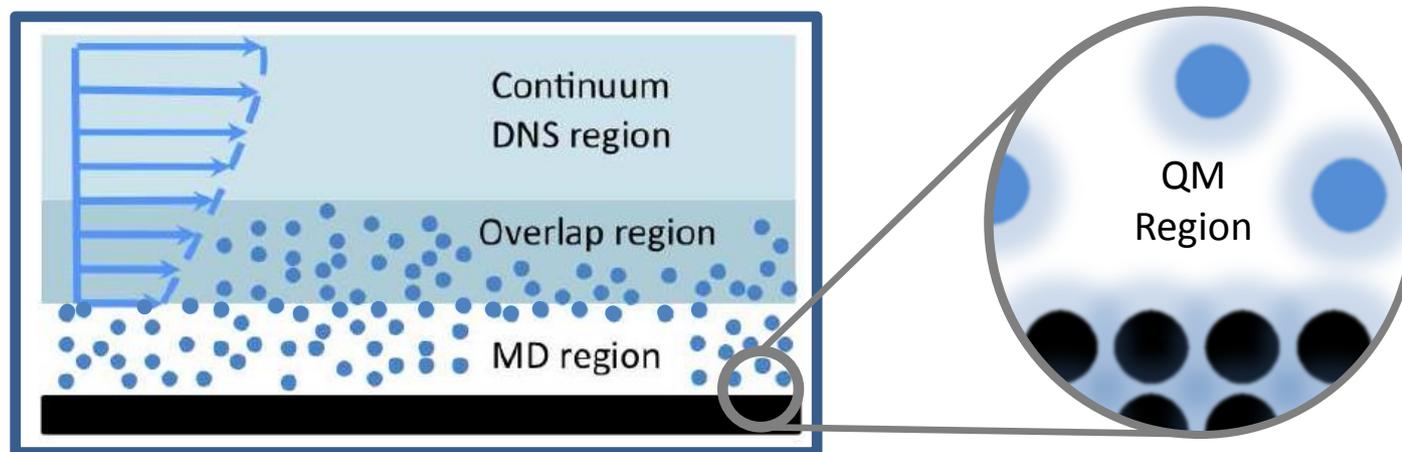
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- **Long term goal is to seamlessly link various scales of modelling**
  - Fine/coarse graining as required based on the problem of interest
  - Dynamic resource allocation and load balancing on multi-core architectures



# Motivation

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



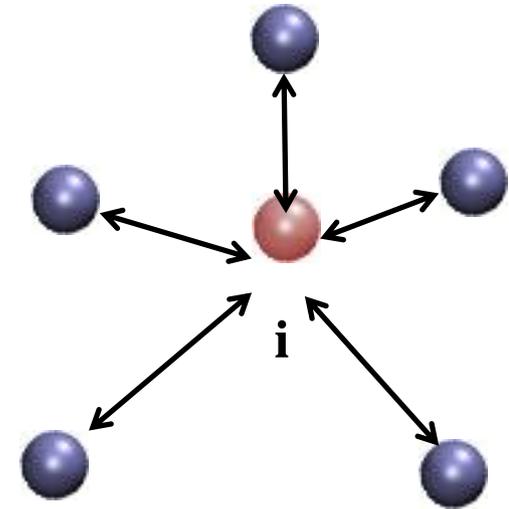
- **Solving similar and relevant problems to quantum mechanics**
  - Relationship between the mathematical framework used to describe a continuous field and a discrete system (The Dirac delta function)
  - Ensuring the dynamics agree in both systems in a physically meaningful manner
  - Interfacing of computational solvers and data exchange
  - Extend the range of quantum modelling, via MD-CFD coupling

# Discrete Models (Molecular Dynamics)

- Discrete molecules in continuous space

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

$$\begin{aligned}\ddot{\mathbf{r}}_i &\rightarrow \dot{\mathbf{r}}_i \\ \dot{\mathbf{r}}_i &\rightarrow \mathbf{r}_i(t)\end{aligned}$$



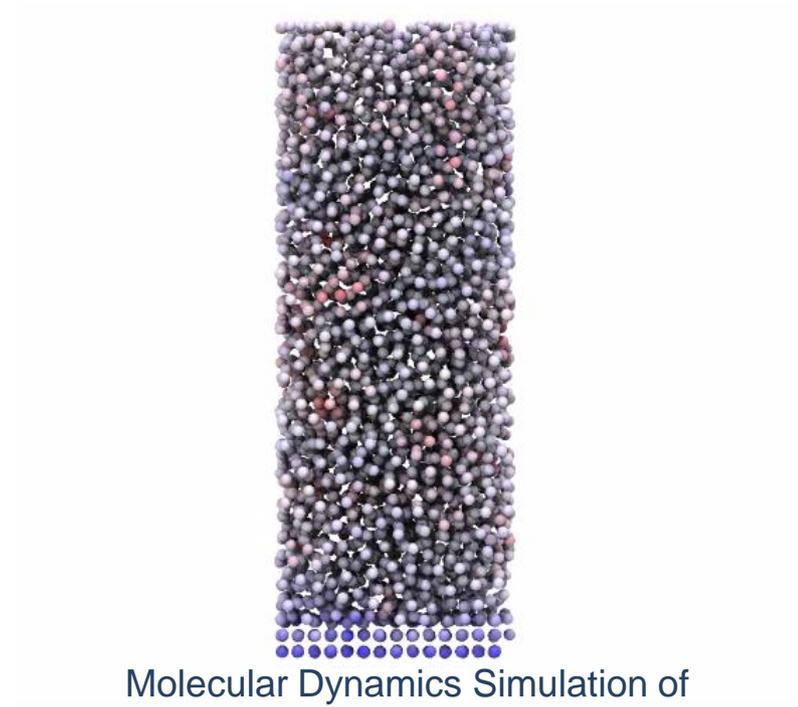
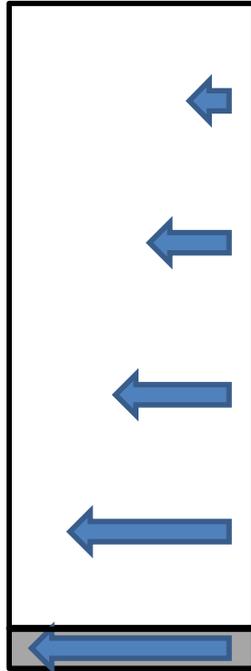
- Acceleration obtained from forces

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

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

# Discrete Models (Molecular Dynamics)

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Molecular Dynamics Simulation of  
Couette Flow

# Continuum Field Equations

- Assumed continuous at every point in space
  - Mass Conservation

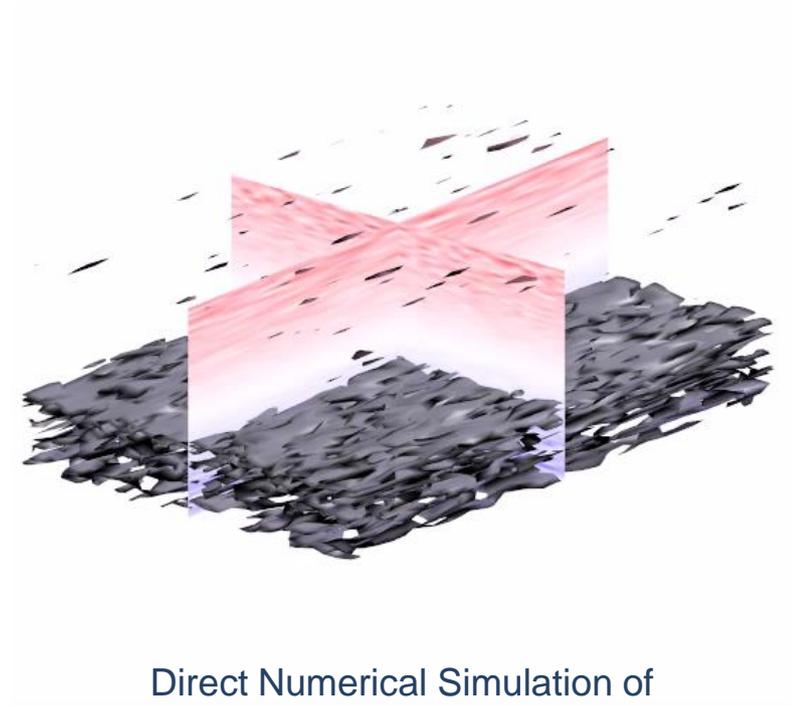
$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}$$

- Momentum Balance (Newton's Law)

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

- Energy Conservation

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



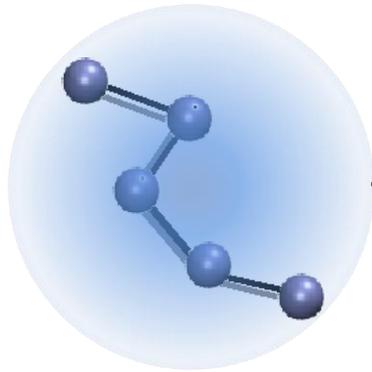
Direct Numerical Simulation of  
Turbulent Couette Flow

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# Mathematical Formulation for Coupling

# Coupling Schematic

Insertion of molecules

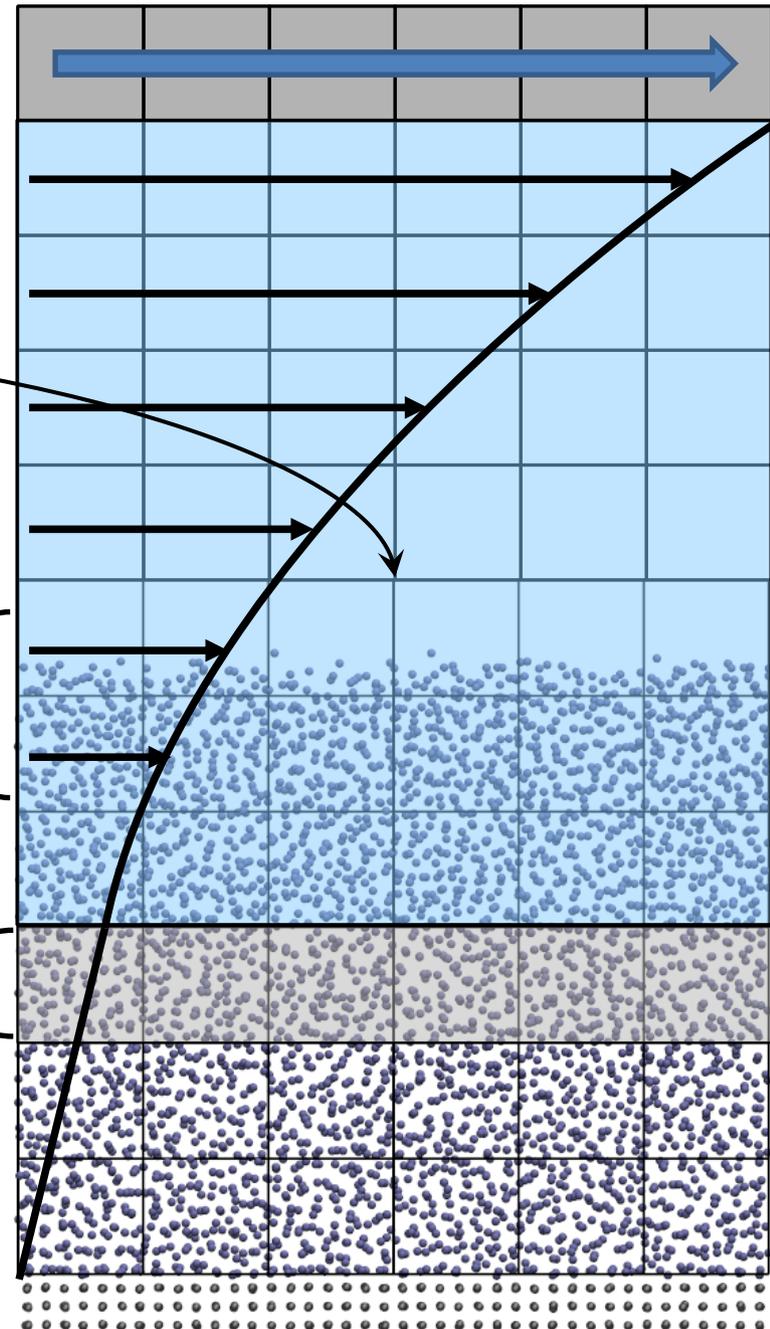


Consistent Framework

CFD→MD  
Boundary  
condition

MD→CFD  
Boundary  
condition

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



# Irving and Kirkwood (1950)

$$\langle \alpha; f \rangle \equiv \int \dots \int \alpha(\mathbf{r}^N, \mathbf{p}^N) f(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N$$

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \sum_{i=1}^N \left\langle \frac{\partial \alpha}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i + \frac{\partial \alpha}{\partial \mathbf{p}_i} \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i}; f \right\rangle$$

$$\alpha = \sum_{i=1}^N m_i \delta(\mathbf{r} - \mathbf{r}_i)$$

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

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was not been observed. If the preferred interpretation is correct, the group of Raman bands, 769, 778, 819, and 829  $\text{cm}^{-1}$ , are related to each other in much the same manner as similar groups in the spectra of  $\text{CO}_2$  and  $\text{CS}_2$ .

ACKNOWLEDGMENTS

The writers wish to express their indebtedness to Dr. C. F. Hamner and E. L. du Pont de Nemours and Company for the samples; to Doctors Isabella and Jerome Kafke for electron diffraction data; and to Dr. E. K. Plyler and the National Bureau of Standards for data in the long wave-length region.

JUNE, 1950

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

J. I. IRVING and J. G. KIRKWOOD  
 Gates and Crellin Laboratories of Chemistry, University of California, Los Angeles, California  
 (Received November 21, 1949)

The equations of hydrodynamics—continuity, momentum, and equation of energy transport—are derived by means of the statistical mechanical theory of transport processes for the stress tensor and heat current in terms of molecular velocities and momenta. The contributions of intermolecular forces to the stress tensor and heat current are expressed, respectively, as quadrupoles of the density and current densities 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 statistical mechanics. In particular, the equations 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 in terms of quadrature involving the potential of intermolecular force and the density of the sum of the potential of intercurrent density involving the density and current density in the configuration space of a pair of molecules. The results were previously stated in this series<sup>1</sup> when this derivation 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 work was supported by the U. S. ONR under Contract N00r-244 with the California Institute of Technology. J. G. Kirkwood, J. Chem. Phys. 14, 50 (1946).

TRANSPORT PROCESSES

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The probability distribution function (relative density of representative points in phase space) we denote by

$$f(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N, t)$$

satisfying the normalization condition

$$\int \dots \int f d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{p}_1 \dots d\mathbf{p}_N = 1 \quad (2.1)$$

where  $d\mathbf{R}_k$  stands for a volume element in the configuration space and  $d\mathbf{p}_k$  a volume element in the momentum space of the  $k$ th molecule.  $f$  changes in time according to the well-known Liouville equation

$$\frac{df}{dt} = \sum_{i=1}^N \left[ \frac{\partial f}{\partial \mathbf{r}_i} \cdot \mathbf{v}_i + \nabla_{\mathbf{p}_i} \cdot \mathbf{F}_i \right] f \quad (2.2)$$

where  $U$  is the potential energy of the entire system. Any dynamical variable,  $\alpha(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N, t)$  has an expectation value given at time  $t$  by

$$\langle \alpha; f \rangle = \int \dots \int \alpha(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N, t) f d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \quad (2.3)$$

We thus denote by  $\langle \alpha; f \rangle$  the expectation value of  $\alpha$  for a distribution function  $f$ . (It is merely the inner product of  $\alpha$  and  $f$  taken over phase space.) Providing  $\alpha$  does not depend on time explicitly, the rate of change of the expectation value of  $\alpha$  is given by

$$\frac{d}{dt} \langle \alpha; f \rangle = \left\langle \frac{\partial \alpha}{\partial t} \right\rangle + \sum_{i=1}^N \left\langle \left[ \alpha; -\frac{\partial \alpha}{\partial \mathbf{p}_i} \cdot \nabla_{\mathbf{p}_i} \right] \right\rangle \quad (2.4)$$

By Green's theorem applied in the space of  $\mathbf{R}_k$

$$\left\langle \left[ \alpha; -\frac{\partial \alpha}{\partial \mathbf{p}_i} \cdot \nabla_{\mathbf{p}_i} \right] \right\rangle = \int \dots \int \left[ \alpha; -\frac{\partial \alpha}{\partial \mathbf{p}_i} \cdot \nabla_{\mathbf{p}_i} \right] f d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \quad (2.5)$$

providing the integrated part vanishes, i.e., providing the system is bounded or  $f$  falls off sufficiently rapidly as  $\mathbf{R}_k \rightarrow \infty$ . Likewise, since  $\mathbf{F}_i$  is independent of  $\mathbf{p}_i$ , momentum  $\mathbf{p}_i$ , and since  $\mathbf{F}_i$  falls off rapidly as  $\mathbf{p}_i \rightarrow \infty$ , use of Green's theorem in the momentum space also yields

$$\left\langle \left[ \alpha; -\frac{\partial \alpha}{\partial \mathbf{p}_i} \cdot \nabla_{\mathbf{p}_i} \right] \right\rangle = - \left\langle \alpha; \mathbf{F}_i \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i} \right\rangle \quad (2.5)$$

Thus, (2.4) becomes

$$\frac{d}{dt} \langle \alpha; f \rangle = \sum_{i=1}^N \left\langle \left[ \alpha; -\frac{\partial \alpha}{\partial \mathbf{p}_i} \cdot \nabla_{\mathbf{p}_i} - \mathbf{F}_i \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i} \right] \right\rangle \quad (2.7)$$

Consequently,  $\langle \alpha; \mathbf{F}_i \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i} \rangle$  is the product of this mean momentum by the probability per unit volume that the  $k$ th molecule be at  $\mathbf{r}$ ; i.e., it is the contribution of the  $k$ th molecule to the momentum per unit volume (mass current density). The total momentum density

# Irving and Kirkwood (1950) cont.

- Density in the molecular system is defined

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = \frac{\partial}{\partial t} \sum_{i=1}^N \left\langle m_i \delta(\mathbf{r} - \mathbf{r}_i); f \right\rangle \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}$$

- Time evolution from the Irving and Kirkwood procedure

$$\frac{\partial}{\partial t} \left\langle \alpha; f \right\rangle = \sum_{i=1}^N \left\langle \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial \alpha}{\partial \mathbf{r}_i} - \mathbf{F}_i \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i}; f \right\rangle \quad \alpha = \sum_{i=1}^N m_i \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{i=1}^N \left\langle m_i \delta(\mathbf{r} - \mathbf{r}_i); f \right\rangle &= \sum_{i=1}^N \left\langle \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} m_i \delta(\mathbf{r} - \mathbf{r}_i) \right. \\ &\quad \left. - \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} m_i \delta(\mathbf{r} - \mathbf{r}_i); f \right\rangle \\ &= -\frac{\partial}{\partial \mathbf{r}} \cdot \sum_{i=1}^N \left\langle \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i); f \right\rangle \end{aligned}$$

# Mass Conservation Equation

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- Continuum mass conservation

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

- Molecular Equivalent

$$\frac{\partial}{\partial t} \underbrace{\sum_{i=1}^N \langle m_i \delta(\mathbf{r} - \mathbf{r}_i); f \rangle}_{\rho} = -\nabla \cdot \underbrace{\sum_{i=1}^N \langle \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i); f \rangle}_{\rho \mathbf{u}}$$

- Similarly for the time evolution of momentum (and beyond)

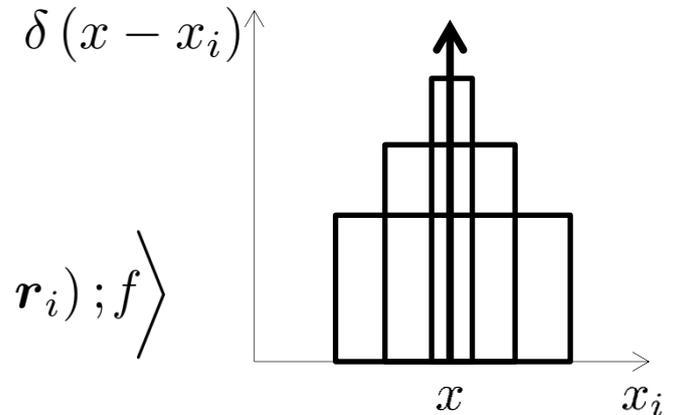
$$\frac{\partial}{\partial t} \rho \mathbf{u} = -\nabla \cdot [\rho \mathbf{u} \mathbf{u} + \mathbf{\Pi}]$$

# Selecting Functions

- **The Dirac delta selects molecules at a point**

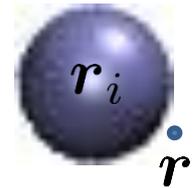
- Infinitely high, infinitely thin peak
- Equivalent to the continuum differential formulation at a point

$$\nabla \cdot \mathbf{A} \equiv \lim_{V \rightarrow 0} \frac{1}{V} \oint_S \mathbf{A} \cdot d\mathbf{S} \quad \rho(\mathbf{r}, t) = \sum_{i=1}^N \left\langle m_i \delta(\mathbf{r} - \mathbf{r}_i); f \right\rangle$$



- **In a molecular simulation  $r$  is never exactly equal to  $r_i$**

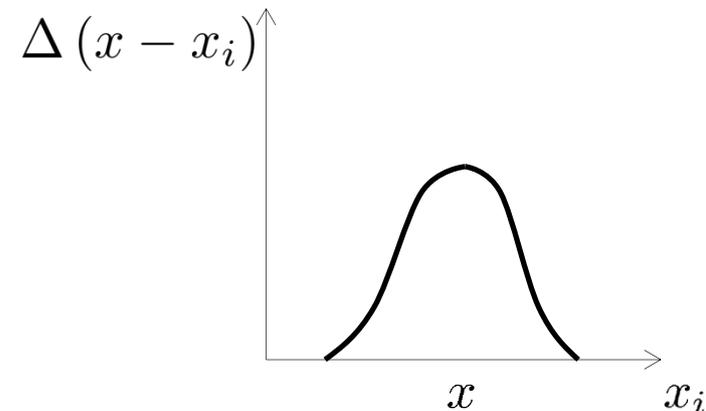
- Other difficulties with the Dirac delta function



- **Relaxed weighting functions**

- By Hardy(1981), Hoover (2009), Murdoch (2010) and others

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



# The Control Volume (CV)

- A finite volume with fluxes and forces acting over its surfaces

- Mass Conservation

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

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

- Momentum Balance (Newton's Law)

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

$$\frac{\partial}{\partial t} \int_V \rho \mathbf{u} dV = - \oint_S \rho \mathbf{u} \mathbf{u} \cdot d\mathbf{S} + \mathbf{F}_{\text{surface}}$$

- Energy Conservation

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

$$\frac{\partial}{\partial t} \int_V \rho \mathcal{E} dV = - \oint_S \rho \mathcal{E} \mathbf{u} \cdot d\mathbf{S} - \oint_S \mathbf{\Pi} \cdot \mathbf{u} \cdot d\mathbf{S} + \mathbf{q} \cdot d\mathbf{S}$$

# The Control Volume (CV)

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- Writing the molecular system in terms of control volumes

- Mass

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

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

- Momentum

$$\rho \mathbf{u} = \sum_{i=1}^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\int_V \rho \mathbf{u} dV = \sum_{i=1}^N \mathbf{p}_i \int_V \delta(\mathbf{r} - \mathbf{r}_i) dV$$

- Energy

$$\rho \mathcal{E} = \sum_{i=1}^N e_i \delta(\mathbf{r} - \mathbf{r}_i)$$

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

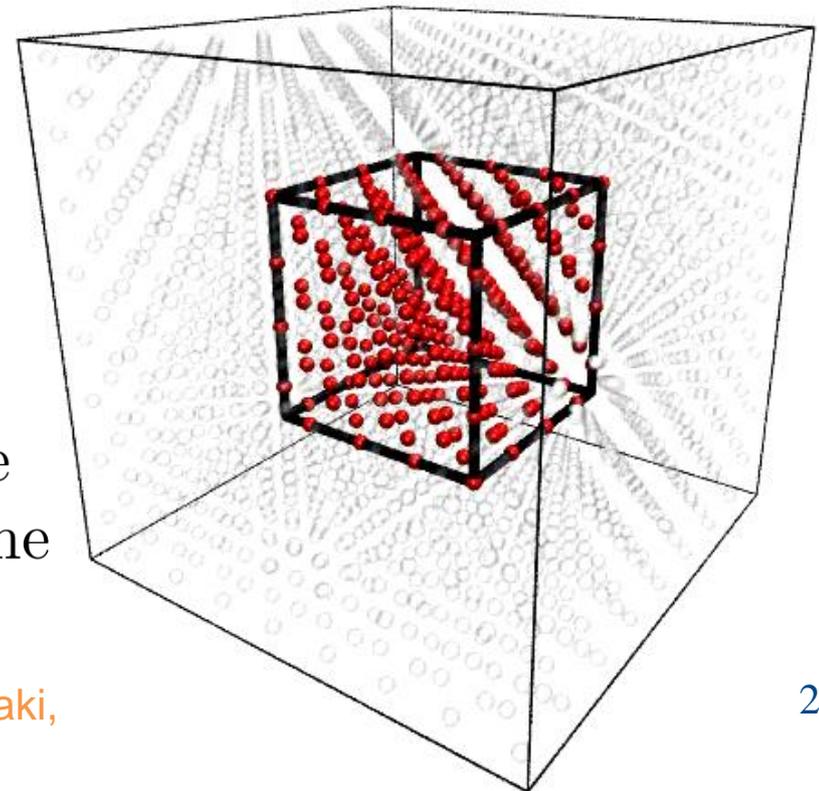
# Control Volume Function

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

$$\begin{aligned}\vartheta_i &\equiv \int_{x^-}^{x^+} \int_{y^-}^{y^+} \int_{z^-}^{z^+} \delta(x_i - x) \delta(y_i - y) \delta(z_i - z) dx dy dz \\ &= [H(x^+ - x_i) - H(x^- - x_i)] \\ &\quad \times [H(y^+ - y_i) - H(y^- - y_i)] \\ &\quad \times [H(z^+ - z_i) - H(z^- - z_i)]\end{aligned}$$

- Or in words

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



# Derivatives yields the Surface Fluxes

- Taking the Derivative of the CV function

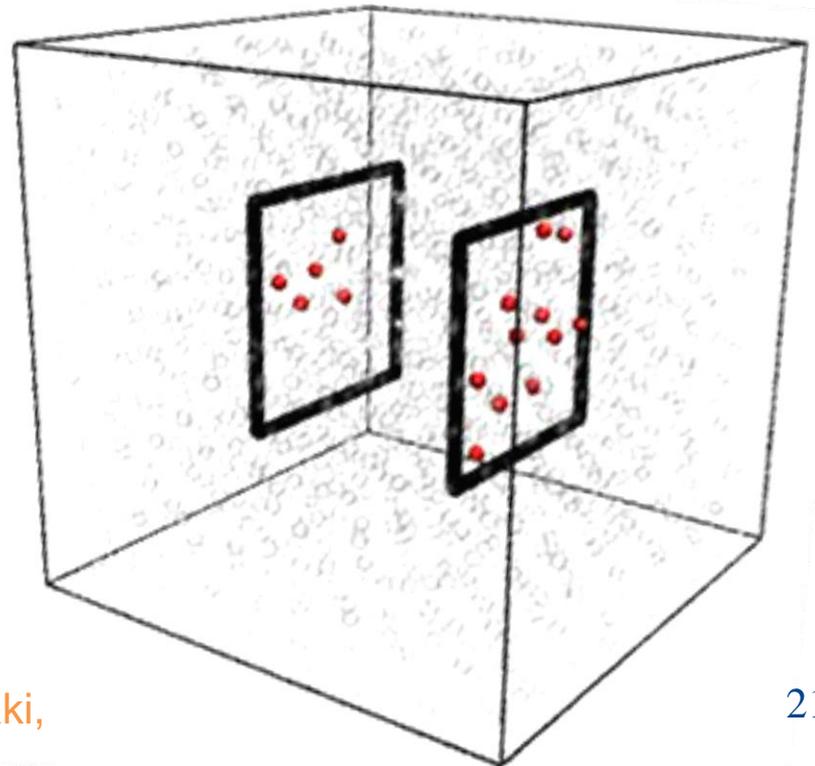
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = [\delta(x^+ - x_i) - \delta(x^- - x_i)] \\ \times [H(y^+ - y_i) - H(y^- - y_i)] \\ \times [H(z^+ - z_i) - H(z^- - z_i)]$$

- Vector form defines six surfaces

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

- Or in words

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



# Applying the Control Volume Function

- Molecular mass in a control volume can be defined

$$\frac{\partial}{\partial t} \int_V \rho dV = \frac{\partial}{\partial t} \sum_{i=1}^N \left\langle m_i \vartheta_i; f \right\rangle \qquad \frac{\partial}{\partial t} \int_V \rho dV = - \oint_S \rho \mathbf{u} \cdot d\mathbf{S}$$

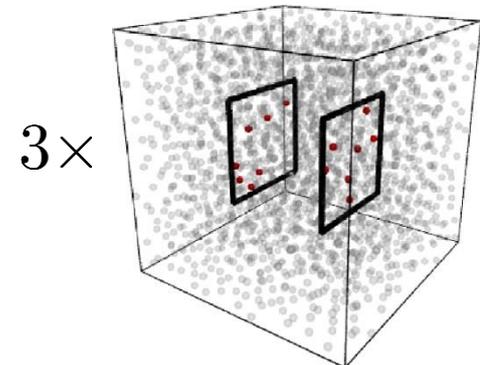
- Simple mathematical operations using the control volume function

$$\frac{\partial}{\partial t} \left\langle \alpha; f \right\rangle = \sum_{i=1}^N \left\langle \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial \alpha}{\partial \mathbf{r}_i} - \mathbf{F}_i \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i}; f \right\rangle \qquad \alpha = \sum_{i=1}^N m_i \vartheta_i$$

$$\frac{\partial}{\partial t} \sum_{i=1}^N \left\langle m_i \vartheta_i; f \right\rangle = \sum_{i=1}^N \left\langle \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial m_i \vartheta_i}{\partial \mathbf{r}_i} - \mathbf{F}_i \cdot \frac{\partial m_i \vartheta_i}{\partial \mathbf{p}_i}; f \right\rangle$$

$$= \sum_{i=1}^N \left\langle \mathbf{p}_i \cdot \frac{\partial \vartheta_i}{\partial \mathbf{r}_i}; f \right\rangle$$

$$= - \sum_{i=1}^N \left\langle \mathbf{p}_i \cdot d\mathbf{S}_i; f \right\rangle$$



# Reynolds' Transport Theorem

- Mass, momentum and energy equations

- Mass Conservation

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

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

- Momentum Balance

$$\begin{aligned} \frac{d}{dt} \sum_{i=1}^N m_i \mathbf{v}_i \vartheta_i &= - \sum_{i=1}^N m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i \\ &\quad + \frac{1}{2} \sum_{i,j}^N \mathbf{f}_{ij} \vartheta_{ij} \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t} \int_V \rho \mathbf{u} dV &= - \oint_S \rho \mathbf{u} \mathbf{u} \cdot d\mathbf{S} \\ &\quad + \mathbf{F}_{\text{surface}} \end{aligned}$$

- Energy Conservation

$$\begin{aligned} \frac{d}{dt} \sum_{i=1}^N e_i \vartheta_i &= - \sum_{i=1}^N e_i \mathbf{v}_i \cdot d\mathbf{S}_i \\ &\quad + \frac{1}{2} \sum_{i=1}^N \sum_{i \neq j}^N \frac{\mathbf{p}_i}{m_i} \cdot \mathbf{f}_{ij} \vartheta_{ij} \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t} \int_V \rho \mathcal{E} dV &= - \oint_S \rho \mathcal{E} \mathbf{u} \cdot d\mathbf{S} \\ &\quad - \oint_S \mathbf{\Pi} \cdot \mathbf{u} \cdot d\mathbf{S} + \mathbf{q} \cdot d\mathbf{S} \end{aligned}$$

# Reynolds' Transport Theorem

- Mass, momentum and energy equations

- Mass Conservation

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

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

- Momentum Balance

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

$$\begin{aligned} \frac{\partial}{\partial t} \int_V \rho \mathbf{u} dV &= - \oint_S \rho \mathbf{u} \mathbf{u} \cdot d\mathbf{S} \\ &+ \mathbf{F}_{\text{surface}} \end{aligned}$$

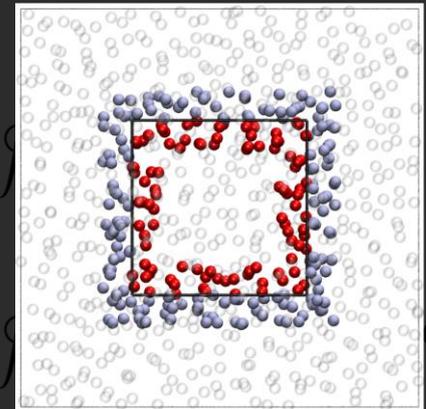
- The difference between two control volume functions for i and j

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

$$\vartheta_{ij} \equiv \vartheta_i - \vartheta_j$$

$$+ \frac{1}{2} \sum_{i=1}^N \sum_{i \neq j} \frac{\mathbf{p}_i}{m_i} \cdot \mathbf{f}_{ij} \vartheta_{ij}$$

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

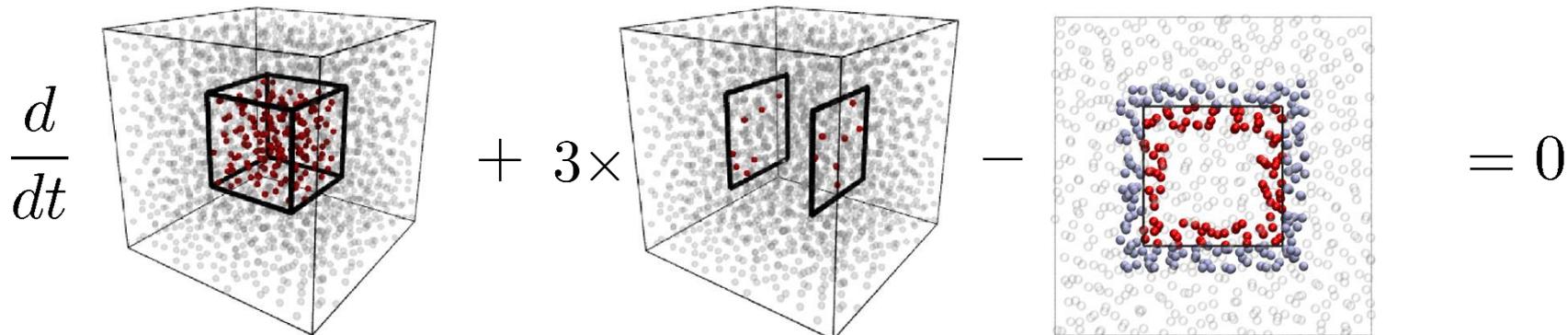


- This is the IK operator for a CV

# Testing Momentum Balance

## • Momentum Balance

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



# The Pressure Tensor

- Continuum Control Volume equations in terms of the pressure tensor

$$\frac{\partial}{\partial t} \int_V \rho u dV = - \oint_S \rho u u \cdot d\mathbf{S} + \mathbf{F}_{\text{surface}} \begin{cases} \rightarrow -\frac{\partial}{\partial \mathbf{r}} \cdot \int_V \boldsymbol{\Pi} dV \\ \rightarrow - \oint_S \boldsymbol{\Pi} \cdot d\mathbf{S} \end{cases}$$

- Molecular Control Volume equations in terms of the pressure tensor

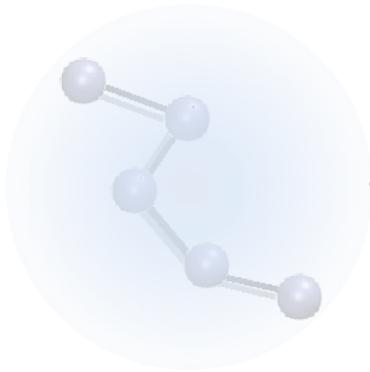
Volume Average

(Lutsko 1988 & Cormier et al 2001)

$$\frac{d}{dt} \sum_{i=1}^N m_i \mathbf{v}_i \vartheta_i = - \sum_{i=1}^N m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2} \sum_{i,j}^N \mathbf{f}_{ij} \vartheta_{ij} \begin{cases} \rightarrow -\frac{\partial}{\partial \mathbf{r}} \cdot \frac{1}{2} \sum_{i,j}^N \mathbf{f}_{ij} \mathbf{r}_{ij} \int_0^1 \vartheta_s ds \\ \rightarrow -\frac{1}{4} \sum_{i,j}^N \boldsymbol{\varsigma}_{ij} \cdot d\mathbf{S}_{ij} \end{cases}$$

# Coupling Using the Control Volume

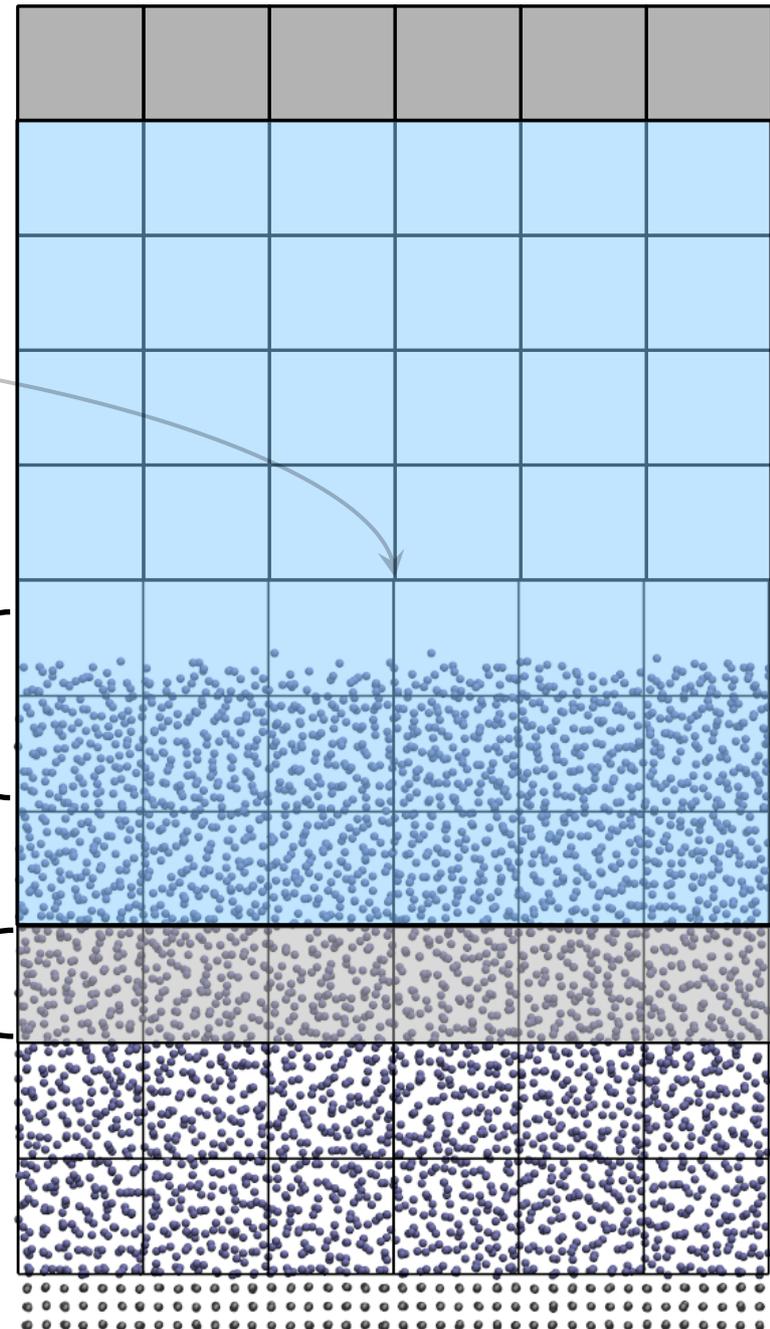
Insertion of molecules



Consistent Framework ✓

CFD → MD  
Boundary  
condition

MD → CFD  
Boundary  
condition



# Coupling Using the Control Volume

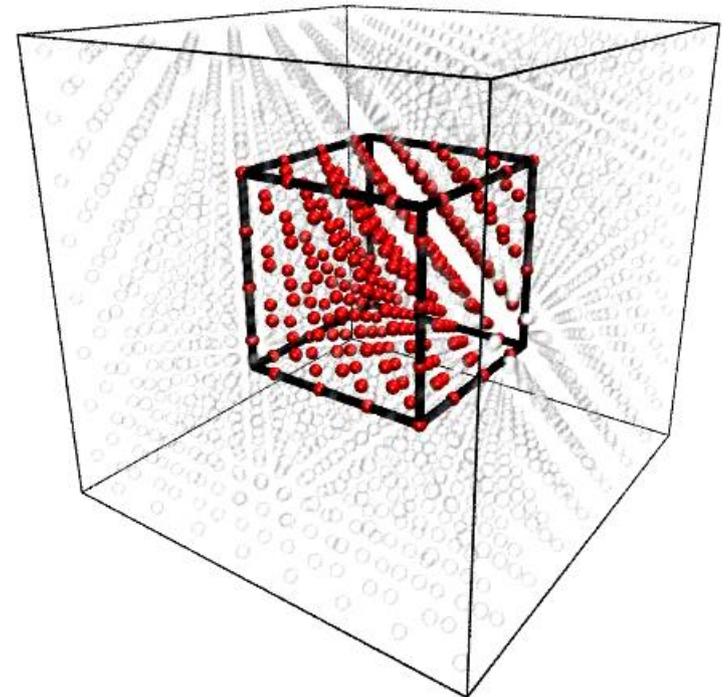
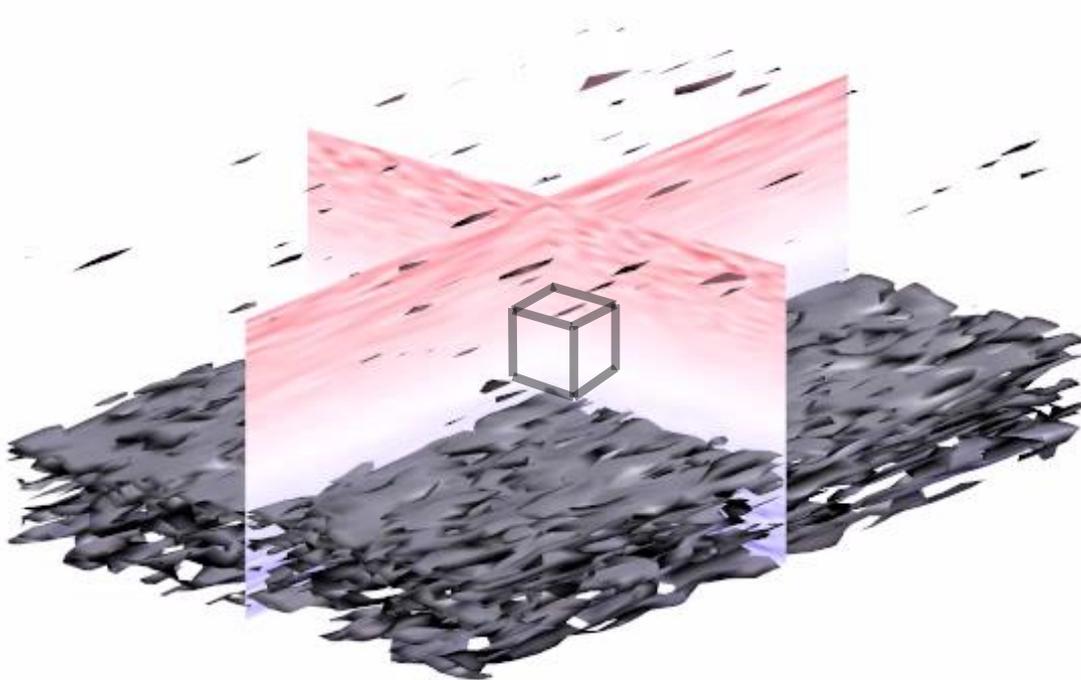
- We now have an equivalent description in both regions
  - Momentum or stresses inside an arbitrary control volume in both domains

$$\int_V \rho u dV = \sum_{i=1}^N m_i \dot{\mathbf{r}}_i \vartheta_i$$

$$\oint_S \boldsymbol{\Pi} \cdot d\mathbf{S} = \frac{1}{4} \sum_{i,j} \boldsymbol{\varsigma}_{ij} \cdot d\mathbf{S}_{ij}$$

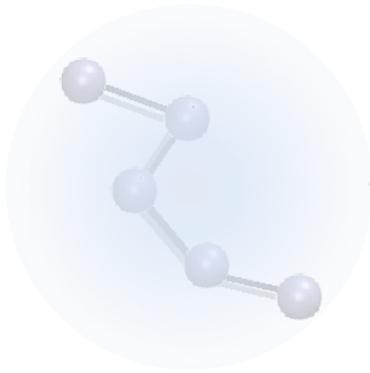
**State Coupling** : O'Connell & Thompson (1995), Nie, Chen, E & Robbins (2004)

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



# Coupling Using the Control Volume

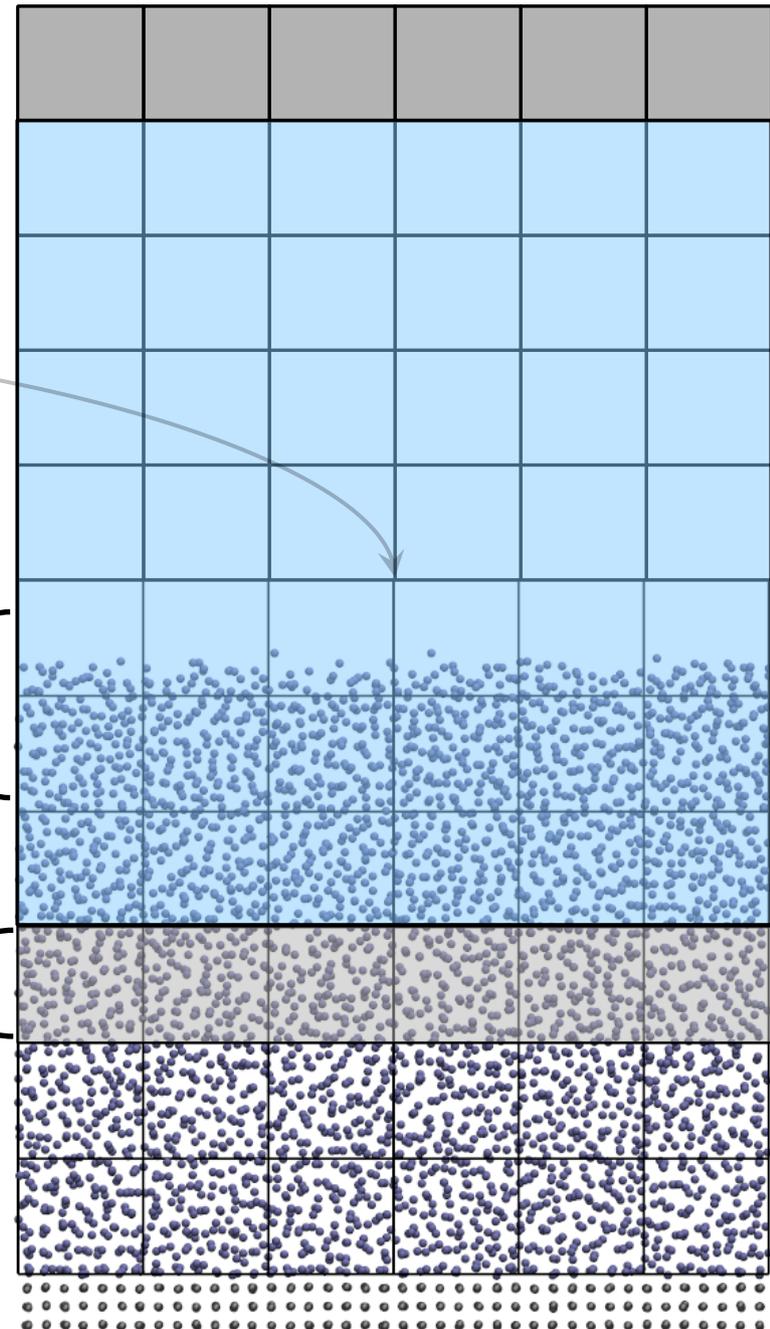
Insertion of molecules



Consistent Framework ✓

**CFD→MD**  
Boundary  
condition

**MD→CFD**  
Boundary  
condition ✓



$$\int_V \rho u dV = \sum_{i=1}^N m_i \dot{\mathbf{r}}_i \vartheta_i$$

# Constrained Control Volume

---

- **Non-unique solution**

- Continuum field properties must specify N molecules

- **Hamilton's principle (subject to a constraint)**

- As close as possible to the true trajectory
- Used in the first fluids coupling scheme (O'Connell and Thompson 1995)

$$\delta A_c = \delta \int_a^b (\mathcal{L} + \boldsymbol{\lambda} \cdot \boldsymbol{g}) dt = 0$$

- **But now we want to apply a constraint localised using the control volume function**

- CV function takes care of the localisation for us

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

# Principle of least action

---

- **The Euler-Lagrange equation is applicable**

- As the constraint is semi-holonomic (Flannery 2004,2011)

$$\frac{d}{dt} \frac{\partial \mathcal{L}_c}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}_c}{\partial q_i} = 0 \qquad \mathcal{L}_c = \mathcal{L} + \lambda \cdot g$$

- **Written in terms of canonical momentum and its time derivative**

$$p_i = \frac{\partial \mathcal{L}_c}{\partial \dot{q}_i}$$

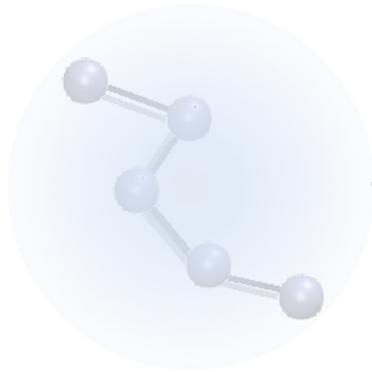
$$\dot{p}_i = \frac{\partial \mathcal{L}_c}{\partial q_i}$$

- **To give equations of motions**

- Applying the MD boundary condition based on Hamilton's principle
- Localised to a region in space (courtesy of the CV function)
- No energy added to the system when applied correctly (i.e. with the CV function)

# Coupling Using the Control Volume

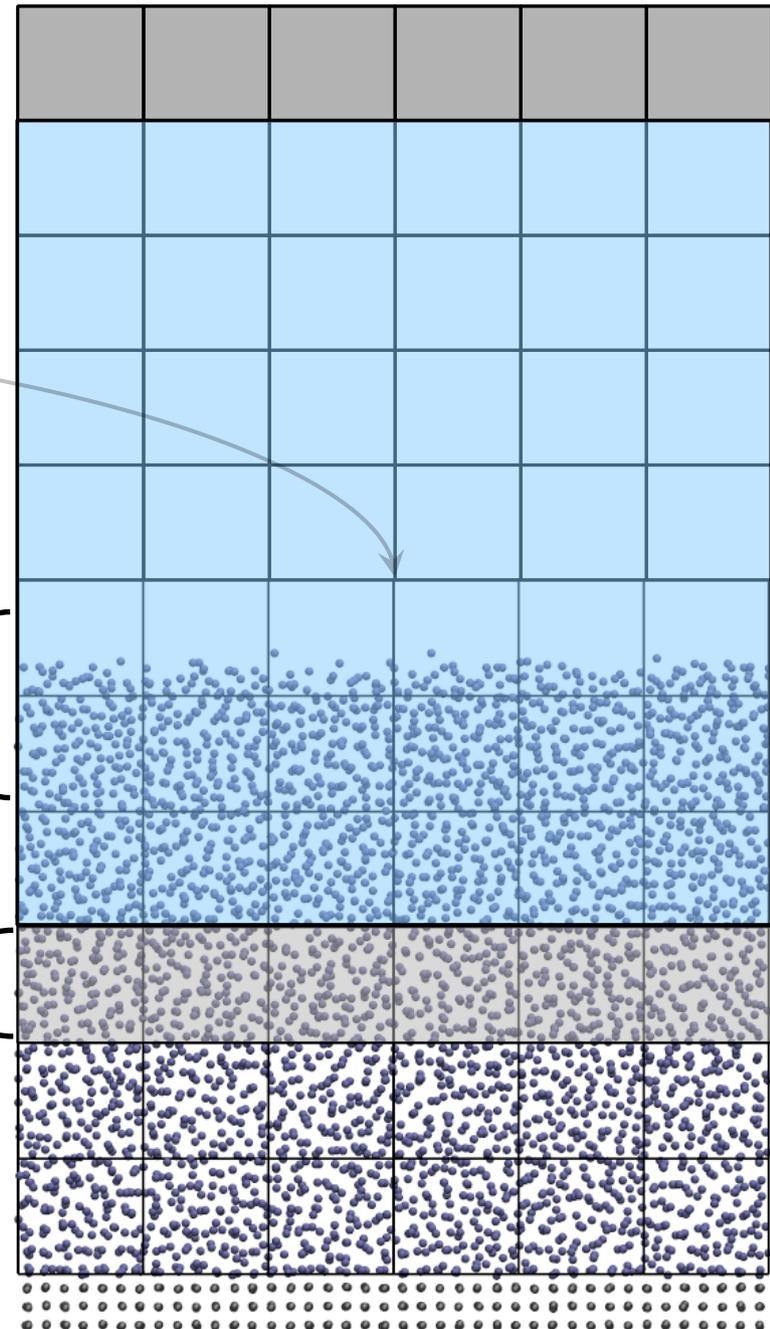
Insertion of molecules



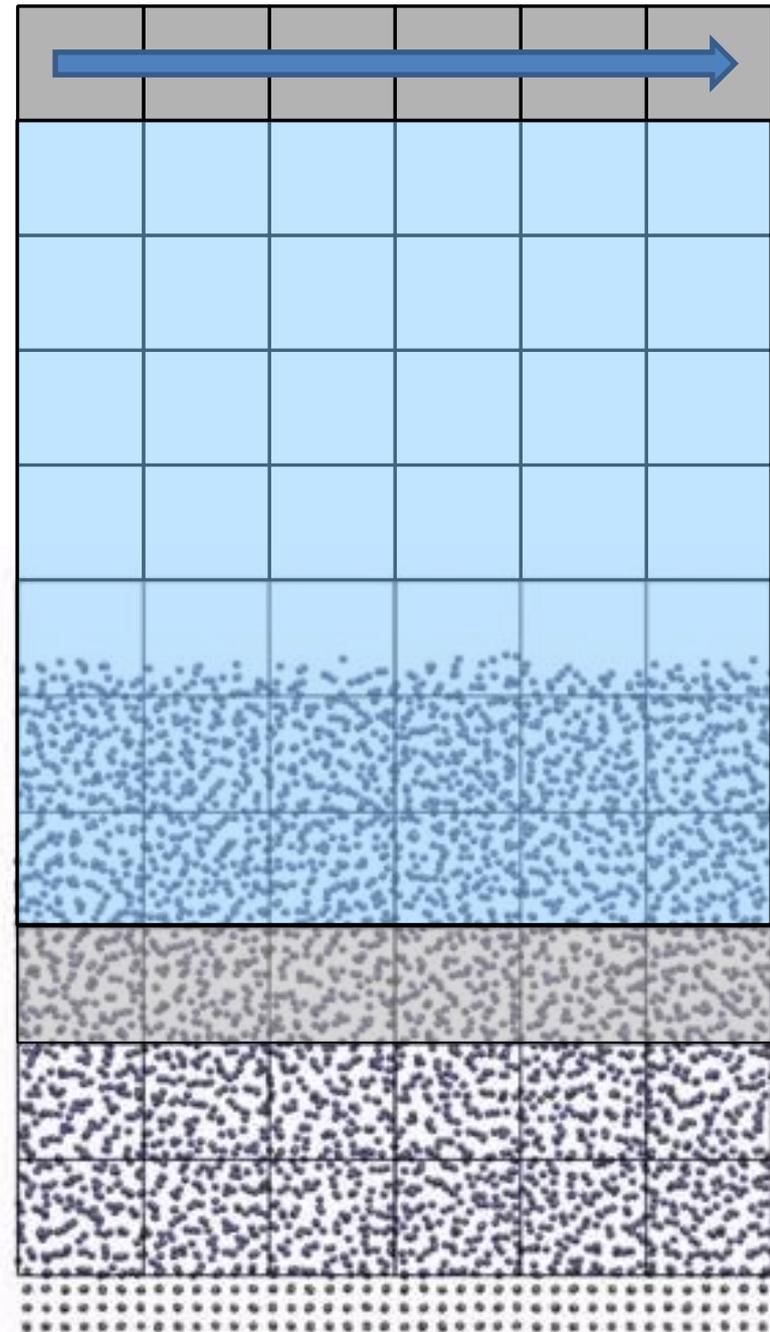
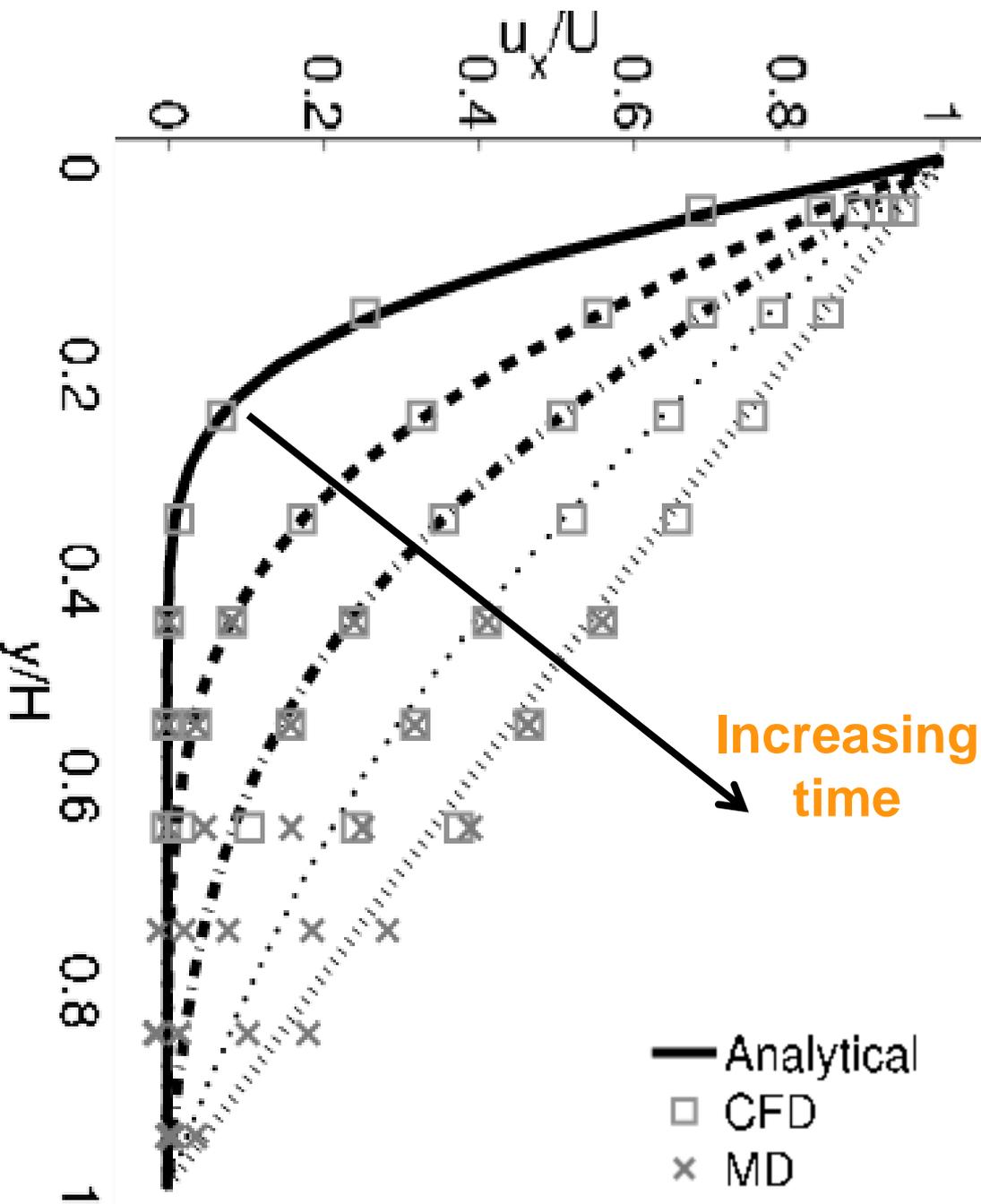
Consistent Framework ✓

CFD → MD  
Boundary condition ✓

MD → CFD  
Boundary condition ✓



# Coupling Results

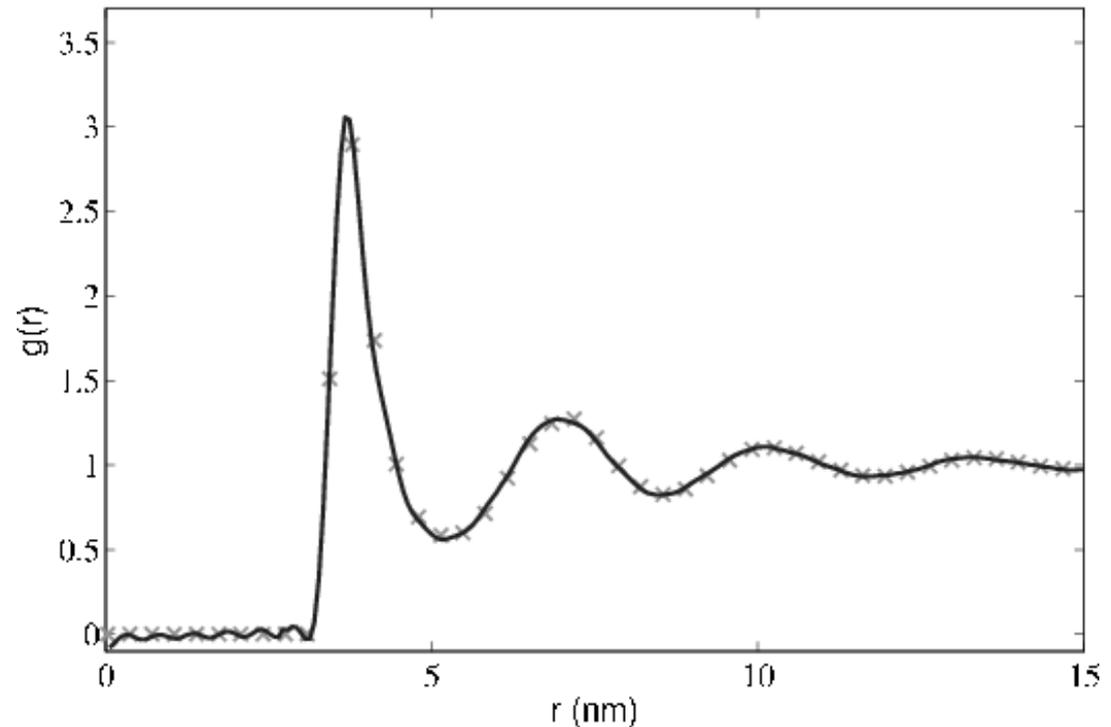
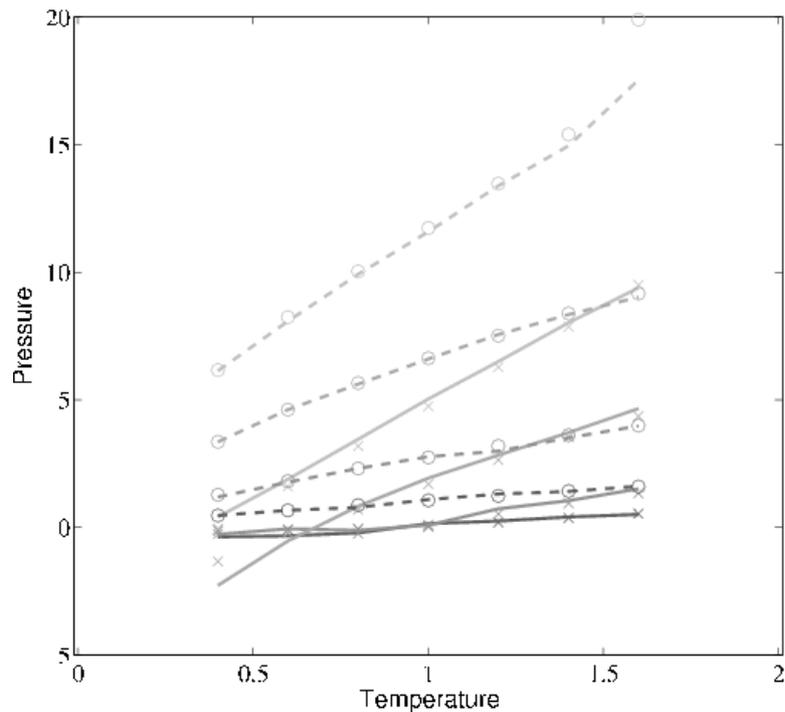


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# Computing Developments

# Molecular Dynamics Solver

- **New parallel molecular dynamics (MD) code**
  - Fortran 90 (including 'modern' 2003 features and python wrappers)
  - Optimised for non-equilibrium molecular dynamics and linking to CFD
- **A range of verification tests using experimental data and literature benchmarks**
  - Phase diagrams
  - Radial Distribution Function (related to the scattering function)



# MD Computing – Serial optimisations

- **All pairs simulation uses local cell/neighbour lists**

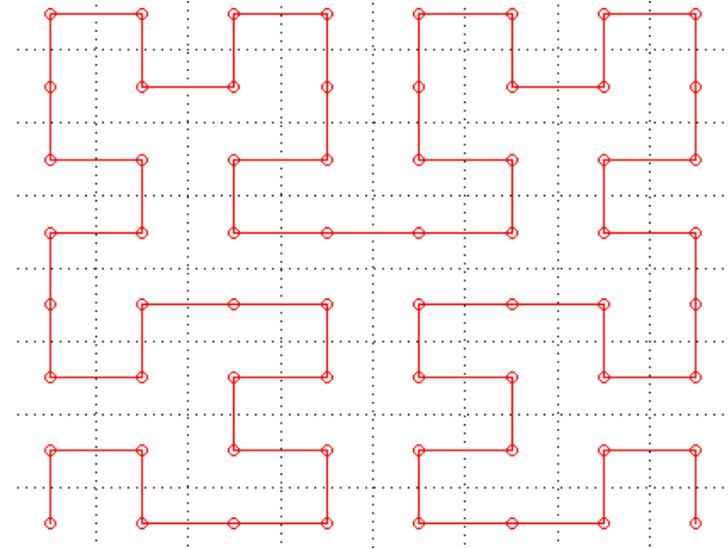
- $N^2$  calculation reduced to order  $N$
- Linked lists are used in order to manipulate data
- Result in non-contiguous data access

- **Hilbert curve sorting improves cache efficiency of operations**

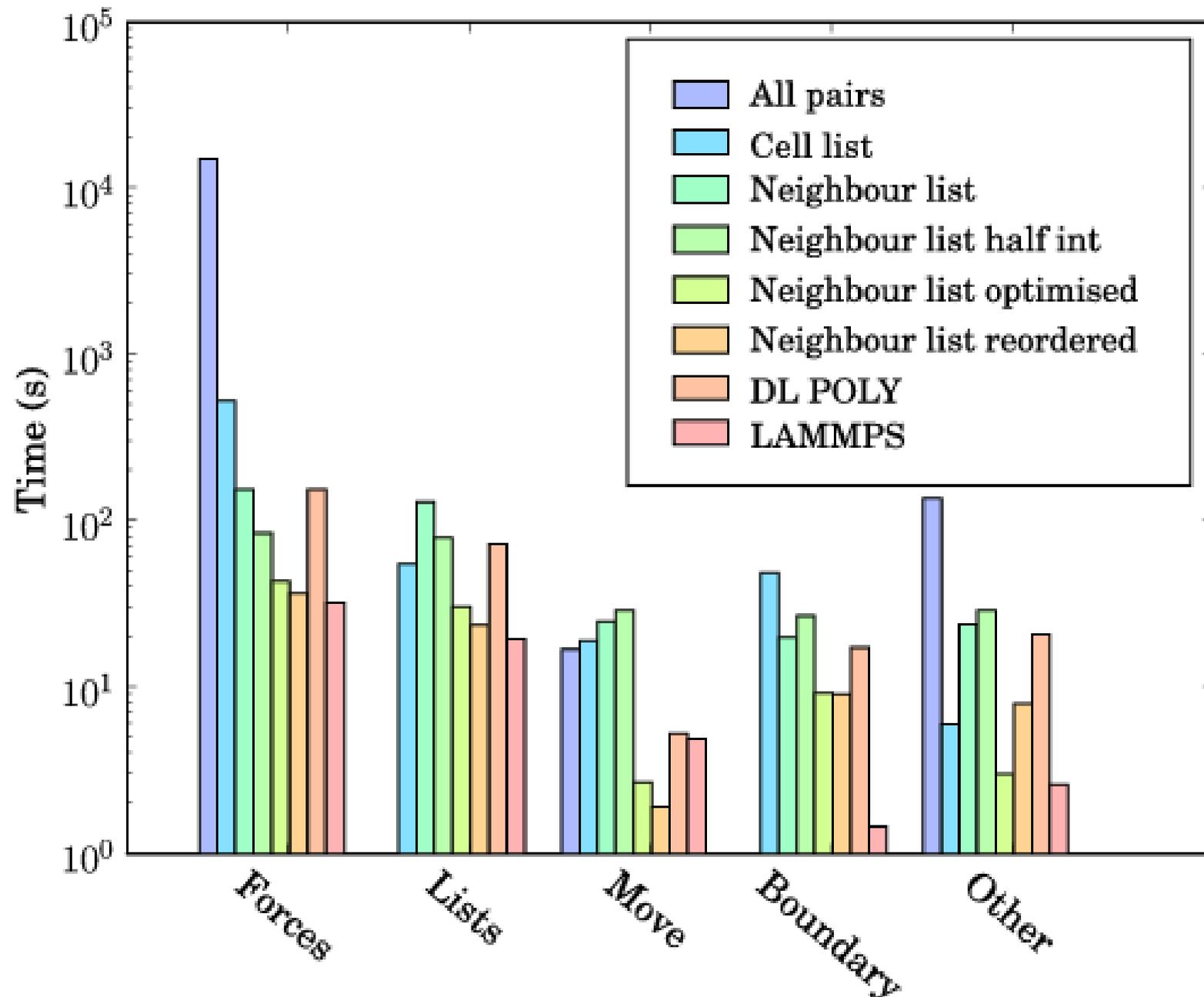
- Improvement becomes greater on larger systems
- Some tuning required

- **Heaviside function implemented in assembly language**

- `cmplesd xmm1,xmm0`      `#Check input less than 0.0; true=zeros, false=ones`
- `movsd xmm0,xmm2`      `#Save 1.0 into xmm0`
- `andpd xmm0,xmm1`      `#AND 1.0 with all zeros/ones`

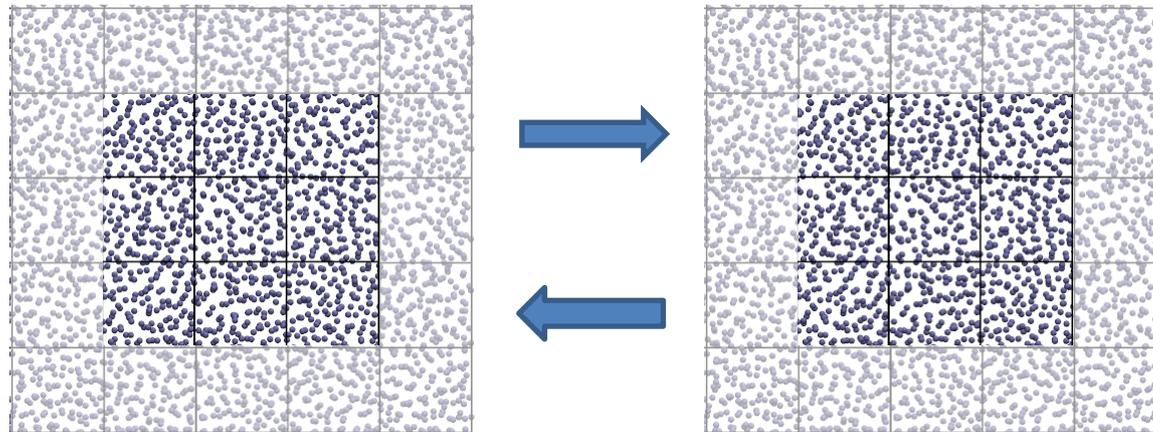


# MD Computing – Serial optimisations



# MD Computing – Parallel optimisations

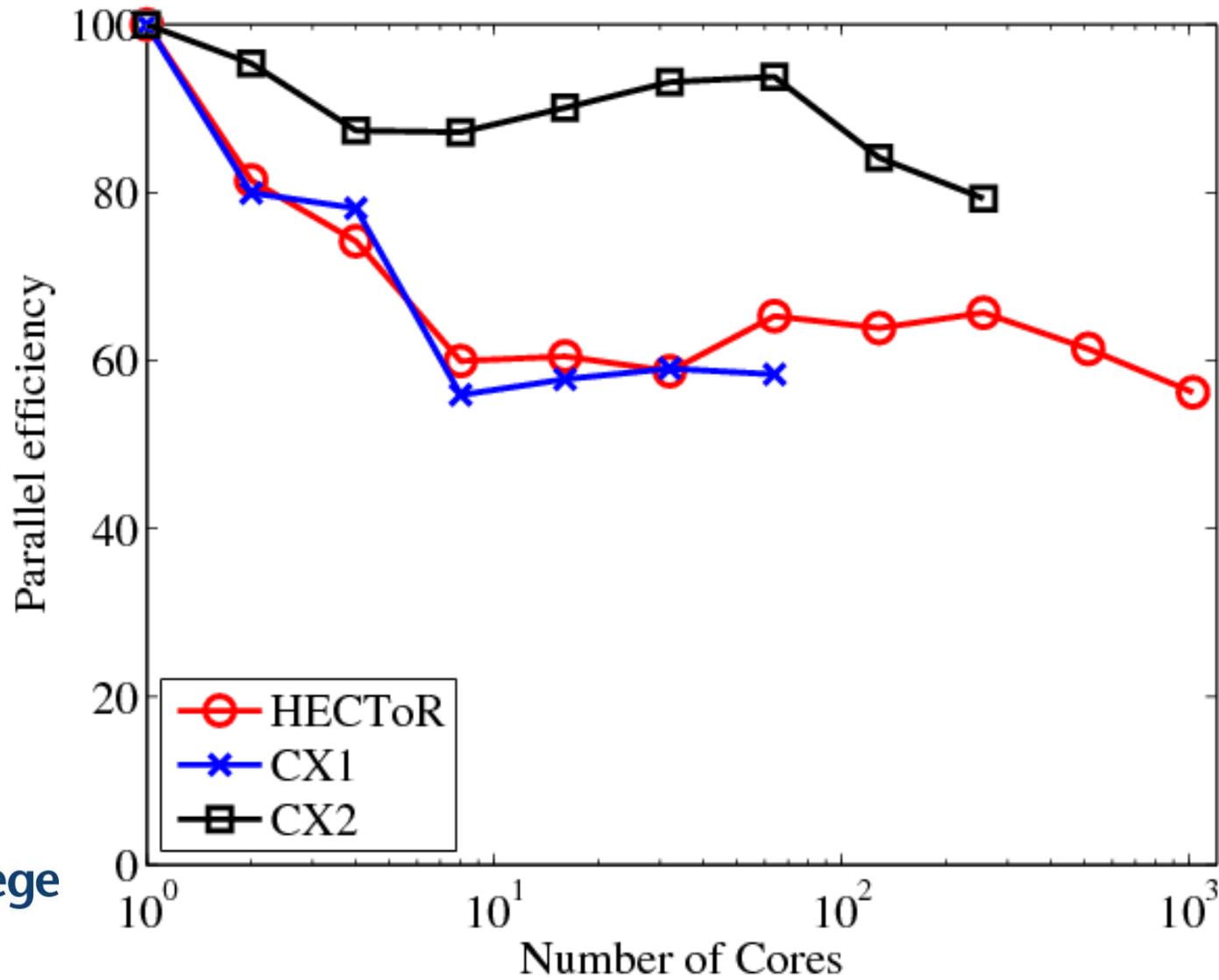
- **Localisations lends itself to parallel computing using MPI**
  - Spatial decomposition employed
  - Halo cells (ghost molecules) are used to link adjacent regions



- **Halo exchange of variable amounts of data**
  - MPI\_Send, MPI\_Probe and MPI\_Recv employed
- **CUDA implementation developed but found to be too inflexible to justify the speedup (especially in parallel)**
  - 30x speedup reported if entire code on GPU (Anderson et al 2008)
  - Speedup negated by transfer, multi-GPU implementation challenging

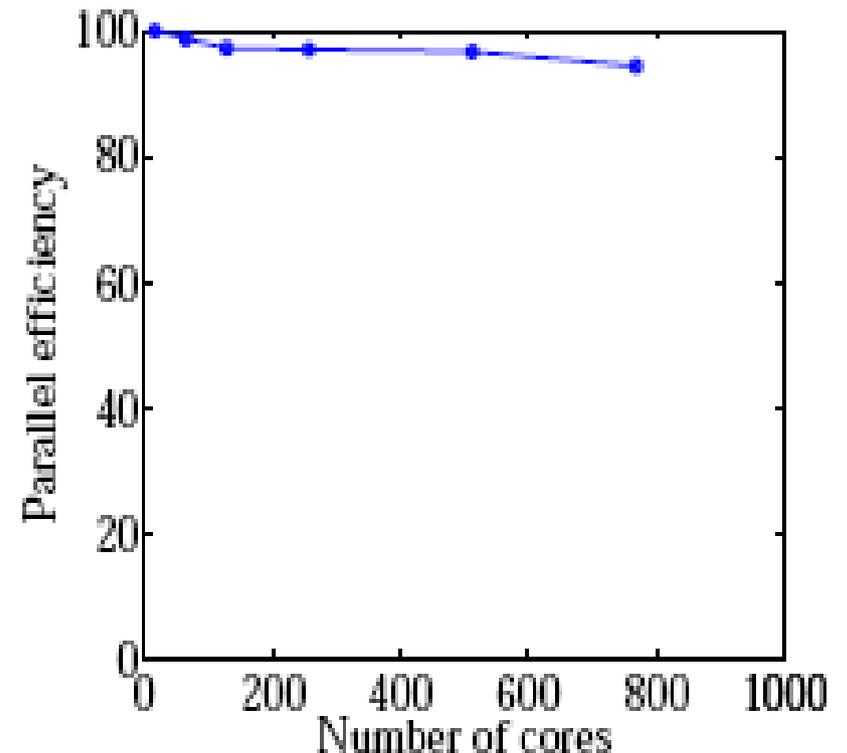
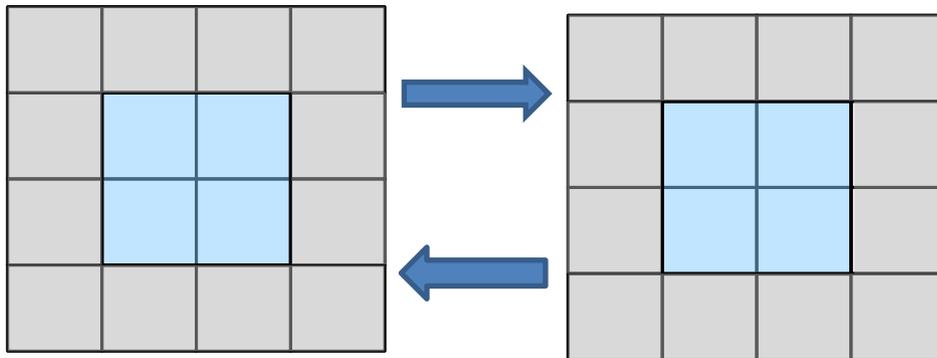
# MD Computing – Parallel optimisations

- Strong scaling vs 1 core with 3,322,336 molecules
  - On HECToR and Imperial's supercomputers CX1/CX2
  - Efficiency of 90% when comparing 1024 cores to 8 cores



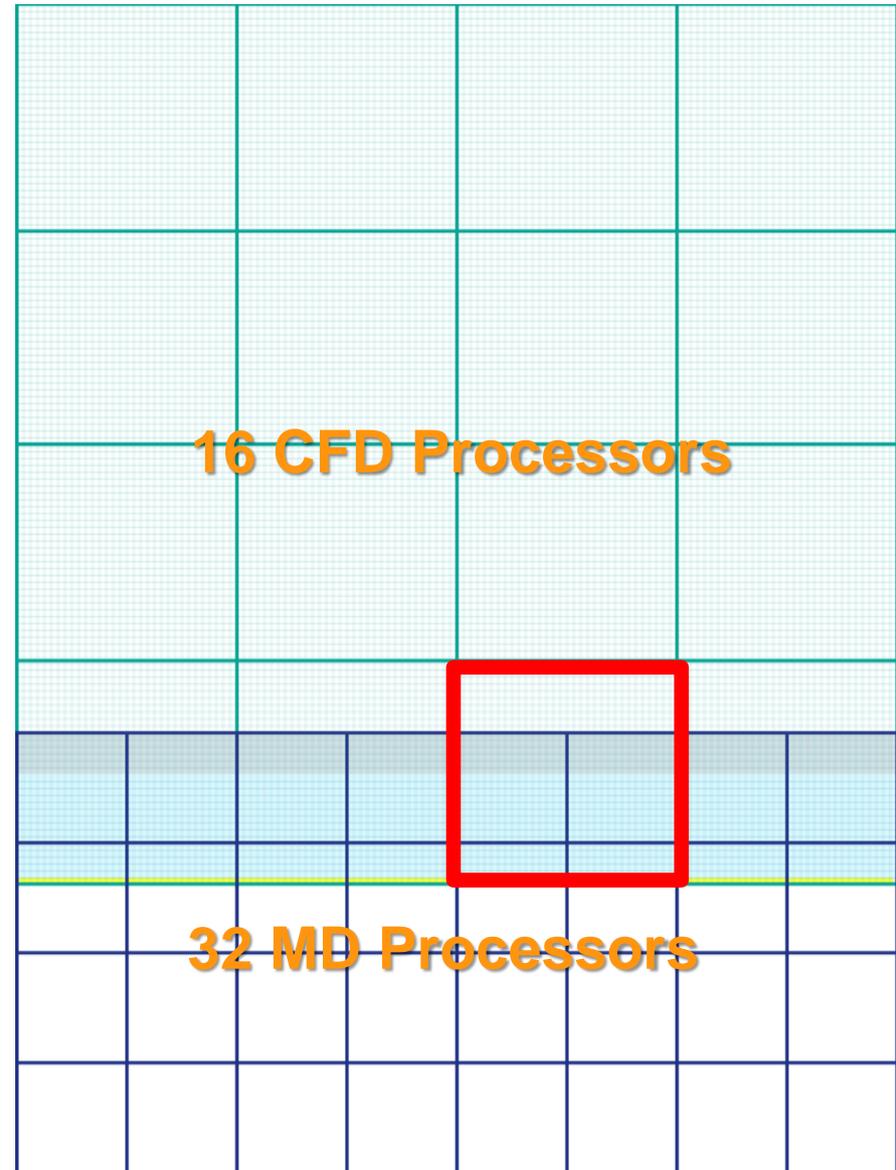
# Computational Fluid Dynamics

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



# 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`**

# CPL\_LIBRARY Key Routines

---

- **Setup**

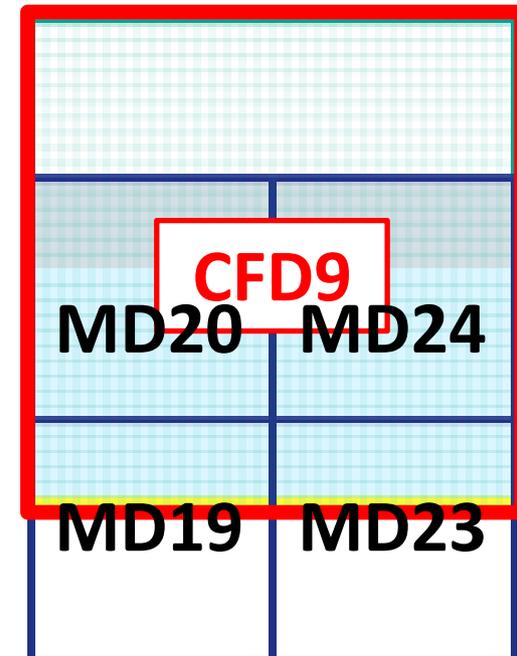
- `CPL_create_comm` – Split intra-comms and create inter-comms
- `CPL_CFD_init` / `CPL_MD_init` – Define mapping between domains. Every processor stores a copy of all mappings, communicators and both solvers processor topology

- **Exchange**

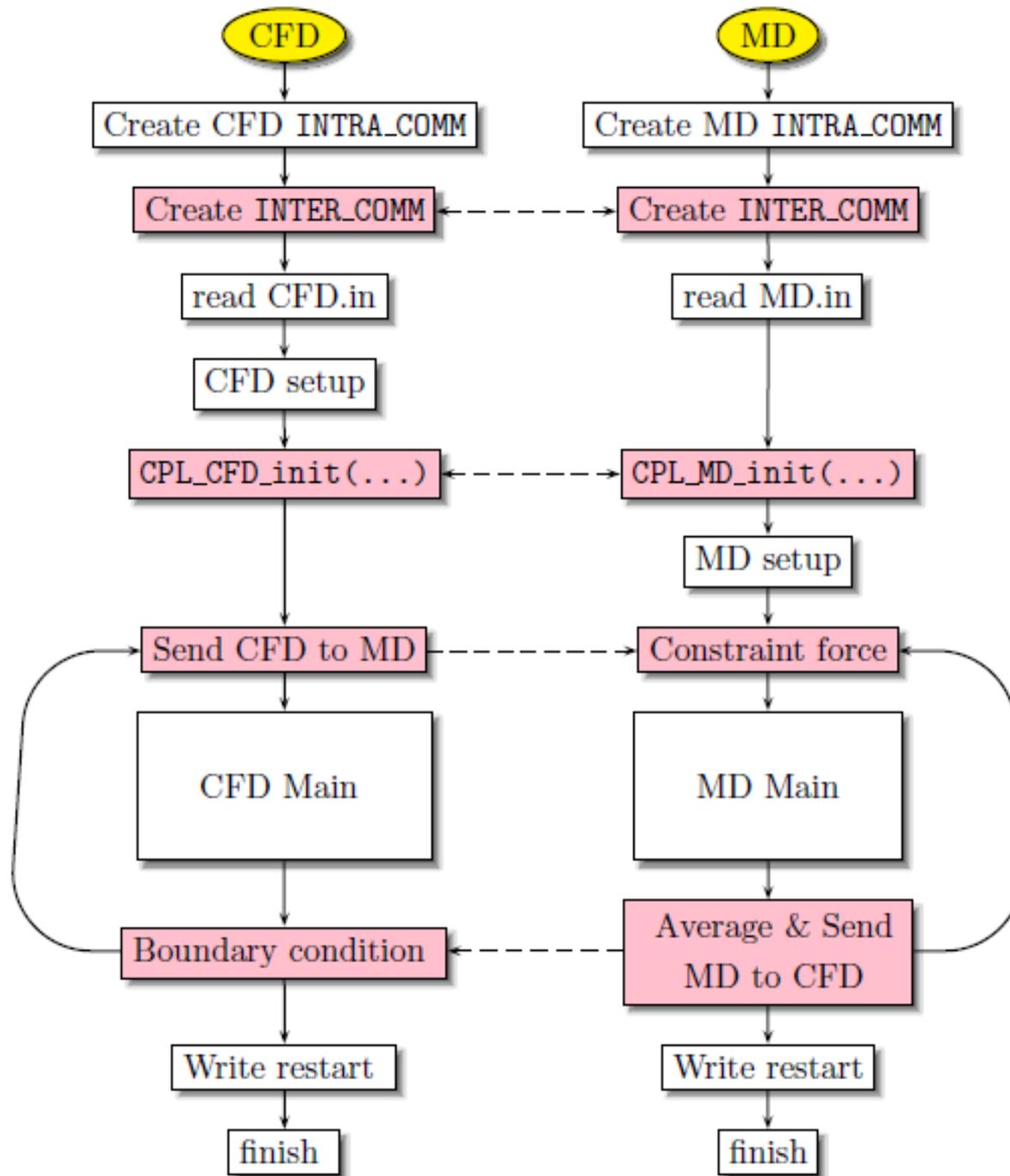
- `CPL_send` / `CPL_recv` – Send and receive data between overlapping processors on the coupling interface
- `CPL_gather` / `CPL_scatter` – Gather/scatter operations implemented efficiently on dedicated communicators linking coupled processors

- **Enquiry**

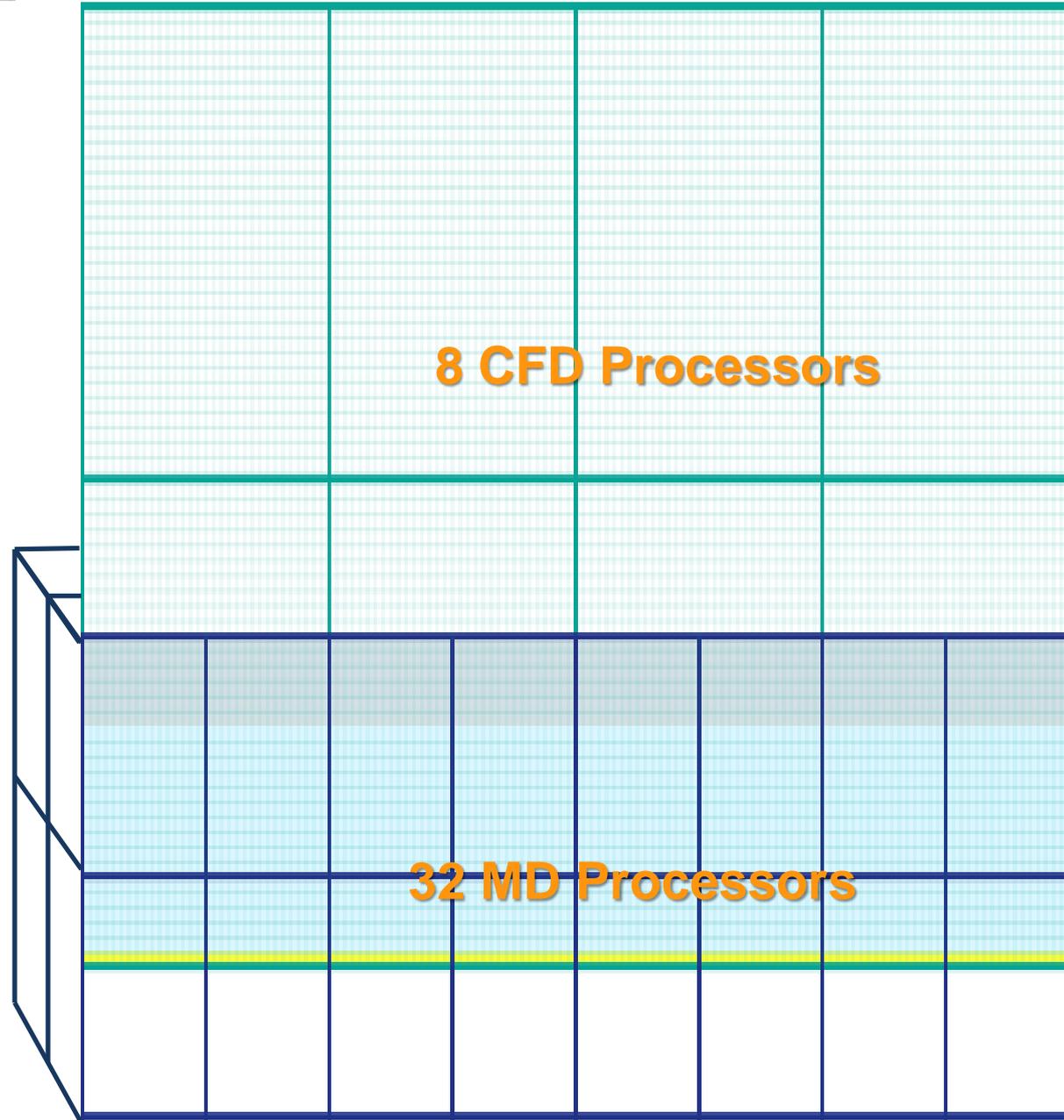
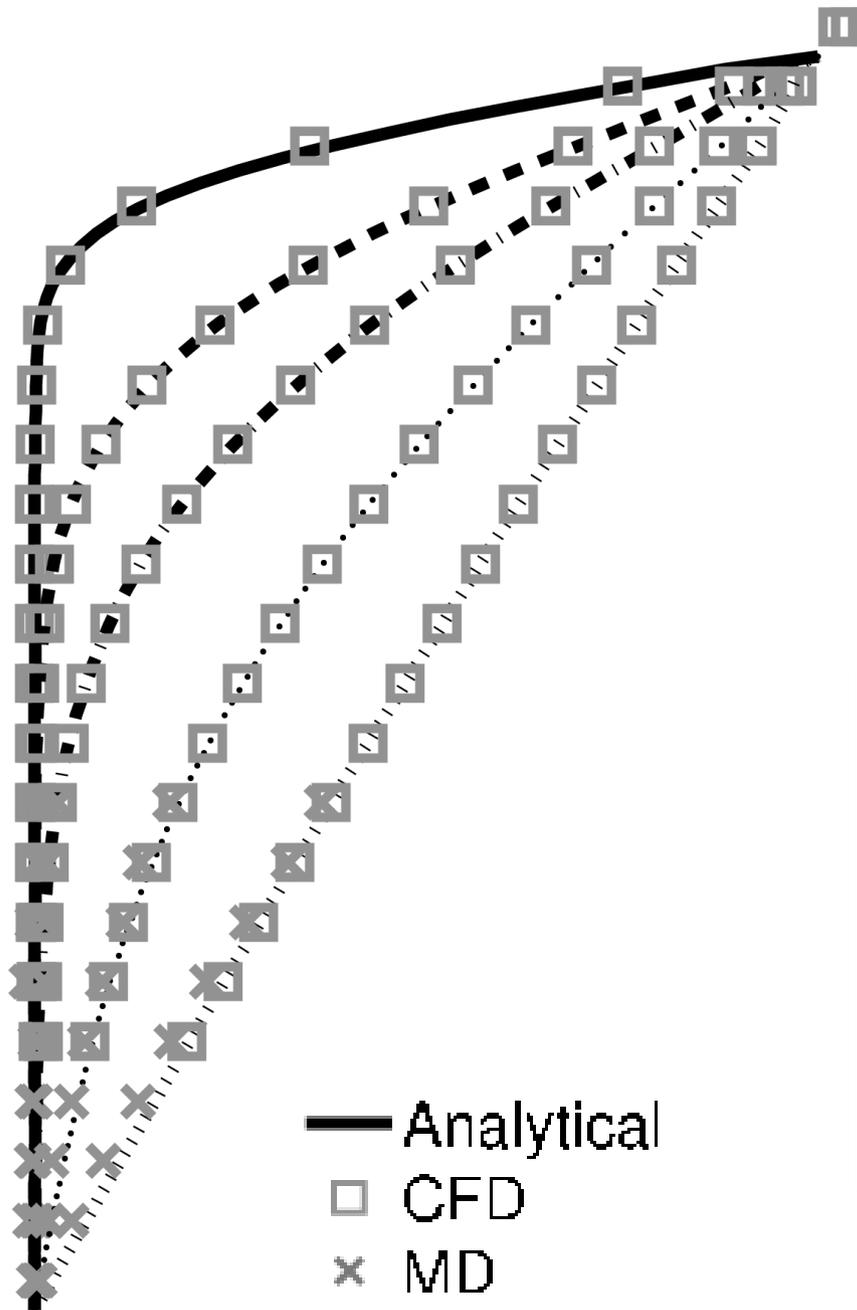
- `CPL_get` – Return copies of protected library internal data
- `CPL_cart_coord` – Coordinate of any processor on either solver
- `CPL_COMM_rank` – Rank of processor in specified communicator
- `CPL_extents` – extents of cells on current processor



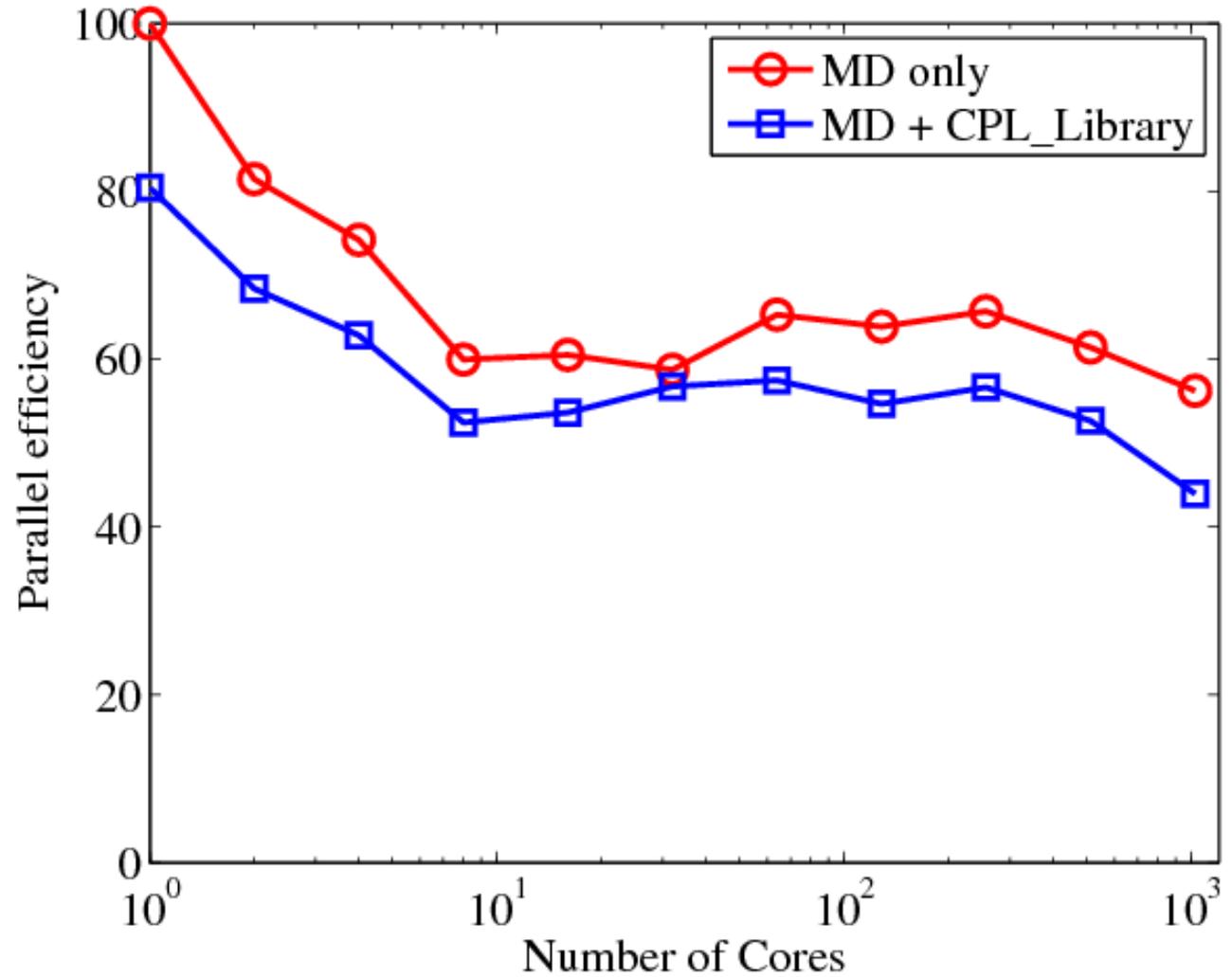
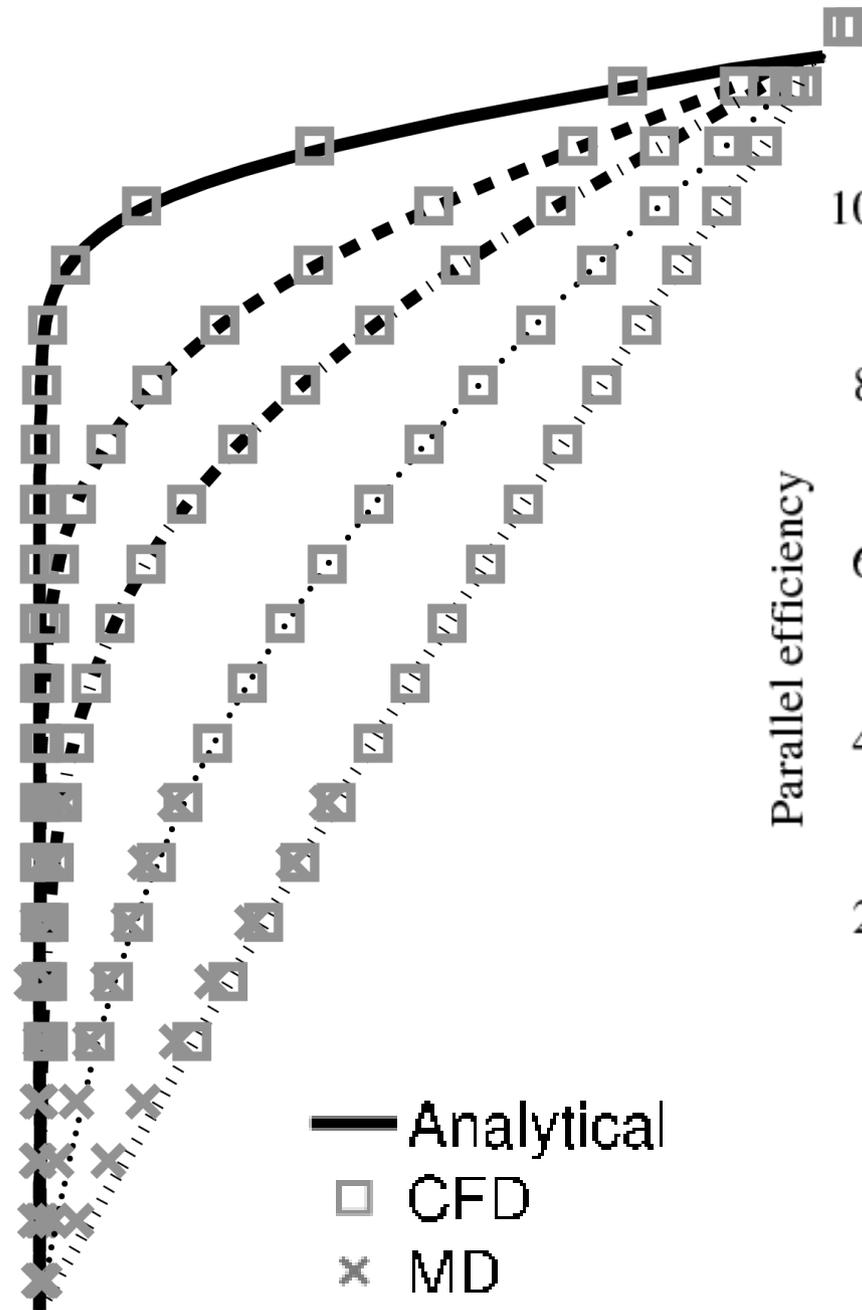
# CPL\_LIBRARY Schematic



# CPL\_Library results



# CPL\_Library results



# Conclusions

---

- **Multi-scale coupling is essential for modern engineering**
  - Implementation of molecular dynamics (and quantum mechanics) where essential and a continuum model to extend to engineering scales
- **Consistent framework for coupling fluid descriptions**
  - Control volume (CV) function expresses continuum and discrete systems in an equivalent formulation (rigours backing to existing coupling)
  - Hamilton's principle, with the CV function, provides a constraint which ensures the descriptions in both domains agree
  - Verified using test cases with known analytical solutions
- **Computational developments**
  - Extensive serial and parallel optimisations applied to the molecular dynamics solver
  - CPL\_library is an open source library to facilitates the exchange of data between two coupled codes (<https://code.google.com/p/cpl-library/>)
  - Verified with test cases on a range of processor topologies

# References

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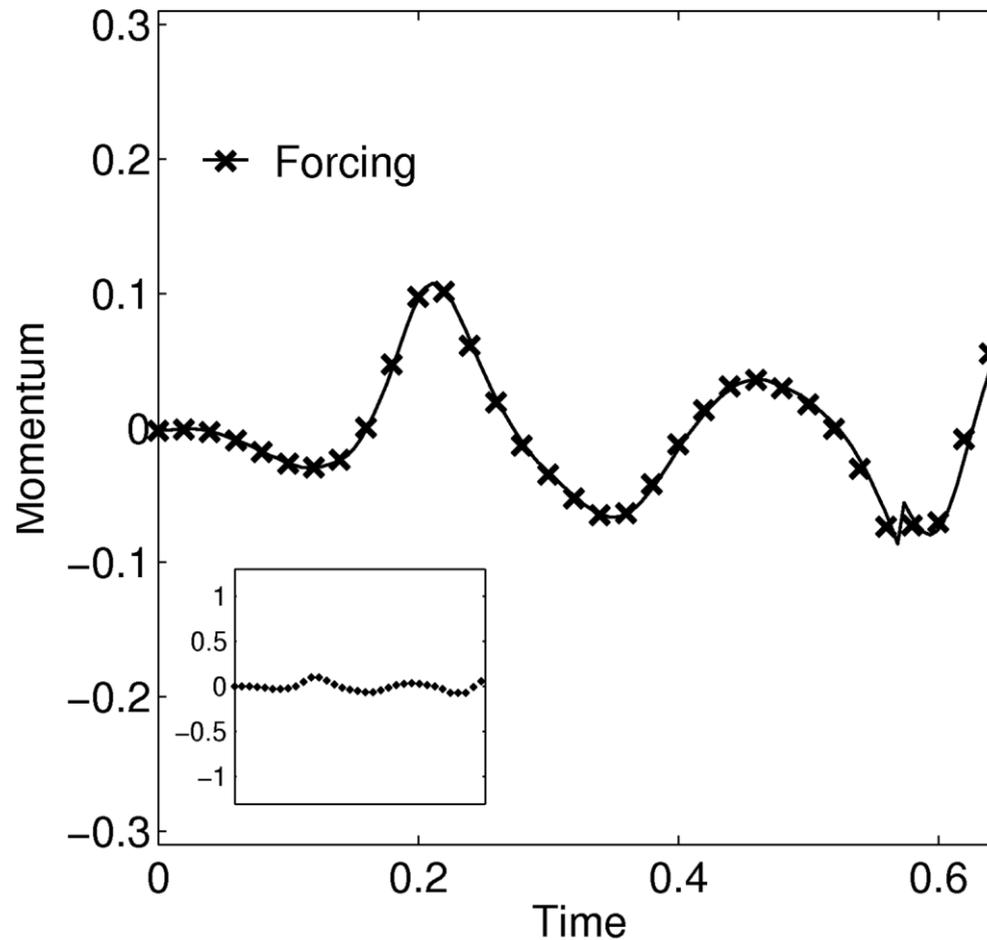
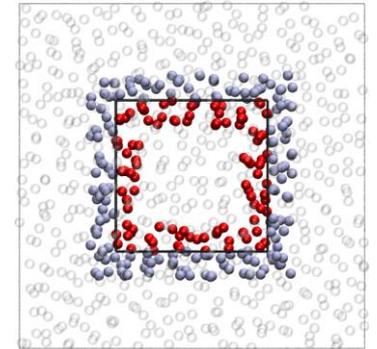
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# Extra Material

# Testing Momentum Balance

- Momentum Balance

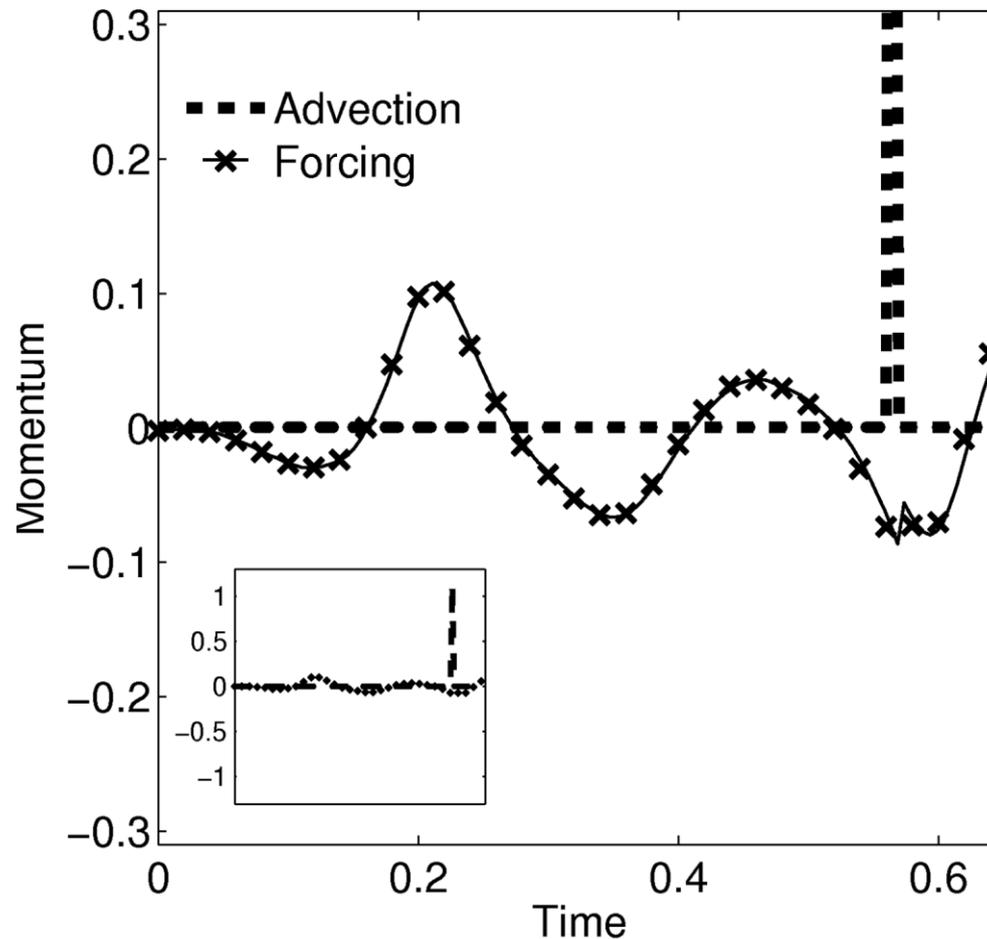
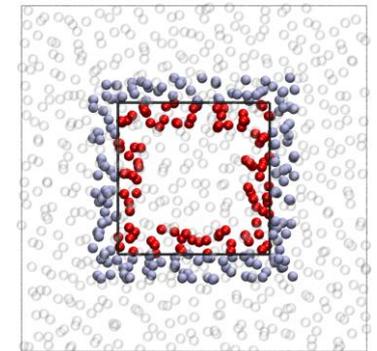
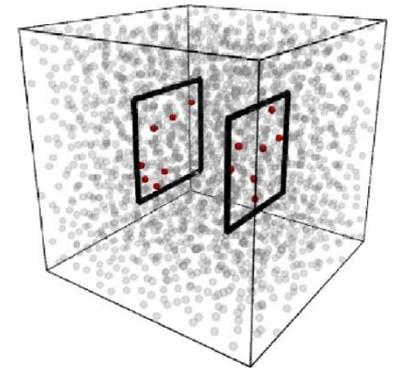
$$\underbrace{\sum_{i=1}^N \sum_{j \neq i}^N \mathbf{f}_{ij} \vartheta_{ij}}_{\text{Forcing}}$$



# Testing Momentum Balance

## • Momentum Balance

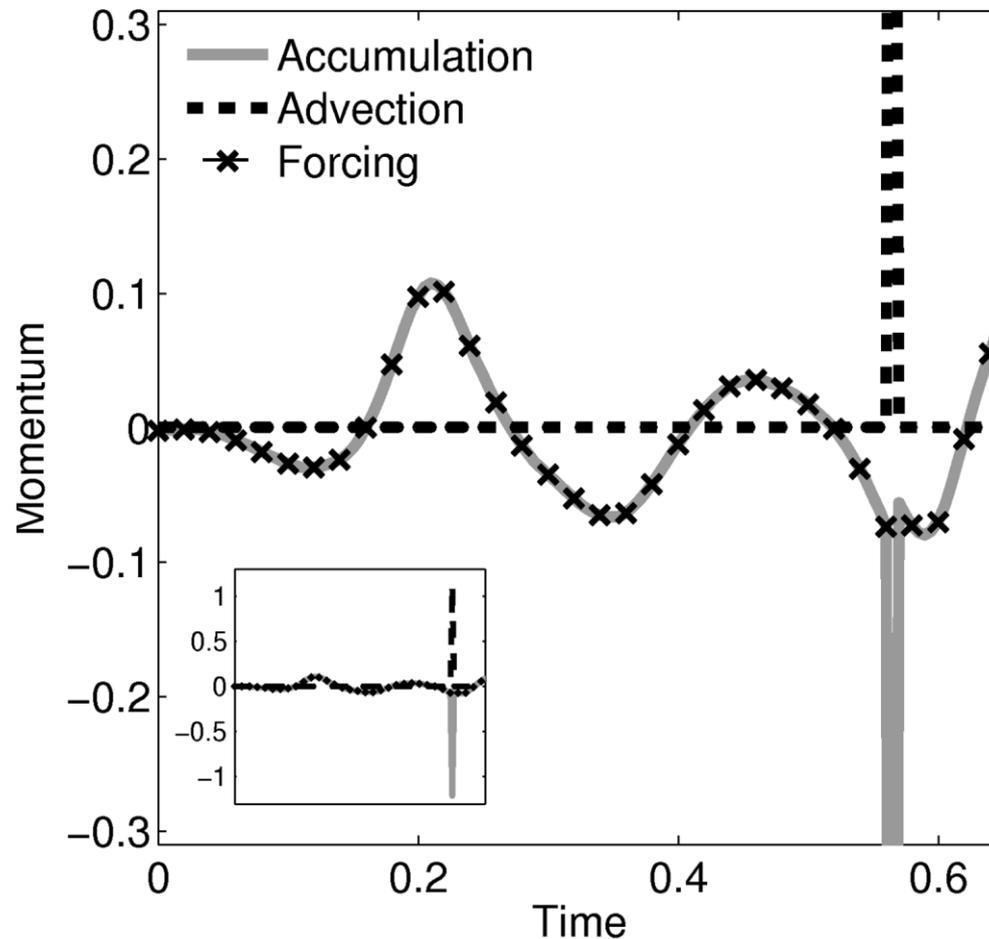
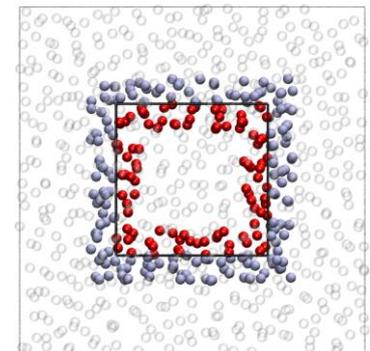
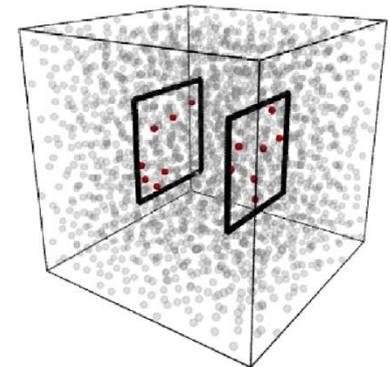
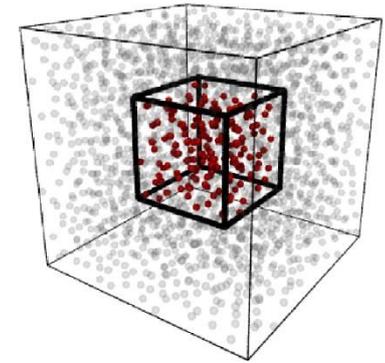
$$-\underbrace{\sum_{i=1}^N m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i}_{\text{Advection}} + \underbrace{\sum_{i=1}^N \sum_{j \neq i}^N \mathbf{f}_{ij} \vartheta_{ij}}_{\text{Forcing}}$$



# Testing Momentum Balance

## • Momentum Balance

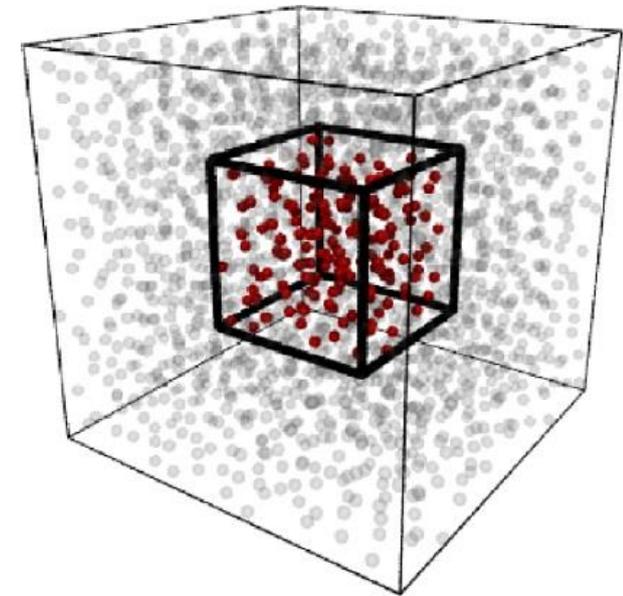
$$\underbrace{\frac{d}{dt} \sum_{i=1}^N m_i \mathbf{v}_i \vartheta_i}_{\text{Accumulation}} = - \underbrace{\sum_{i=1}^N m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i}_{\text{Advection}} + \underbrace{\sum_{i=1}^N \sum_{j \neq i}^N \mathbf{f}_{ij} \vartheta_{ij}}_{\text{Forcing}}$$

 $\frac{d}{dt}$ 


# Control Volume Function (revisited)

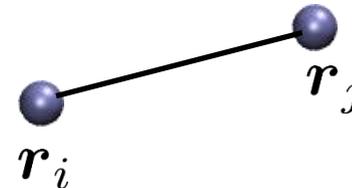
- The Control volume function is the integral of the Dirac delta function in 3 dimensions

$$\begin{aligned}\vartheta_i &\equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i) dV \\ &= [H(x^+ - x_i) - H(x^- - x_i)] \\ &\quad \times [H(y^+ - y_i) - H(y^- - y_i)] \\ &\quad \times [H(z^+ - z_i) - H(z^- - z_i)]\end{aligned}$$



- Replace molecular position with equation for a line

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



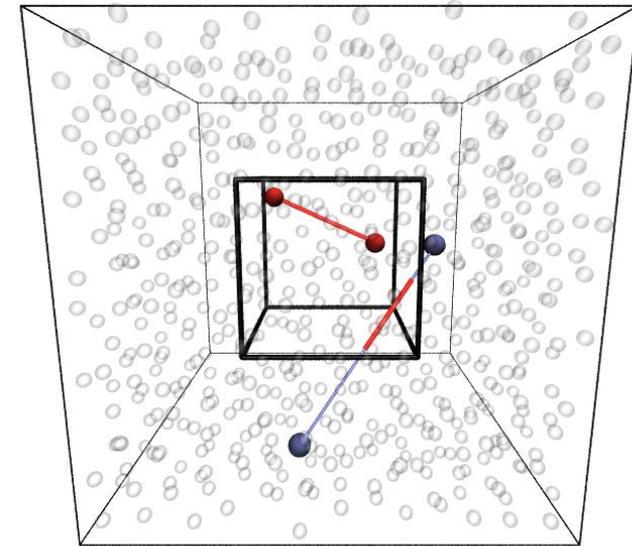
# Control Volume Function (revisited)

- 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

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



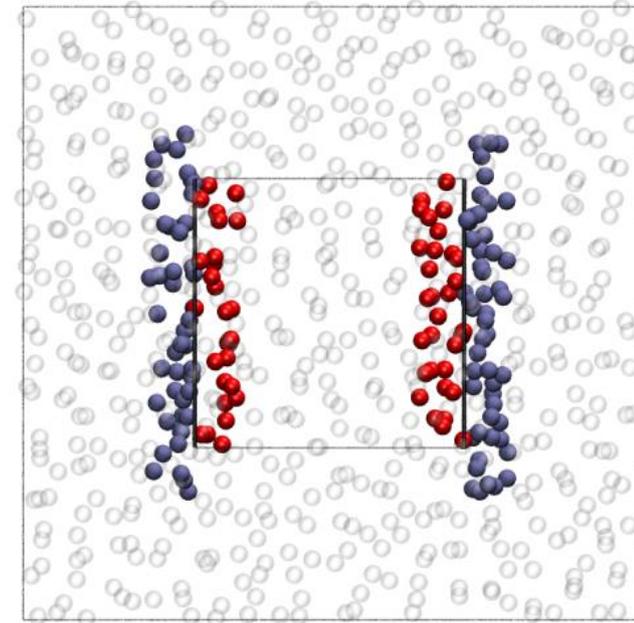
# Derivatives Yield the Surface Forces

- Taking the Derivative of the CV function

$$\frac{\partial \vartheta_s}{\partial x} \equiv \left[ \delta(x^+ - x_i + sx_{ij}) - \delta(x^- - x_i + sx_{ij}) \right]$$

$$\times \left[ H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij}) \right]$$

$$\times \left[ H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij}) \right]$$



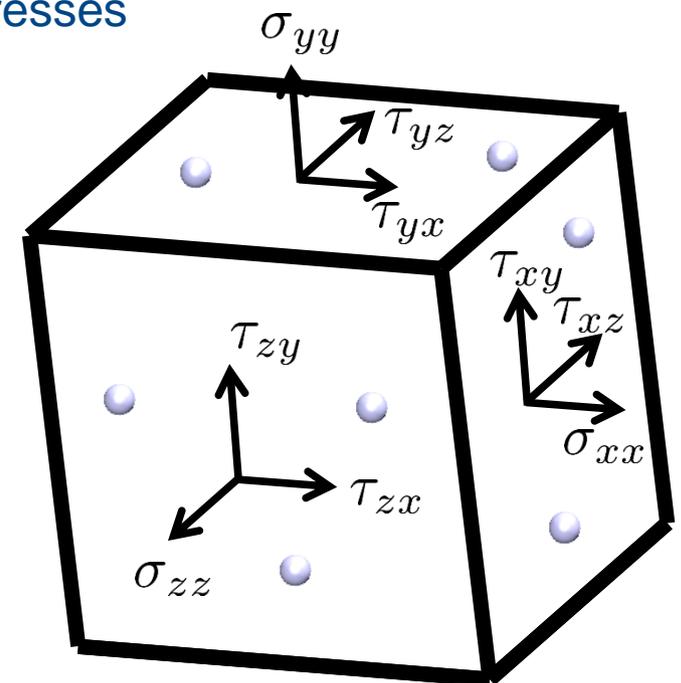
- Surface fluxes over the top and bottom surface

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

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

# 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

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

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

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

- Lagrangian mass conservation

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

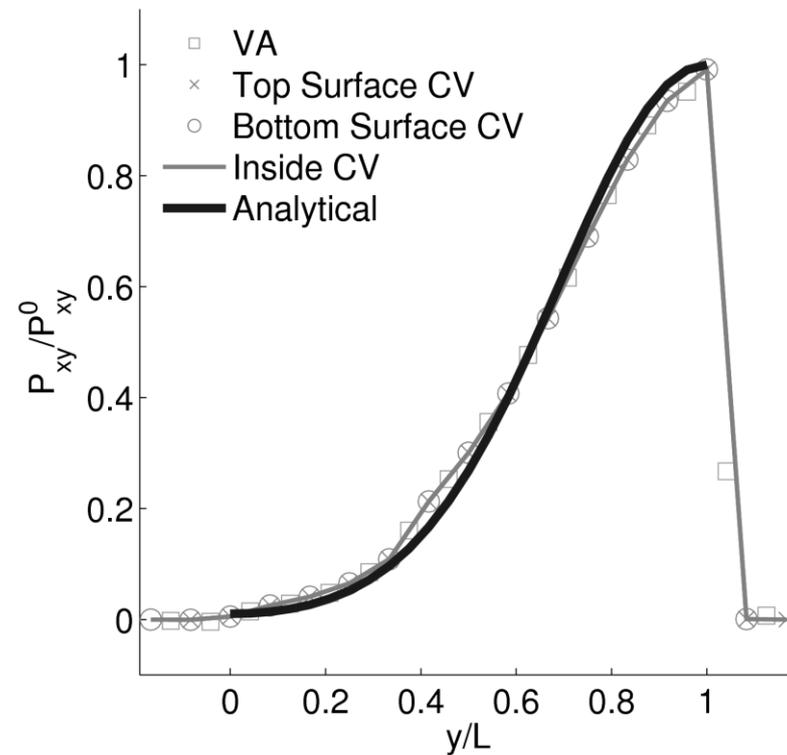
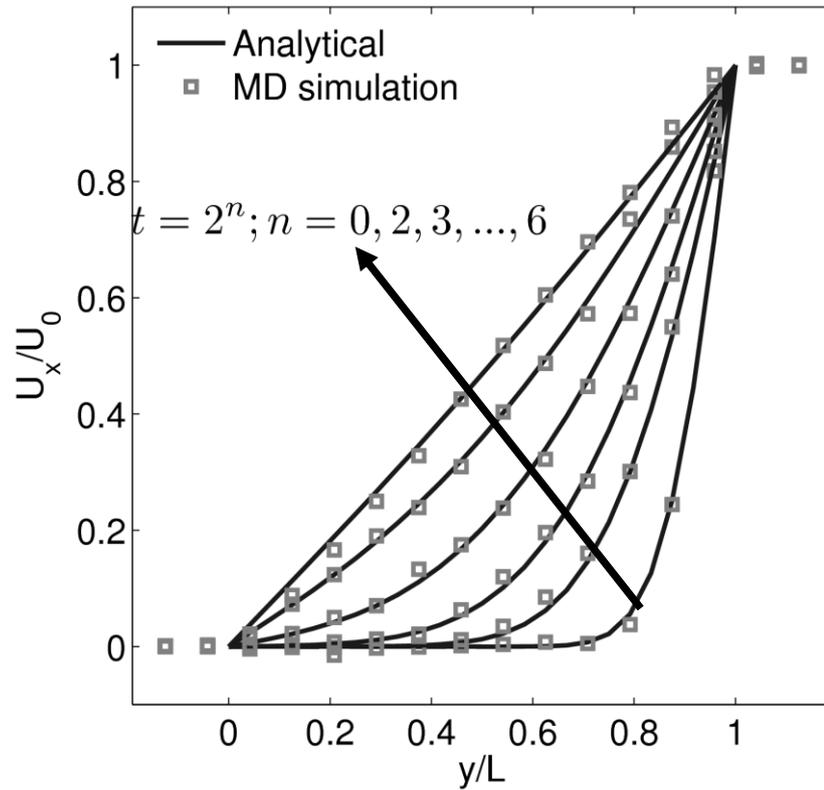
$$\frac{d}{dt} \sum_{i=1}^N m_i \vartheta_i = - \sum_{i=1}^N m_i (\mathbf{v}_i + \bar{\mathbf{u}}) \cdot d\mathbf{S}_i$$

$$\frac{d}{dt} \int_V \rho dV = \oint_S \rho (\mathbf{u} - \bar{\mathbf{u}}) \cdot d\mathbf{S}$$

$$\bar{\mathbf{u}} \cdot d\mathbf{S}_i = \frac{d\mathbf{r}}{dt} \cdot \frac{d\vartheta_i}{d\mathbf{r}}$$

$$\oint_S \rho \mathbf{u} \cdot d\mathbf{S} - \oint_S \rho \bar{\mathbf{u}} \cdot d\mathbf{S} = 0$$

# Continuum Analytical Couette Flow



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

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

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

# Unsteady Couette Flow

## Continuum Analytical

- Simplify the momentum balance (Navier-Stokes) equation

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

- 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

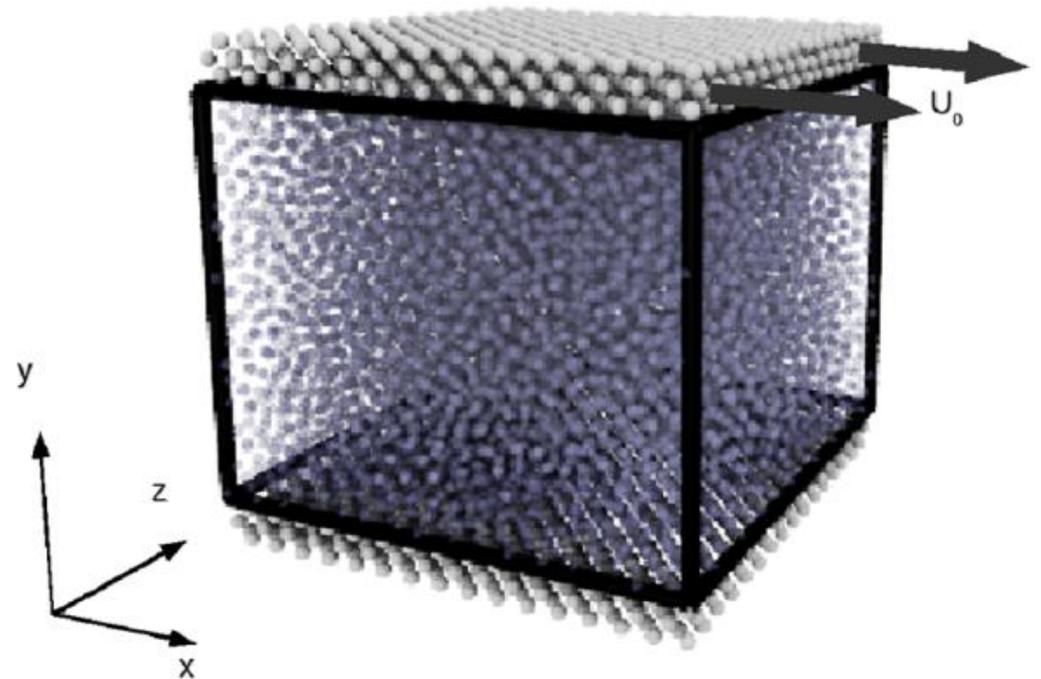
$$u_x(0, t) = 0$$

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

$$u_x(y, 0) = 0$$

## Molecular Dynamics

- Fixed bottom wall, sliding top wall with both thermostatted



# Unsteady Couette Flow

## Continuum Analytical

- Simplify the control volume momentum balance equation

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

- Simplifies for a single control volume

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

- With Boundary Conditions

$$u_x(0, t) = 0$$

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

$$u_x(y, 0) = 0$$

## Molecular Dynamics

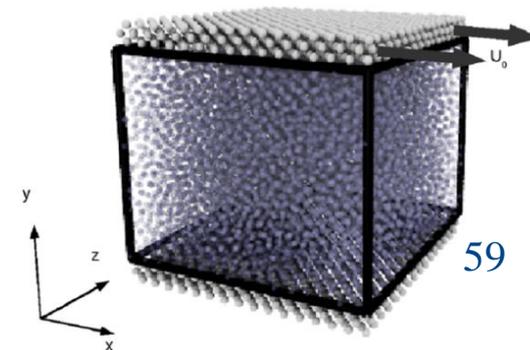
- Discrete form of the Momentum balance equation

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

- Simplifies for a single control volume

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

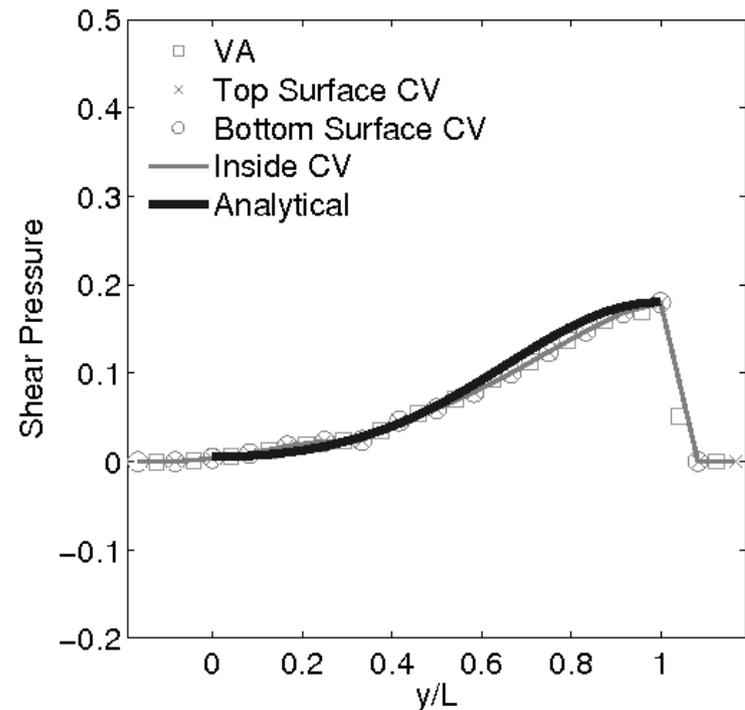
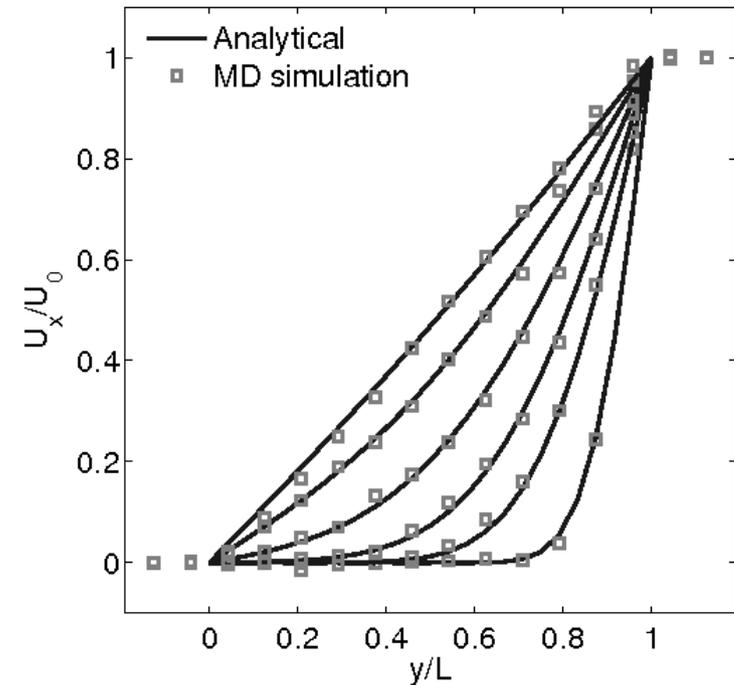
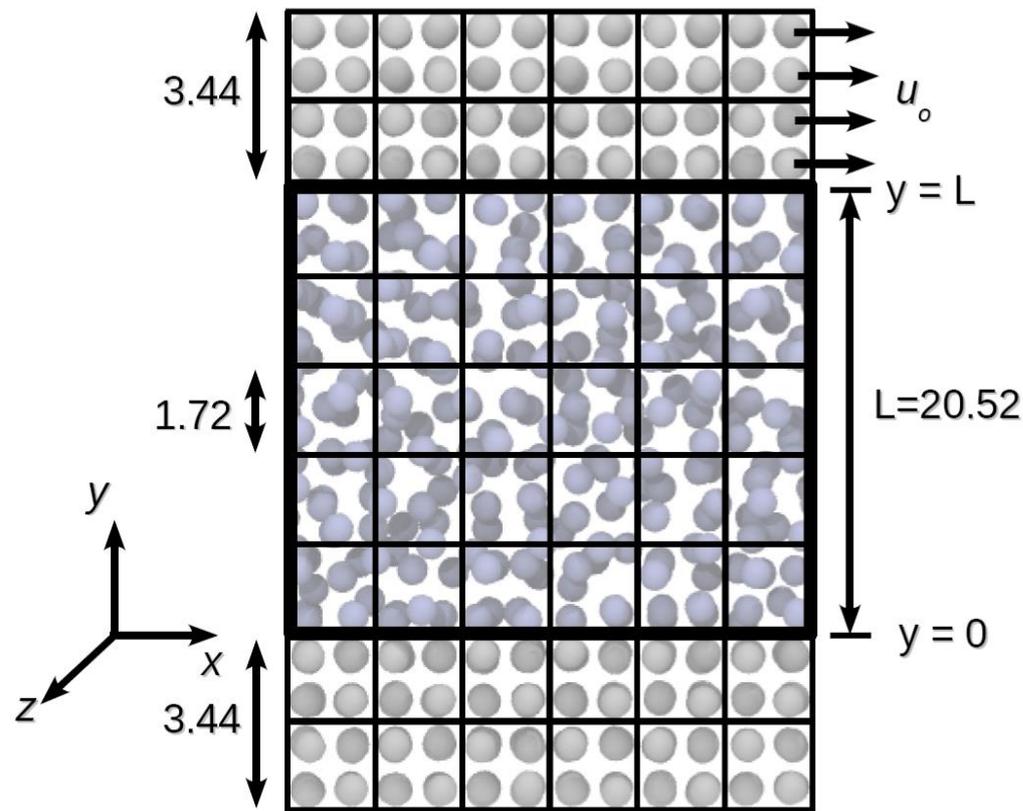
- Fixed bottom wall, sliding top wall with both thermostatted



# Unsteady Couette Flow

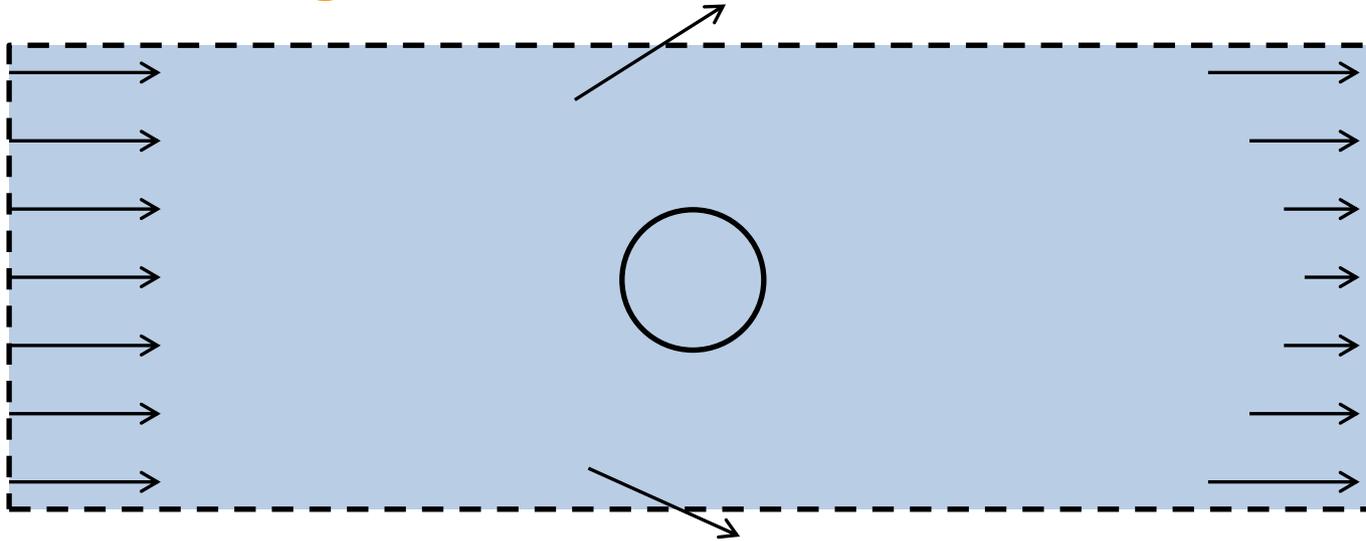
## Simulation setup

- 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

