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Coupling Molecular Dynamics to the Continuum for Fluid Dynamics Simulation

By Edward Smith

Unimore

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Overview

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- Coupling
  - Computational Fluid Dynamics (CFD)
  - Molecular Dynamics (MD)
- Developing a Coupling Framework
  - Control Volume Functional
  - Constrained Dynamics
  - Link to NEMD
- Coupled Simulations
  - Software Development
  - Results

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COUPLING

Computational Fluid Dynamics

Molecular Dynamics

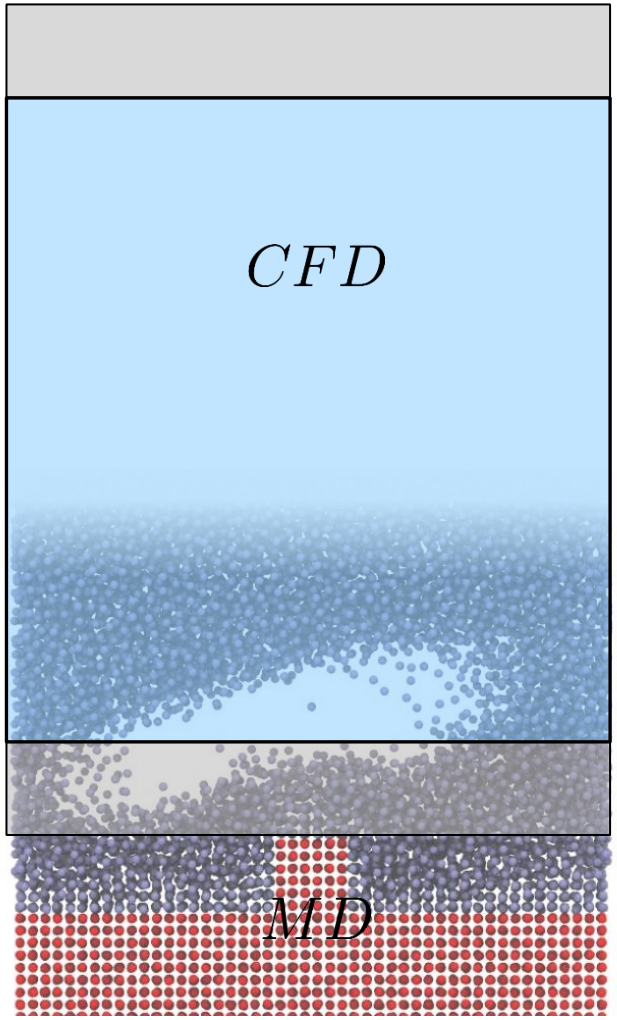
Coupled Simulation

- Assumes a continuous field

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

- Discrete molecules

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



Computational Fluid Dynamics

- Assumed continuous at every point in space
  - Mass Conservation

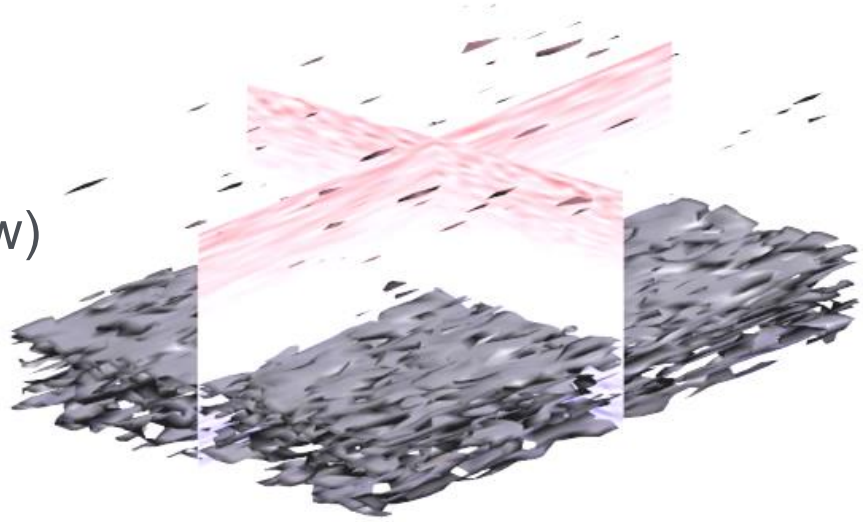
$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \rho \boldsymbol{u}$$

  - Momentum Balance (Newton's Law)

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

  - Energy Conservation

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



Direct Numerical Simulation of Turbulent Couette Flow

Computational Fluid Dynamics

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- Taking Momentum Balance and approximating $\boldsymbol{\Pi}$

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

- Gives the Navier-Stokes Equation

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

Viscosity Coefficient

- Beyond simple flow we need further models
  - Multi-phase interface tracking, phase change, flow of energy, chemical species tracking and reactions, shock waves, slip models near boundaries, etc
  - Each brings in more empirical coefficients

Computational Fluid Dynamics

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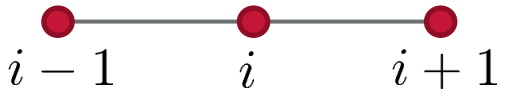
- The Navier-Stokes Equation

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

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

- Finite Difference Method

$$\frac{\partial u_i}{\partial x} \approx \frac{u_{i+1} - u_{i-1}}{2\Delta x}$$



Computational Fluid Dynamics

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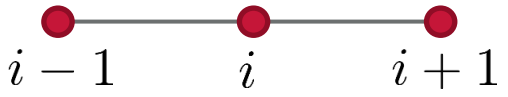
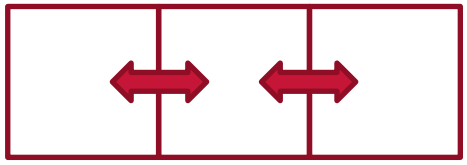


- Finite Volume Method

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



- Other methods: finite element, spectral methods, smooth particle hydrodynamics, lattice Boltzmann, …

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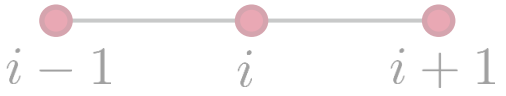

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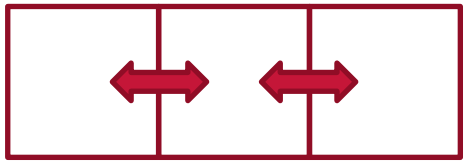

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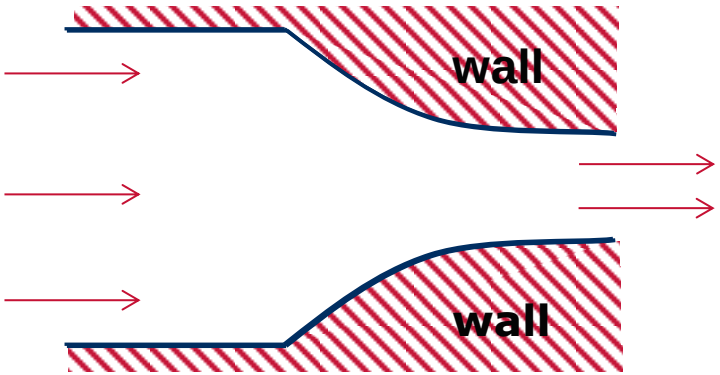
Finite (Control) Volume Formulation

- An integrated Navier-Stokes Equation

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

- Exactly links fluxes to changes inside control volume (CV), consider mass flow in a nozzle



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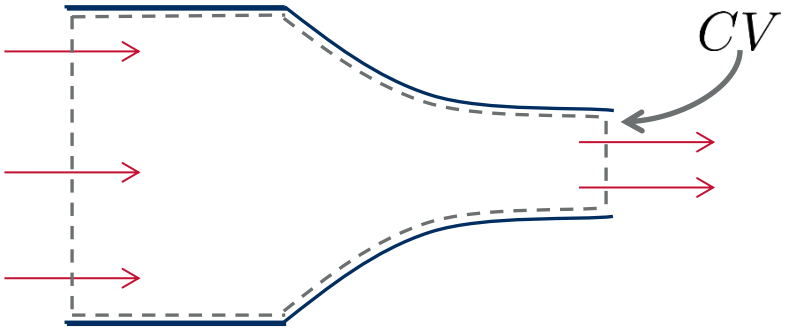

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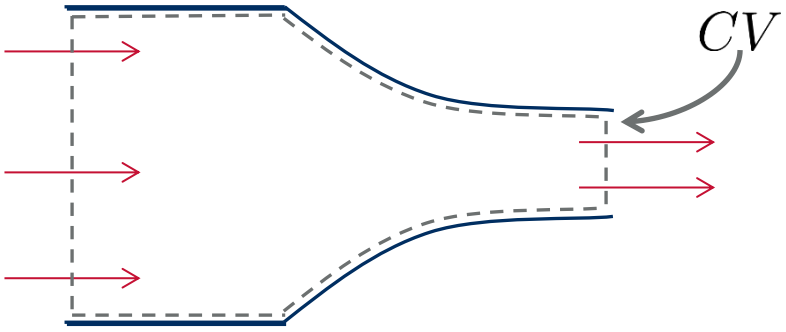
$$\int_{in} \rho \boldsymbol{u}\cdot d\mathbf{S}$$



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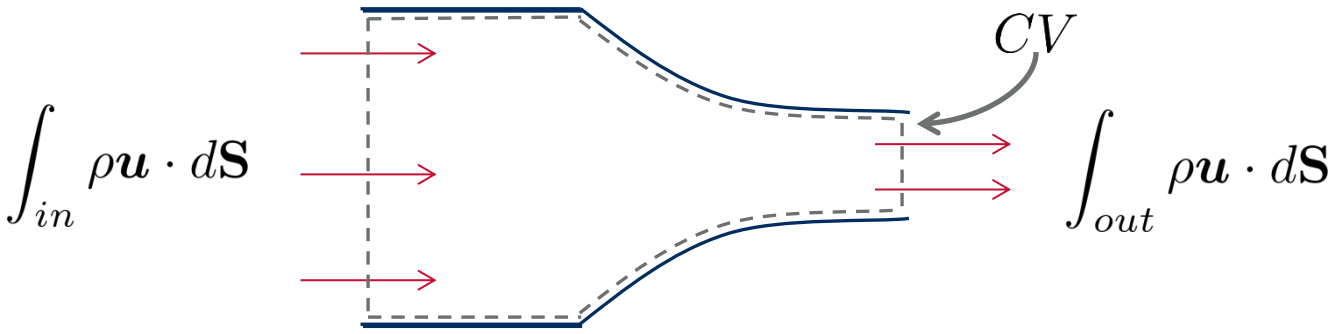

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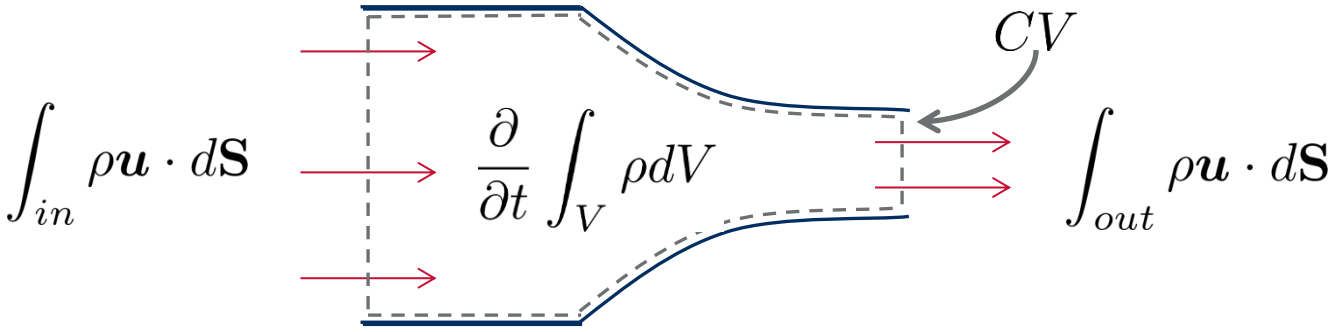

$$\frac{\partial}{\partial t}\int_V \rho dV = \int_{in} \rho \boldsymbol{u}\cdot d\mathbf{S} - \int_{out} \rho \boldsymbol{u}\cdot d\mathbf{S}$$

Finite (Control) Volume Formulation

- An integrated Navier-Stokes Equation

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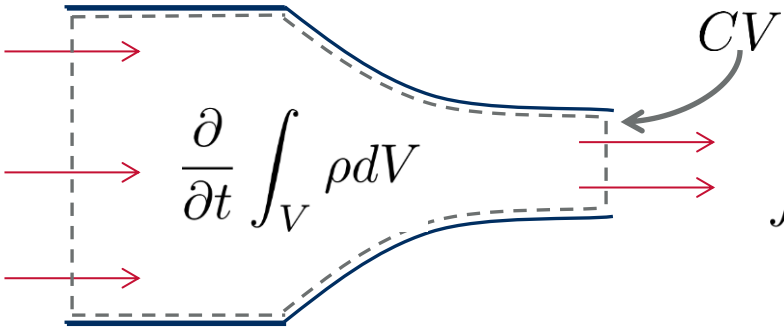


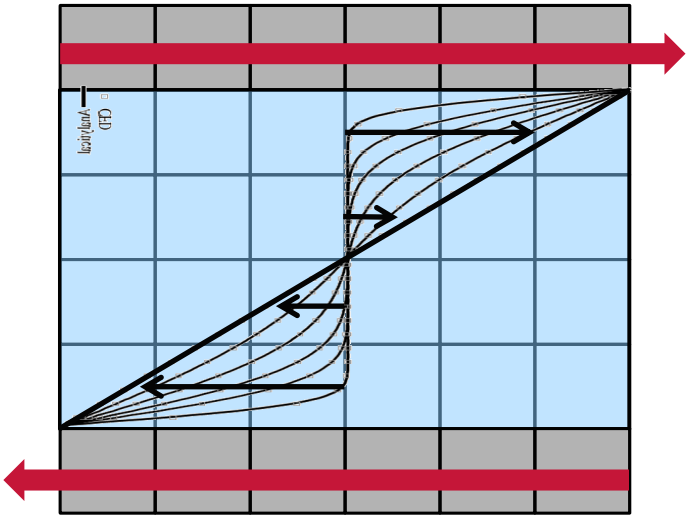
$$\int_{in} \rho \boldsymbol{u}\cdot d\mathbf{S} \qquad \frac{\partial}{\partial t}\int_V \rho dV \qquad \int_{out} \rho \boldsymbol{u}\cdot d\mathbf{S}$$

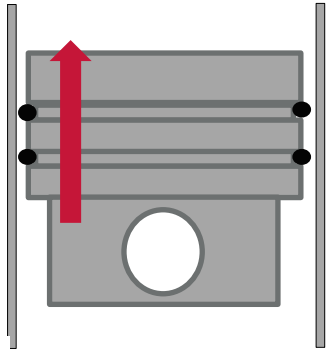
$$\frac{\partial}{\partial t}\int_V \rho dV = \int_{in} \rho \boldsymbol{u}\cdot d\mathbf{S} - \int_{out} \rho \boldsymbol{u}\cdot d\mathbf{S} = -\oint_S \rho \boldsymbol{u}\cdot d\mathbf{S}$$

- Conservative – keeps track of all flow in and out

Computational Fluid Dynamics

- Domain split into a grid of finite volumes
  - Boundary conditions must be specified as fluxes
  - Loop with flux equal between adjacent volume in space
  - Sum of flux over volume surface gives change in time





- Example: Wall driven or Couette flow
  - Two infinite plates with fluid in between
  - A good model for tribological and industrial cases of interest

Molecular Dynamics

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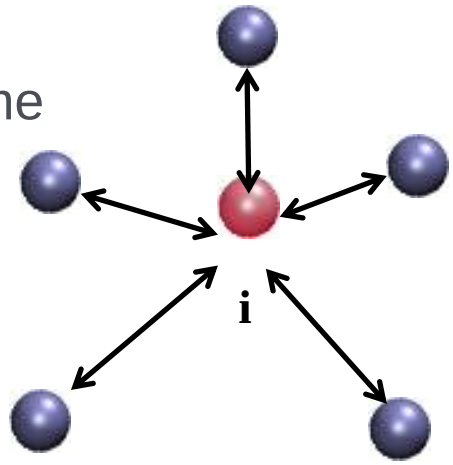
Discrete molecules in continuous space

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

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



Acceleration obtained from forces

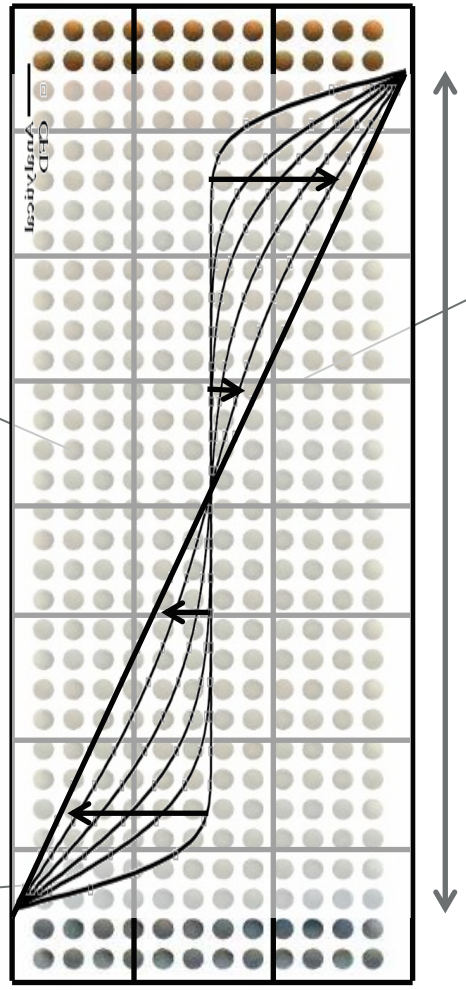
- Governed by Newton's law for an N-body system
- Point particles with pairwise interactions only

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

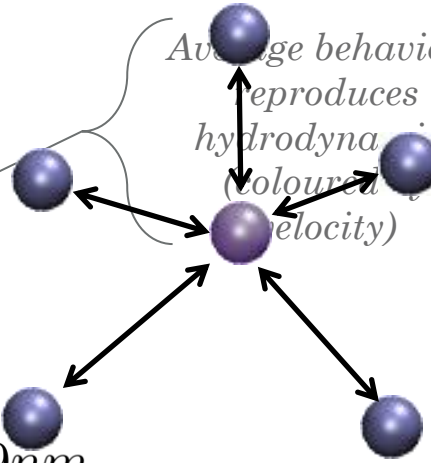
$$\Phi(r_{ij}) = 4\epsilon \left[\left(\frac{\ell}{r_{ij}} \right)^{12} - \left(\frac{\ell}{r_{ij}} \right)^{6} \right]$$

Molecular Dynamics

Liquid structure causes viscosity



Average behaviour reproduces hydrodynamics (coloured by velocity)



$H \approx 9nm$

Stick-slip near walls

Reynolds Number

$Re \approx 15$

with

4096 molecules

Molecular Dynamics
Complex Walls and Fluids

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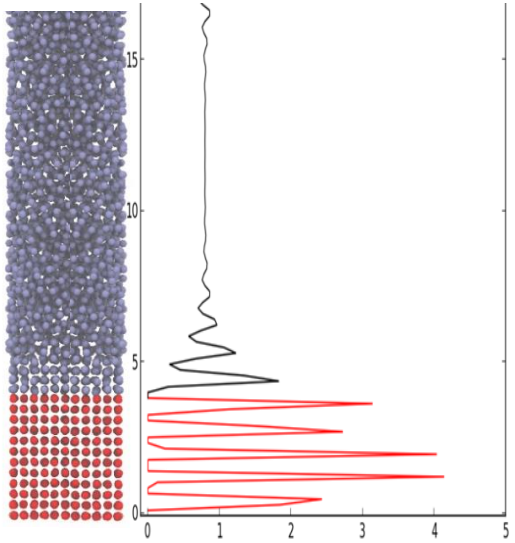
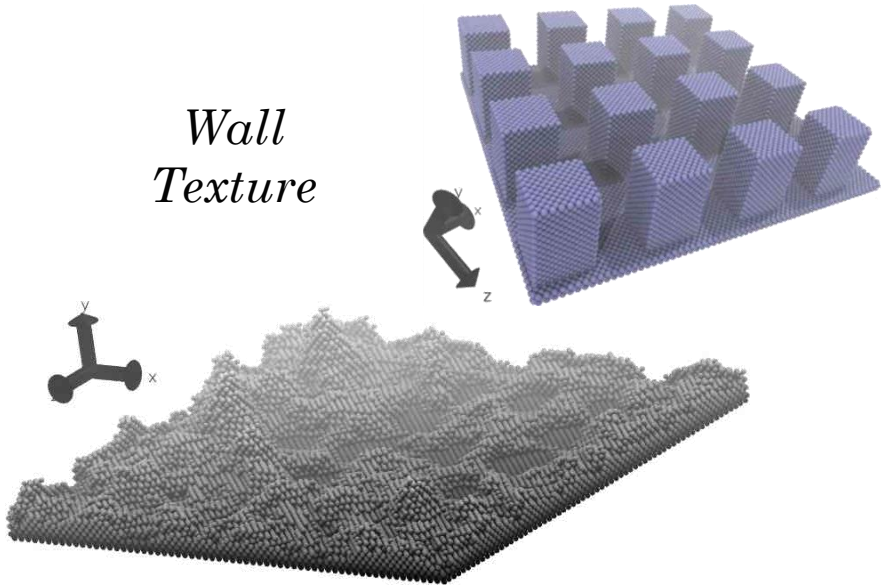
Liquid structure causes viscosity



Wall Texture



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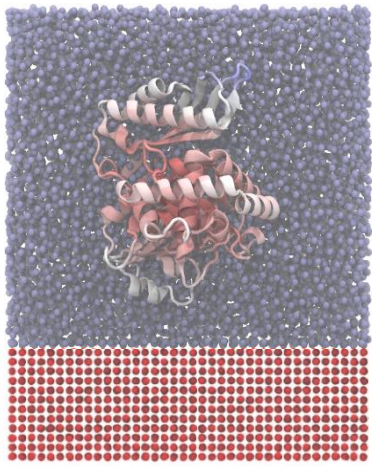
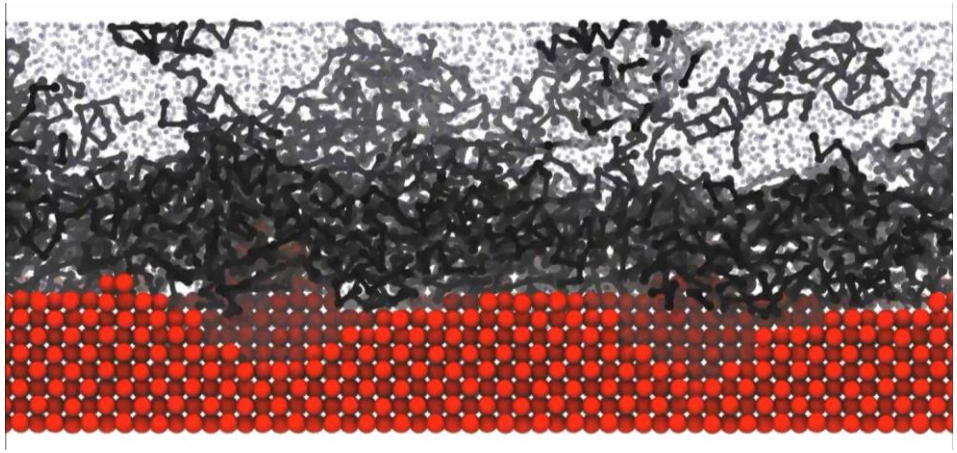


Molecules of arbitrary complexity



Oil, water and textured surface

Molecular Dynamics
Shocks and Multi-Phase

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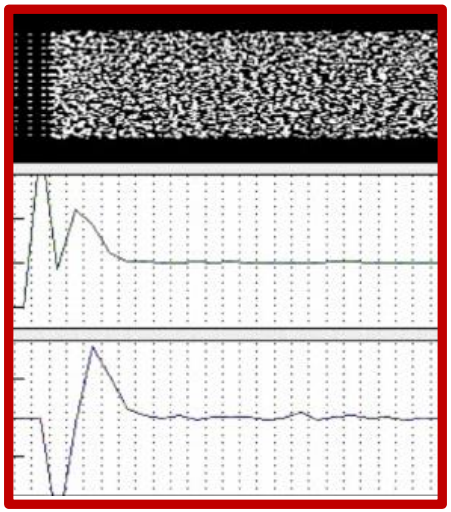
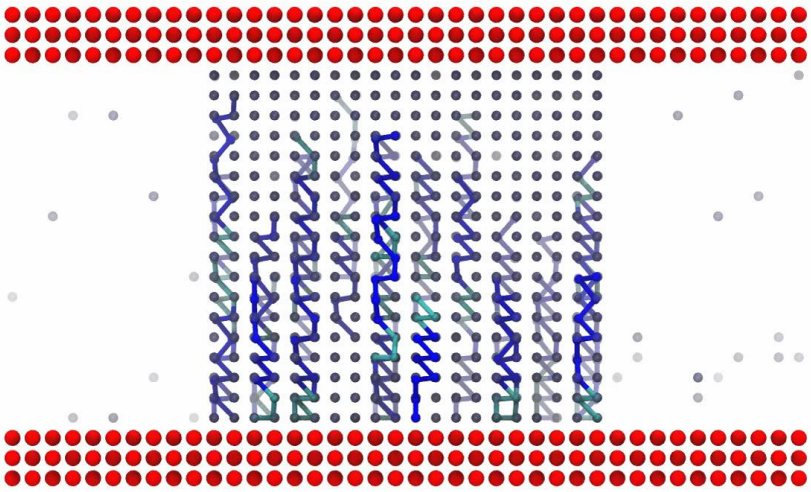
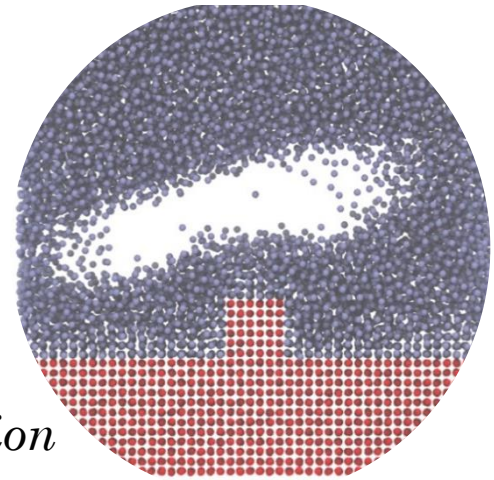
Shockwave



Droplet Formation



Contact line



Nucleation

Coupling Overview

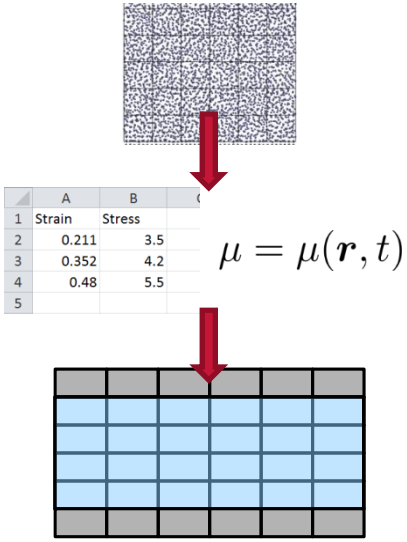
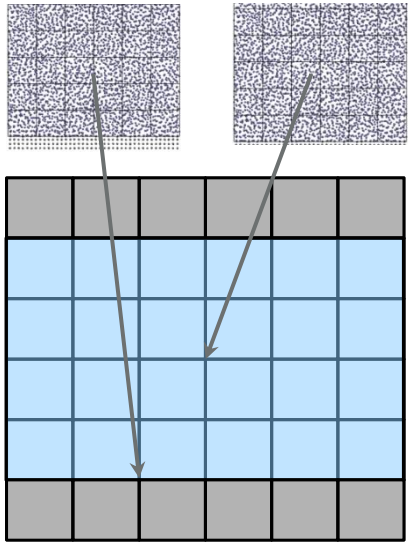


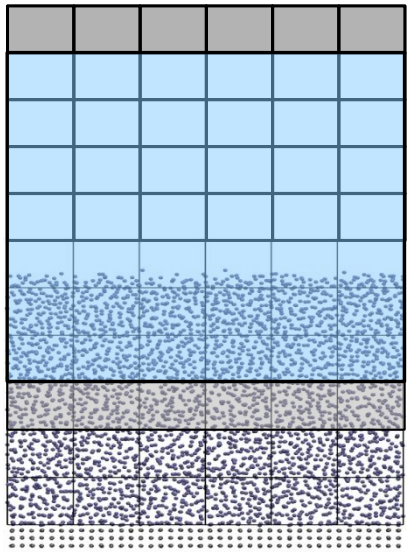
Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data



Embedded Models (HMM)

MD – embedded in a CFD simulation [1)]



Domain Decomposition

MD –CFD linked along an interface [2)]

1) Ren (2007), E et al (2003), Borg et al (2013) 2) O'Connell and Thompson (1995), Flekkøy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni & Coveney, (2003), Mohamed & Mohamad, (2009)

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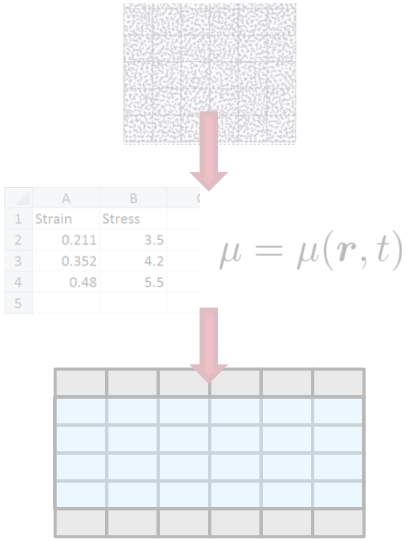

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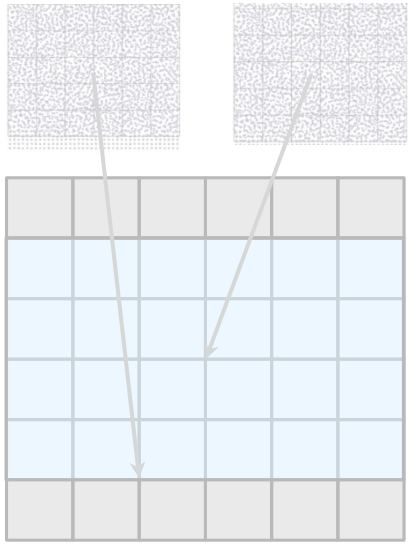

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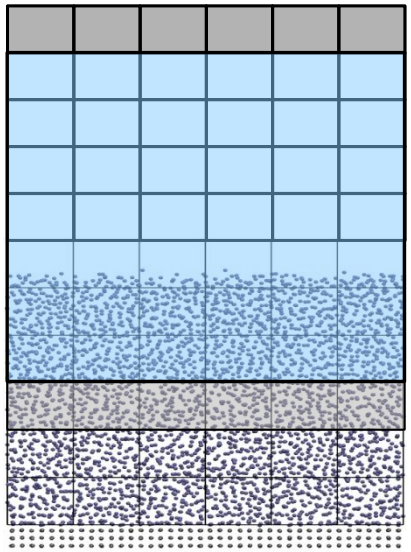

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Coupled Simulation

- Assumes a continuous field

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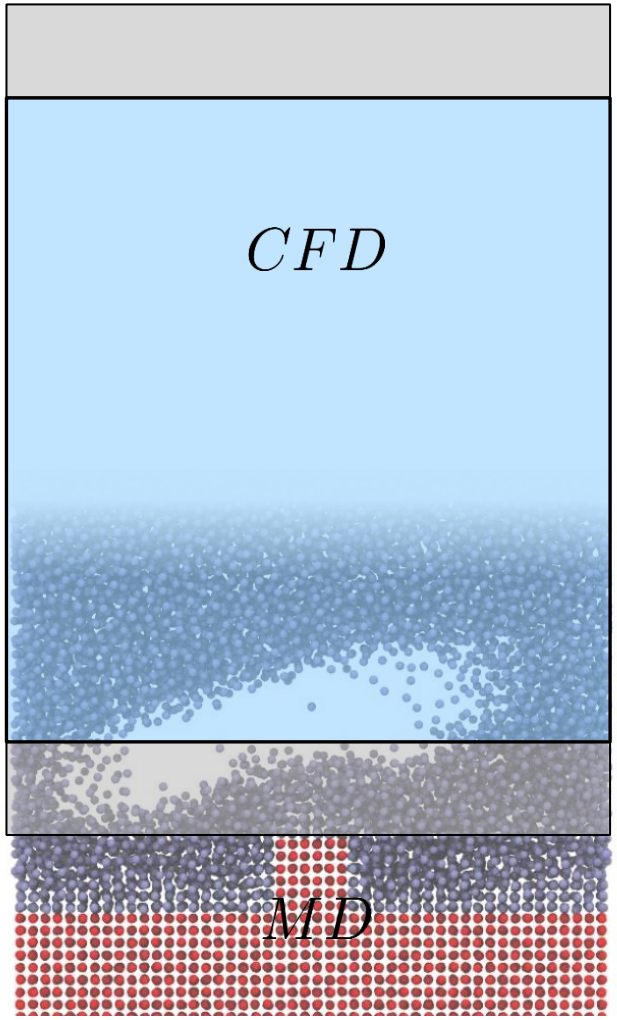
- Discrete molecules

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



Coupled Simulation

- Control (Finite) Volume form

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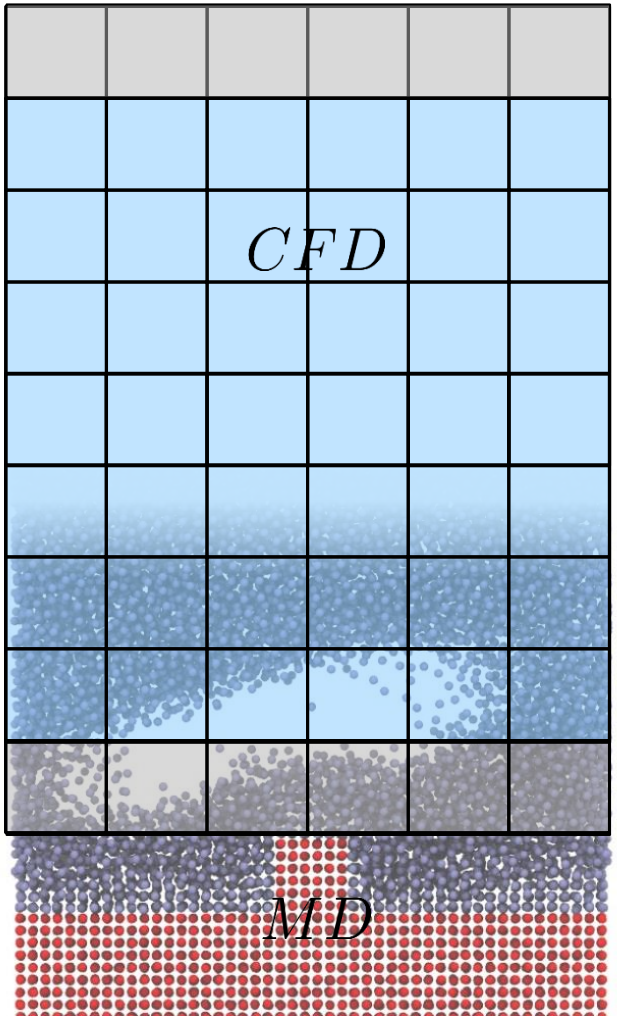

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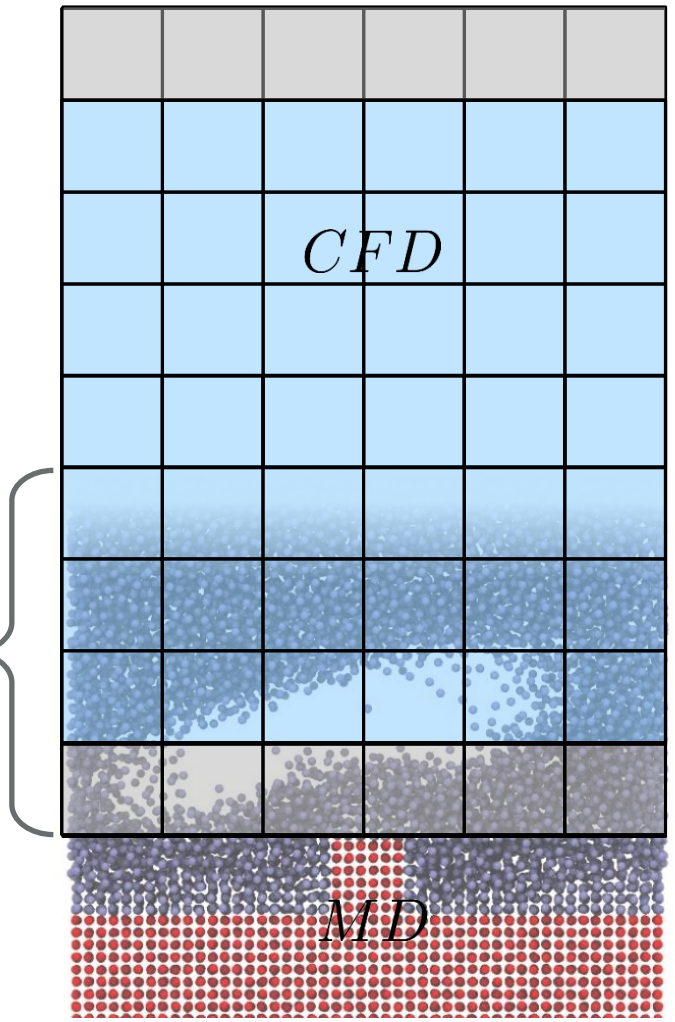

Overlap between CFD and MD

- Discrete molecules

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

O'Connell Thompson (1995)

Coupled Simulation

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

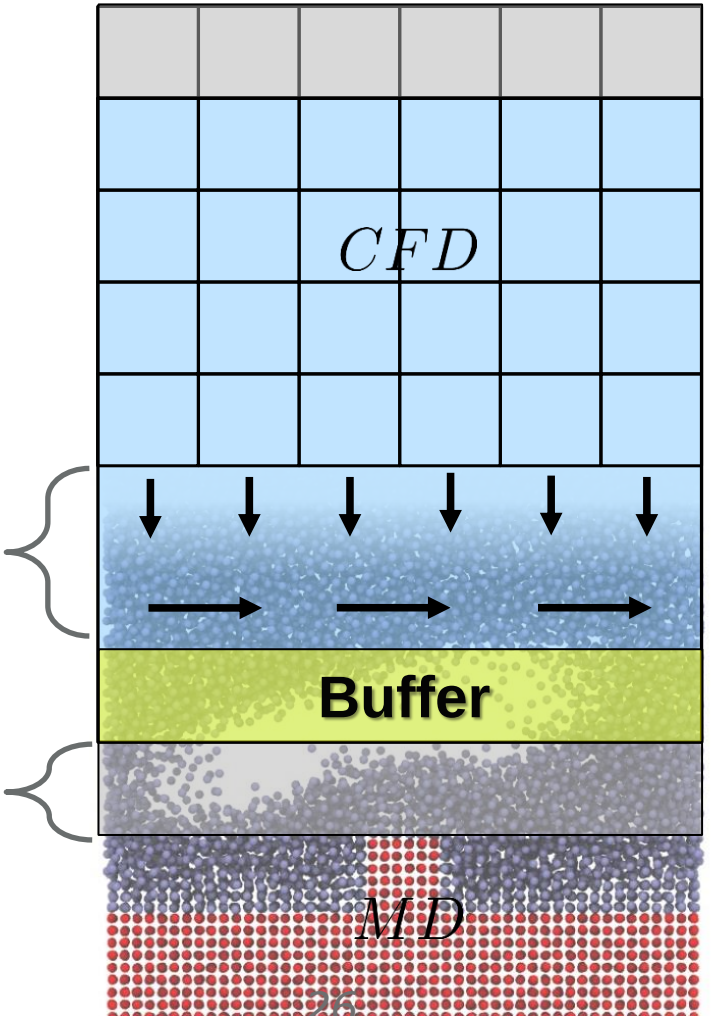
CFD→MD Boundary condition

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

MD→CFD Boundary condition

- Discrete molecules

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



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

Coupled Simulation

- Control (Finite) Volume form

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

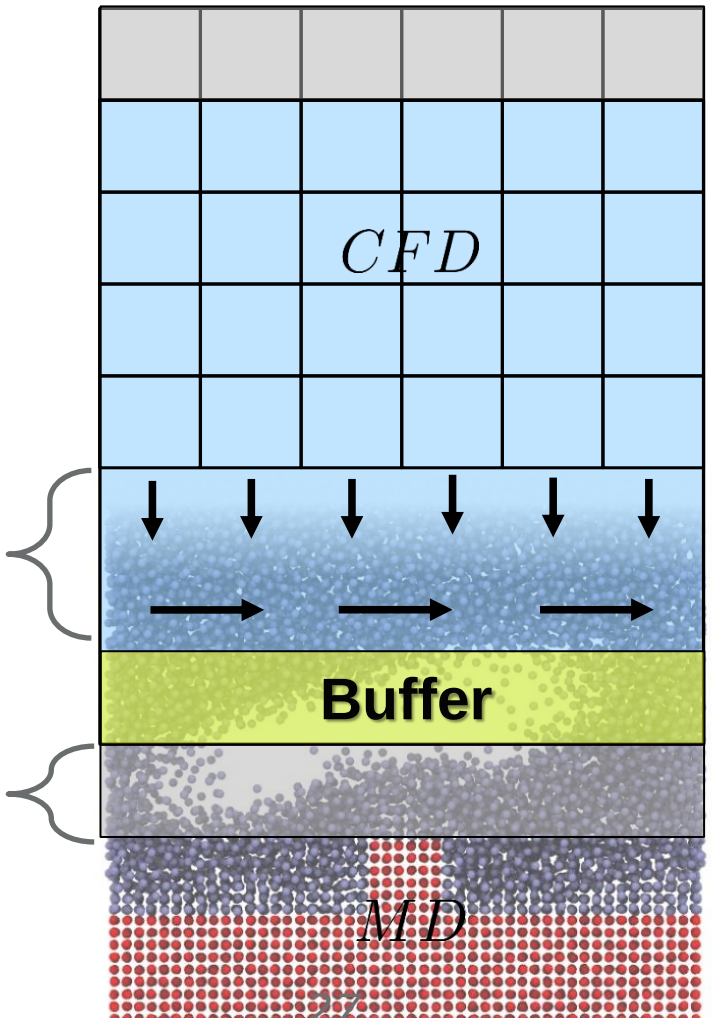
Consistent Framework

CFD→MD Boundary condition

MD→CFD Boundary condition

- Discrete molecules

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



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

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A COUPLING FRAMEWORK

Control Volume Functional
Constrained Dynamics
Link to NEMD

Irving and Kirkwood (1950)

TRANSPORT PROCESSES

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... to the A_u fundamental ... upper-stage band corresponding ... The interpretation of the faint sharp band ... $778+\nu_5-\nu_{11}$ seems more ... cm^{-1} as an upper-stage band, ... interpretation as the B_{1g} combination, plausible than its interpretation as the ... Raman band at 828.7 $210+558$ cm^{-1}. The faint sharp Raman band at 828.7 cm^{-1} has been interpreted as an upper-stage band, $2\times407+\nu_8-\nu_8$, rather than as the B_{2u} difference band $1340-510$ cm^{-1}, because the corresponding sum band has not been observed. If the preferred interpretations are correct, the group of Raman bands, 769, 778, 819, and 829 cm^{-1}, are related to each other in much the same manner as similar groups in the spectra of CO_2 and CS_2.

ACKNOWLEDGMENTS

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

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

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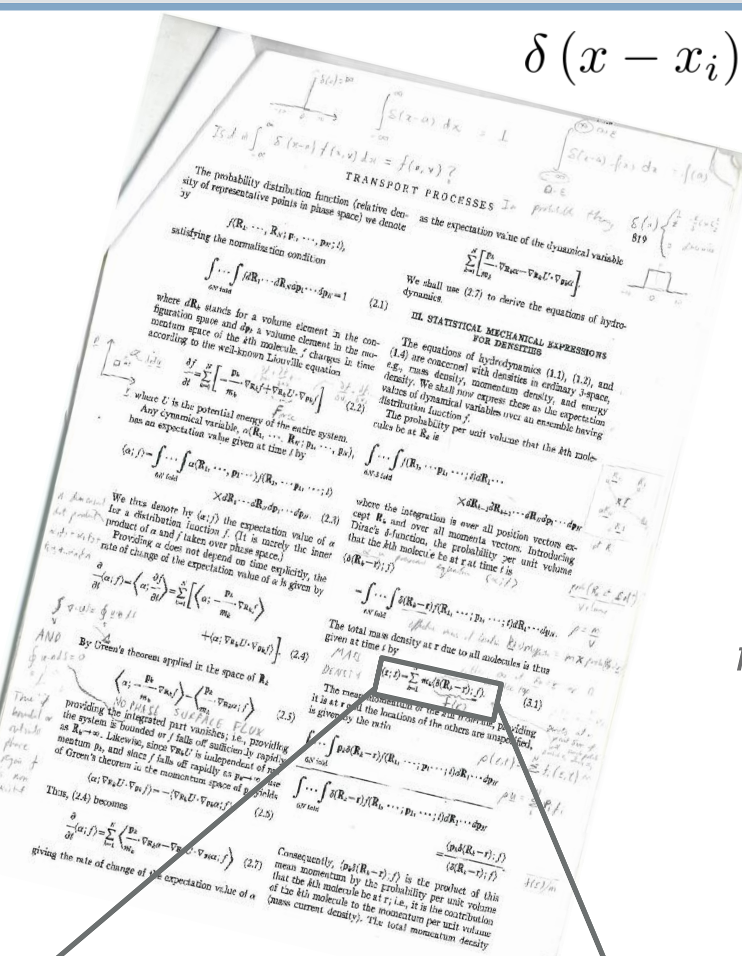
The equations of hydrodynamics—continuity equation, equation of motion, and equation of energy transport—are derived by means of the classical statistical mechanics. Thereby, expressions are obtained for the stress tensor and heat current density in terms of molecular variables. In addition to the familiar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

INTRODUCTION

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

To obtain explicit expressions for the pair probability density and probability current density one would in principle need to solve the Liouville equation [Eq. (2.2)] for the probability distribution in Gibbs phase space and then perform repeated integrations. Since this program is untenable for a liquid, various attempts have been made to obtain a closed equation satisfied approximately by the probability distribution function in the phase space of a pair of molecules. One such equation has been derived by Born and Green[2] using a generalized "superposition" assumption. Another, a generalization of the well-known Fokker-Planck equation of stochastic theory, has been derived by Kirkwood[1] by introducing the concepts of time smoothing and a friction constant. This latter equation has been applied to obtain an expression for the stress tensor linear in gradients of fluid velocity and, thereby, expressions (in terms of molecular variables) for coefficients of shear and volume viscosity.[3] The same equation generalized to non-uniform temperatures, after linearizing in the temperature gradient, leads to an explicit expression for the heat current and thereby to an expression for the coefficient of thermal conductivity.[4] We shall assume, for purposes of mathematical simplicity, a single component, single phase fluid system consisting of molecules which interact under central forces only. It is not difficult to generalize the treatment to a multiple component or multiple ...

* This work was supported by the U. S. ONR under Contract N6onr-244 with the California Institute of Technology.
[1] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).
[2] M. Born and H. S. Green, Proc. Roy. Soc. A188, 10 (1946).
[3] Kirkwood, Buff, and Green, J. Chem. Phys. 17, 988 (1949).
[4] Kirkwood, Standart, and Irving (in preparation). The ... merical evaluation awaits a more precise computation of the ... retical radial distribution function.



TRANSPORT PROCESSES

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

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

satisfying the normalization condition

$$\int\cdots\int_{6N \text{ fold}} f d\mathbf{R}_1\cdots d\mathbf{R}_N d\mathbf{p}_1\cdots d\mathbf{p}_N = 1 \qquad (2.1)$$

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 kth molecule. f changes in time according to the well-known Liouville equation

$$\frac{\partial f}{\partial t} = \sum_{k=1}^{N}\left[-\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k} f + \nabla_{\mathbf{R}_k} U\cdot\nabla_{\mathbf{p}_k} f\right] \qquad (2.2)$$

where U is the potential energy of the entire system.

Any dynamical variable, $\alpha(\mathbf{R}_1, \cdots, \mathbf{R}_N; \mathbf{p}_1, \cdots, \mathbf{p}_N)$, has an expectation value given at time t by

$$\langle\alpha; f\rangle = \int\cdots\int_{6N \text{ fold}} \alpha(\mathbf{R}_1, \cdots, \mathbf{p}_1\cdots) f(\mathbf{R}_1, \cdots \mathbf{p}_1, \cdots; t) \times d\mathbf{R}_1\cdots d\mathbf{R}_N d\mathbf{p}_1\cdots d\mathbf{p}_N. \qquad (2.3)$$

We thus denote by $\langle\alpha; f\rangle$ the expectation value of α for a distribution function f. (It is merely the inner product of α and f taken over phase space.)

Providing α does not depend on time explicitly, the rate of change of the expectation value of α is given by

$$\frac{\partial}{\partial t}\langle\alpha; f\rangle = \left\langle\alpha; \frac{\partial f}{\partial t}\right\rangle = \sum_{k=1}^{N}\left[\left\langle\alpha; -\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k} f\right\rangle + \langle\alpha; \nabla_{\mathbf{R}_k} U\cdot\nabla_{\mathbf{p}_k} f\rangle\right]. \qquad (2.4)$$

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

$$\left\langle\alpha; -\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k} f\right\rangle = \left\langle\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}\alpha; f\right\rangle \qquad (2.5)$$

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

$$\langle\alpha; \nabla_{\mathbf{R}_k} U\cdot\nabla_{\mathbf{p}_k} f\rangle = -\langle\nabla_{\mathbf{R}_k} U\cdot\nabla_{\mathbf{p}_k}\alpha; f\rangle \qquad (2.6)$$

Thus, (2.4) becomes

$$\frac{\partial}{\partial t}\langle\alpha; f\rangle = \sum_{k=1}^{N}\left\langle\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}\alpha - \nabla_{\mathbf{R}_k} U\cdot\nabla_{\mathbf{p}_k}\alpha; f\right\rangle \qquad (2.7)$$

giving the rate of change of the expectation value of α as the expectation value of the dynamical variable

$$\sum_{k=1}^{N}\left[\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}\alpha - \nabla_{\mathbf{R}_k} U\cdot\nabla_{\mathbf{p}_k}\alpha\right].$$

We shall use (2.7) to derive the equations of hydrodynamics.

III. STATISTICAL MECHANICAL EXPRESSIONS FOR DENSITIES

The equations of hydrodynamics (1.1), (1.2), and (1.4) are concerned with densities in ordinary 3-space, e.g., mass density, momentum density, and energy density. We shall now express these as the expectation values of dynamical variables over an ensemble having distribution function f.

The probability per unit volume that the kth molecules be at $\mathbf{R}_k$ is

$$\int\cdots\int_{6N-3 \text{ fold}} f(\mathbf{R}_1, \cdots \mathbf{p}_1, \cdots; t) d\mathbf{R}_1\cdots \times d\mathbf{R}_{k-1} d\mathbf{R}_{k+1}\cdots d\mathbf{R}_N d\mathbf{p}_1\cdots d\mathbf{p}_N$$

where the integration is over all position vectors except $\mathbf{R}_k$ and over all momenta vectors. Introducing Dirac's δ-function, the probability per unit volume that the kth molecule be at $\mathbf{r}$ at time t is

$$\langle\delta(\mathbf{R}_k-\mathbf{r}); f\rangle = \int\cdots\int_{6N \text{ fold}} \delta(\mathbf{R}_k-\mathbf{r}) f(\mathbf{R}_1, \cdots; \mathbf{p}_1, \cdots; t) d\mathbf{R}_1\cdots d\mathbf{p}_N.$$

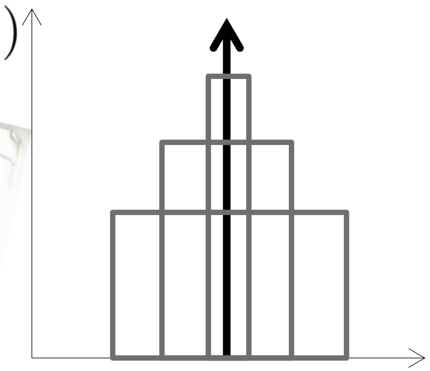
The total mass density at $\mathbf{r}$ due to all molecules is thus given at time t by

$$\rho(\mathbf{r}; t) = \sum_{k=1}^{N} m_k\langle\delta(\mathbf{R}_k-\mathbf{r}); f\rangle. \qquad (3.1)$$

The mean momentum of the kth molecule, providing it is at $\mathbf{r}$ and the locations of the others are unspecified, is given by the ratio

$$\frac{\int\cdots\int_{6N \text{ fold}} \mathbf{p}_k\delta(\mathbf{R}_k-\mathbf{r}) f(\mathbf{R}_1, \cdots; \mathbf{p}_1\cdots; t) d\mathbf{R}_1\cdots d\mathbf{p}_N}{\int\cdots\int_{6N \text{ fold}} \delta(\mathbf{R}_k-\mathbf{r}) f(\mathbf{R}_1, \cdots; \mathbf{p}_1, \cdots; t) d\mathbf{R}_1\cdots d\mathbf{p}_N} = \frac{\langle\mathbf{p}_k\delta(\mathbf{R}_k-\mathbf{r}); f\rangle}{\langle\delta(\mathbf{R}_k-\mathbf{r}); f\rangle}.$$

Consequently, $\langle\mathbf{p}_k\delta(\mathbf{R}_k-\mathbf{r}); f\rangle$ is the product of this mean momentum by the probability per unit volume that the kth molecule be at $\mathbf{r}$; i.e., it is the contribution of the kth molecule to the momentum per unit volume (mass current density). The total momentum density ...



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

The Dirac delta infinitely high, infinitely thin peak formally equivalent to the continuum differential formulation

Coupled Simulation

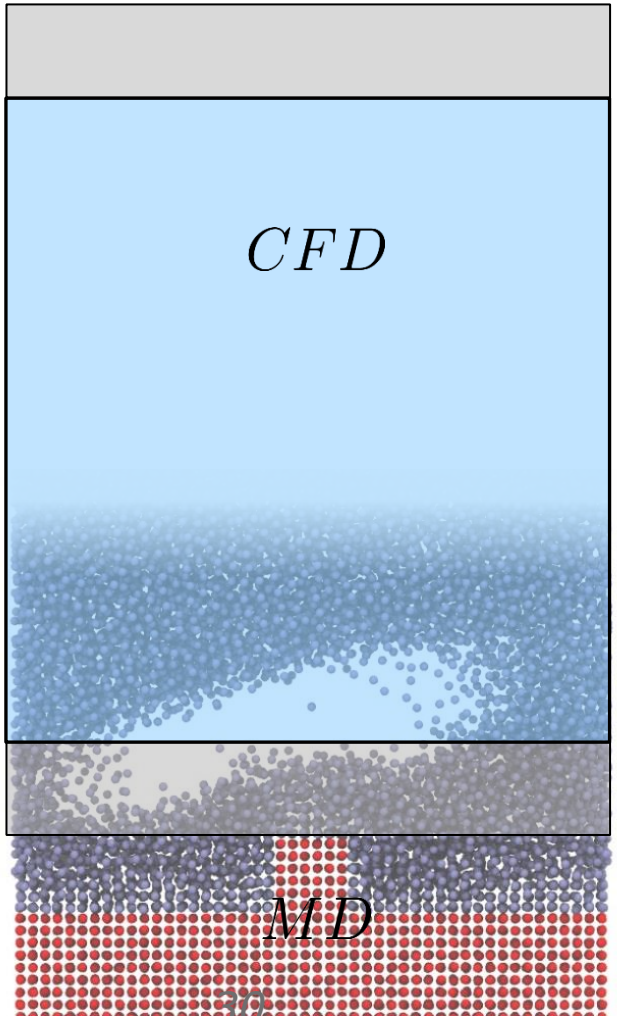
- Density at a point

$$\rho(\boldsymbol{r}, t)$$

Share the same **time** and **length** scales

- Discrete molecules

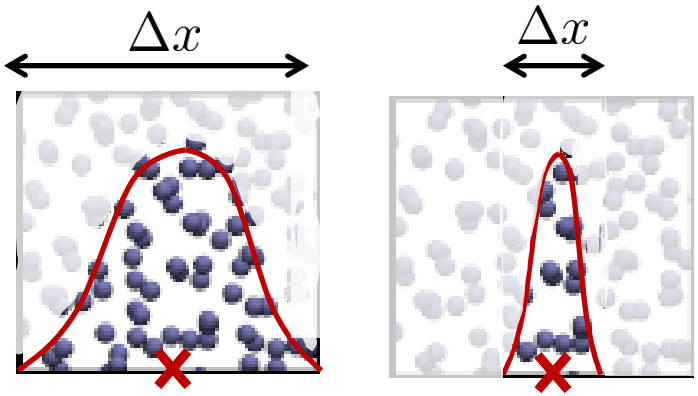
$$m_i \text{ for all i in N}$$



Linking the two formulations

- Irving and Kirkwood (1950) express field based quantities using the Dirac delta functional and ensemble averages

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



- Same **temporal** scale

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

$$\delta(x)=\lim_{\Delta x\to 0}\frac{1}{\Delta x}e^{x^2/\Delta x^2}$$

- Same **spatial** scale
  - » Dirac delta formally correct but no molecule ever at point r
  - » Any approximation to the Dirac delta is no longer formally correct
  - » A discrete system can only be approximately represented using a continuous field

The Control Volume (Weak) Form

- The “weak formulation” expressed the equations in integrated form

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

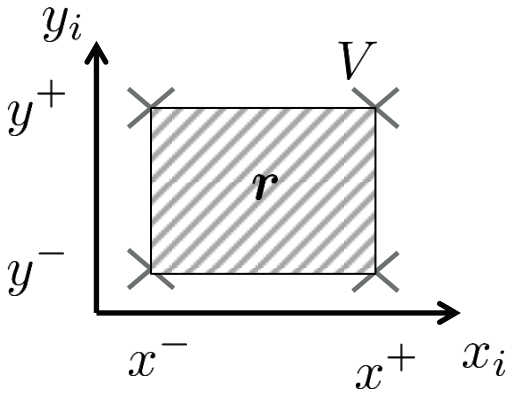
- Integrating the Dirac delta function exactly provides a combination of Heaviside functions

Derivation

- Integrating the Dirac delta function

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

- Over a 2D volume



The Control Volume Functional

- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

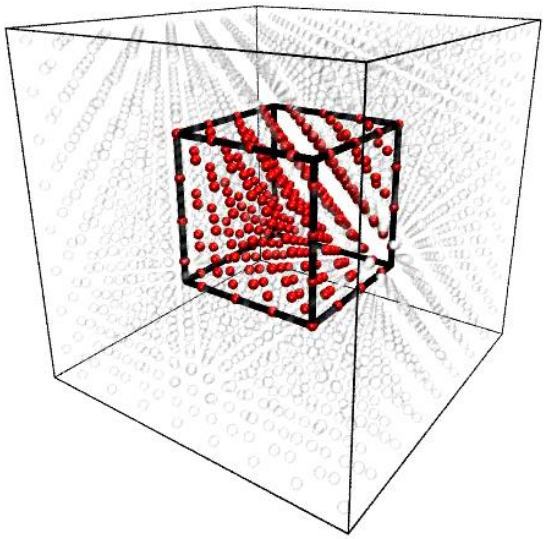
$$= \left[H(x^+ - x_i) - H(x^- - x_i)\right]$$

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

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

- In words

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



Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

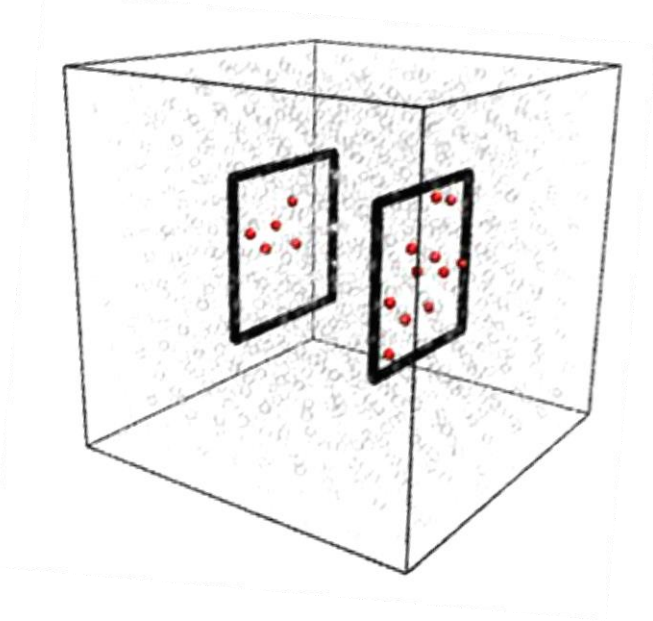
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

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



The Control Volume (Weak) Form

- The “weak formulation” expressed the equations in integrated form

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

Time Evolution

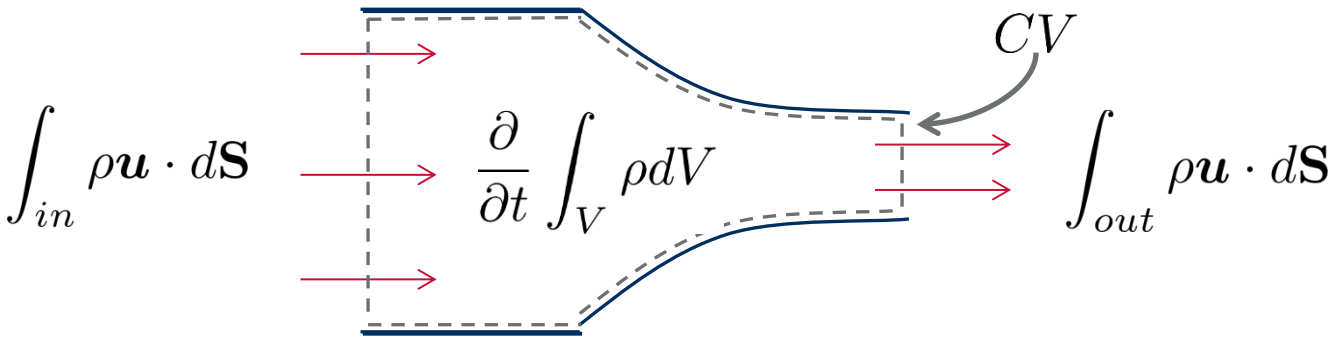
$$\frac{d}{dt}\sum_{i=1}^{N} m_i\vartheta_i = \sum_{i=1}^{N} m_i \frac{d\boldsymbol{r}_i}{dt}\cdot\frac{\vartheta_i}{d\boldsymbol{r}_i} = \sum_{i=1}^{N} m_i \boldsymbol{v}_i \cdot d\mathbf{S}_i$$

Surface Flux

  - Integrating the Dirac delta function exactly provides a combination of Heaviside functions, which can:
    - » Be mathematically manipulated to give fluxes and forces
    - » Be implemented directly in MD codes
    - » Be linked to the continuum control volume (or finite volume) equations as they are no expressed in the same form

Finite (Control) Volume Formulation

- Recall control volume exactly links fluxes to changes inside, consider mass flow in a nozzle

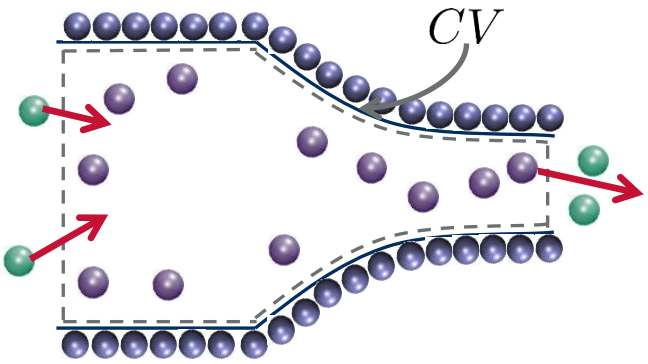


$$\frac{\partial}{\partial t} \int_V \rho dV = \int_{in} \rho \boldsymbol{u} \cdot d\mathbf{S} - \int_{out} \rho \boldsymbol{u} \cdot d\mathbf{S} = - \oint_S \rho \boldsymbol{u} \cdot d\mathbf{S}$$

- Conservative – keeps track of all flow in and out

Finite (Control) Volume Formulation

- Recall control volume exactly links fluxes to changes inside, consider mass flow in a nozzle

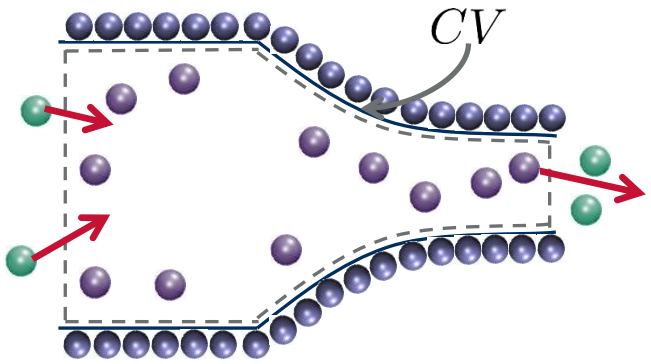


- Conservative – keeps track of all flow in and out

Finite (Control) Volume Formulation

- Recall control volume exactly links fluxes to changes inside, consider mass flow in a nozzle

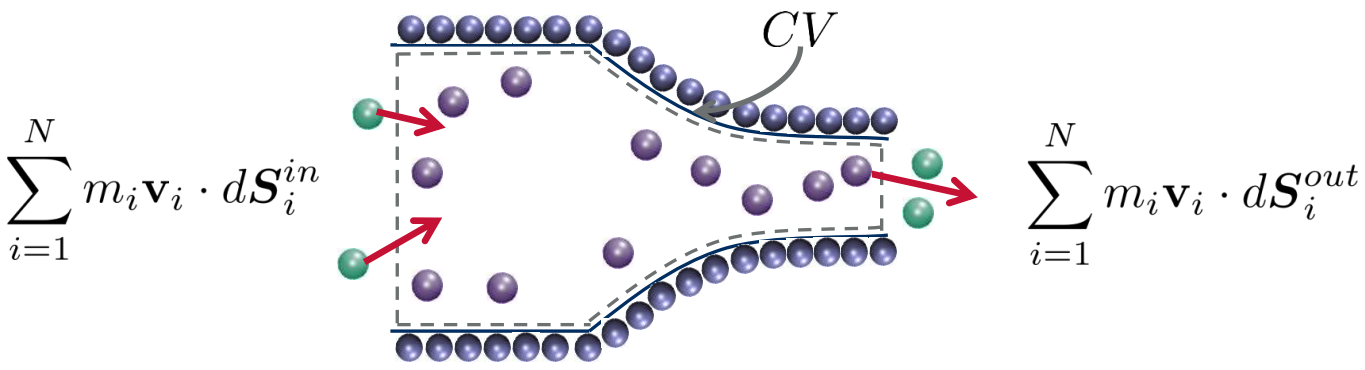
$$\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i^{in}$$



- Conservative – keeps track of all flow in and out

Finite (Control) Volume Formulation

- Recall control volume exactly links fluxes to changes inside, consider mass flow in a nozzle



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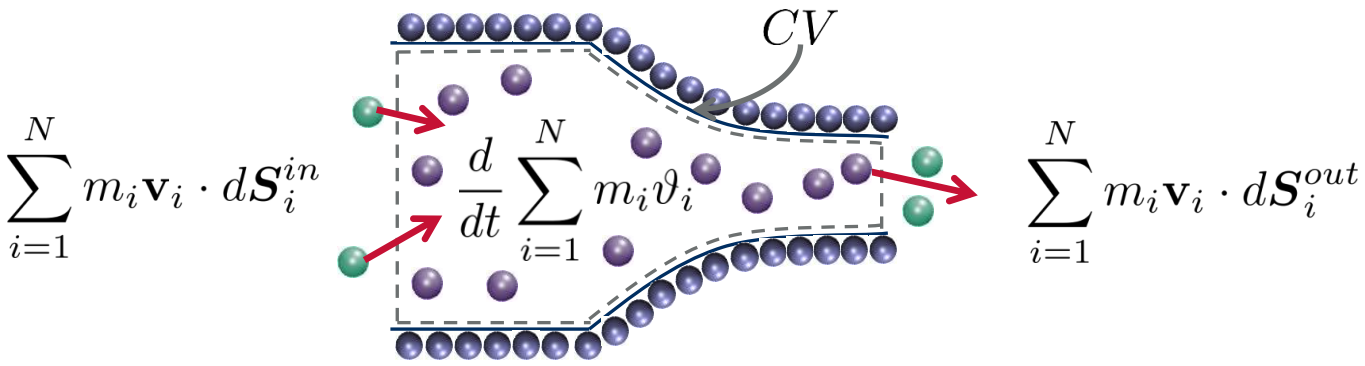
Finite (Control) Volume Formulation

- Recall control volume exactly links fluxes to changes inside, consider mass flow in a nozzle

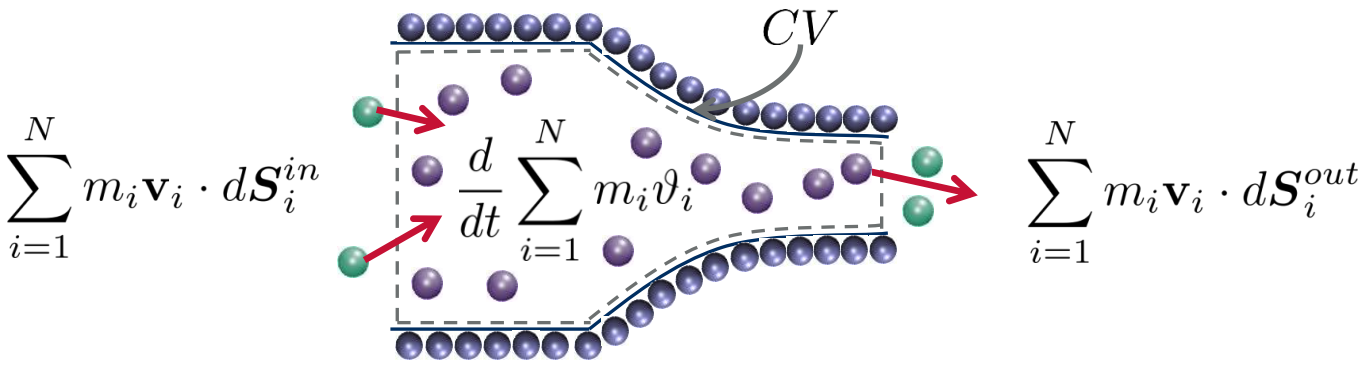


$$\frac{d}{dt} \sum_{i=1}^{N} m_i \vartheta_i = \sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i^{in} - \sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i^{out}$$

- Conservative – keeps track of all flow in and out

Finite (Control) Volume Formulation

- Recall control volume exactly links fluxes to changes inside, consider mass flow in a nozzle



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

- Conservative – keeps track of all flow in and out

The Control Volume Equations

- Mass Conservation

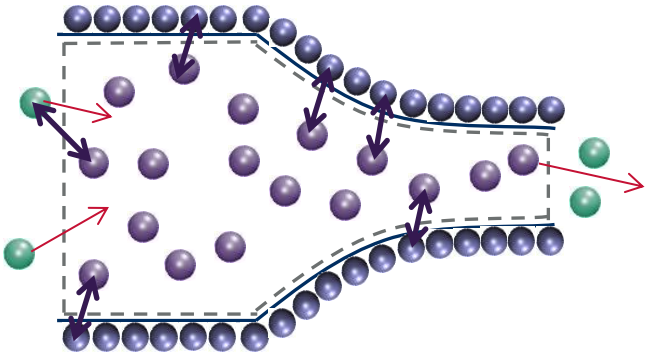
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i$$

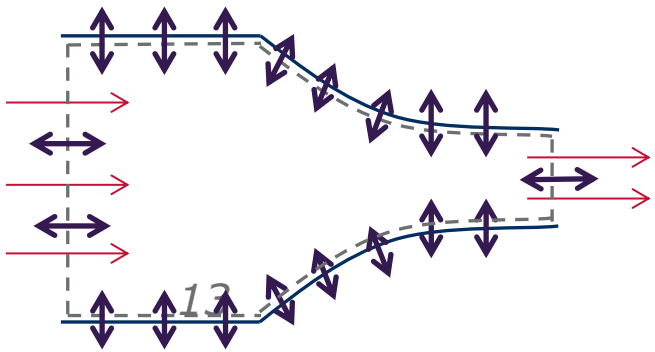
$$\frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u} \cdot d\mathbf{S}$$

- Momentum Balance

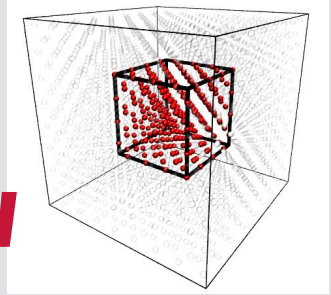
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\mathbf{n} \cdot d\mathbf{S}_{ij}$$

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





Exact Conservation for a cubic CV



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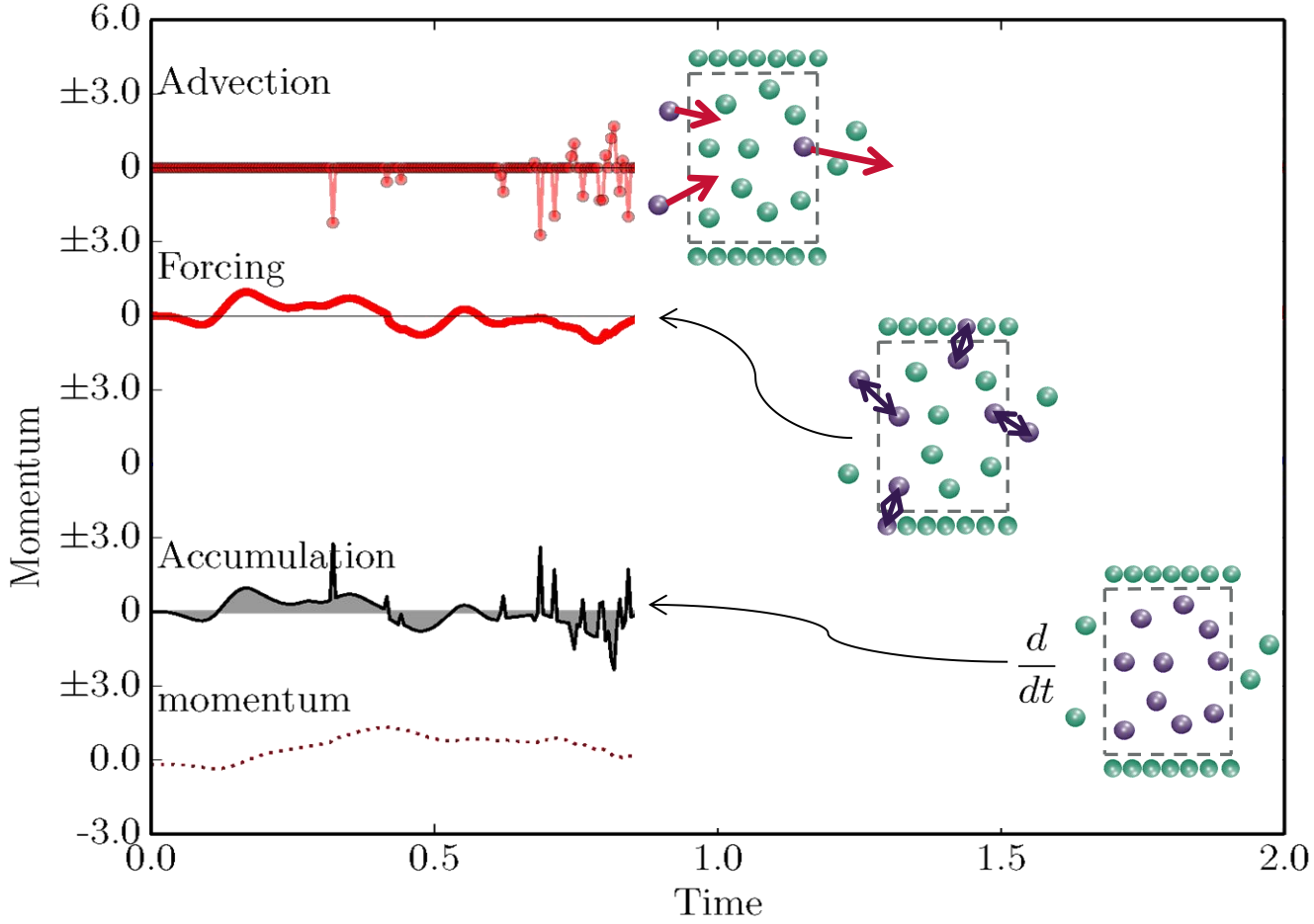
Accumulation = Forcing + Advection

Momentum evolution from integral of Accumulation



Method of Planes on 6 surfaces

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

$$= \underbrace{\frac{d}{dt} \sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\textit{Accumulation}}$$

A more general Control Volume Functional

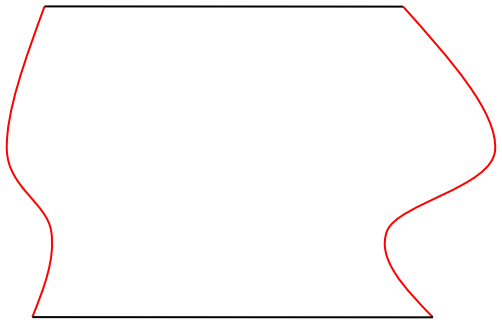
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

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



- In words

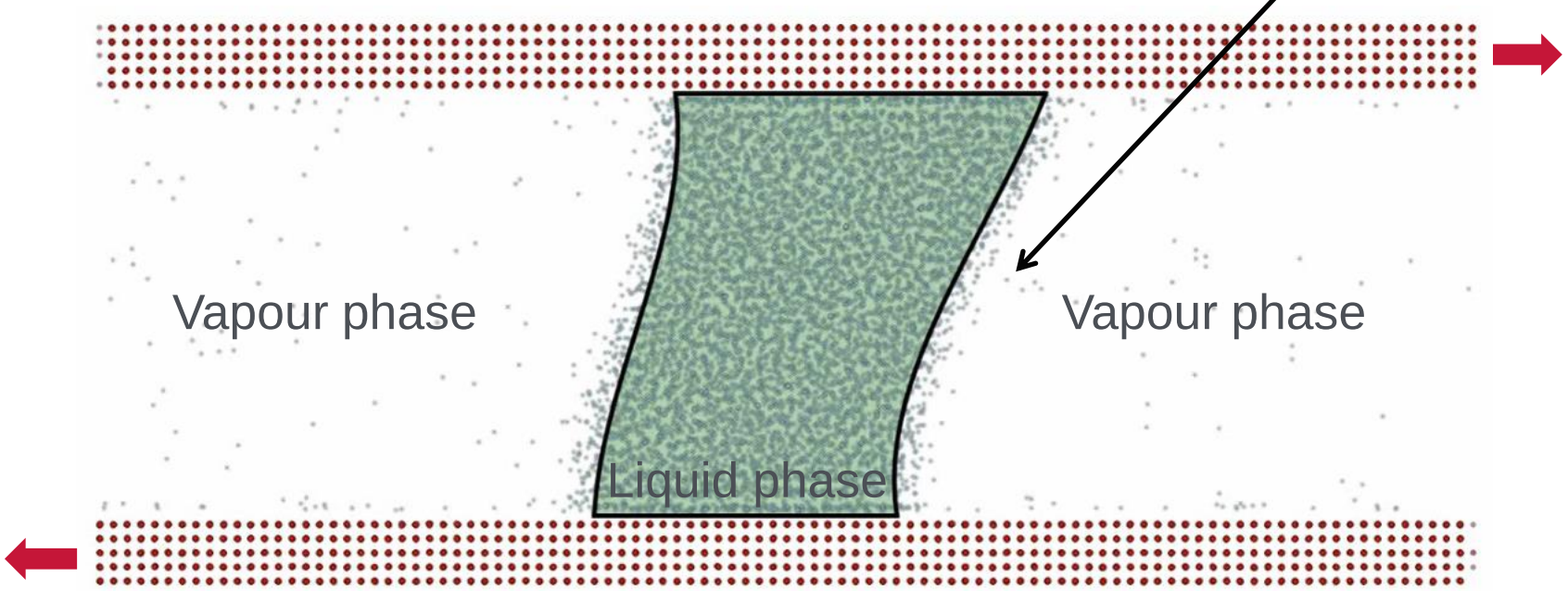
$$\vartheta \equiv \begin{cases} 1 & \text{if molecule is inside volume} \\ 0 & \text{if molecule is outside volume} \end{cases}$$

Moving liquid-vapour interfaces

- Derivative now includes terms for moving surface, curvature, etc

$$dS_{xi}^{+} = \left[\dot{x} - \dot{x}_i + \dot{y}_i \frac{\partial \xi^{+}}{\partial y_i} + \dot{z}_i \frac{\partial \xi^{+}}{\partial z_i} + \frac{\partial \xi^{+}}{\partial t}\right] \delta\left(x^{+} + \xi^{+} - x_i\right) \times \left[H\left(y^{+} - y_i\right) - H\left(y^{-} - y_i\right)\right] \times \left[H\left(z^{+} - z_i\right) - H\left(z^{-} - z_i\right)\right]$$

- Allows MOP stresses to be obtained on arbitrary surfaces



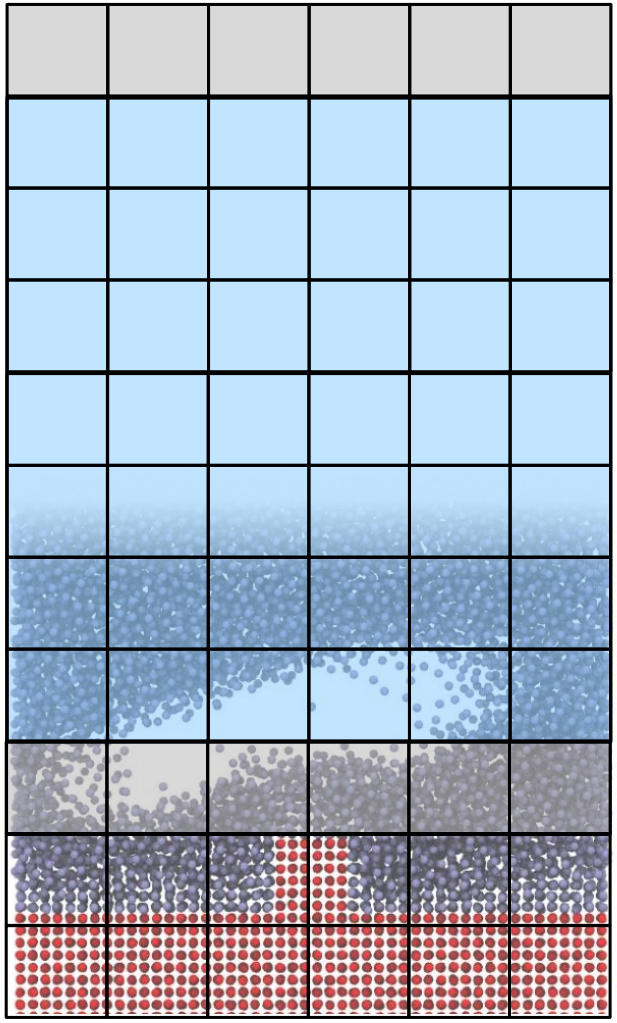
Sliding Solid walls (tethered)

Coupled Simulation

- Only volume averages, fluxes and stresses

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

Use the same volumes



- *Exact sum of discrete molecules in volume, fluxes and stresses (method of planes)*

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

Control Volume Summary

1. It is problematic to discuss continuous fields in a discrete system
   - » We can **never** know values at a point in space in a discrete system
   - » So we should accept this and only ever use spatial averages…
2. Control volume (or weak) formulations expresses the equations of motion as the fluxes, forces and values inside arbitrary volumes
   - » *"It is of philosophical interest to interject here a thought, that perhaps such weak formulation are indeed the requirement of nature as opposed to differential equations"*

     Zienkiewicz (1975) Finite Elements in Fluid, 1st Edition
3. Demonstrate mass, momentum and energy laws are exactly satisfied
   - » Linking the non-unique pressure tensor to momentum change inside a volume (c.f. Schofield and Henderson 1982)
   - » Provides an exact bookkeeping, useful for a number of applications
   - » CV functional mathematical localises to a volume allowing derivation of local constraints for nonequilibrium molecular dynamics (NEMD)

Coupled Simulation

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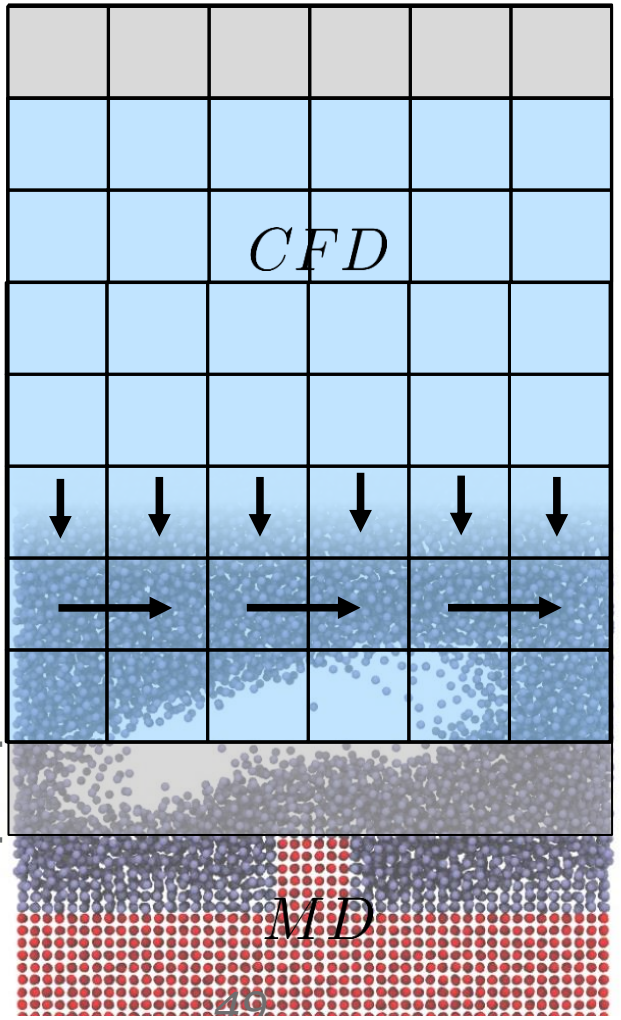
Consistent Framework ✓

CFD→MD Boundary condition

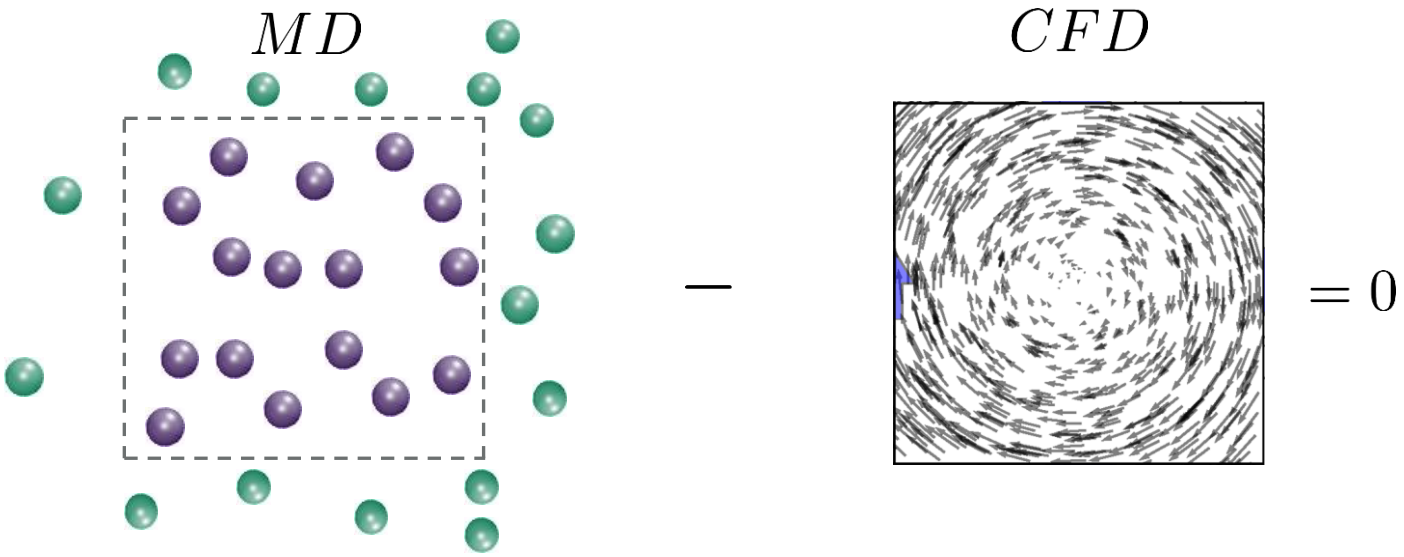
MD→CFD Boundary condition ✓



Constrained Control Volume

- Constrain the momentum in a control volume
  - Fix MD volume to have the same momentum as the CFD

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



Constrained Control Volume

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

- We use the principle of least action $\mathcal{L}_c \equiv \mathcal{L} + \boldsymbol{\lambda} \cdot \boldsymbol{g}$
  - Valid as constraint is semi-holonomic
  - Least action constrained Lagrangian → Euler Lagrange

$$\delta A_c = \delta \int_a^b \mathcal{L}_c dt = 0 \qquad \frac{d}{dt}\frac{\partial \mathcal{L}_c}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}_c}{\partial q_i} = 0,$$

Least Action used by O'Connell Thompson (1995)

Constrained Control Volume

- Constrain the momentum in a control volume
  - Fix MD volume to have the same momentum as the CFD

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

- The conjugate momentum is,

$$\boldsymbol{p}_i = \frac{\partial \mathcal{L}_c}{\partial \dot{\boldsymbol{q}}_{\boldsymbol{i}}} = m_i \dot{\boldsymbol{q}}_i + m_i \vartheta_i \boldsymbol{\lambda}$$

- And the constrained Euler Lagrange equation,

$$\dot{\boldsymbol{p}}_i = \frac{\partial \mathcal{L}_c}{\partial \boldsymbol{q}_{\boldsymbol{i}}} = \boldsymbol{F}_i - \boldsymbol{\lambda} m_i \dot{\boldsymbol{q}}_i \cdot d\mathbf{S}_i$$

Constrained Control Volume

- Substituting into the constraint and solving for lambda

$$\boldsymbol{\lambda} = \frac{1}{\sum_{n=1}^{N} m_n \vartheta_n^2} \left[\sum_{n=1}^{N} \boldsymbol{p}_n \vartheta_n - \int_V \rho \boldsymbol{u} dV \right],$$

- Gives the following equations of motion

$$\dot{\boldsymbol{q}}_i = \frac{\boldsymbol{p}_i}{m_i} - \frac{\vartheta_i}{M_I} \left[\sum_{n=1}^{N} \boldsymbol{p}_n \vartheta_n - \int_V \rho \boldsymbol{u} dV \right],$$

$$\dot{\boldsymbol{p}}_i = \boldsymbol{F}_i - \frac{m_i \dot{\boldsymbol{q}}_i \cdot d\mathbf{S}_i}{M_I} \left[\sum_{n=1}^{N} \boldsymbol{p}_n \vartheta_n - \int_V \rho \boldsymbol{u} dV \right],$$

Constrained Control Volume

- Combining the equations we get Newton's law

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

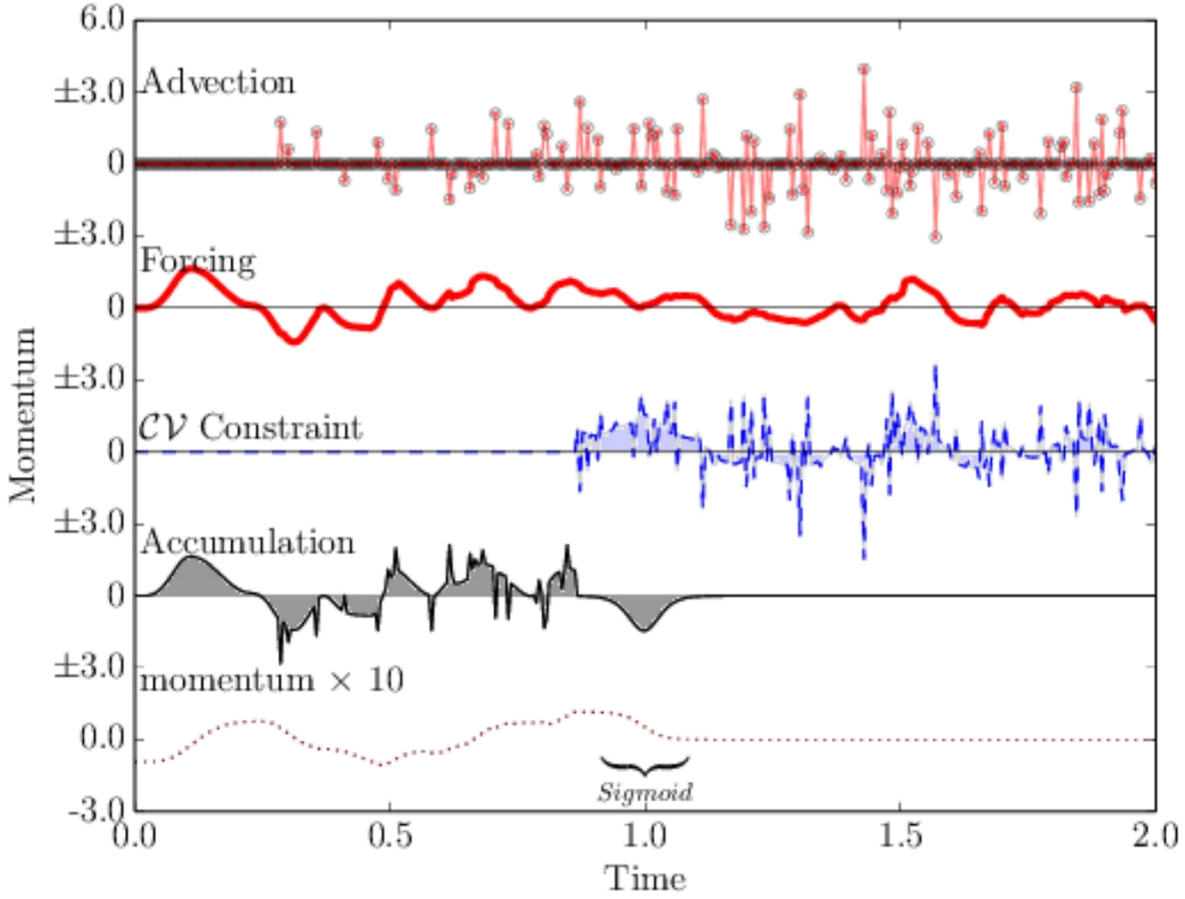
$$\boldsymbol{F}_i^C \equiv \frac{m_i \vartheta_i}{M_I}\left[\frac{d}{dt}\int_V \rho \boldsymbol{u} dV - \overbrace{\left(-\sum_{n=1}^{N} m_i \dot{\boldsymbol{r}}_{\boldsymbol{n}} \dot{\boldsymbol{r}}_n \cdot d\mathbf{S}_n\right)}^{\text{Advection}} + \overbrace{\sum_{n,m}^{N} \boldsymbol{f}_{nm}\mathbf{n}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

- The same equation can be obtained by applying Gauss' principle of least constraint with same ***g***

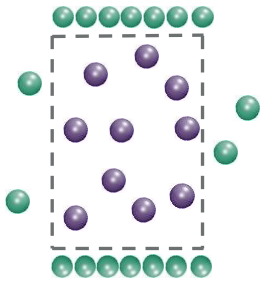
$$\frac{\partial}{\partial \boldsymbol{r}_{ij}} \sum_{i=1}^{N} \left[\boldsymbol{F}_i - \boldsymbol{r}_{ij}\right]^2 - \boldsymbol{\lambda} \cdot \boldsymbol{g} = 0$$

Constrained Control Volume

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

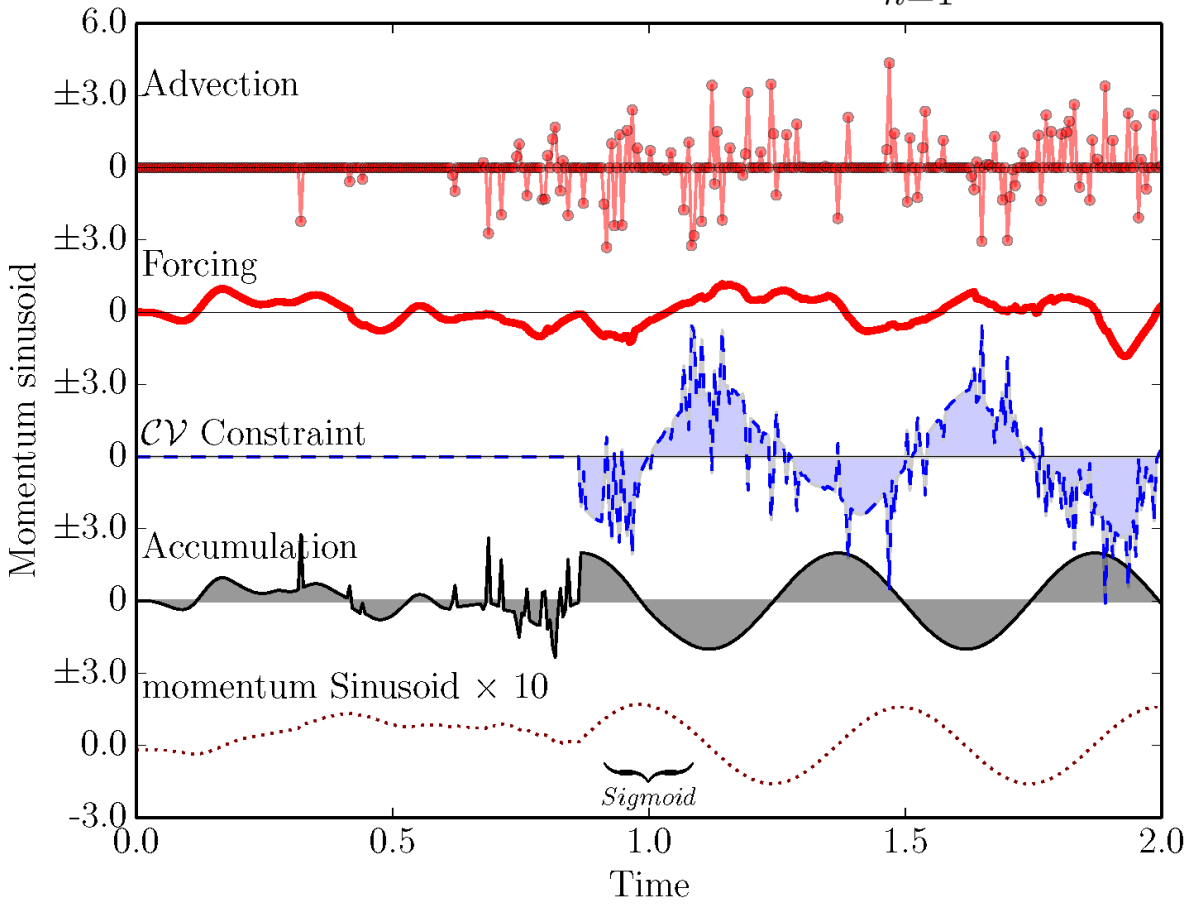


- Zero time evolution applied
- No momentum evolution results
- Exact control of momentum using **iteration**

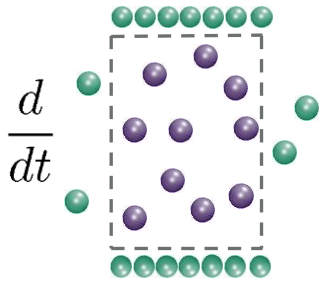
$$\frac{d}{dt}$$  $$= 0$$

Constrained Control Volume

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



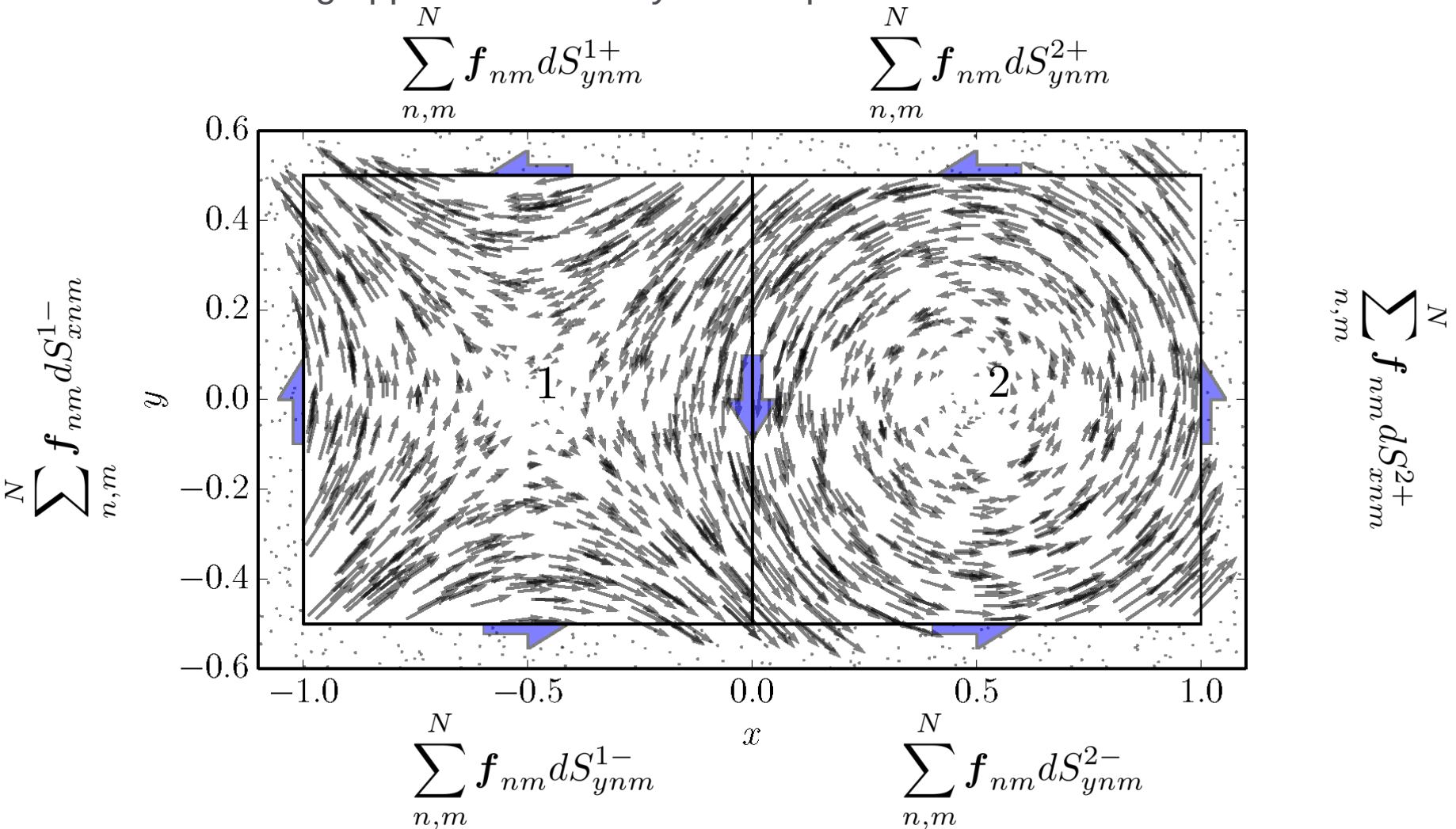
- Cosinusoidal time evolution applied
- Sinusoidal velocity evolution results
- Exact control of momentum using iteration



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

Using linear weighting between surfaces

- Forcing applies an arbitrary 18 component 3D stress field



Using linear weighting between surfaces

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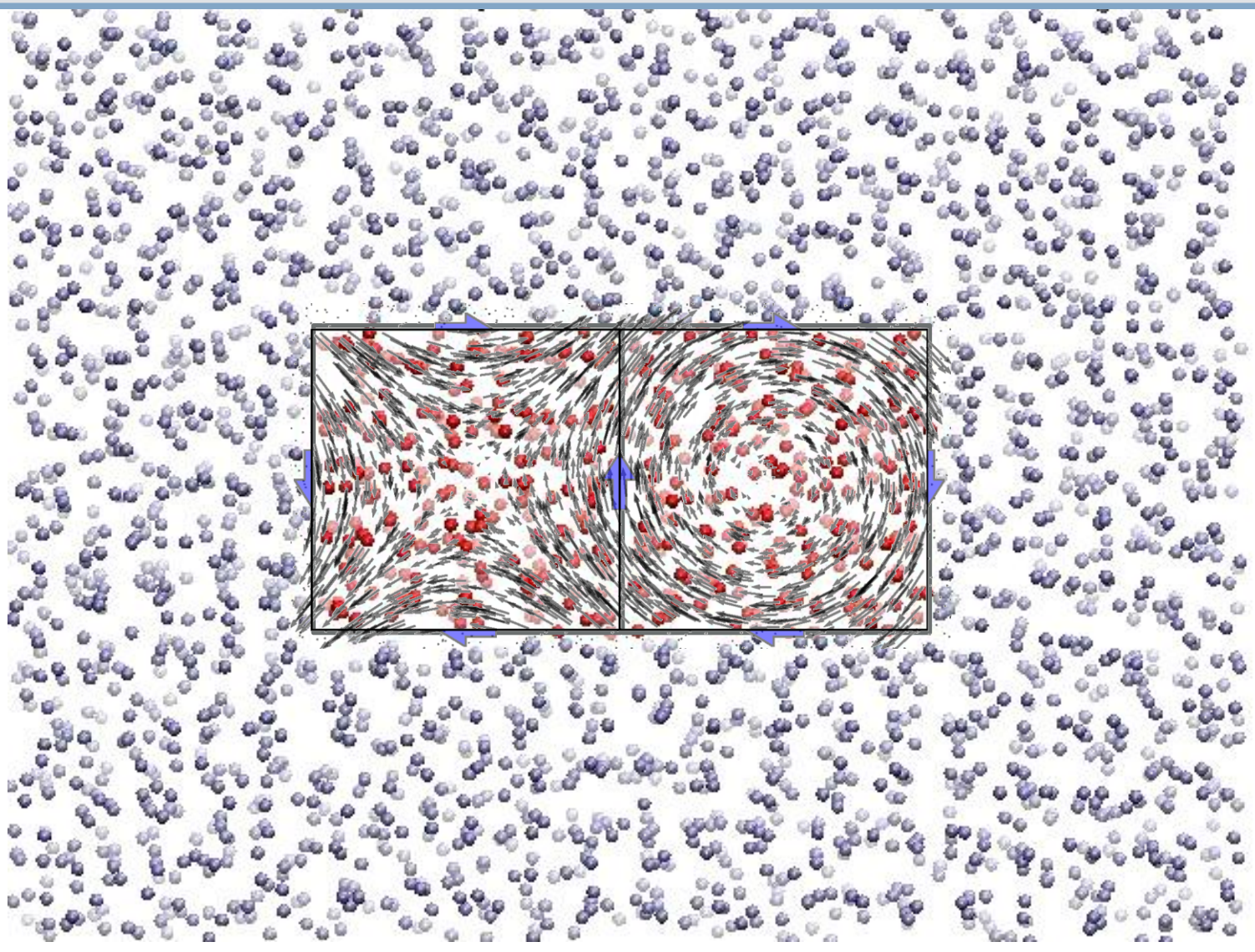
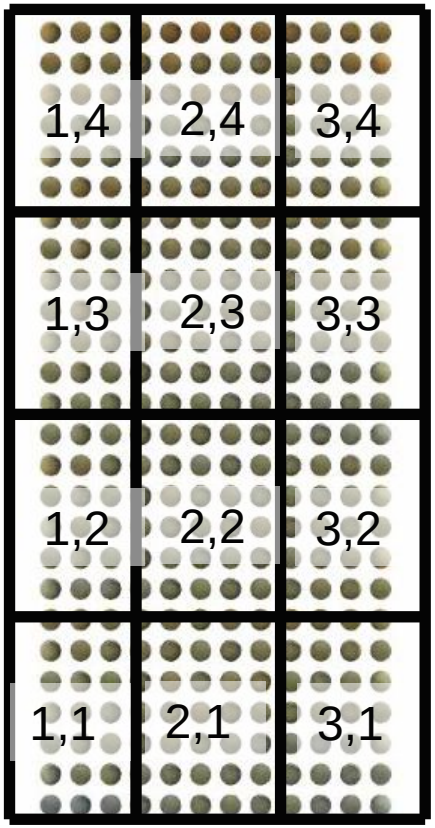


Link to SLLOD

- We can apply the constraint in a grid of control volumes with indices *I,J,K*

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



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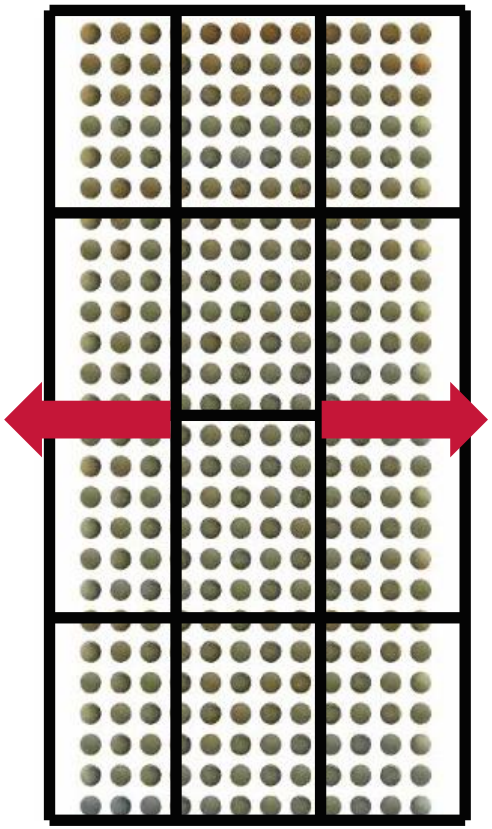
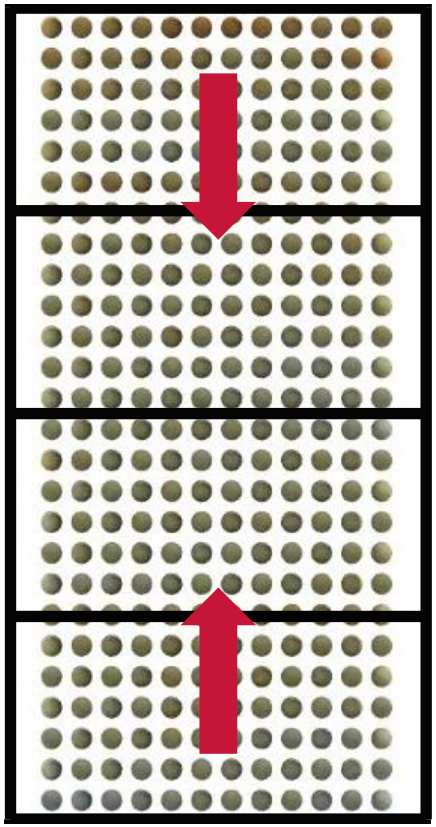


- SLLOD is the limiting case with
  - No CFD time evolution
  - Infinitely wide volumes

Link to SLLOD

- We can apply the constraint in a grid of control volumes with indices *I,J,K*

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



- SLLOD is the limiting case with
  - No CFD time evolution
  - Infinitely wide volumes
  - Infinitesimally thin volumes

Link to SLLOD

- We can apply the constraint in a grid of control volumes with indices *I,J,K*

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

- SLLOD is the limiting case with
  - No CFD time evolution
  - Infinitely wide volumes
  - Infinitesimally thin volumes
- Resulting energy addition in this limiting case is the same as SLLOD

$$\int_{-\infty}^{\infty} \lim_{\Delta x \to \infty} \lim_{\Delta y \to 0} \lim_{\Delta z \to \infty} \dot{\boldsymbol{r}}_i \cdot \boldsymbol{F}_i^{C_{IJK}} dy$$

$$= \boldsymbol{\nabla u} : \boldsymbol{\Pi}_{MD} = \dot{\mathcal{H}}_{SLLOD}$$

Phase Space Compressibility

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- Phase space compressibility κ is defined as,

$$\kappa = \sum_{i=1}^{N} \left[\frac{\partial}{\partial \boldsymbol{p}_i} \cdot \dot{\boldsymbol{p}}_i + \frac{\partial}{\partial \boldsymbol{q}_i} \cdot \dot{\boldsymbol{q}}_i \right]$$

- Substituting in the equations of motion and working through gives an expression in terms of surface fluxes

$$\kappa = \frac{(\mathcal{D}-1)}{M_I} \sum_{i=1}^{N} (m_i \boldsymbol{\lambda} \vartheta_i - \boldsymbol{p}_i \vartheta_i - M_I \boldsymbol{\lambda}) \cdot d\mathbf{S}_i$$

- Where

$$\boldsymbol{\lambda} = \frac{1}{\sum_{n=1}^{N} m_n \vartheta_n^2} \left[\sum_{n=1}^{N} \boldsymbol{p}_n \vartheta_n - \int_V \rho \boldsymbol{u} dV \right],$$

Constraint Summary

- Apply localised momentum constraint using CV function, ϑ_i

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

- The resulting equations use the exact CV bookkeeping
  - » Iterate, like SHAKE, to ensure time evolution of momentum is EXACTLY controlled (apply force, get flux, correct force, get flux)
  - » Only possible by counting flux of every molecule and all stresses
- A useful NEMD constraint?
  - » Phase space compression is all due to surface flux
  - » Limiting case of infinitesimal volumes adds the same energy as the SLLOD algorithm
  - » Could be applied to localised thermostats or control other quantities in an NEMD simulation

Coupled Simulation

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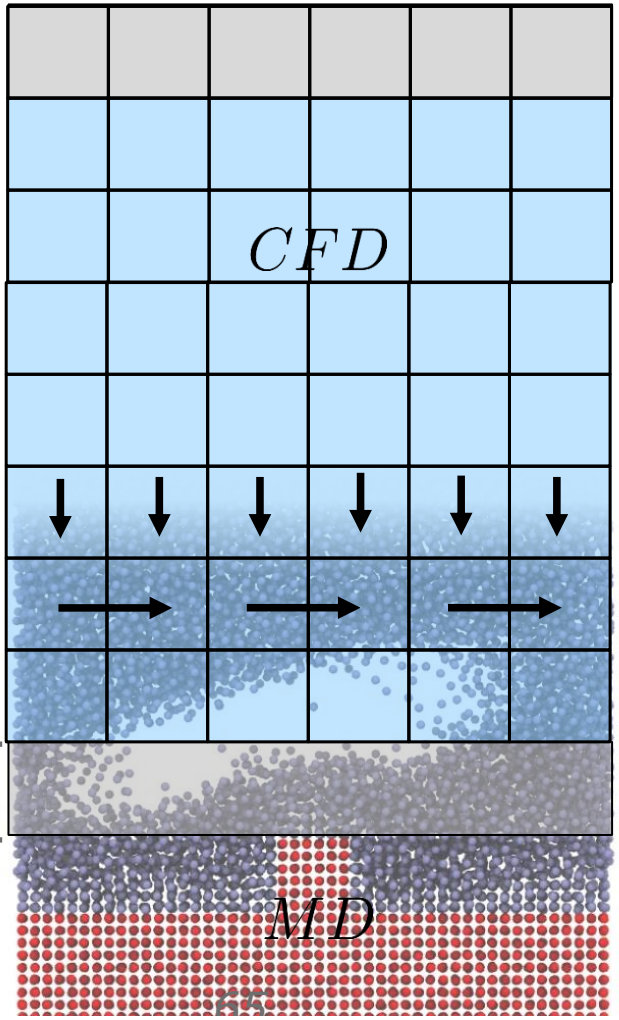
Consistent Framework ✓

CFD→MD Boundary condition ✓

MD→CFD Boundary condition ✓



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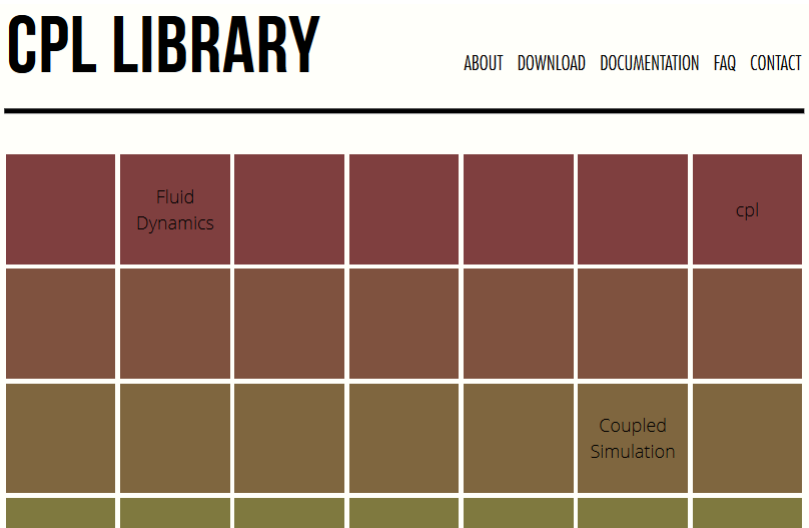
COUPLED SIMULATION

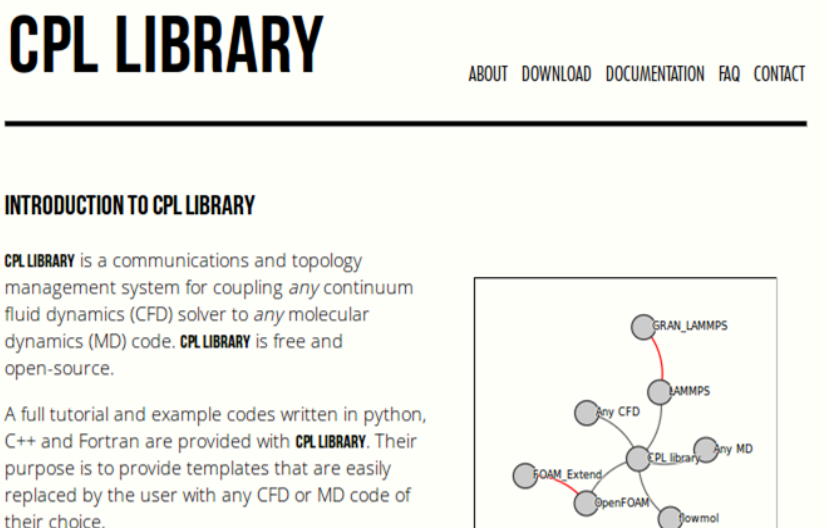
Software Developments

Results

CPL library

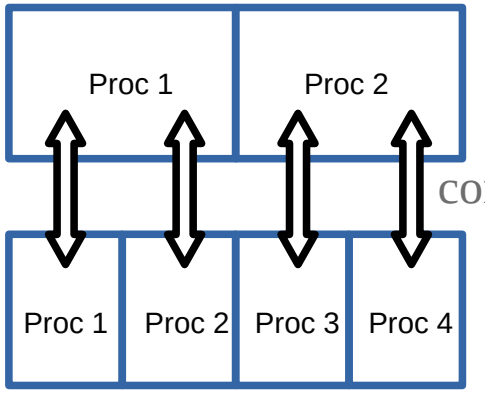
- Open Source (www.cpl-library.org) Fortran, C, C++ and Python bindings
- Designed to facilitate the linking of massively parallel codes with minimal impact on performance of each code (based on MPI)
- Shared library with no external dependencies beyond standard packages
- Minimal set of functions and examples with Python and google tests with key functionality (and examples) subject to continuous integration testing
- Aims to lower barrier to entry for coupled simulation



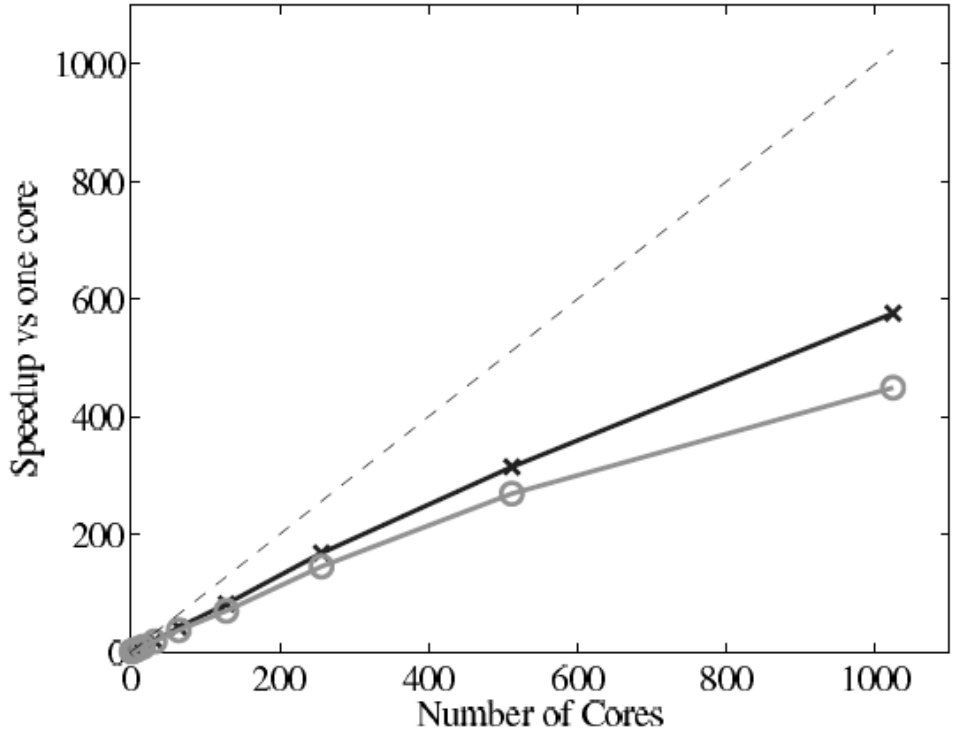


CPL library

- Developed for linking of particle and continuum code
- Previous focus on scalability (for supercomputers)



All MPI communications are local

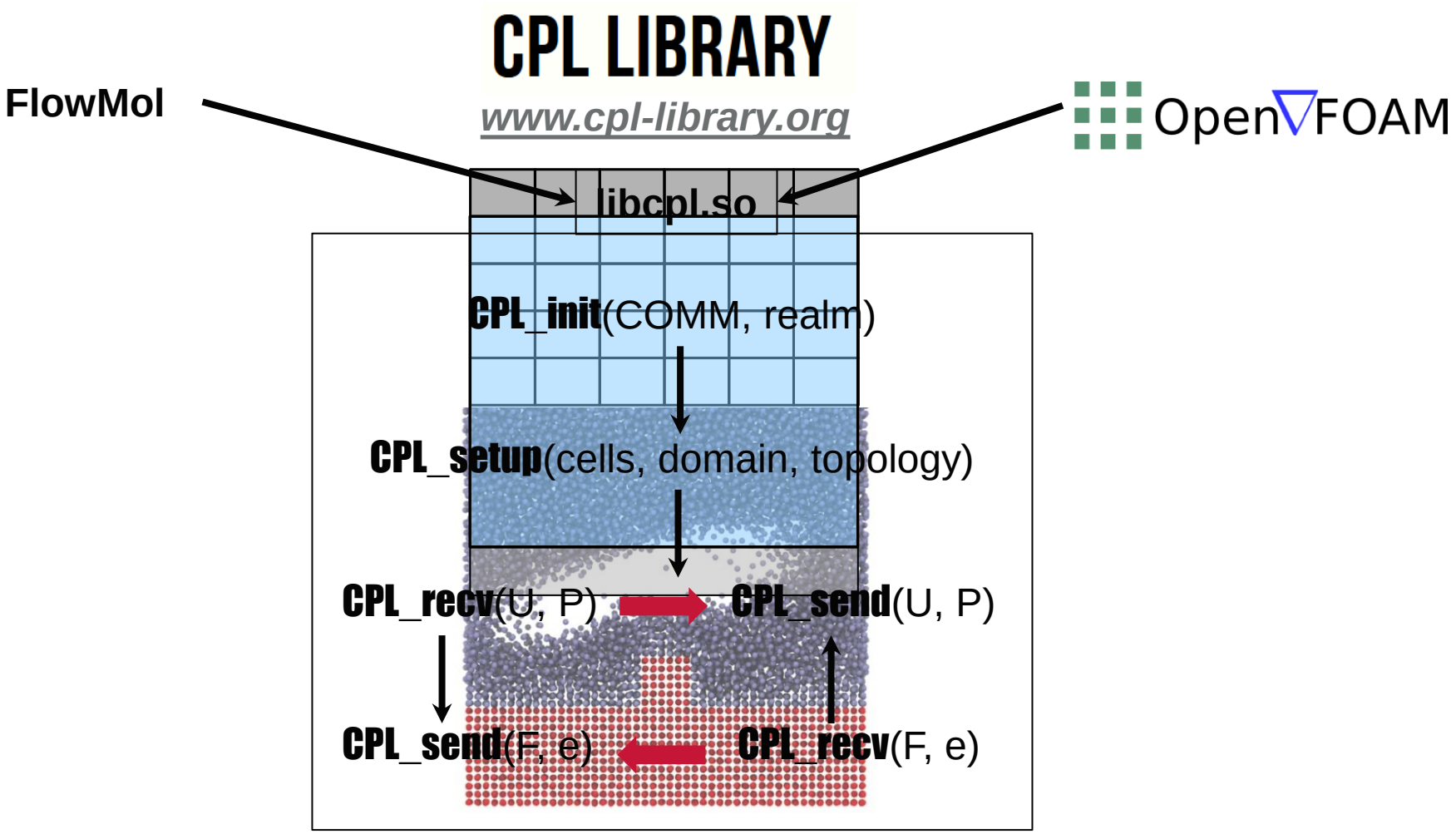


(a) Parallel speedup of the MD solver only (×), coupled code (○) against the ideal speedup (−−)

- Current focus on reliability and ease of use
- Maintains separate scope of each code by linking shared library

Weak scaling
- Particle only x
- Particle Coupled o

Coupled Simulation Software



Coupled Simulation Software

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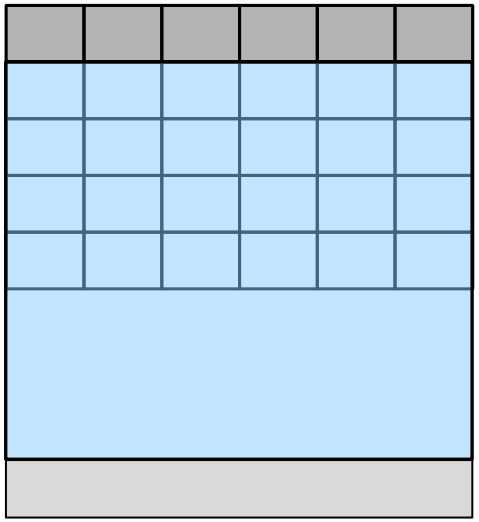
CPL Mock MD

CPL LIBRARY

www.cpl-library.org

OpenFOAM



libcpl.so

CPL_init(COMM, realm)

CPL_setup(cells, domain, topology)

CPL_recv(U, P) → **CPL_send**(U, P)

CPL_send(F, e) ← **CPL_recv**(F, e)

MD_Mock.py

```
CPL_recv(A)
asset A==TestA

CPL_send(testB)
```

Coupled Simulation Software

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CPL LIBRARY

www.cpl-library.org

FlowMol

CPL Mock CFD

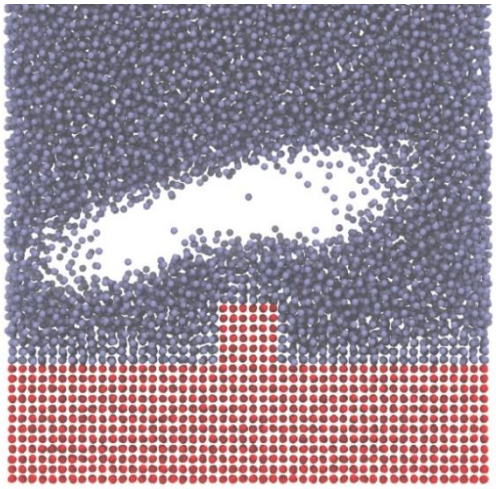
libcpl.so

CPL_init(COMM, realm)

CPL_setup(cells, domain, topology)

CPL_recv(U, P) → **CPL_send**(U, P)

CPL_send(F, e) ← **CPL_recv**(F, e)



CFD_Mock.py

```
CPL_send(TestA)


CPL_recv(B)

asset B==TestB
```

Extending to use LAMMPS

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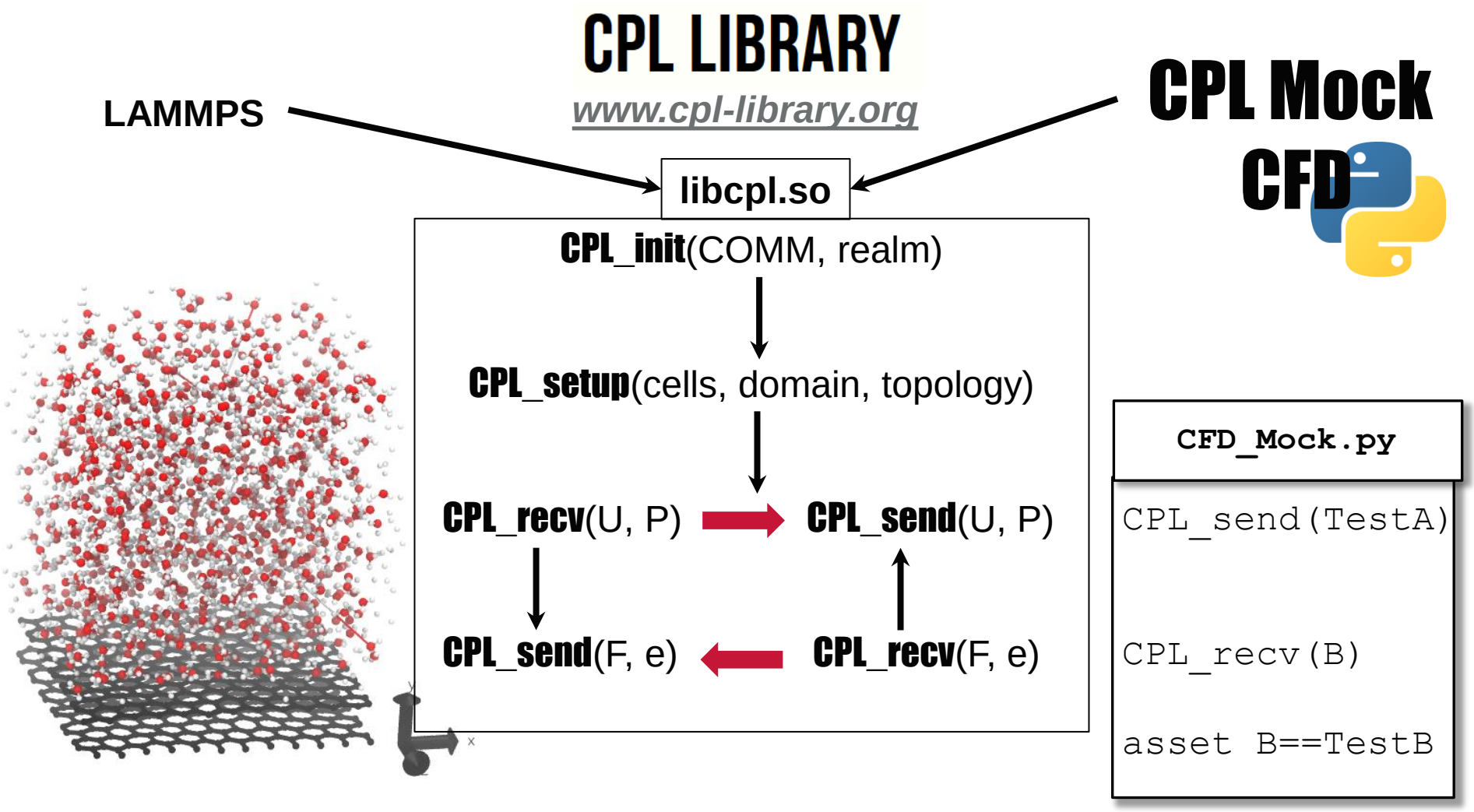
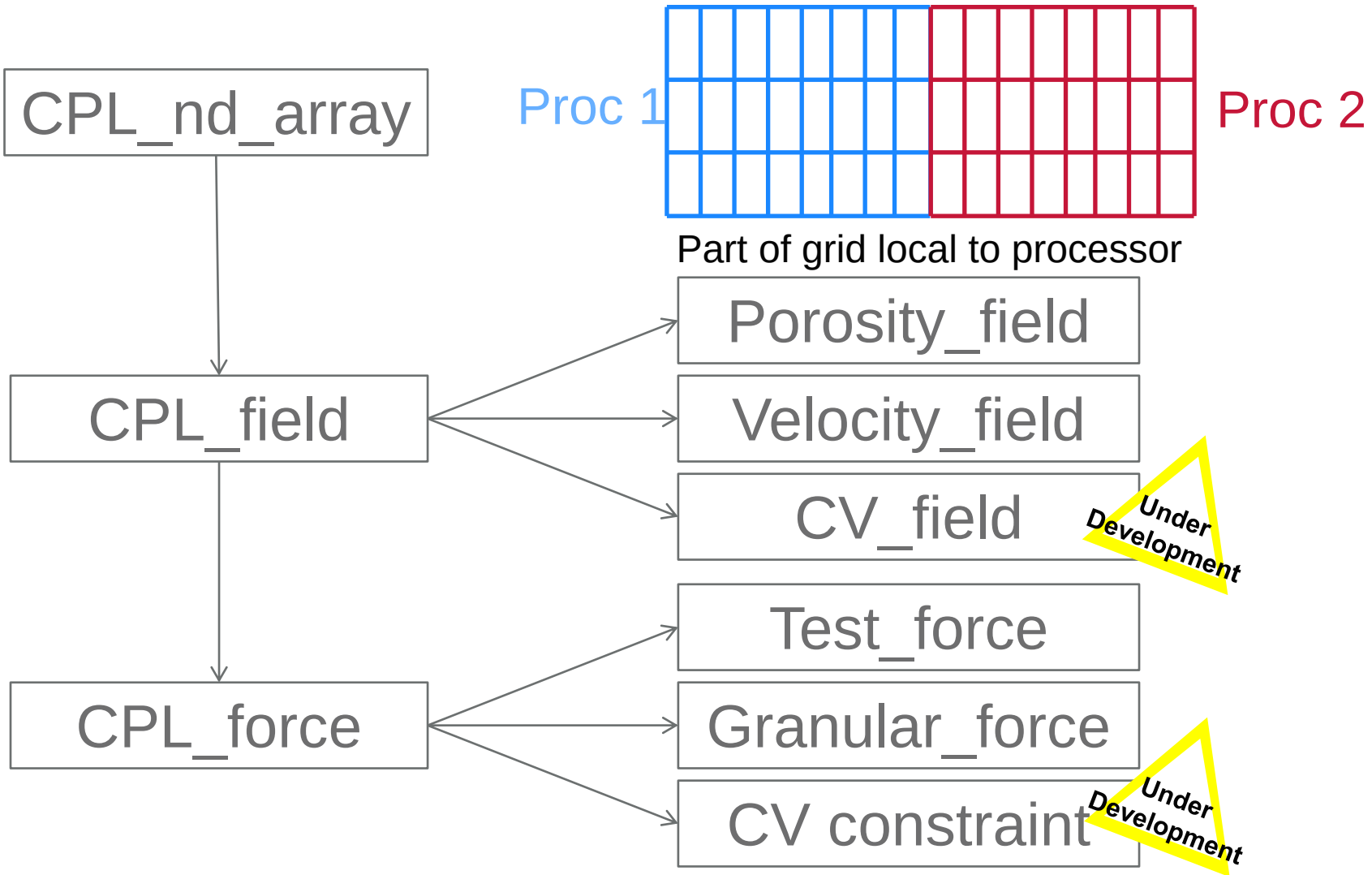


Extending to use LAMMPS



All Developed with Unit Testing

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- Testing the basic units of code

```
TEST_F(CPL_Force_Test, test_CPL_array_size) {
    int nd = 9;
    int icell = 3;
    int jcell = 3;
    int kcell = 3;
    CPL::ndArray<double> buf;
    int shape[4] = {nd, icell, jcell, kcell};
    buf.resize (4, shape);

    //Test sizes and shapes
    ASSERT_EQ(buf.size(), nd*icell*jcell*kcell);
    ASSERT_EQ(buf.shape(0), nd);
    ASSERT_EQ(buf.shape(1), icell);
    ASSERT_EQ(buf.shape(2), jcell);
    ASSERT_EQ(buf.shape(3), kcell);

};
```

Coupling Results – Couette Flow

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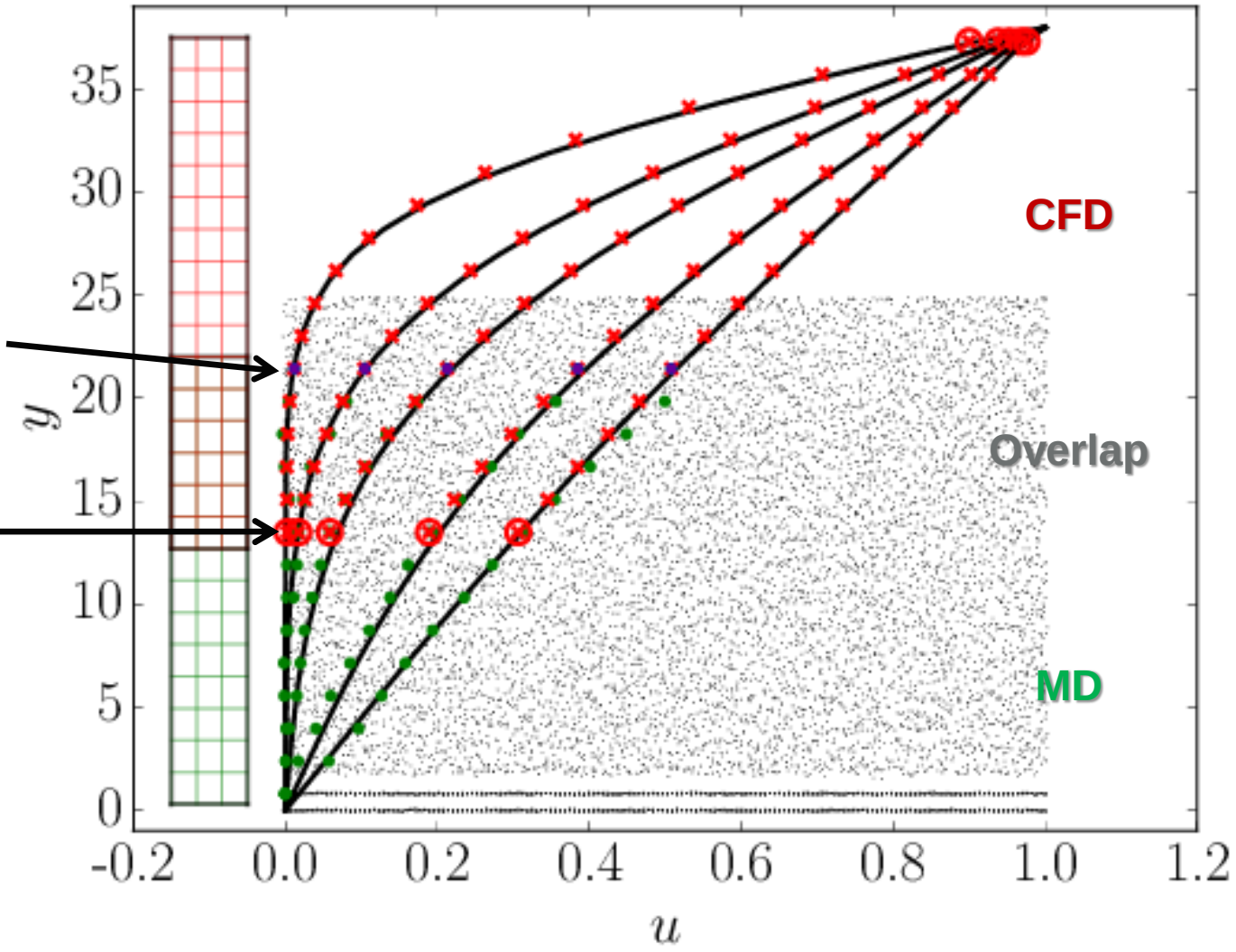
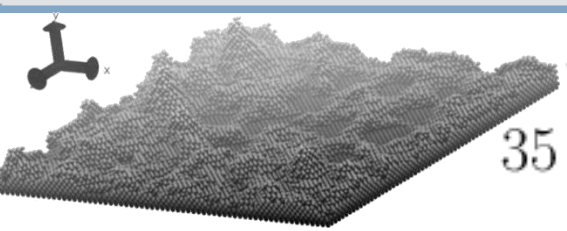
Constraint

CFD Boundary



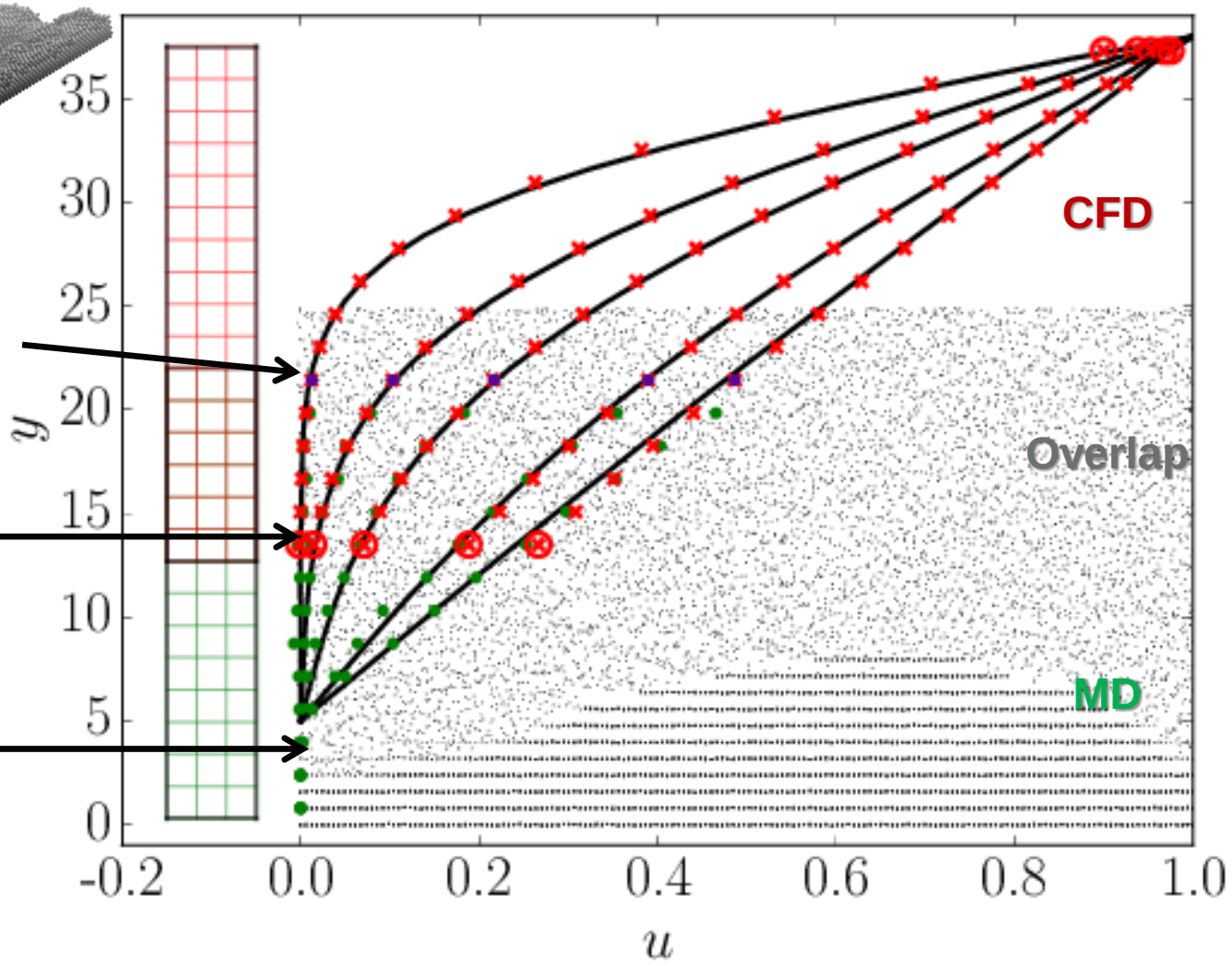
Coupling Results – Couette Flow



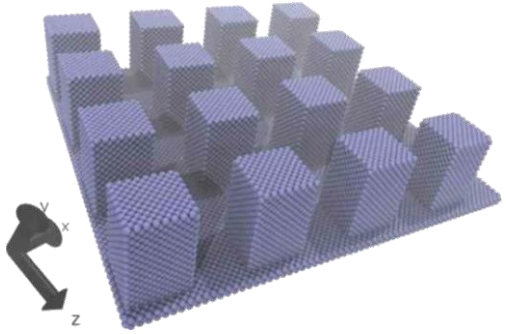
Constraint

CFD Boundary

Rough wall shifts zero velocity location



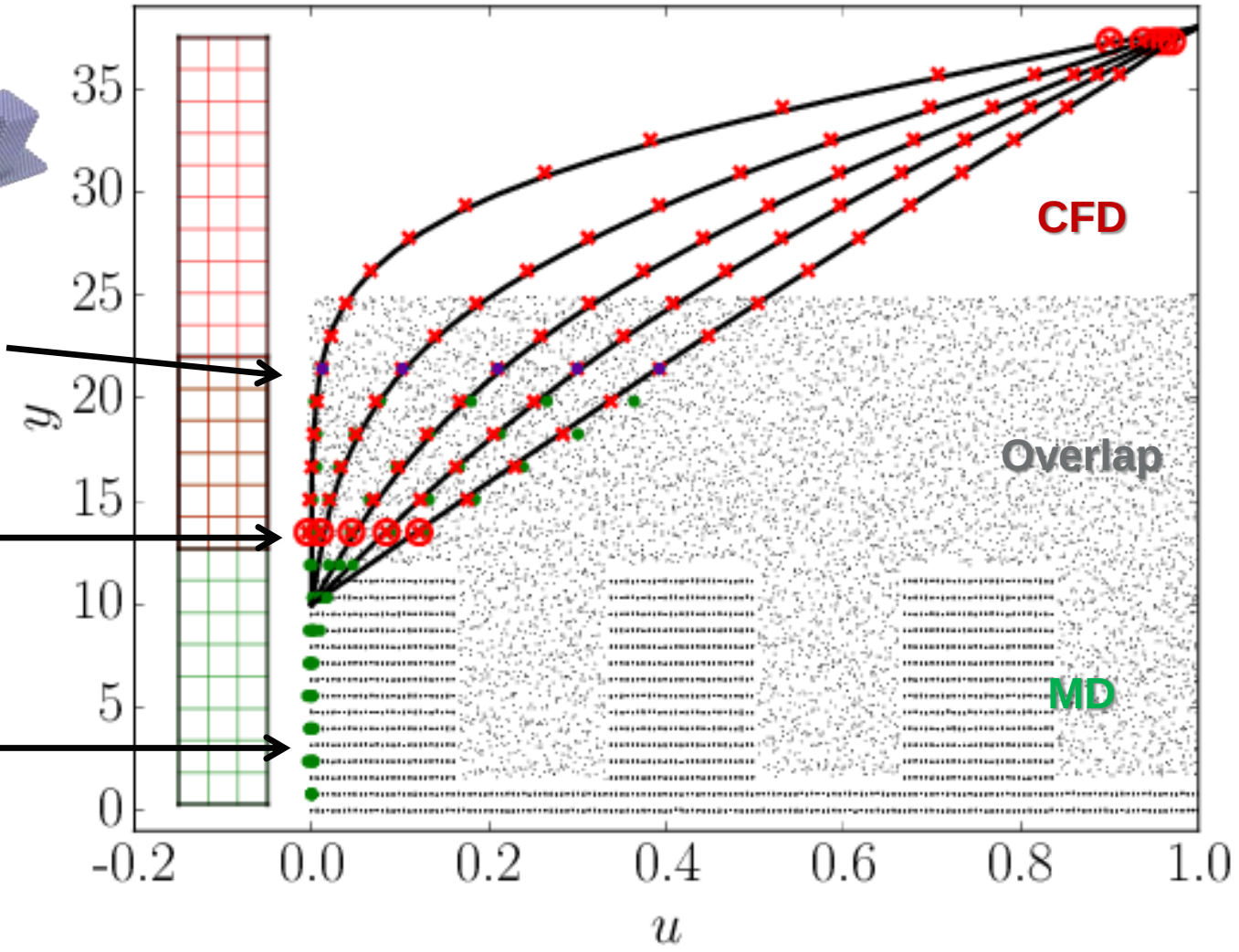
Coupling Results – Couette Flow



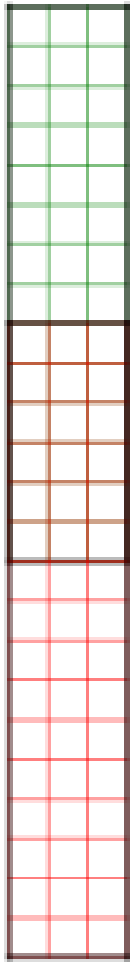
Constraint

CFD Boundary

Posts shifts zero velocity location



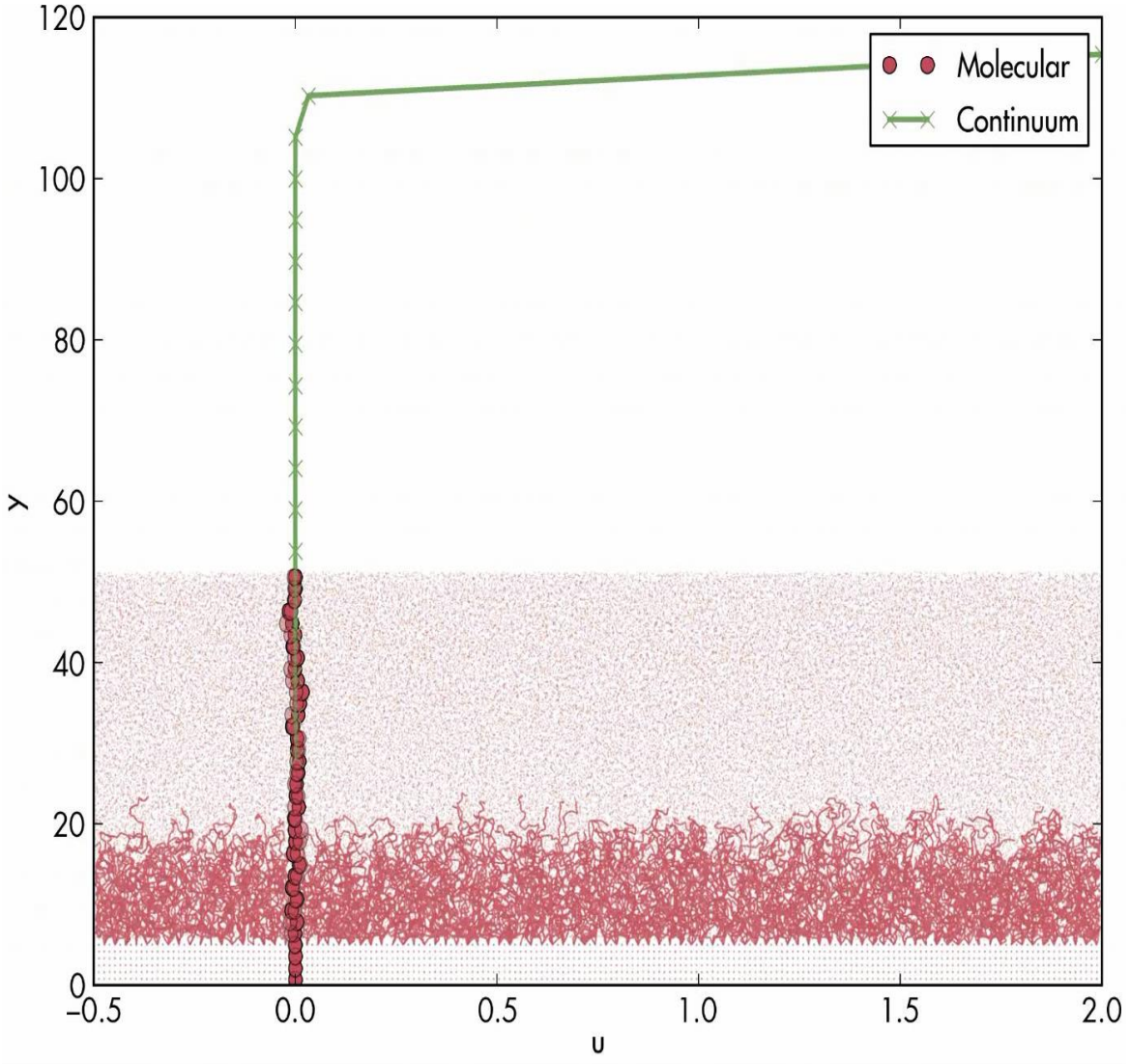
Coupling Results – Polymer Brushes



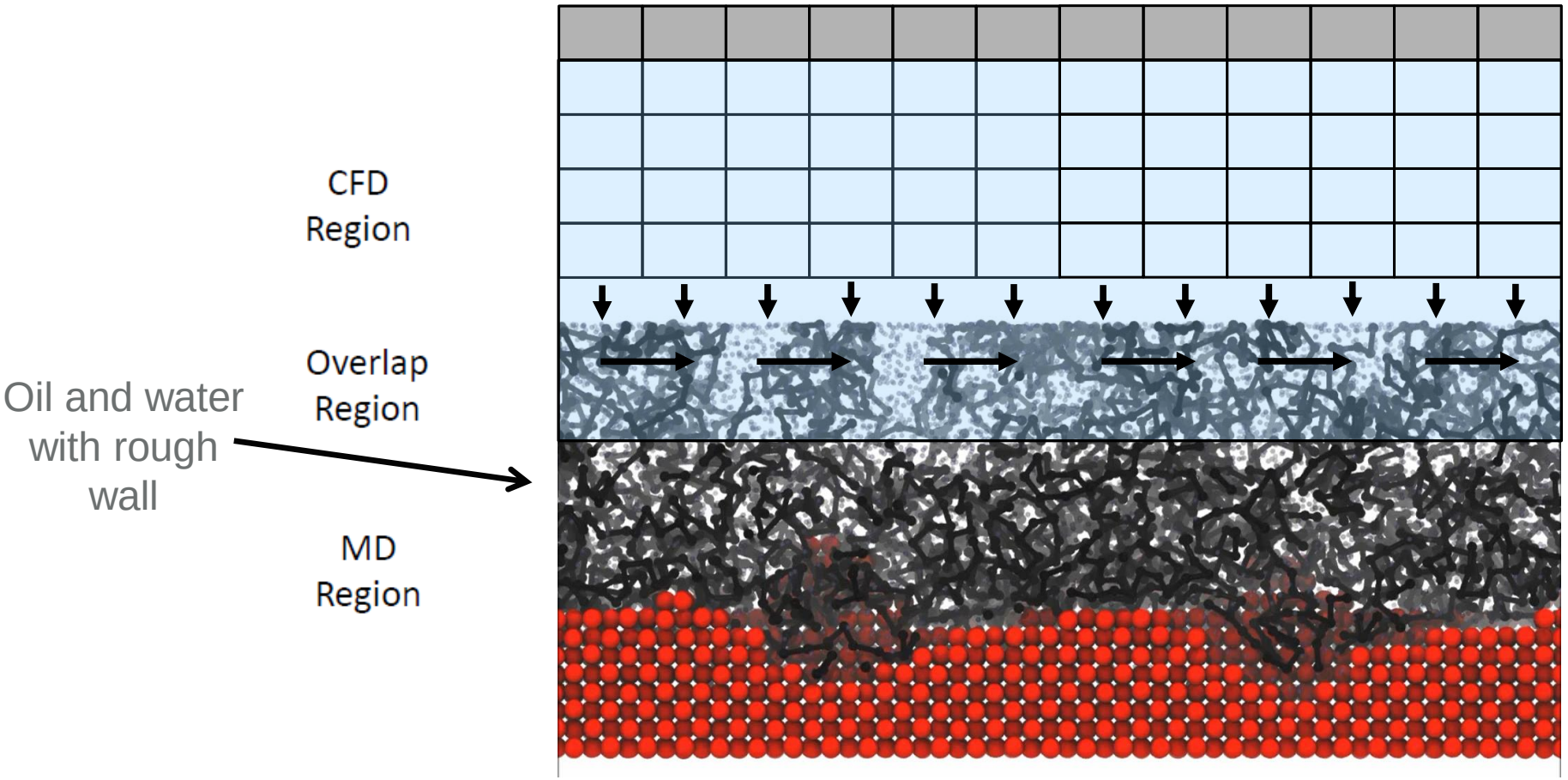
CFD Region

Overlap Region

MD Region



Coupling Results – Couette Flow



Molecular Simulation of Turbulence

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Molecular Simulation of Turbulence

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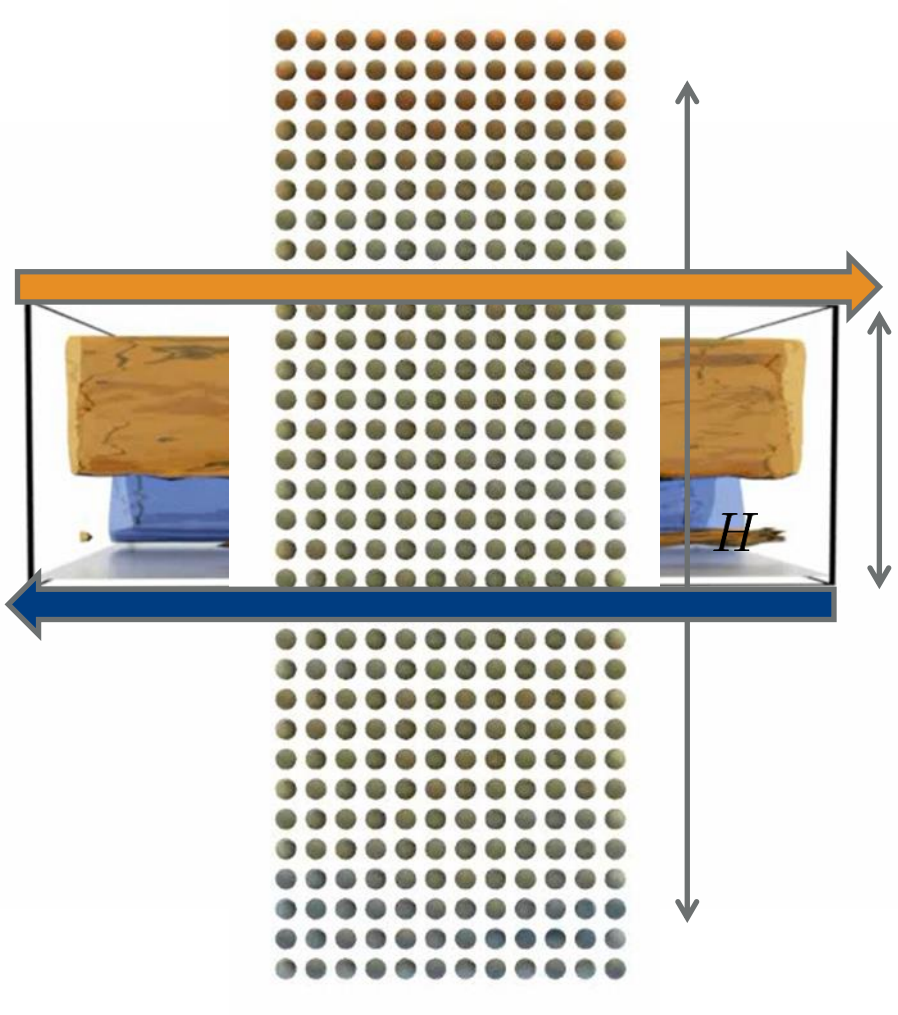

Reynolds Number

$Re \approx 400$

with

300 million molecules

Molecular Simulation of Turbulence

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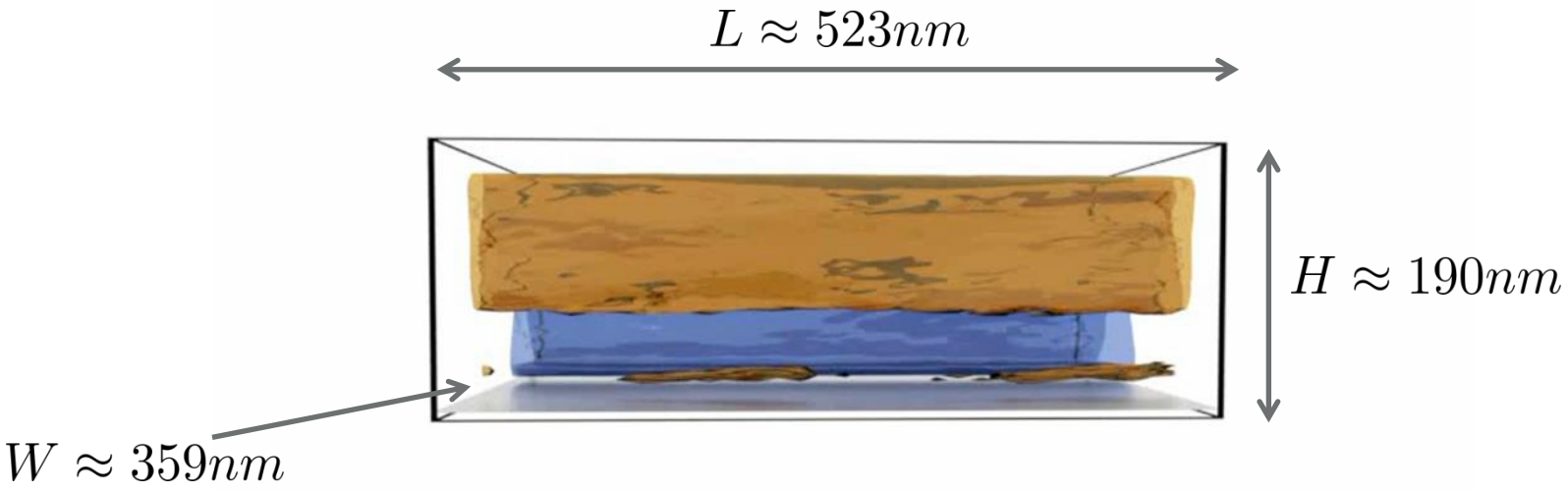
Minimal channel Couette flow



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Molecular Simulation of Turbulence

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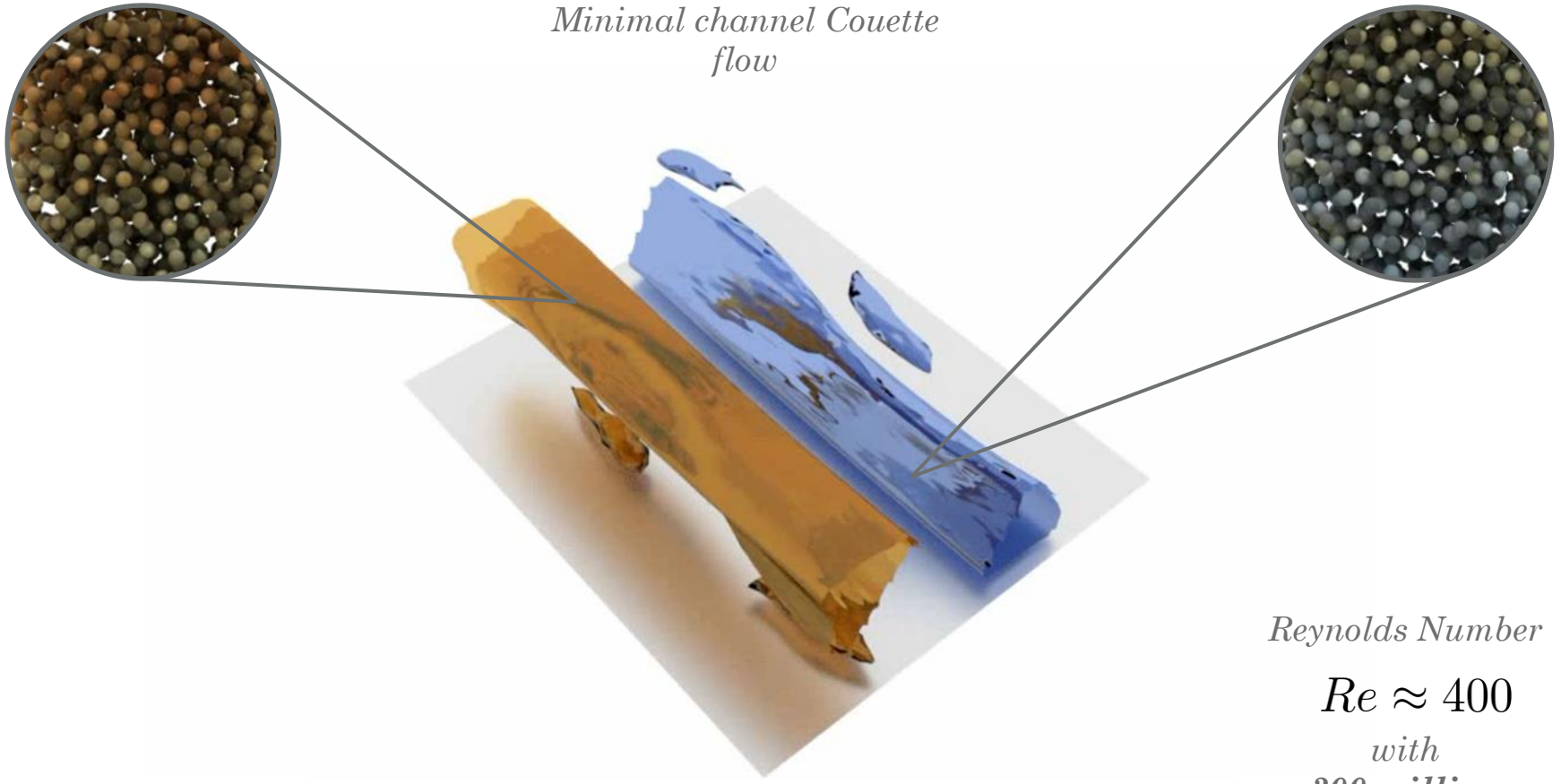
Minimal channel Couette flow



Isosurfaces of turbulent kinetic energy coloured by velocity

Reynolds Number

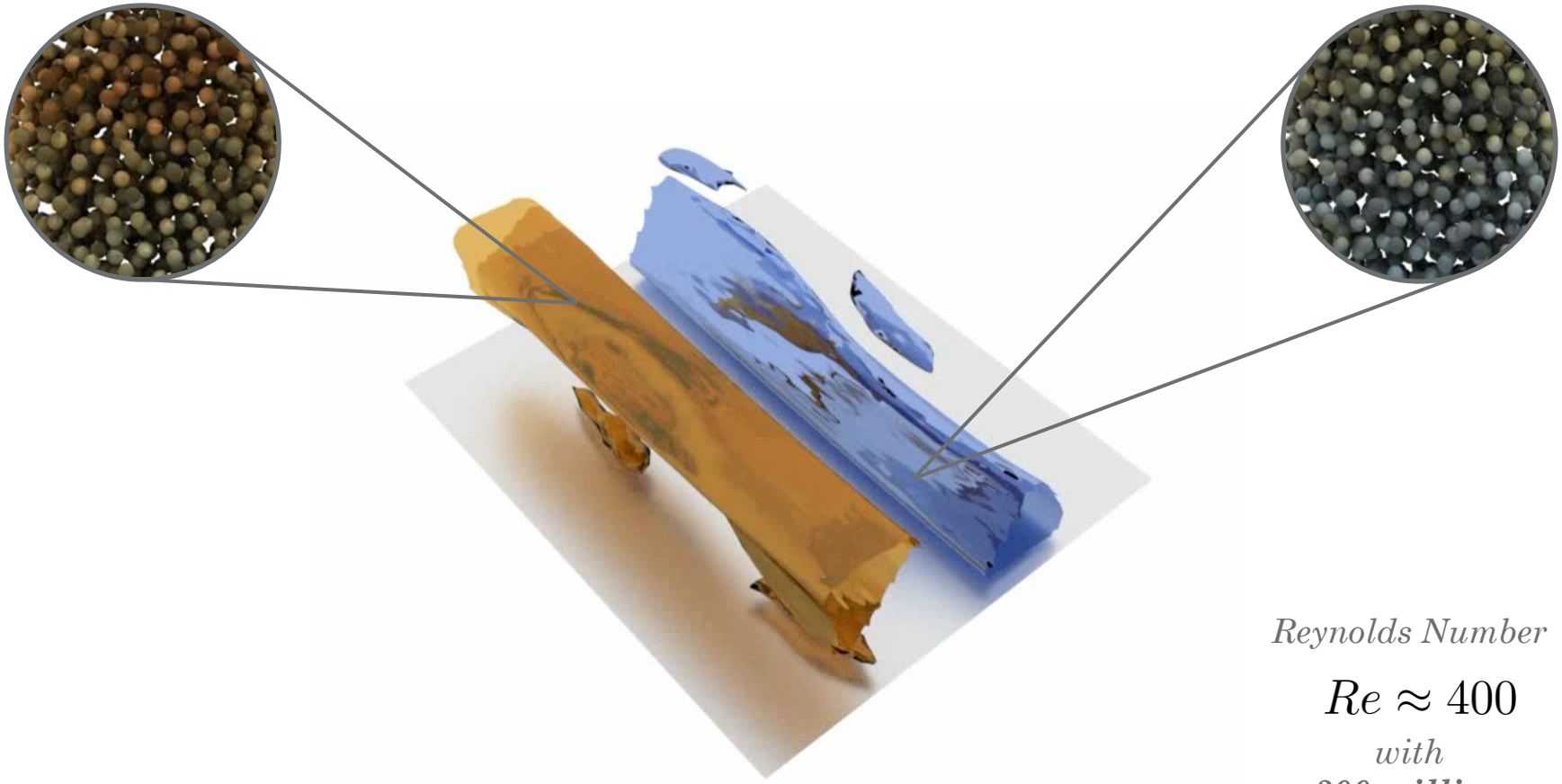
$Re \approx 400$

with

300 million molecules

Molecular Simulation of Turbulence

Brunel University London



Isosurfaces of turbulent kinetic energy coloured by velocity

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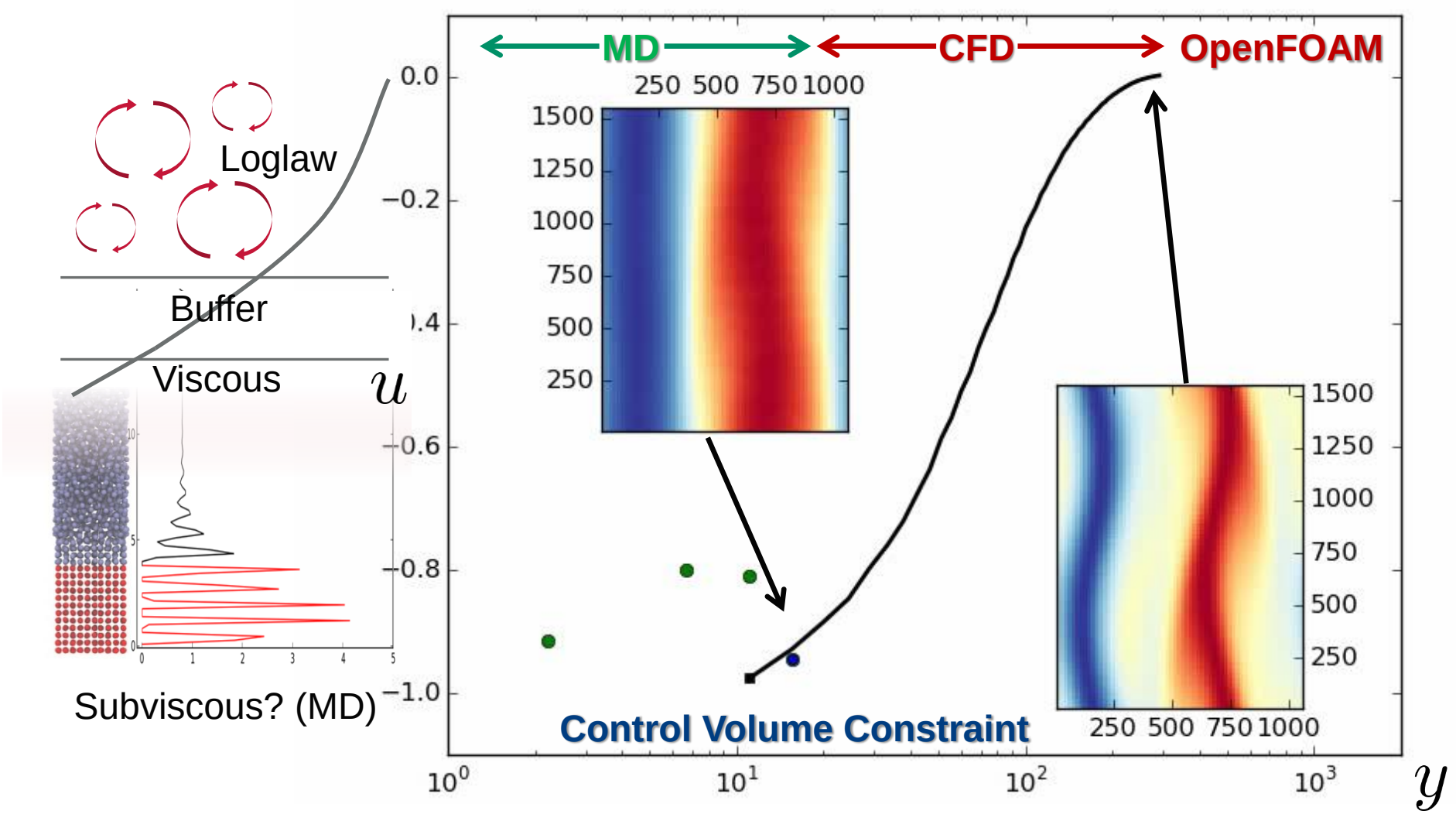
Coupling Results – Turbulent Couette



Molecular Dynamics simulation of Nucleation

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Wall w
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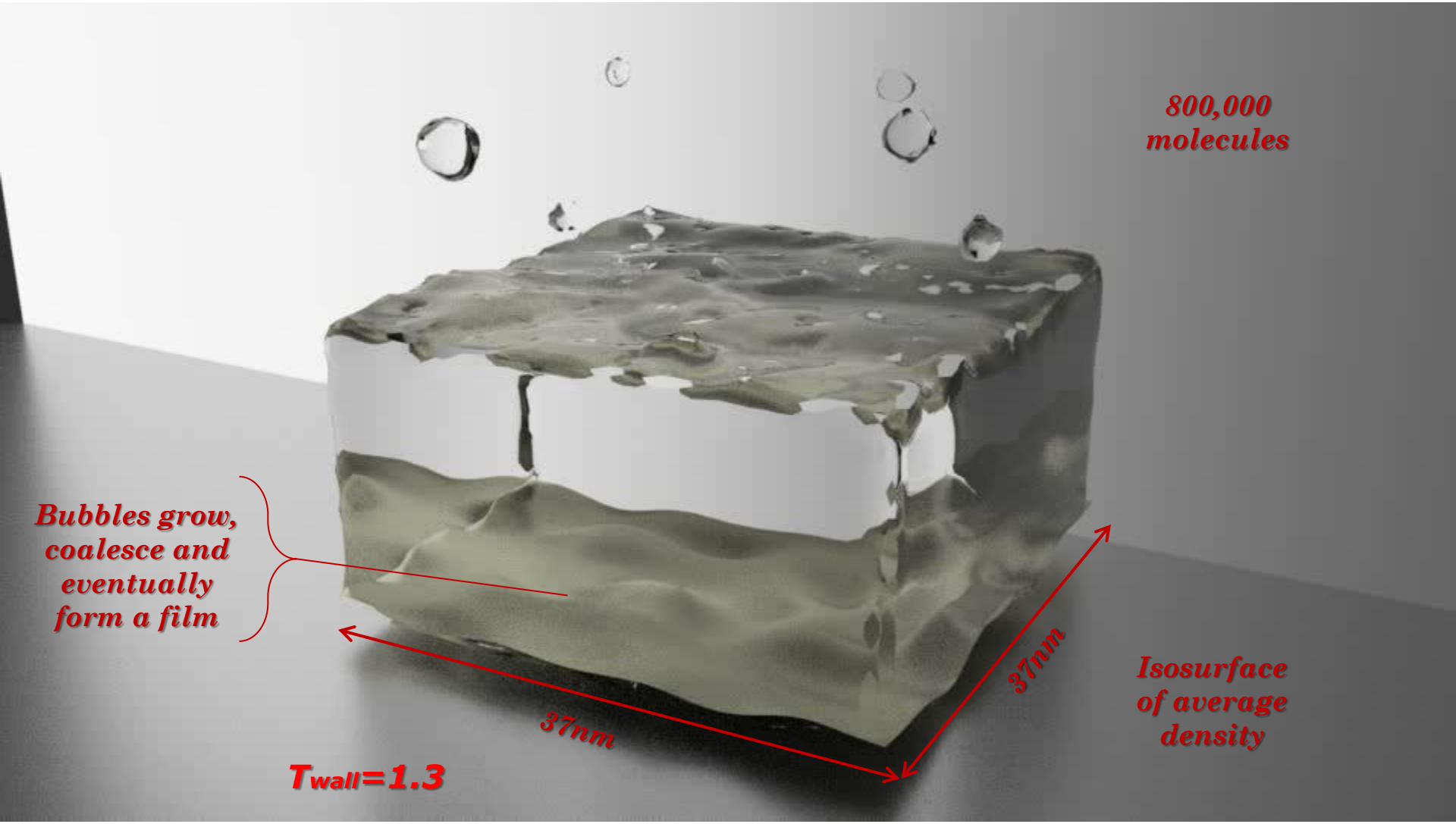
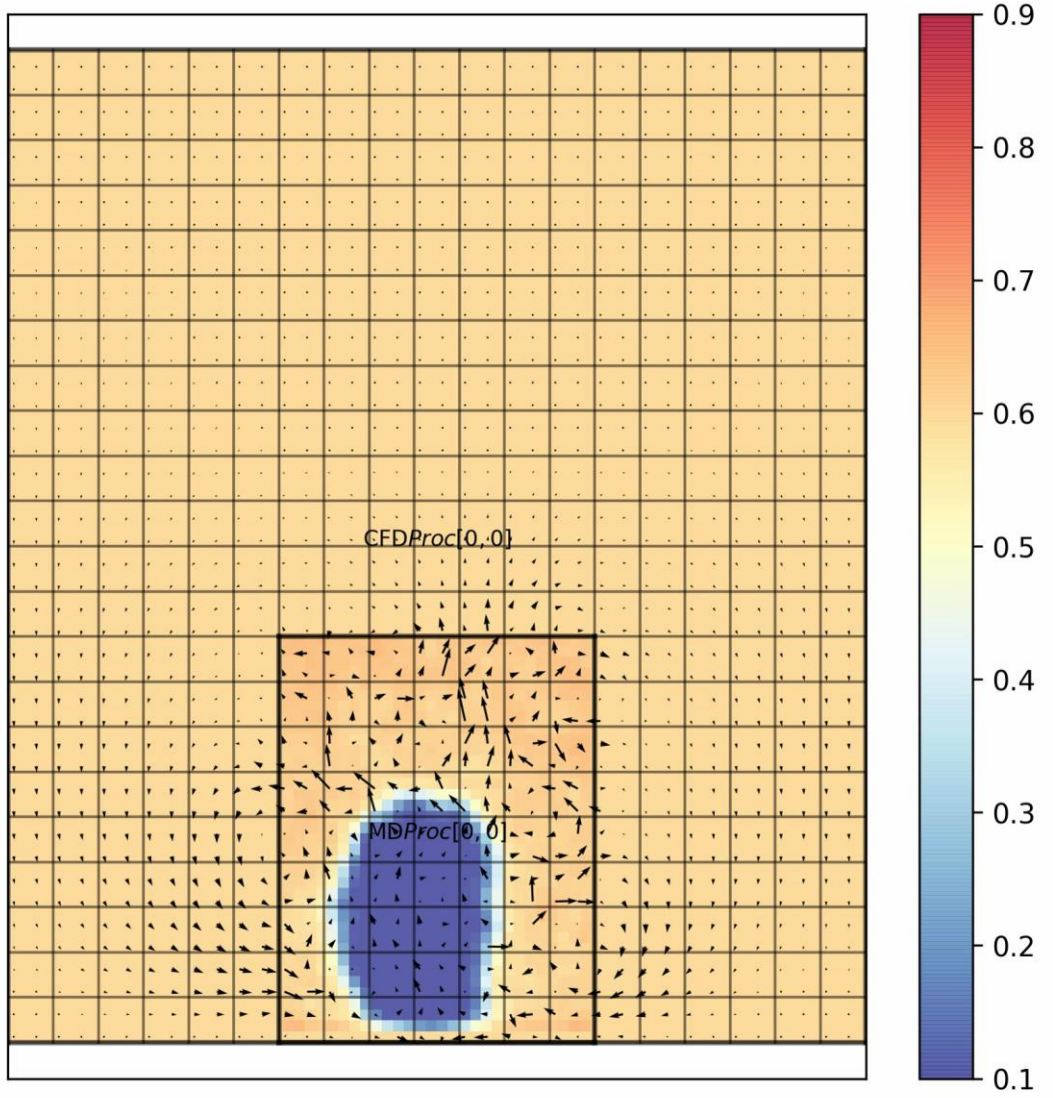
Isosurface of Density



Coupled Simulation of Boiling

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



Overview

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- Coupling
  - Computational Fluid Dynamics (CFD)
  - Molecular Dynamics (MD)
- Developing a Coupling Framework
  - Control Volume Functional
  - Constrained Dynamics
  - Link to NEMD
- Coupled Simulations
  - Software Development
  - Results

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EXTRA SLIDES

Constrained Dynamics

Interaction Control Volume

Constrained Control Volume

- Constrain the momentum in a control volume
  - Fix MD volume to have the same momentum as the CFD

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

- Derivatives we'll need to apply constraint as $\frac{\partial \mathcal{L}_c}{\partial x} = \frac{\partial \mathcal{L}}{\partial x} + \frac{\partial g}{\partial x}$

$$\frac{\partial g}{\partial \boldsymbol{q}_i} = \frac{\partial}{\partial \boldsymbol{q}_i}\left[\sum_{j=1}^{N} m_j \dot{\boldsymbol{q}}_j \vartheta_j - \int_V \rho \boldsymbol{u} dV\right] = m_i \dot{\boldsymbol{q}}_i \cdot \frac{\partial \vartheta_i}{\partial \boldsymbol{q}_i} = m_i \dot{\boldsymbol{q}}_i \cdot d\mathbf{S}_i$$

$$\frac{\partial g}{\partial \dot{\boldsymbol{q}}_i} = \frac{\partial}{\partial \dot{\boldsymbol{q}}_i}\left[\sum_{j=1}^{N} m_j \dot{\boldsymbol{q}}_j \vartheta_j - \int_V \rho \boldsymbol{u} dV\right] = m_i \vartheta_i$$

Constrained Control Volume

- Constrain the momentum in a control volume
  - Fix MD volume to have the same momentum as the CFD

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

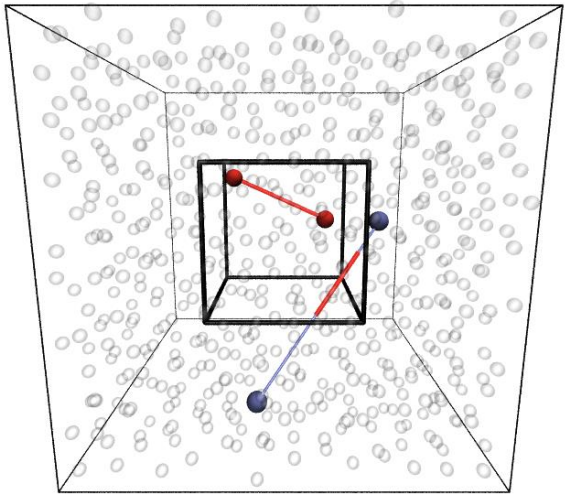
- Constraint is Semi-holonomic if $\frac{d}{dt}\frac{\partial g}{\partial \dot{q}_i} - \frac{\partial g}{\partial q_i} = 0$
- Which we see is true by substituting in constraint derivatives

$$m_i \frac{d\vartheta_i}{dt} - m_i \dot{\boldsymbol{q}}_i \cdot d\mathbf{S}_i = m_i \frac{d\boldsymbol{q}_i}{dt} \cdot \frac{d\vartheta_i}{d\boldsymbol{q}_i} - m_i \dot{\boldsymbol{q}}_i \cdot d\mathbf{S}_i = 0$$

The Control Volume Functional

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

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



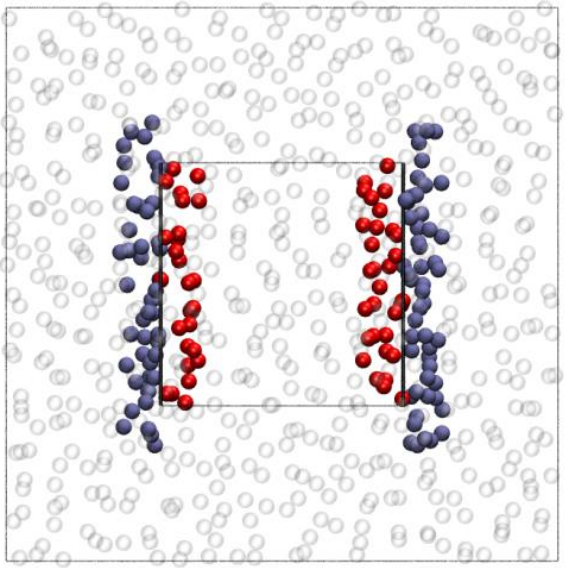
- Length of interaction inside the CV

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

Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

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



- Surface fluxes over the top and bottom surface

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

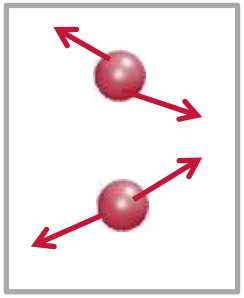
$$dS^+_{xij} = \frac{1}{2} \underbrace{\left[sgn(x^+ - x_i) - sgn(x^+ - x_j)\right]}_{MOP} \boxed{S_{xij}}$$

Volume Average Heat Flux

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$

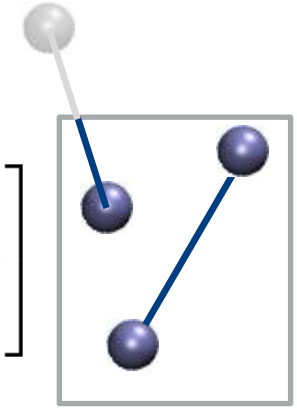
Kinetic

$$\mathbf{J}_{qV}^{K}\left(\mathbf{r}_m, t\right) = \frac{1}{\Delta V}\left[\sum_{i=1}^{N} e_i \mathbf{v}_i \vartheta_i - \bar{\mathbf{v}}\left(\mathbf{r}_m, t\right) \sum_{i=1}^{N} e_i \vartheta_i\right]$$



Configurational

$$\mathbf{J}_{qV}^{\phi}\left(\mathbf{r}_m, t\right) = -\frac{1}{\Delta V}\frac{1}{2}\left[\sum_{i,j}^{N} \mathbf{r}_{ij}\mathbf{F}_{ij} \cdot \mathbf{v}_i \ell_{ij} - \left(\sum_{i,j}^{N} \mathbf{r}_{ij}\mathbf{F}_{ij}\ell_{ij}\right) \cdot \bar{\mathbf{v}}\left(\mathbf{r}_m\right)\right]$$

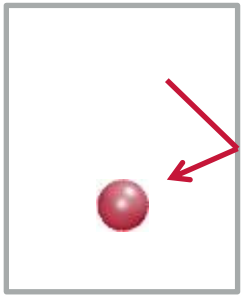


Surface (MOP) Heat Flux

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$

Kinetic

$$J^K_{qA,x} = \frac{1}{\Delta A_x} \sum_{i=1}^{N} e_i \left(v_{ix} - \bar{v}_x \left(r_m\right)\right) \delta \left(x_i - x_+\right) S_{xi}$$



Configurational

$$J^\phi_{qA,x} = -\frac{1}{\Delta A_{x+}} \frac{1}{2} \sum_{i,j}^{N} \mathbf{F}_{ij} \cdot \left(\mathbf{v}_i - \bar{\mathbf{v}} \left(\mathbf{r}_{x+}\right)\right) S_{ij} \left(x_+\right)$$