The Control Volume Formulation for Non-Equilibrium Molecular Dynamics Simulations

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Working with:
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Overview

- What is a Control Volume (CV)?

- How do we apply it to Molecular Dynamics (MD)?

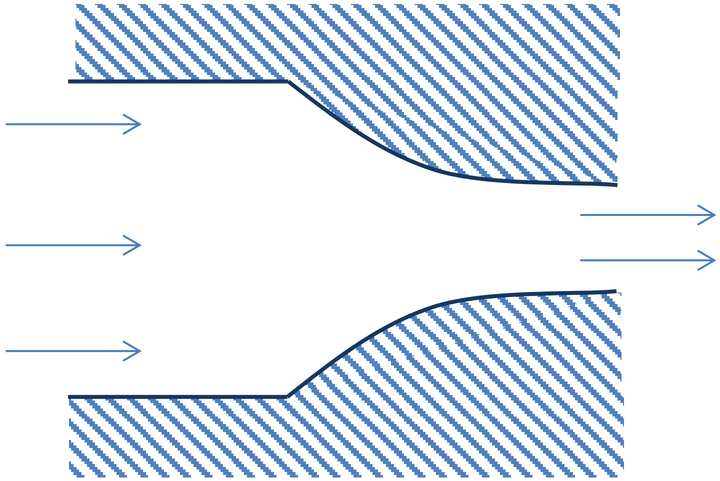
- How is it useful?

Overview

- **What is a Control Volume (CV)?**
- **How do we apply it to Molecular Dynamics (MD)?**
- **How is it useful?**

The Continuum Equations in CV Form

- **The Control Volume is a purely conceptual closed surface used to analyse fluid flow**



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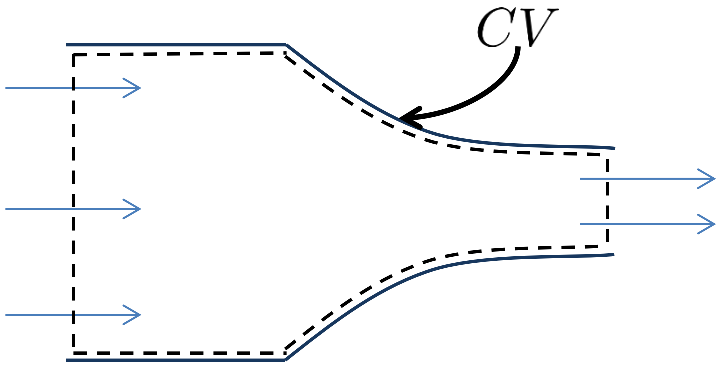

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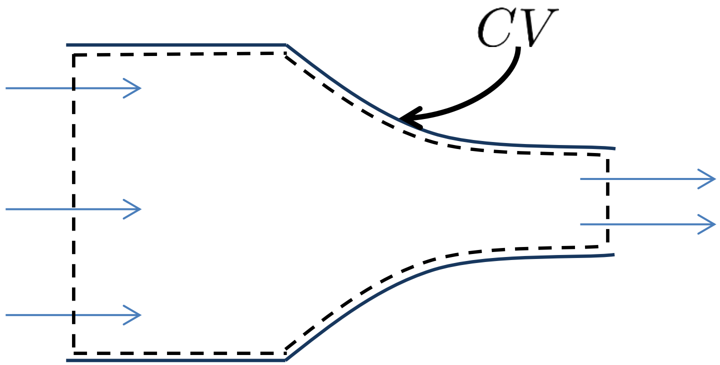
$$\int_{in} \rho \boldsymbol{u} \cdot d\mathbf{S}$$



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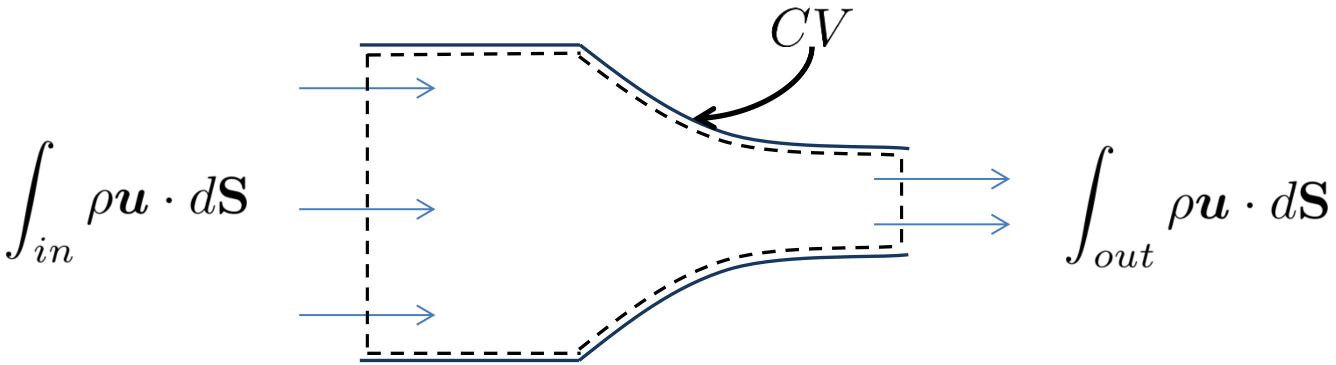

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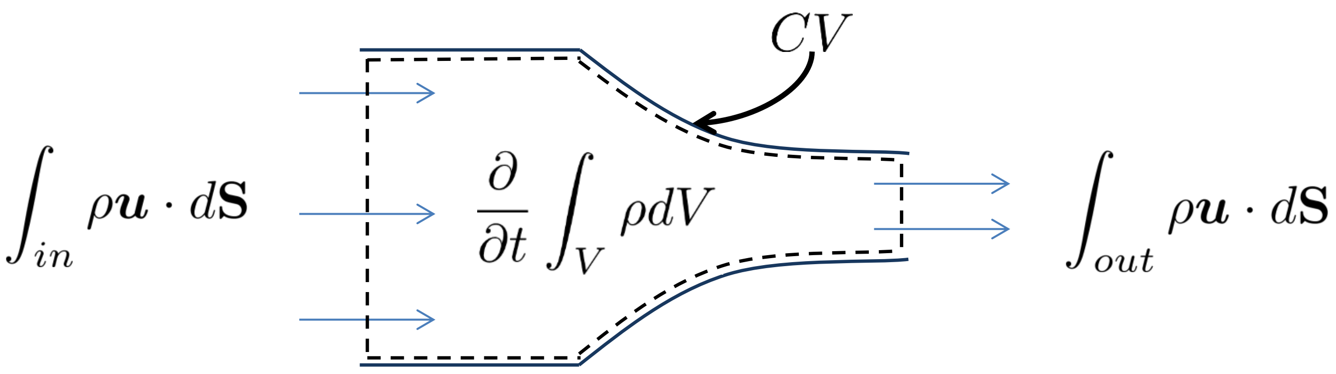

- **What flows into a volume, minus what flows out**
  - Mass conservation

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

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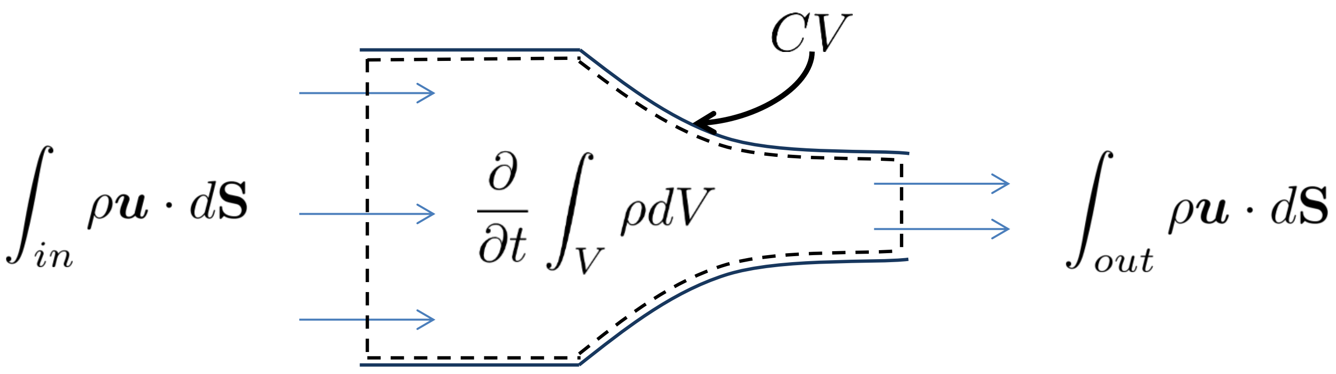

- **What flows into a volume, minus what flows out**
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$$\frac{\partial}{\partial t} \int_V \rho dV = - \oint_S \rho \boldsymbol{u} \cdot d\mathbf{S}$$

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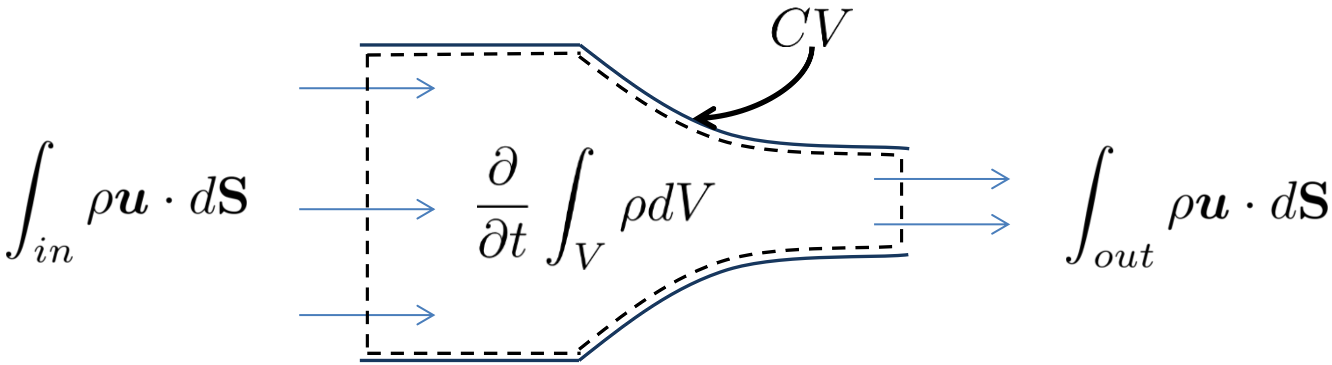

- **What flows into a volume, minus what flows out**
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$$\frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u} \cdot d\mathbf{S}$$

  - Momentum Balance

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

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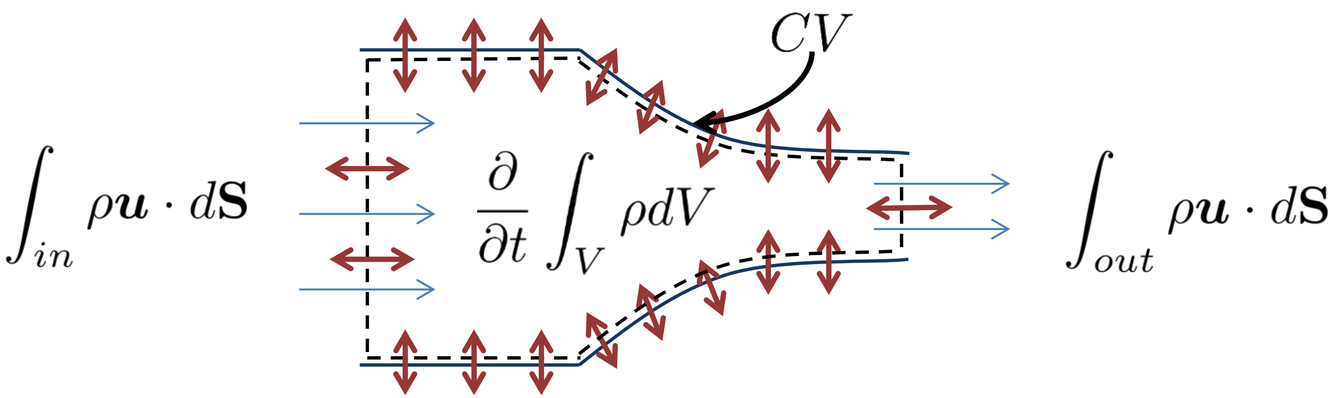

- **What flows into a volume, minus what flows out + Forces**
  - Mass conservation

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

  - Momentum Balance

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

$$+\mathbf{F}_{\text{surface}}$$

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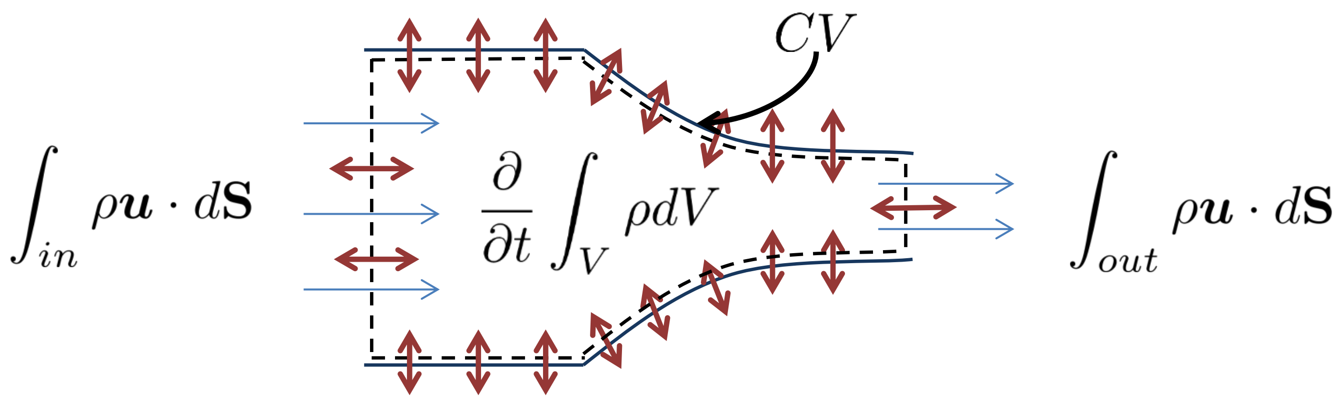


- **What flows into a volume, minus what flows out + Pressure**
  - Mass conservation

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

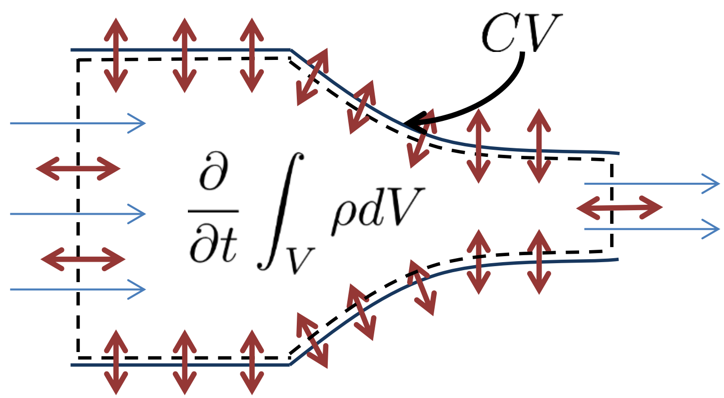
  - Momentum Balance

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

The Continuum Equations in CV Form

- **The Control Volume is a purely conceptual closed surface used to analyse fluid flow**

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



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

- **What flows into a volume, minus what flows out + Pressure**
  - Mass conservation

$$\frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u} \cdot d\mathbf{S} \quad \underset{\lim\limits_{V \to 0}}{\overset{\int_V \ldots dV}{\rightleftarrows}} \quad \frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \rho \boldsymbol{u}$$

  - Momentum Balance

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

The Control Volume Form

- **The Control Volume is a purely conceptual closed surface used to analyse fluid flow**
  - Can be defined anywhere in space with any shape
- **An alternate expression of the equations of motion**
  - Mass conservation, momentum balance (Newton's law) and energy conservation
  - Changes inside a volume exactly equal fluxes and forces over the surface
  - More fundamental[1] and general[2] as the continuum assumption is not required
- **The MD system can be expressed in the same form, as a result:**
  - Both continuum and discrete systems are expressed in the same manner
  - The surface fluxes and forces are the Method of Planes (MOP) form of stress
  - Nine MOP Stress can be obtained and exactly linked to the change of momentum inside the volume
  - Provides a unified framework for coupled simulations

1 - Zienkiewicz The Finite Element Method for Fluid Dynamics 3rd edition
2 - Kolditz (2001) -- Compuational Methods in Environmental Fluid Mechanics C7 p132: *integral formulations are required where discontinuous solutions are possible … the integral formulation is the only physical meaningful problem description*

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The Molecular Equations in CV Form

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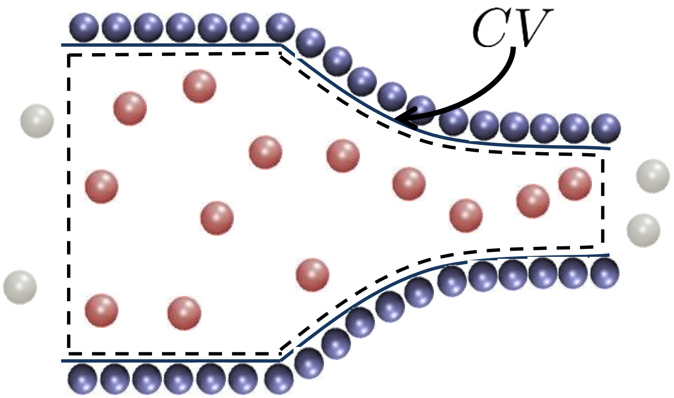
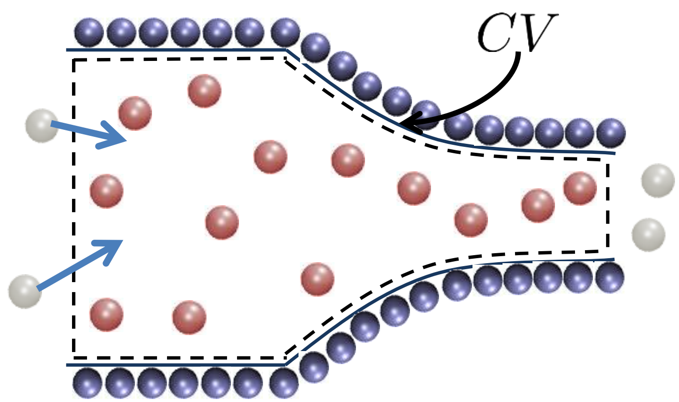


The Molecular Equations in CV Form

- The Control Volume is a purely conceptual closed surface used to analyse fluid flow

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



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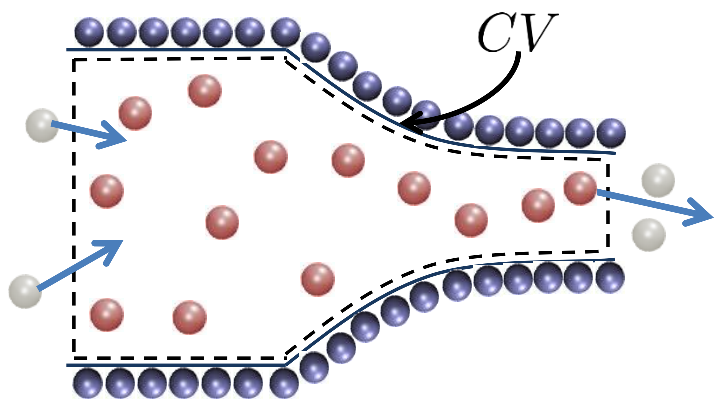

$$\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i^{out}$$

The Molecular Equations in CV Form

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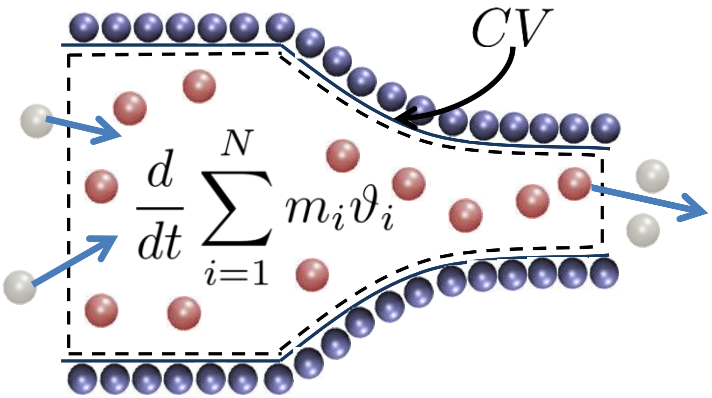
$$\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i^{in}$$



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

- **What flows into a volume, minus what flows out**
  - Mass conservation

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

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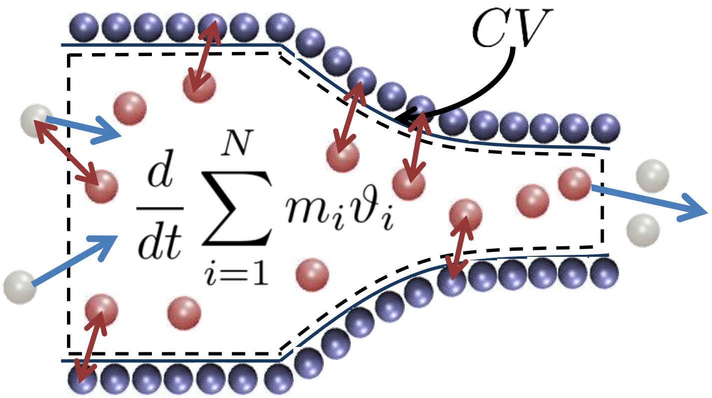

$$\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i^{out}$$

- **What flows into a volume, minus what flows out + Forces**
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$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i$$

  - Momentum Balance

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

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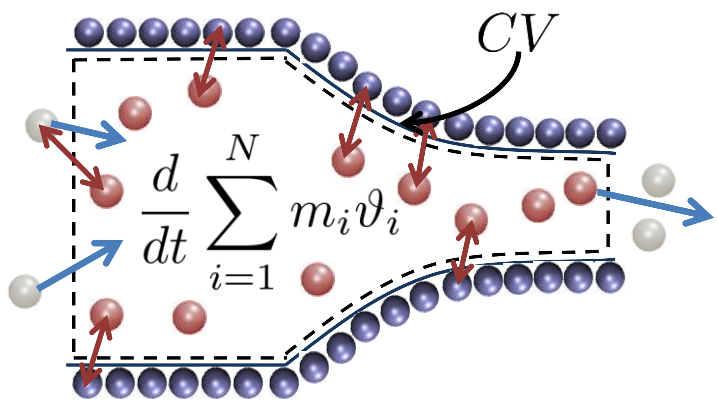
- **The Control Volume is a purely conceptual closed surface used to analyse fluid flow**

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



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  - Mass conservation

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

$$\int_V \dots dV \qquad \lim_{V \to 0}$$

$$\frac{d}{dt}\sum_{i=1}^{N} m_i \delta(\boldsymbol{r}-\boldsymbol{r}_i) = \dots$$

  - Momentum Balance

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

  - Irving and Kirkwood Equations

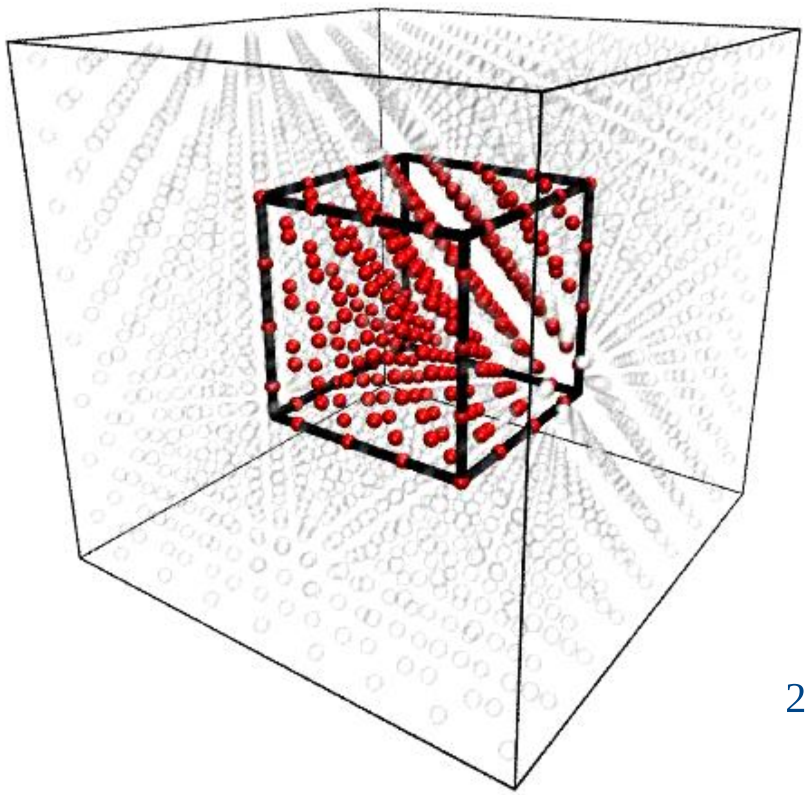
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \boldsymbol{v}_i \delta(\boldsymbol{r}-\boldsymbol{r}_i) = \dots + \frac{1}{2}\boldsymbol{\nabla}\cdot\sum_{i,j}^{N} \boldsymbol{f}_{ij}\boldsymbol{r}_{ij} O_{ij} \delta(\boldsymbol{r}-\boldsymbol{r}_i)$$

Control Volume Function

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

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

$$= \left[H(x^+ - x_i) - H(x^- - x_i)\right]$$
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$
$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$



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Derivatives yields the Surface Fluxes

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

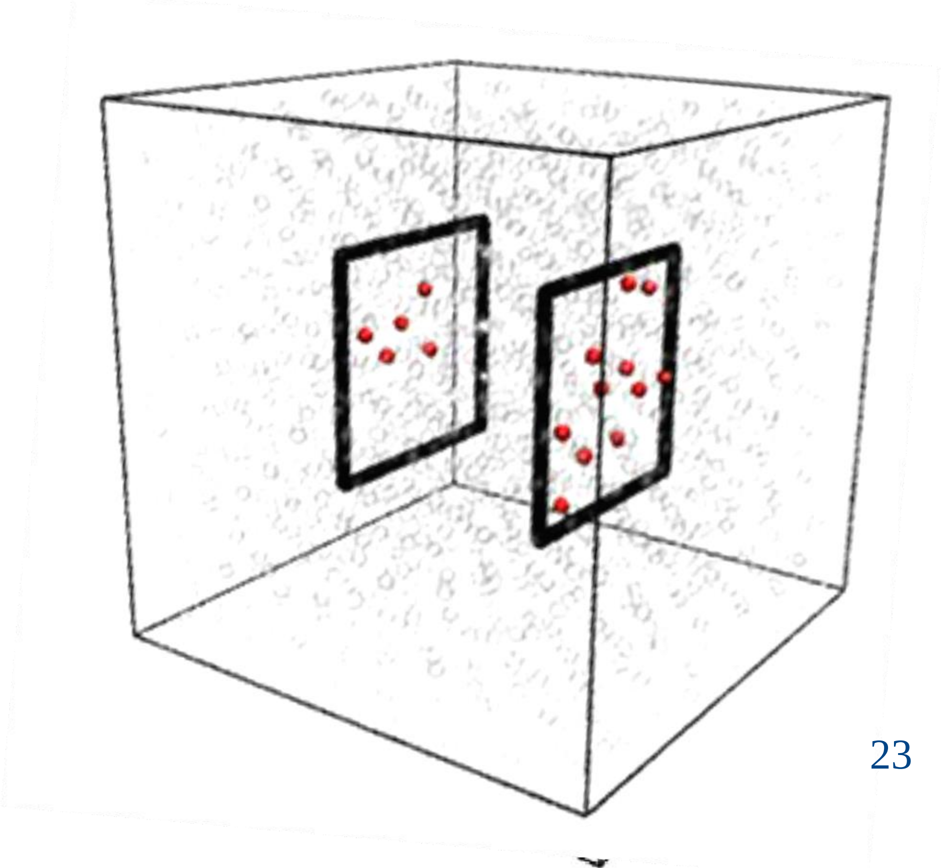
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - \ x_i) - \delta(x^- - \ x_i)\right]$$
$$\times \left[H(y^+ - y_i) - H(y^- - \ y_i)\right]$$
$$\times \left[H(z^+ - z_i) - H(z^- - \ z_i)\right]$$

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

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

- **Vector form defines six surfaces**

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



Control Volume Functional

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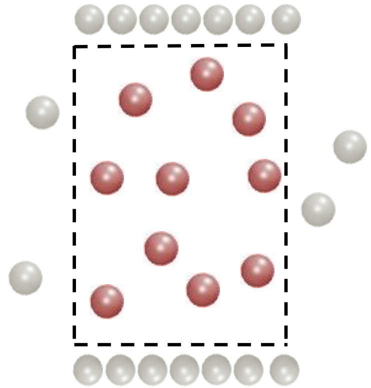
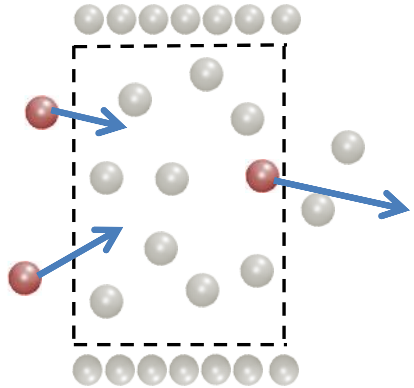


$$\vartheta_i \equiv \int_V \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

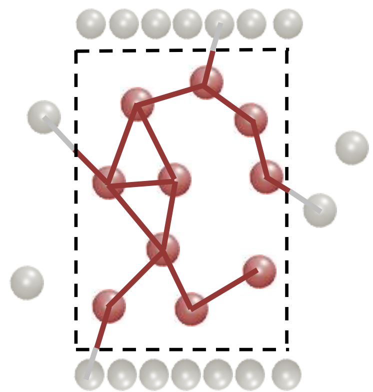
- **Its derivative gives the fluxes over the surface**



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

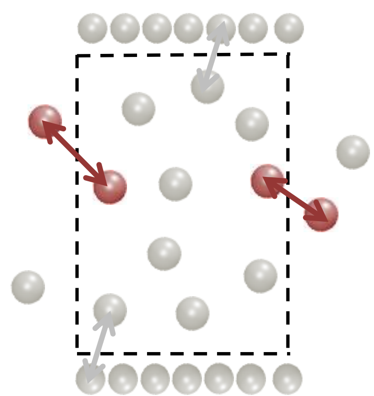
Control Volume Functional - Forces

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



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

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



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

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

Localised to the surface by Heaviside functions

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The Control Volume Equations

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

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

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

  - Momentum Balance

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

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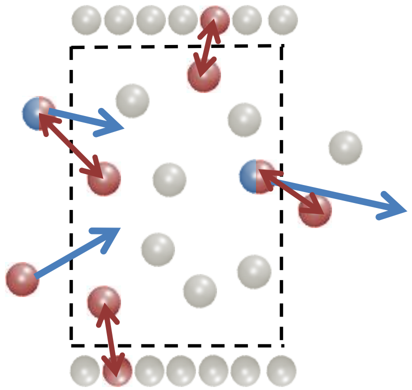

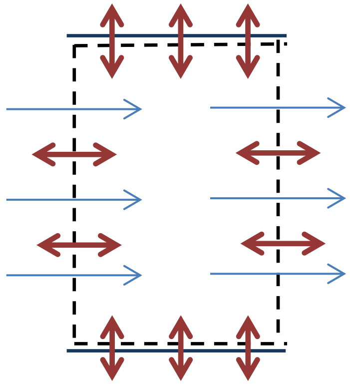

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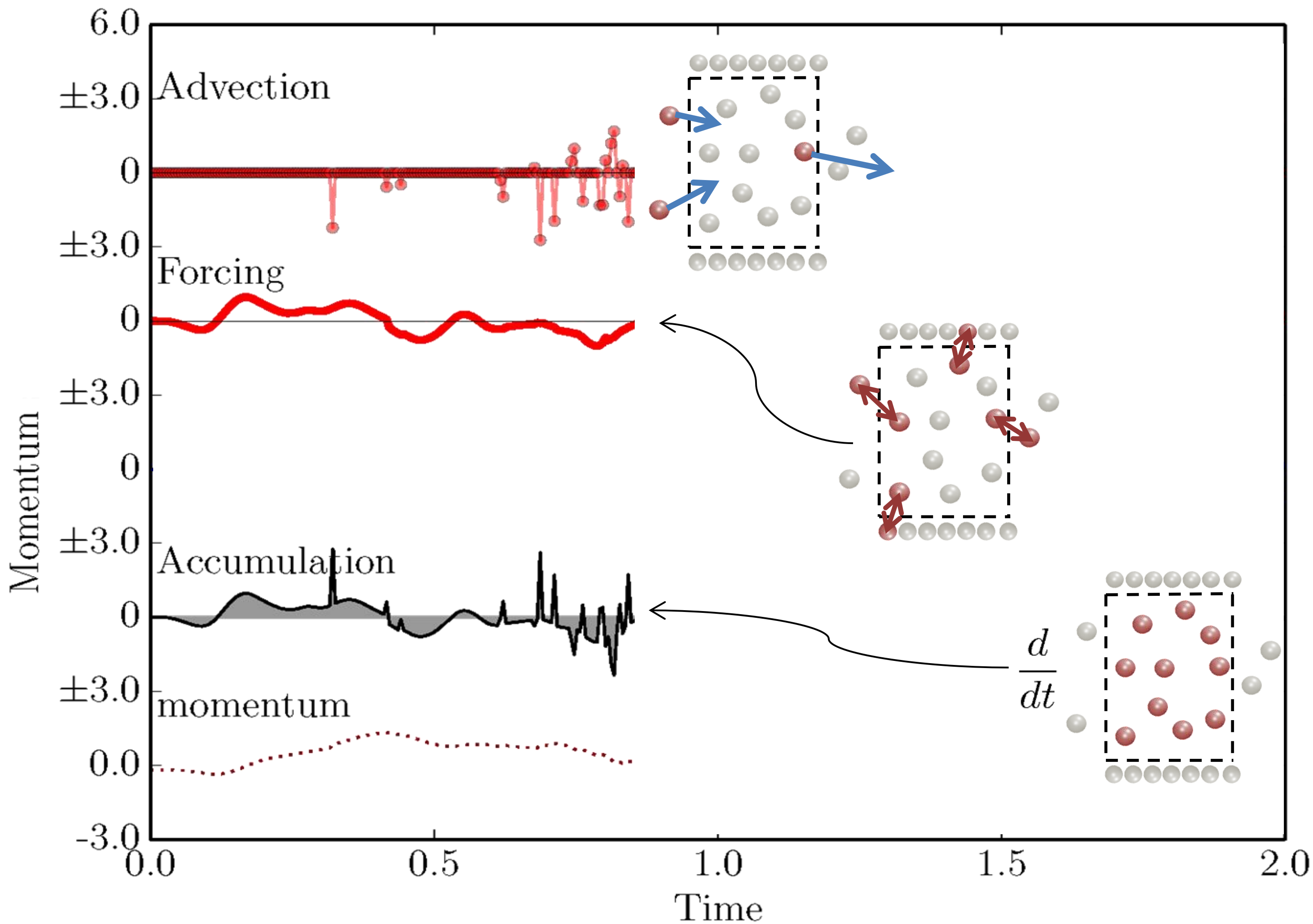
Exact Conservation

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



$$\underbrace{\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i}_{\text{Advection}}$$

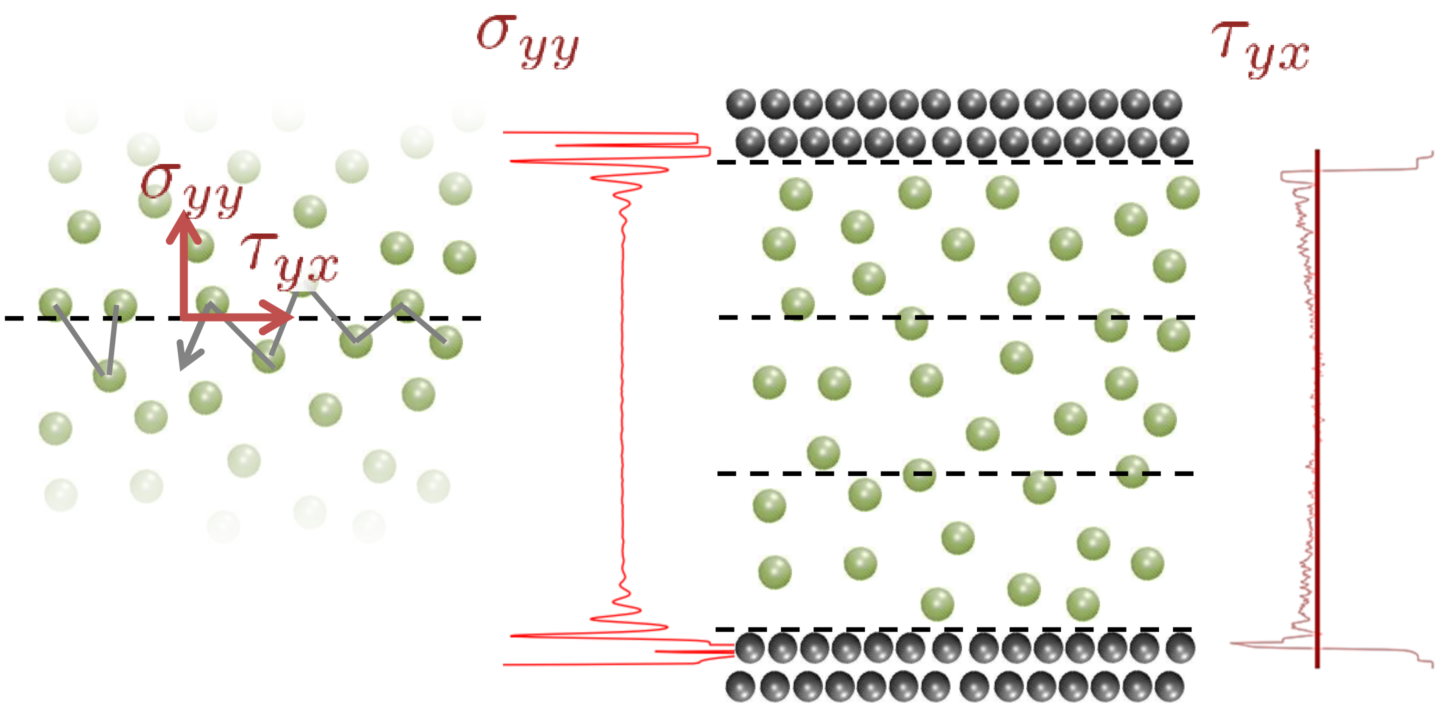
$$-\underbrace{\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij} \mathbf{n} \cdot d\mathbf{S}_{ij}}_{\text{Forcing}}$$

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

The MD Stress Tensor

- **The Method of Planes form of stress (Todd et al 1995)**

$$\sigma = F/A$$



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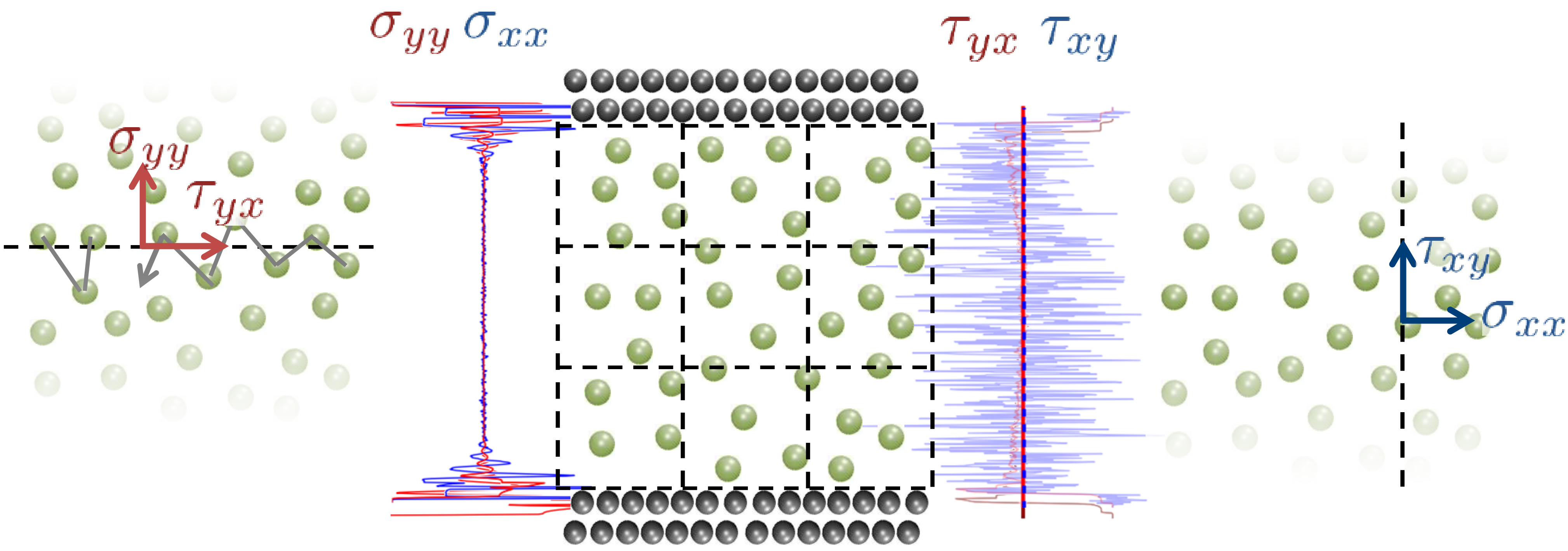

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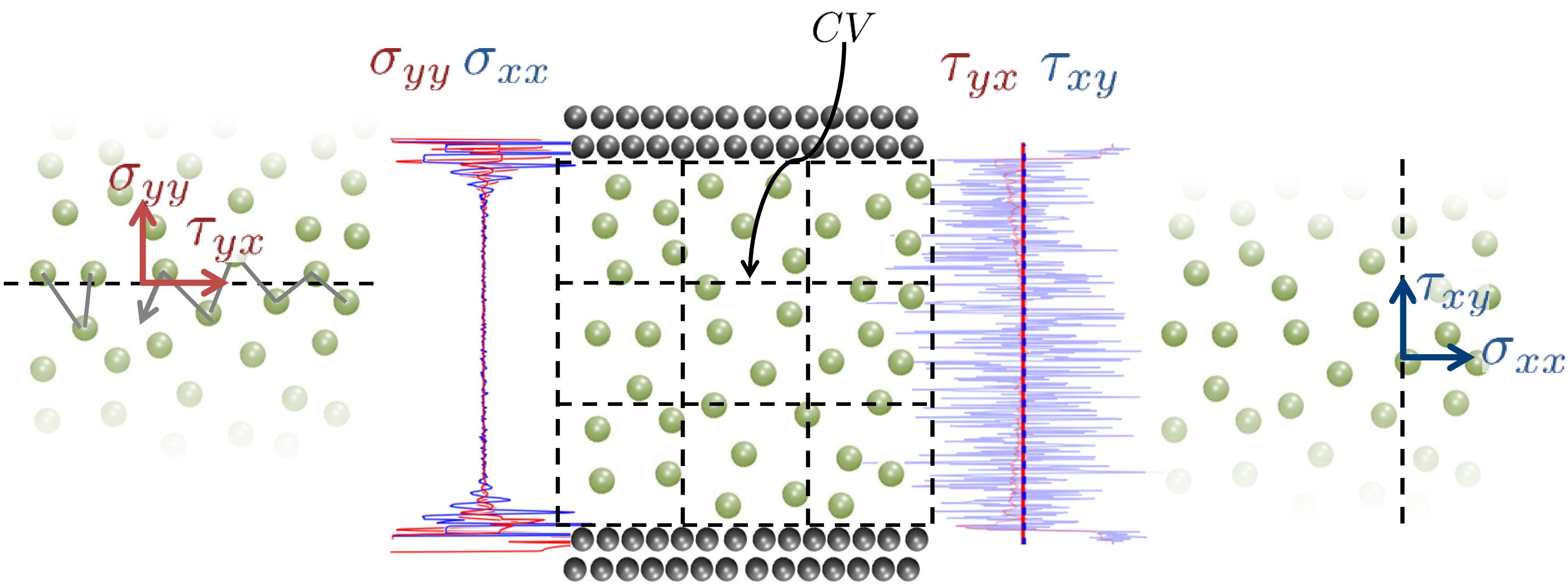
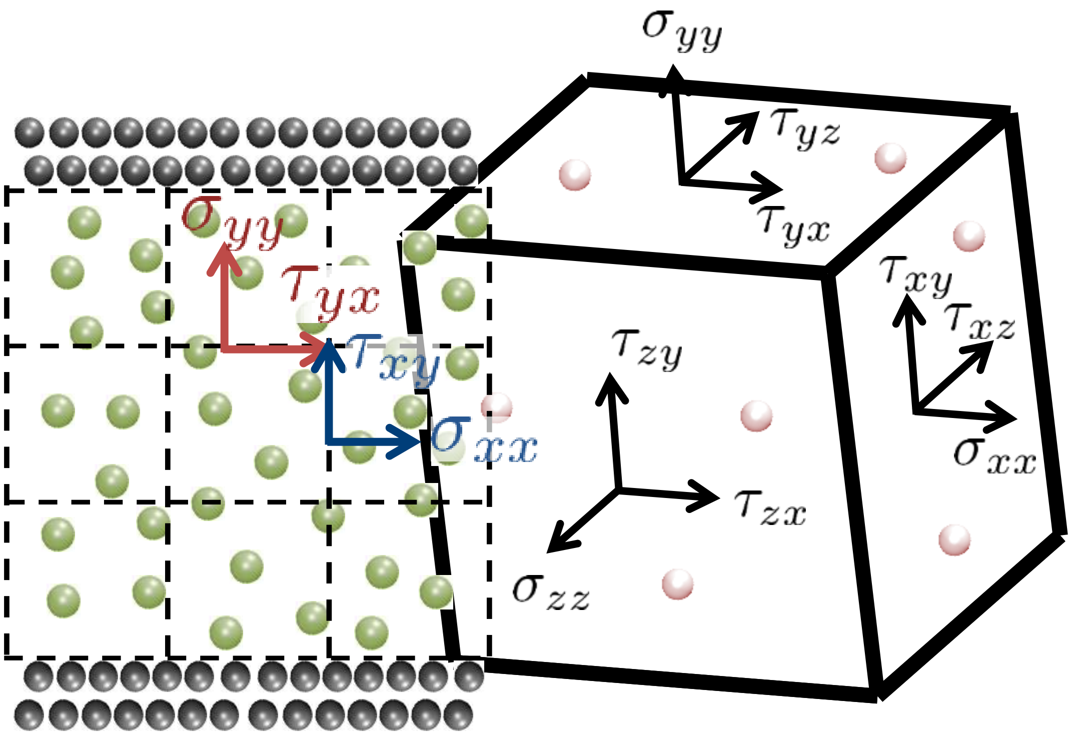


The MD Stress Tensor

- **The Method of Planes form of stress (Todd et al 1995) appears naturally in the control volume equations**
  - Different surfaces provide nine stress components (Cauchy stress theorem)
  - Localised MOP (Han and Lee 2004)



- **Non-uniqueness of the stress tensor is due to choice of volume**
  - Stress is exactly linked to momentum change inside the volume

Constrained Control Volume

- **NEMD simulations often require applied constraints**
  - Typical constraints include barostats, thermostats, etc
  - For coupled simulation, we need a "momentostat"
- **The constraint is localised using the control volume function**
  - The CV function takes care of the localisation for us
  - Momentum control in a CV requires the non-holonomic constraint

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

- **Gauss Principle of Least Constraint applied**
  - Valid for any form of constraint and provides physically meaningful trajectories
  - CV function is mathematically well defined so we just work through the algebra

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

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Constrained Control Volume

- **Gauss Principle of Least Constraint applied**
  - Resulting constrained equations are differential e.g. the evolution of momentum is matched to a target momentum time evolution

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

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

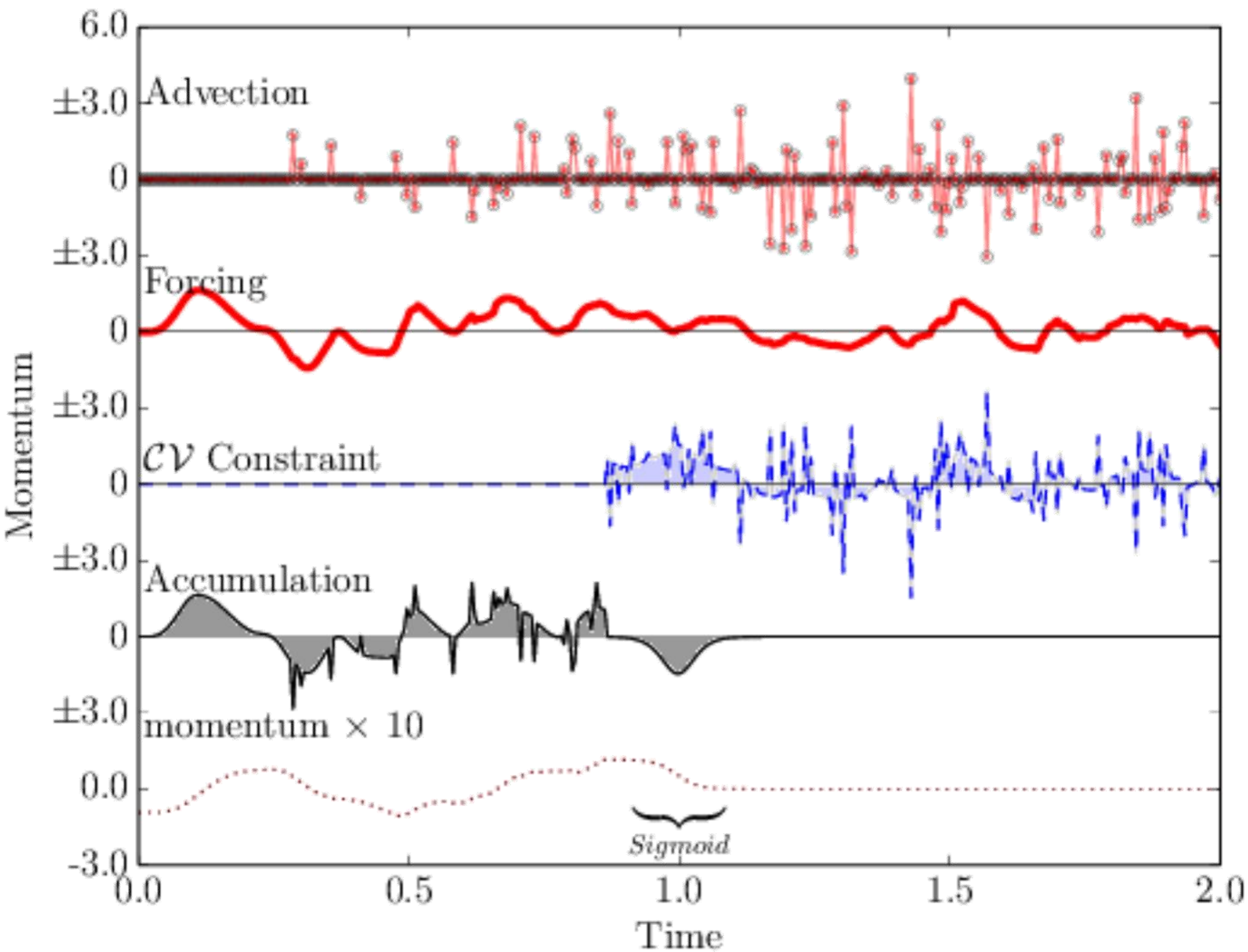
$$m_i\ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i \vartheta_i}{M_I}\left[\frac{d}{dt}\int_V \rho \boldsymbol{u} dV + \overbrace{\sum_{n=1}^{N} m_i \dot{\boldsymbol{r}}_{\boldsymbol{n}} \dot{\boldsymbol{r}}_n \cdot d\mathbf{S}_n}^{\text{Advection}} - \overbrace{\sum_{n,m}^{N} \boldsymbol{f}_{nm}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

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

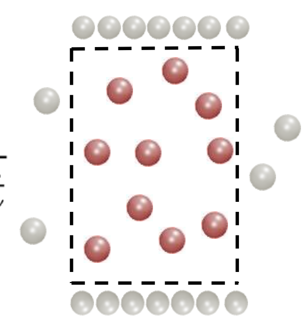
Constrained Control Volume

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

$$m_i\ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i\vartheta_i}{M_I}\left[\cancelto{0}{\frac{d}{dt}\int_V \rho \boldsymbol{u} dV} + \overbrace{\sum_{n=1}^{N} m_i \dot{\boldsymbol{r}}_{\boldsymbol{n}} \dot{\boldsymbol{r}}_n \cdot d\mathbf{S}_n}^{\text{Advection}} - \overbrace{\sum_{n,m}^{N} \boldsymbol{f}_{nm}\mathbf{n} \cdot dS_{nm}}^{Forcing}\right]$$



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

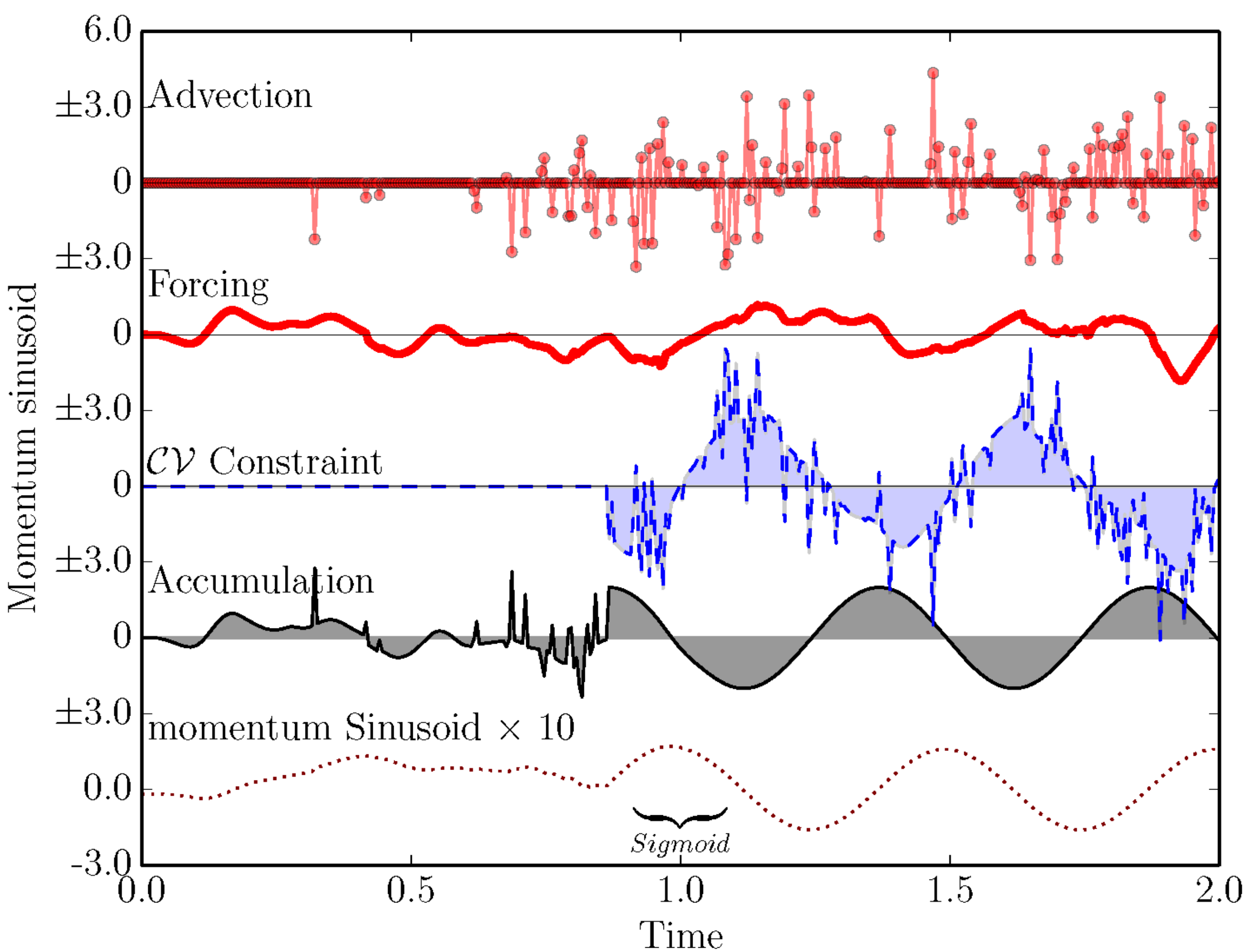
$\frac{d}{dt}$  $= 0$

Constrained Control Volume

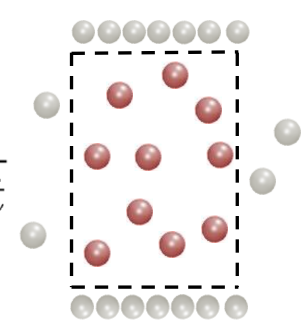
- **Provides a method of controlling a volume's velocity and stress**

$\sim cos(t)$

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



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

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

Constrained Control Volume

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

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

  - Forcing applies an arbitrary 18 component 3D stress field

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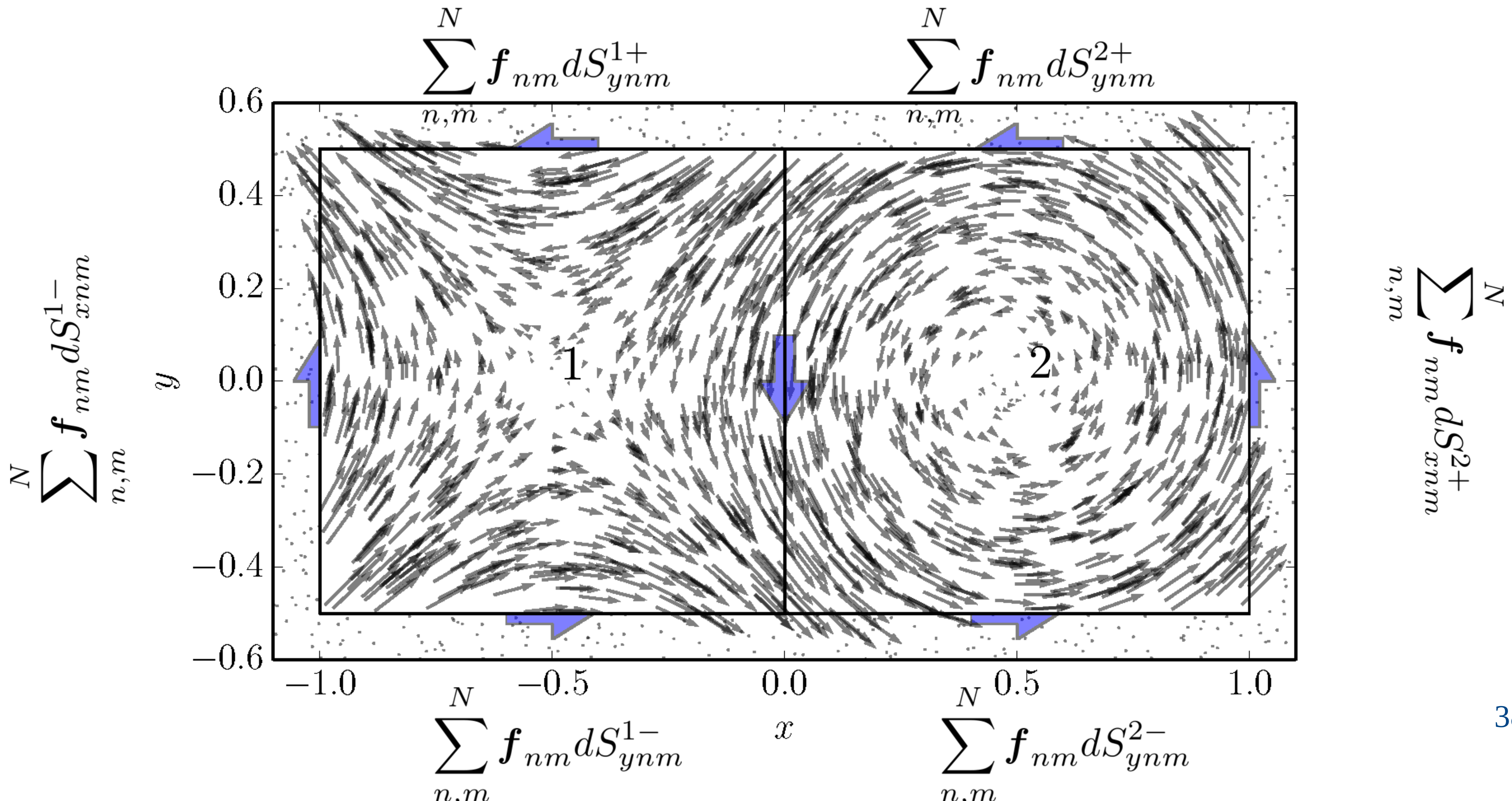
Constrained Control Volume

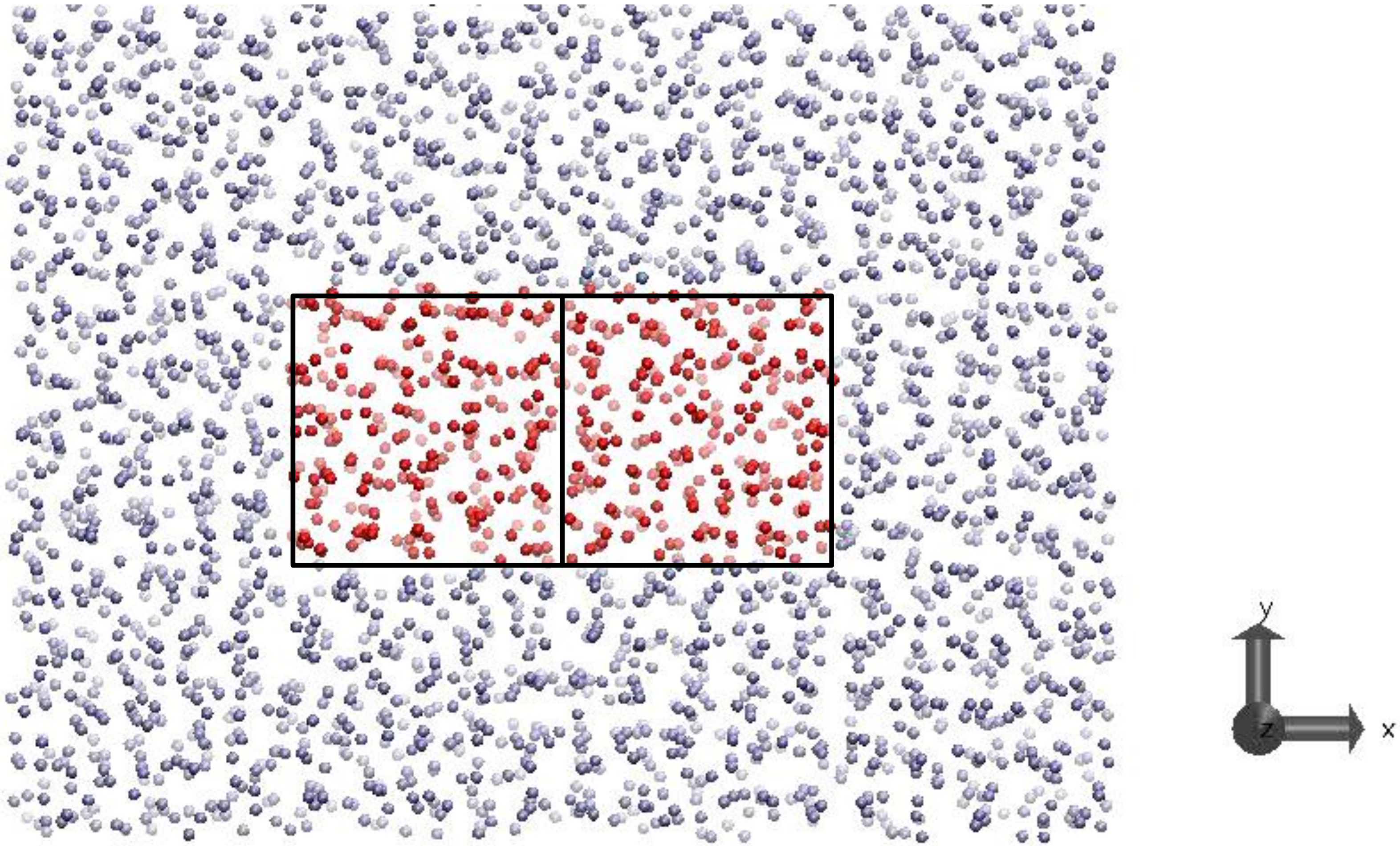
- **Provides a method of controlling a volume's velocity and stress**

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

  - Forcing applies an arbitrary 18 component 3D stress field

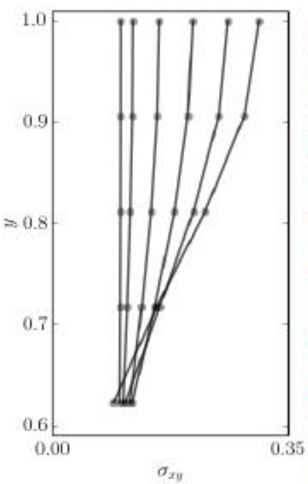


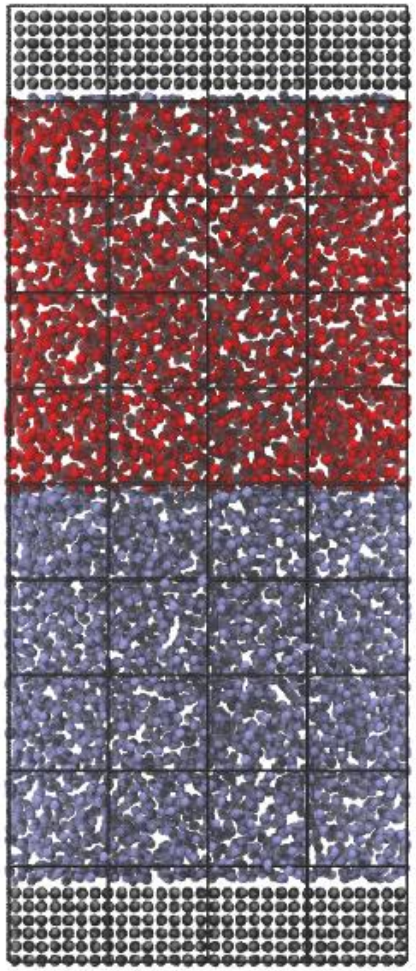
Constrained Control Volume

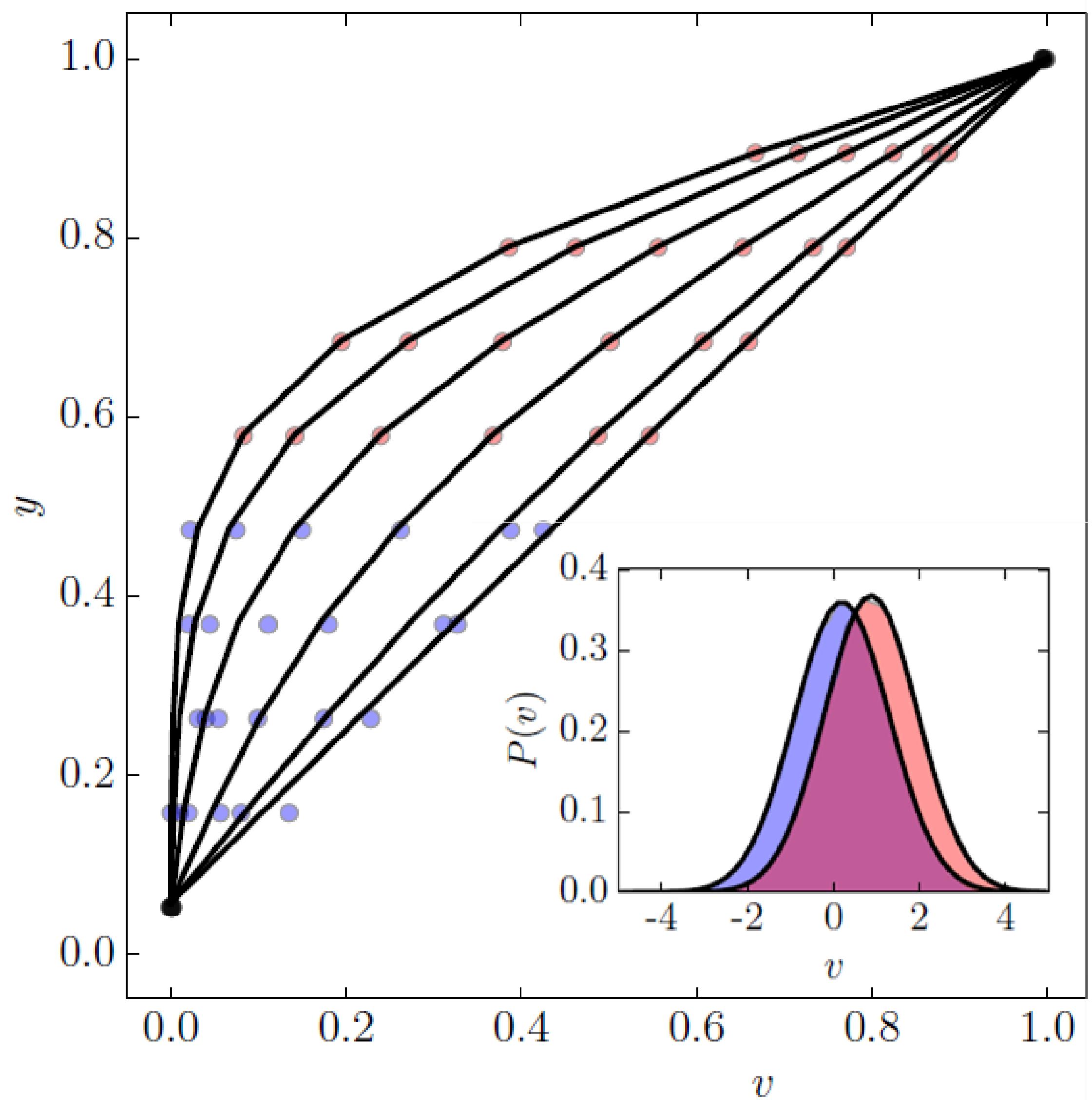


Couette Flow

- **Applying Couette stresses and velocity evolution**

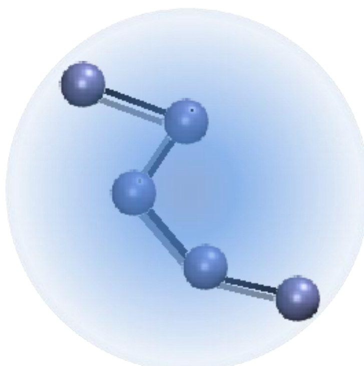


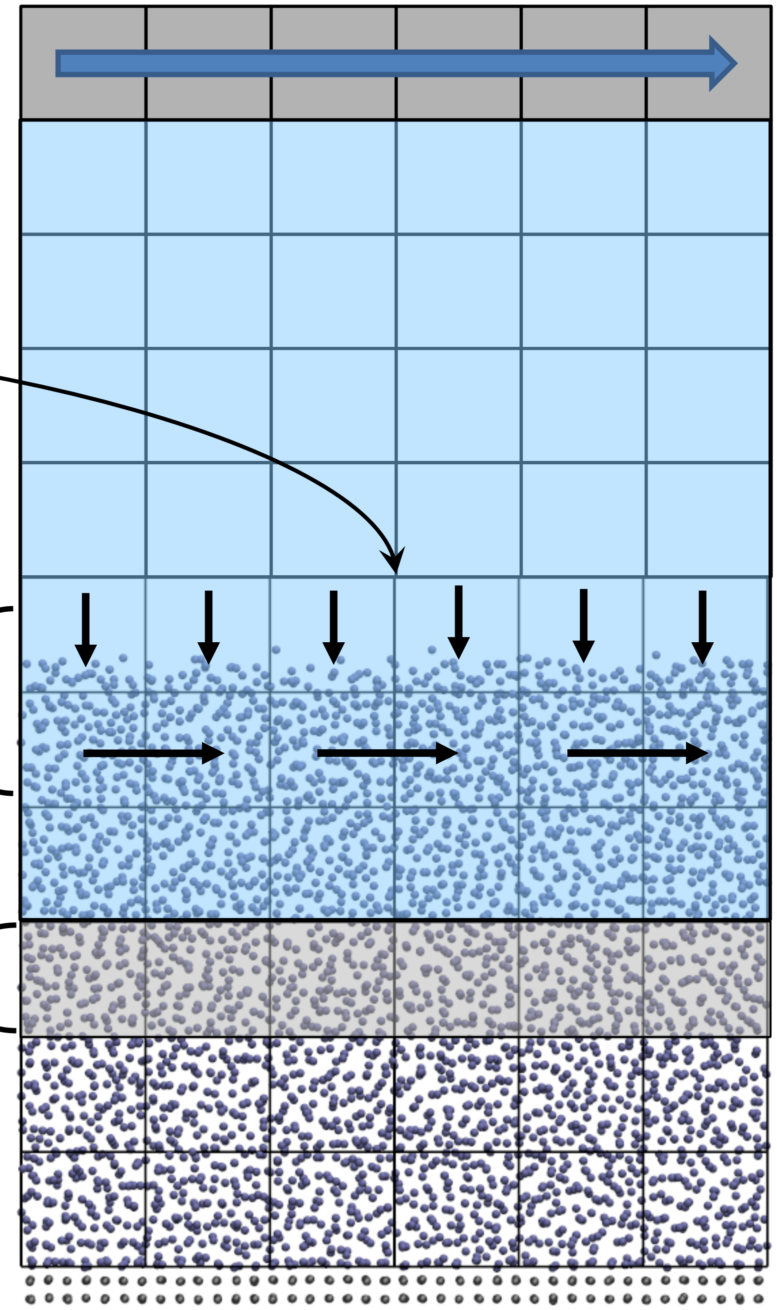




Coupling

Boundary force and insertion of molecules





Consistent Framework

CFD→MD Boundary condition

MD→CFD Boundary condition

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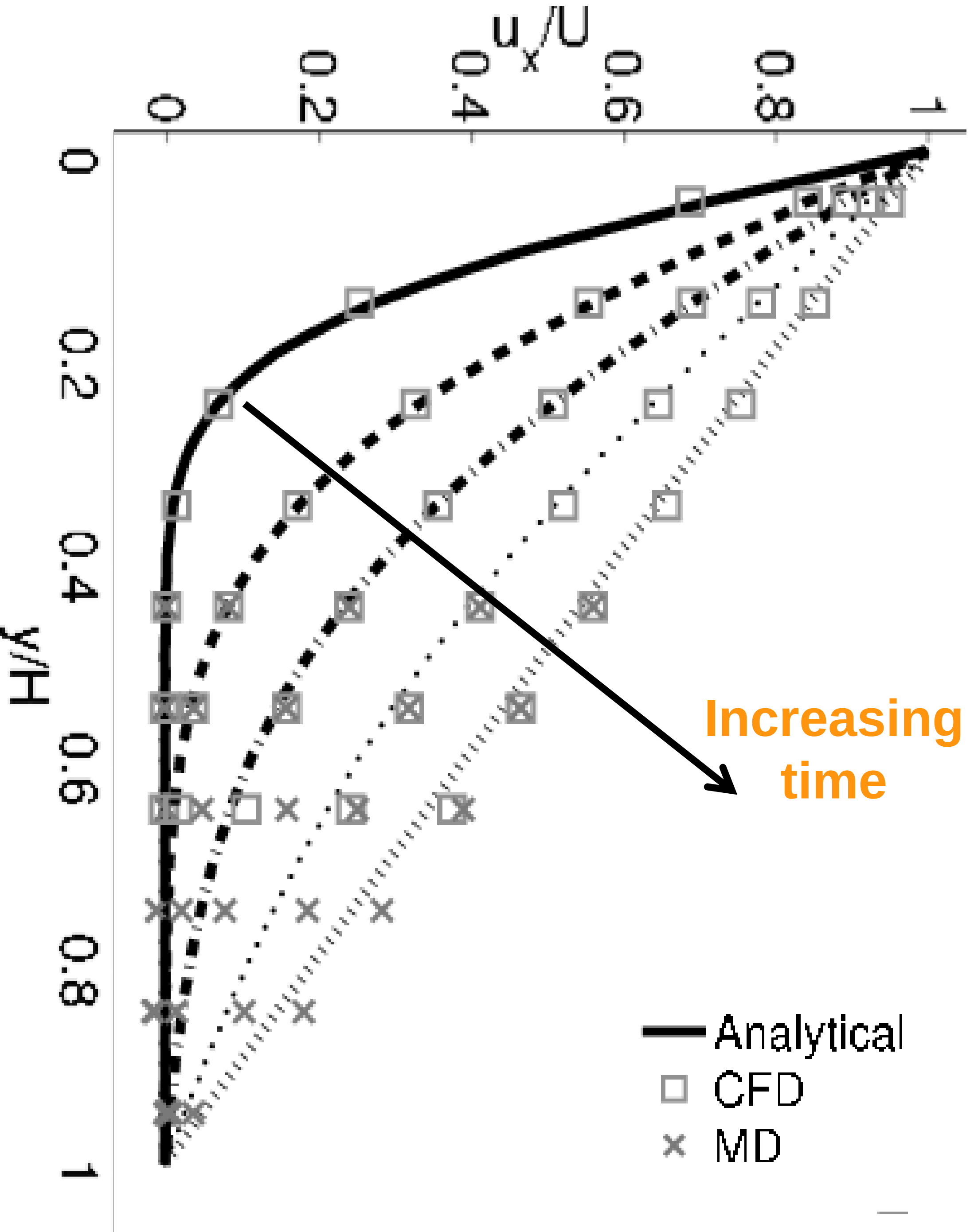
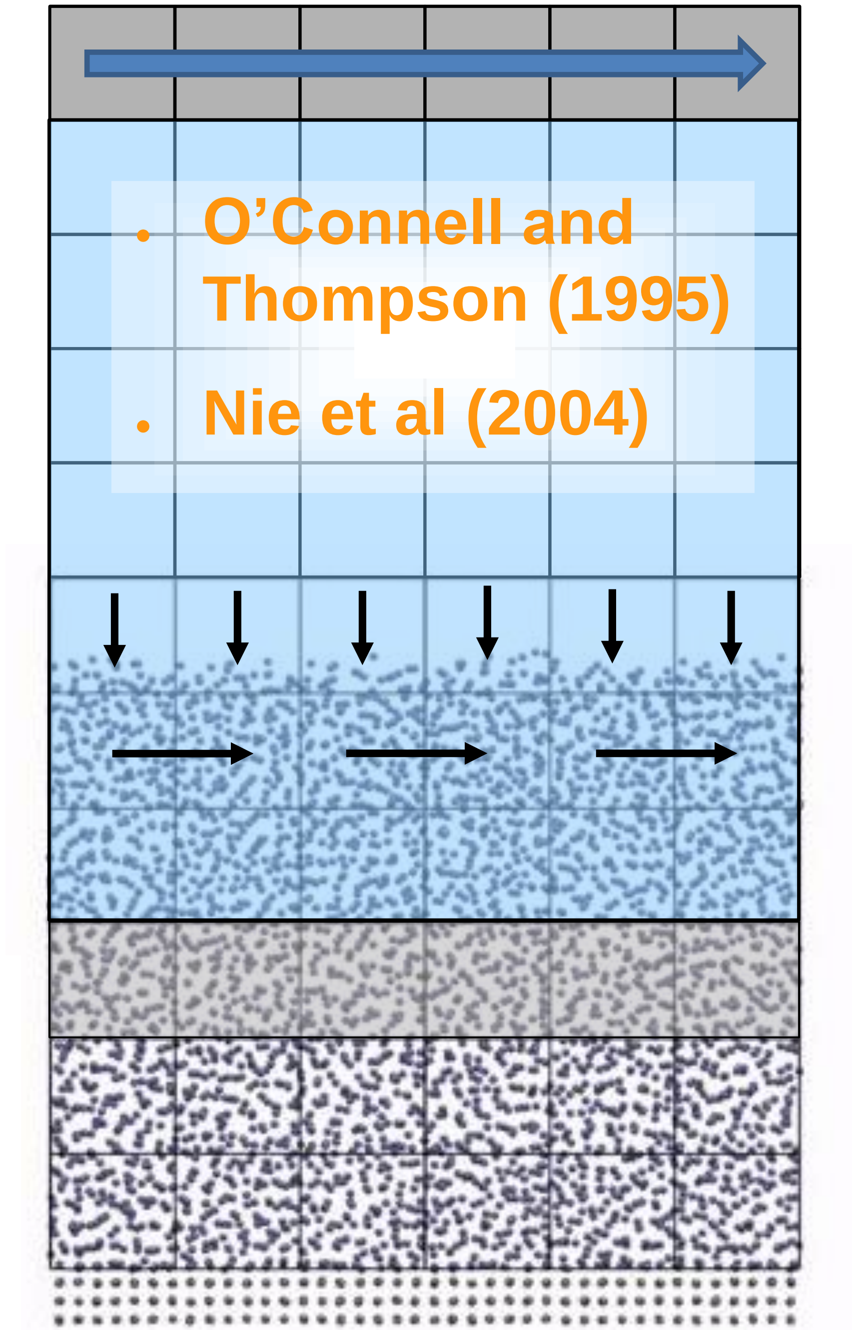
Coupling Results – Couette Flow





- O'Connell and Thompson (1995)
- Nie et al (2004)

Summary

- **What is a Control Volume (CV)?**
  - Gives the equations of motion in integral form
  - The only meaningful form for a discrete system
- **How do we apply it to Molecular Dynamics (MD)?**
  - Integrate the Irving and Kirkwood (1950) equations
  - You can then differentiate the CV functionals to get fluxes and forces
- **How is it useful?**
  - Exact course graining of the MD equations (by selecting functionals)
  - Providing nine Method of Planes stress components and exactly linking then to momentum evolution inside the CV
  - Deriving Exact Constraints localised to a region in space
  - Expressing MD in the same form as the CFD solver for coupled simulation

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- **References**

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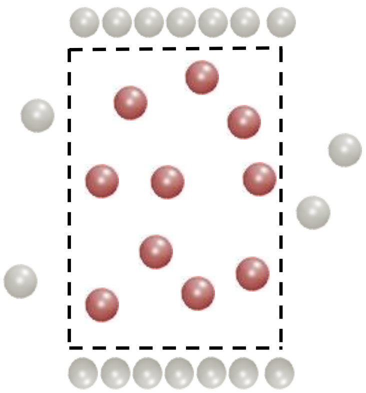
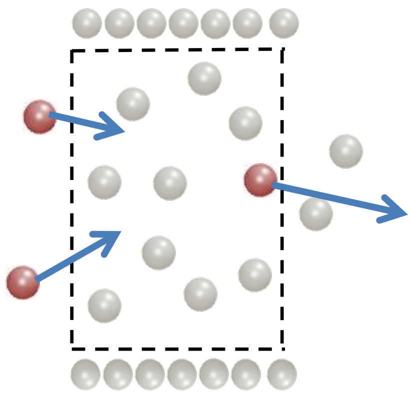
Extra Material

Exact Conservation

- **Mass Conservation**

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

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

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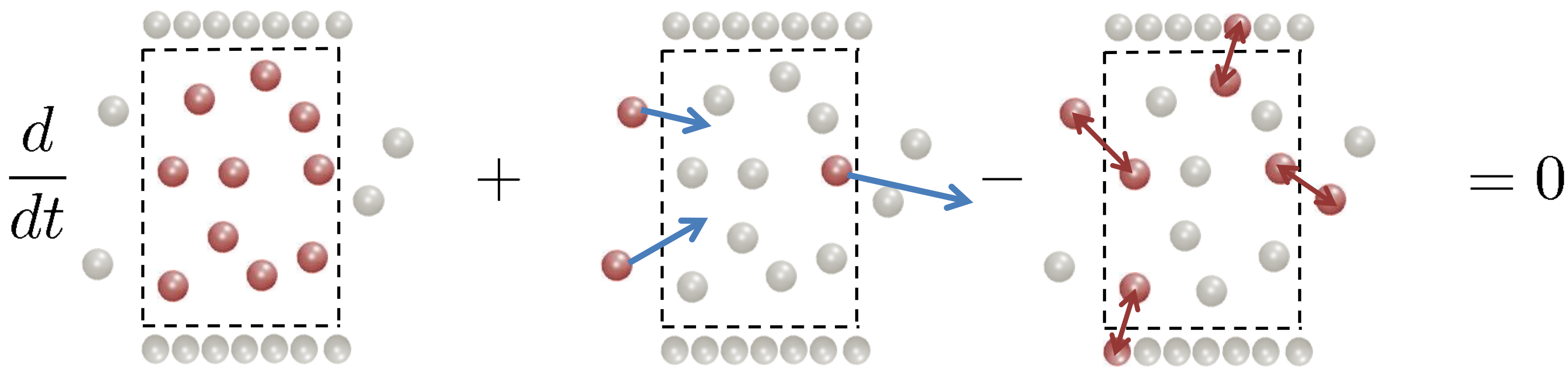
Exact Conservation

- **Momentum Balance**

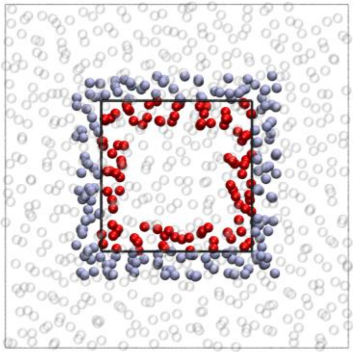
$$\underbrace{\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\textit{Accumulation}} + \underbrace{\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i}_{\textit{Advection}} - \underbrace{\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij} \mathbf{n} \cdot d\mathbf{S}_{ij}}_{\textit{Forcing}}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

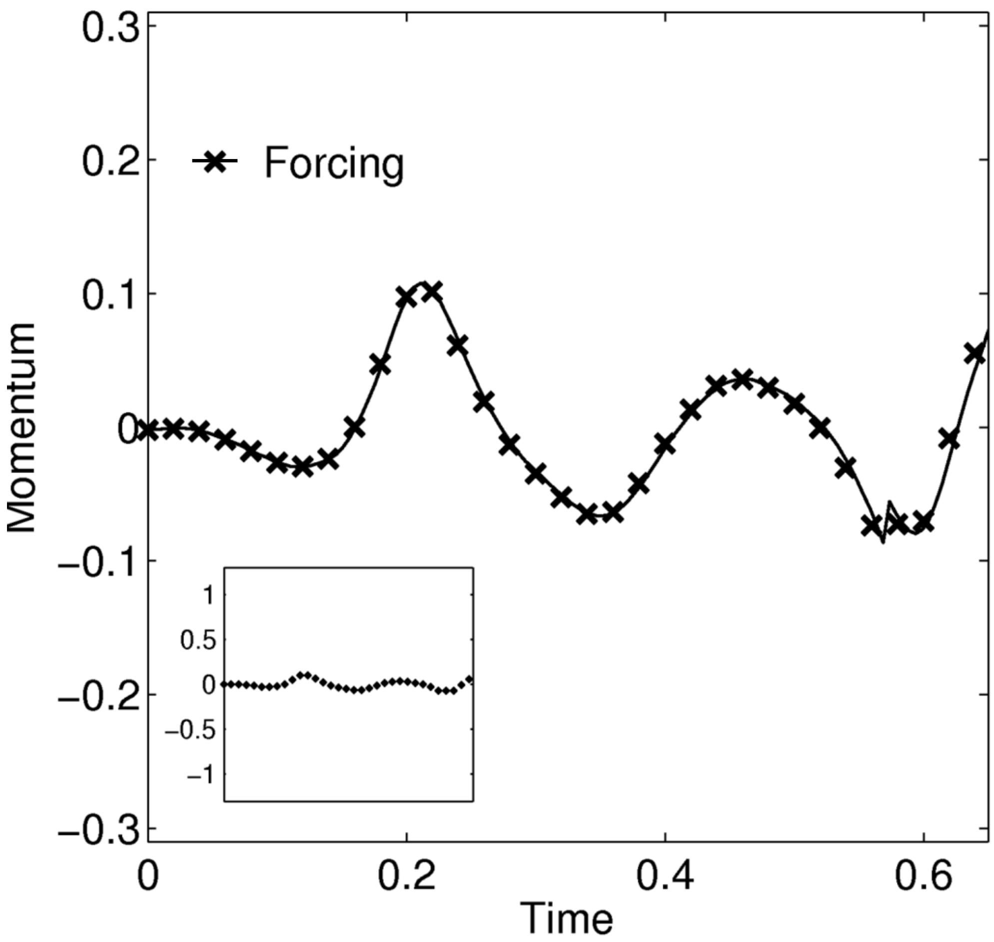


Testing Momentum Balance

- **Momentum Balance**

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

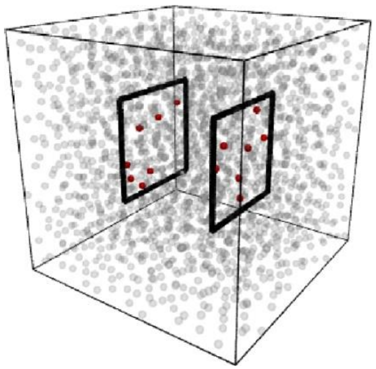


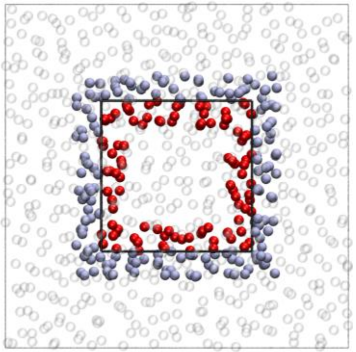


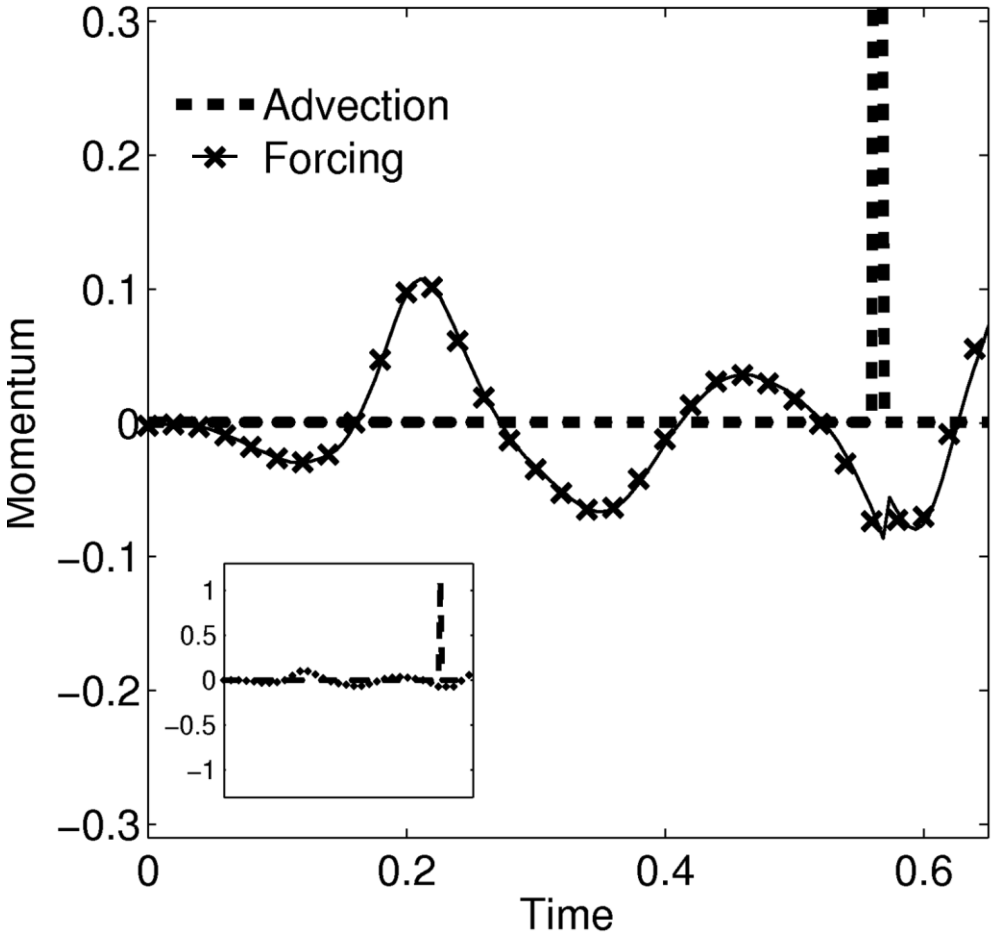
Testing Momentum Balance

- **Momentum Balance**

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







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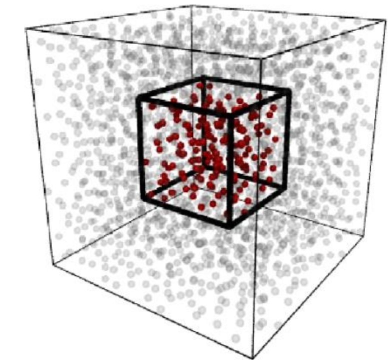
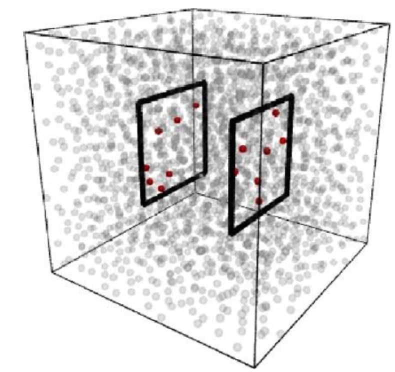
Testing Momentum Balance

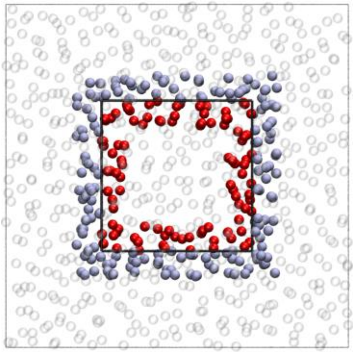
- **Momentum Balance**

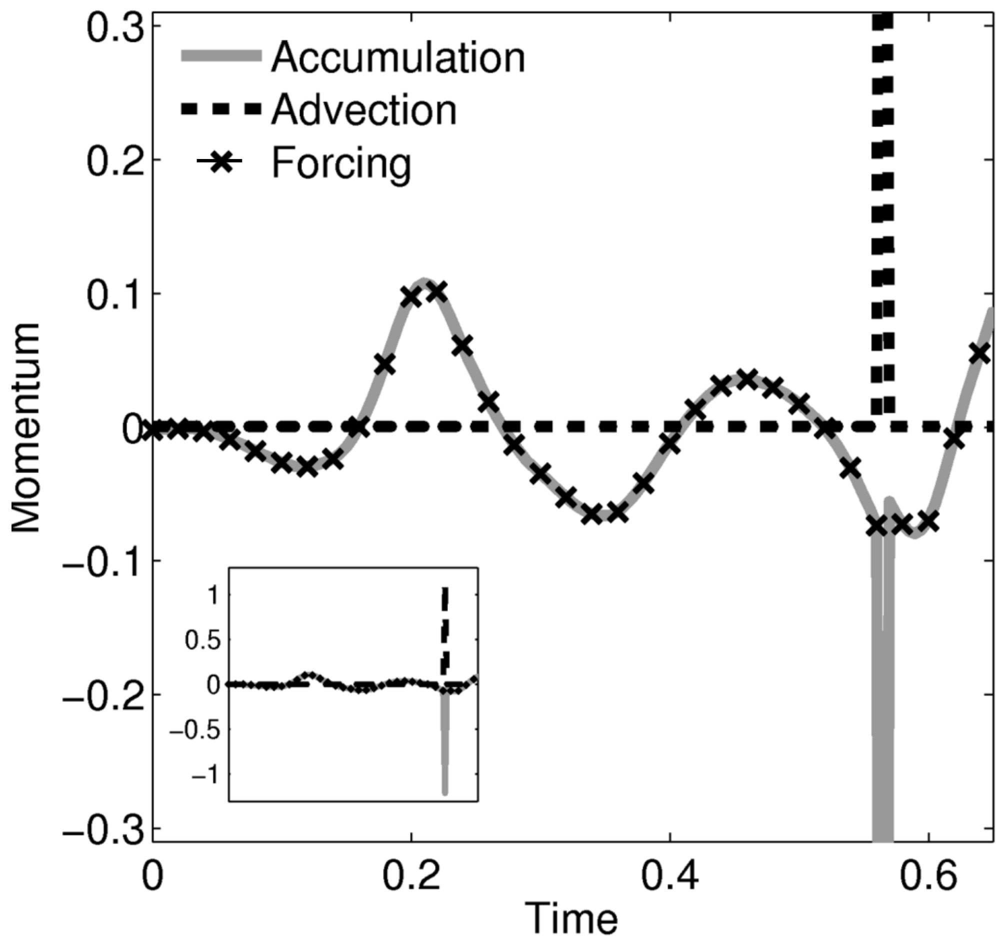
$$\underbrace{\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\textit{Accumulation}} = \underbrace{-\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\boldsymbol{S}_i}_{\textit{Advection}} + \underbrace{\sum_{i=1}^{N}\sum_{j\neq i}^{N} \mathbf{f}_{ij}\vartheta_{ij}}_{\textit{Forcing}}$$

$$\frac{d}{dt}$$









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Control Volume Function (revisited)

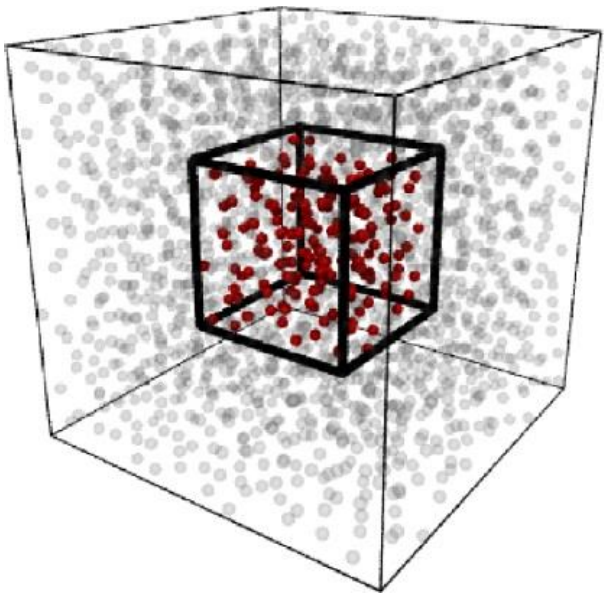
- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

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

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

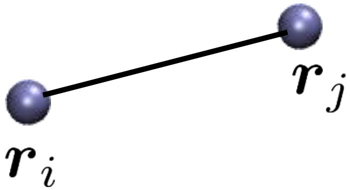
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

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



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

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



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

Control Volume Function (revisited)

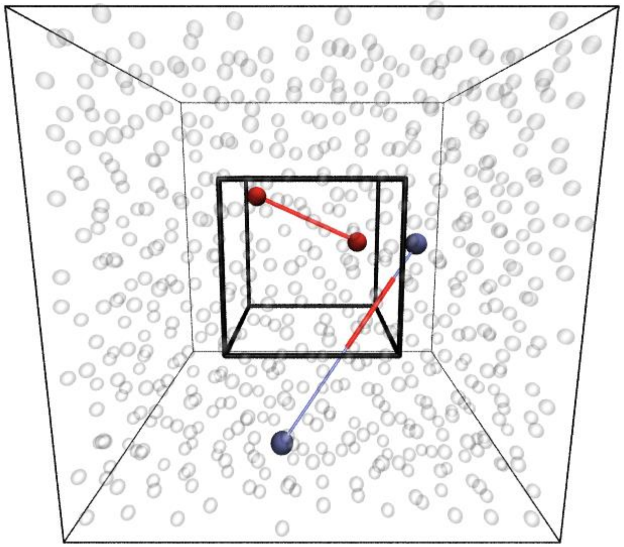
- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

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

$$\left[H(x^+ - x_i + sx_{ij}) - H(x^- - x_i + sx_{ij})\right]$$

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

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



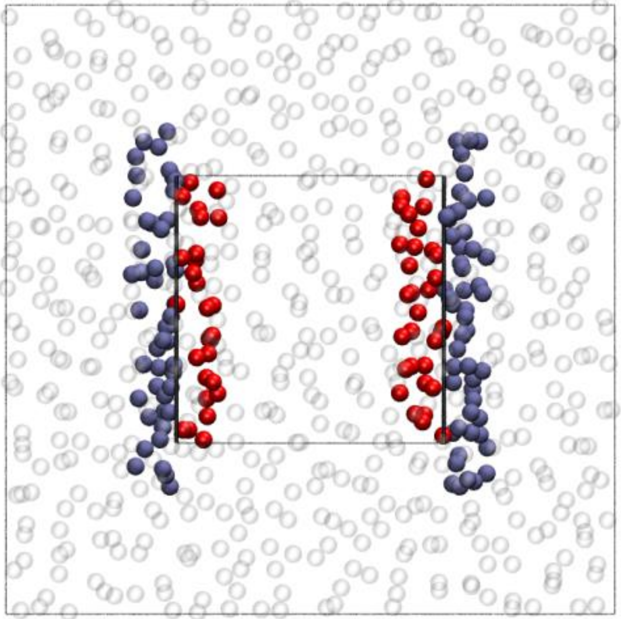
- **Length of interaction inside the CV**

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

Derivatives Yield the Surface Forces

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

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



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

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

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

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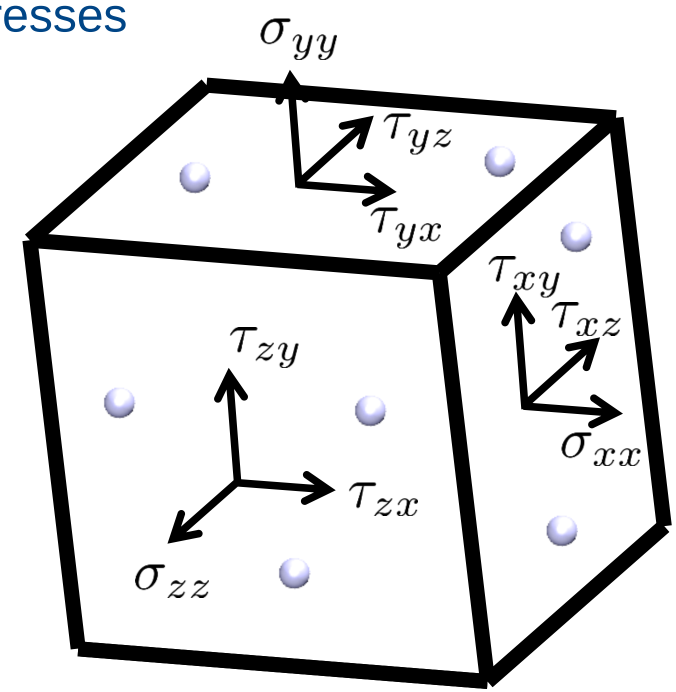
More on the Pressure Tensor

- **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



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Moving reference frame

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

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

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

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

  - Lagrangian mass conservation

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

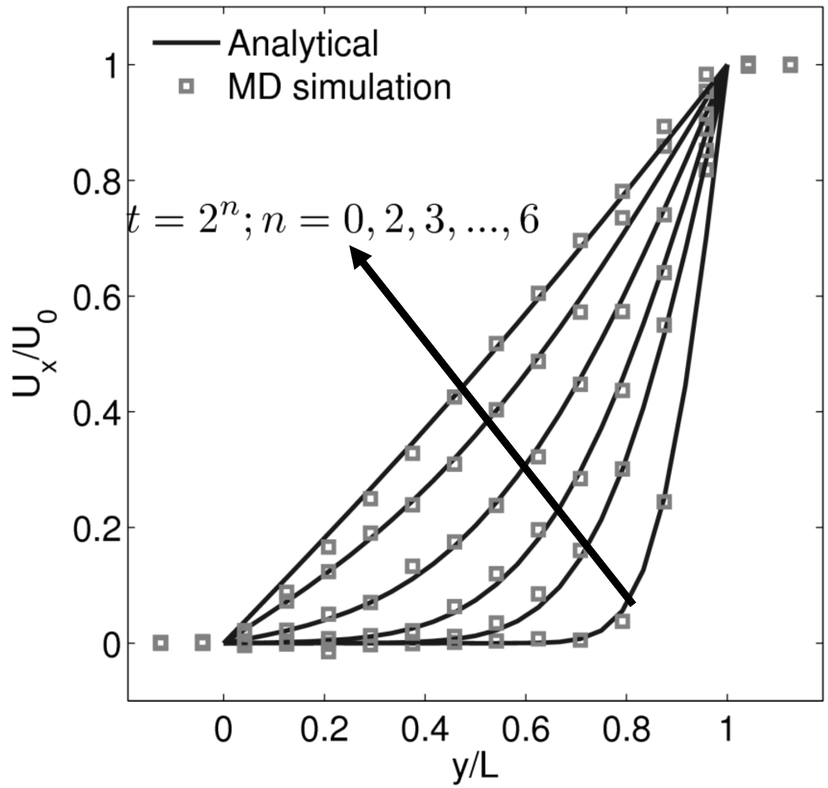
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \left(\mathbf{v}_i + \overline{\boldsymbol{u}}\right) \cdot d\boldsymbol{S}_i$$

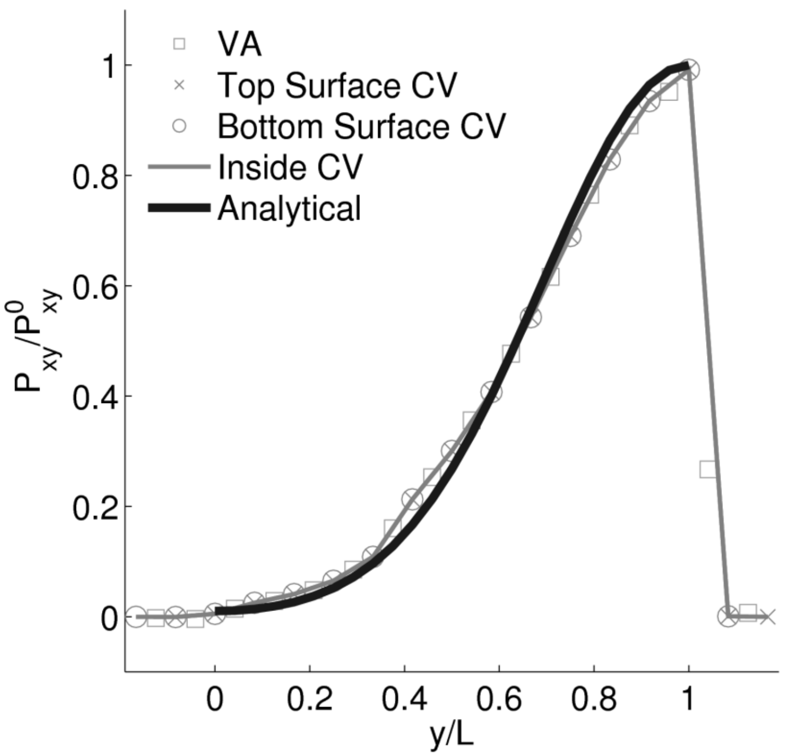
$$\frac{d}{dt}\int_V \rho dV = \oint_S \rho \left(\boldsymbol{u} - \overline{\boldsymbol{u}}\right) \cdot d\boldsymbol{S}$$

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

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

Continuum Analytical Couette Flow





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

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

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

Unsteady Couette Flow

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

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

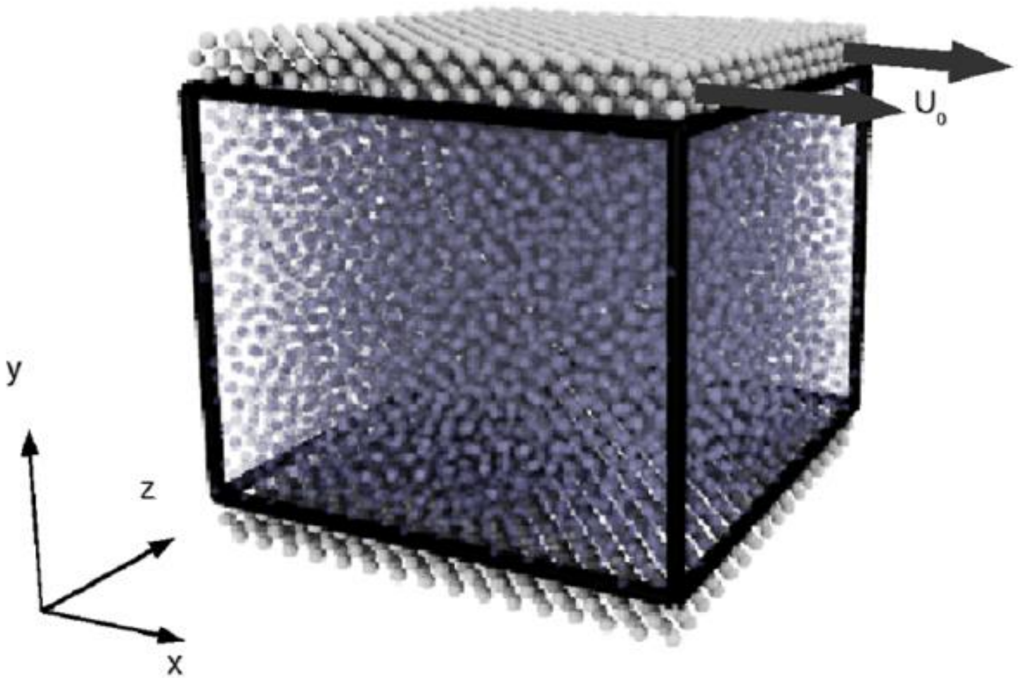
  - Solve the 1D unsteady diffusion equation.

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

  - With Boundary Conditions

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

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



Unsteady Couette Flow

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

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

  - Simplifies for a single control volume

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

  - With Boundary Conditions

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

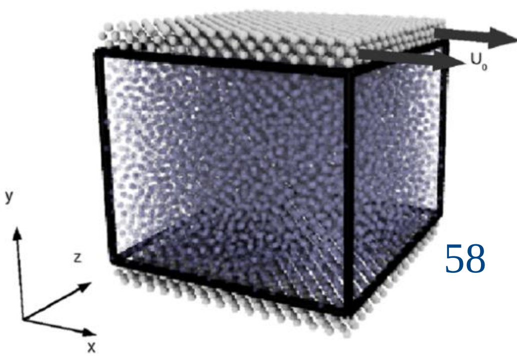
- ## Molecular Dynamics
  - Discrete form of the Momentum balance equation

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

  - Simplifies for a single control volume

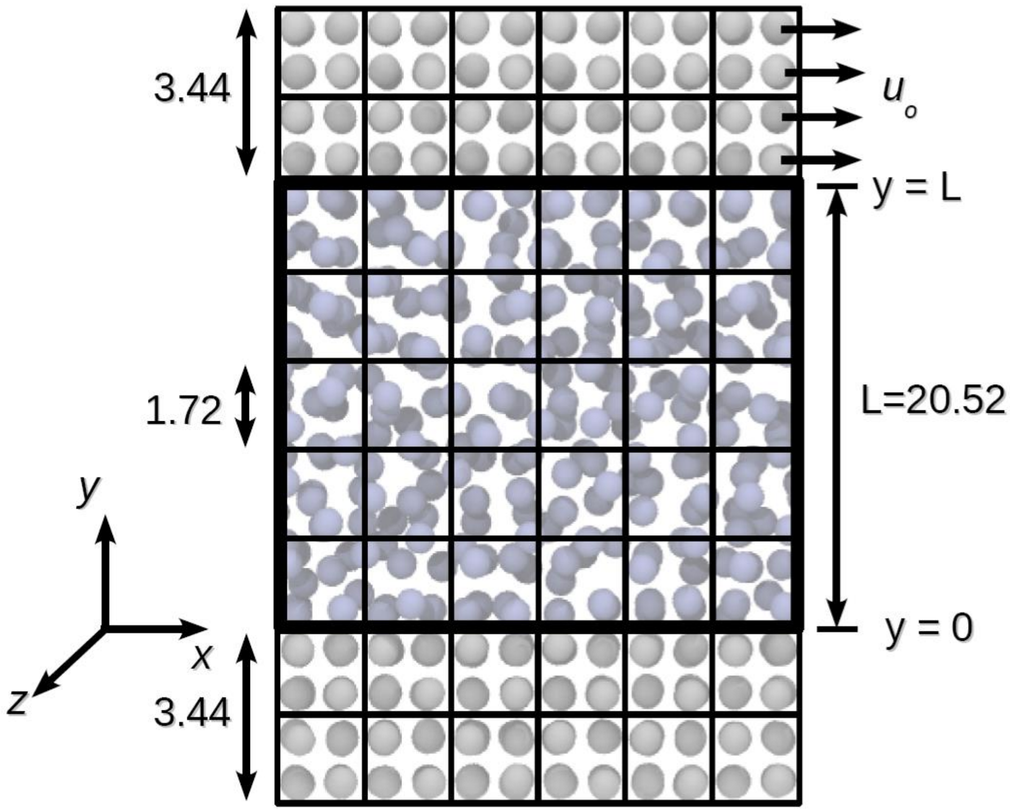
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = \sum_{i,j}^{N} f_{xij} dS_{yij}^+ - \sum_{i,j}^{N} f_{xij} dS_{yij}^-$$

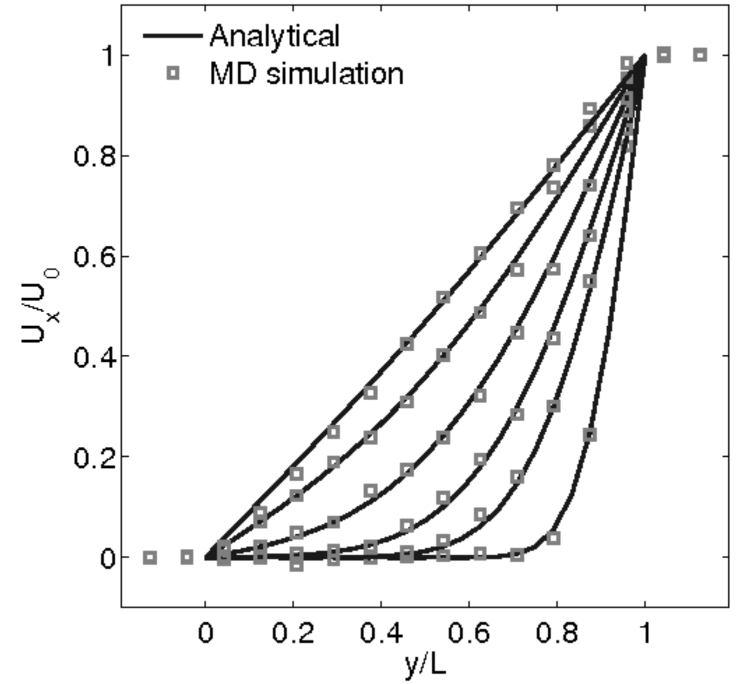
  - Fixed bottom wall, sliding top wall with both thermostatted

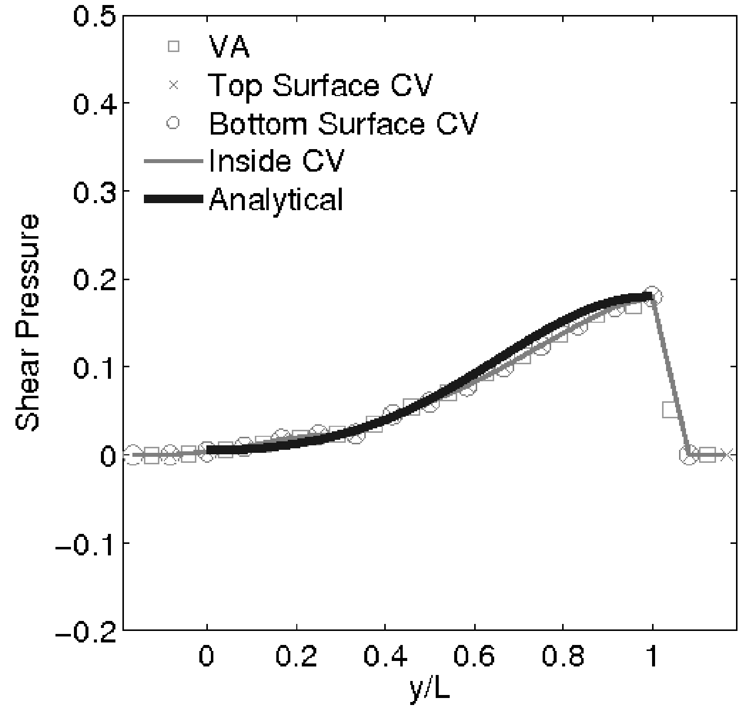


Unsteady Couette Flow

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

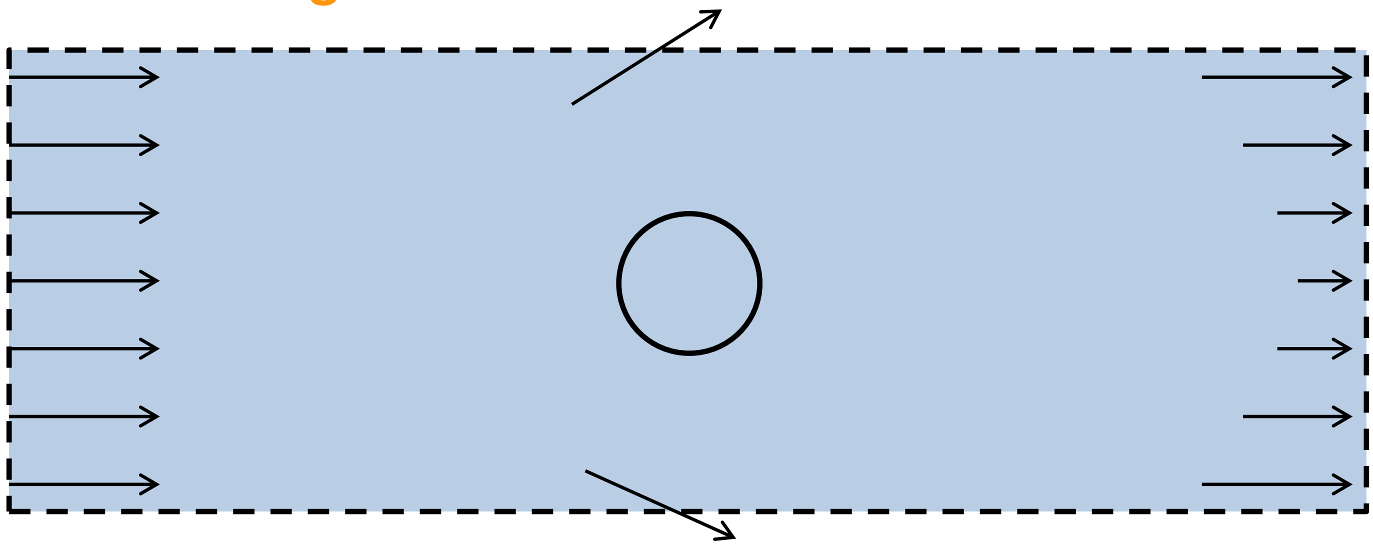






Flow past a cylinder

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



- Drag over a Carbon Nano-tube can be determined