# Control Volume Formulation Applied to Molecular Dynamics

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# Outline

- **Introduction**
  - Continuum Mechanics
  - Molecular Dynamics
  - Irving and Kirkwood (1950) and the Dirac delta
- **The Molecular Control Volume**
  - The Control Volume function
  - Governing equations
  - Exact conservation
- **Applications**
  - The pressure tensor
  - Unsteady Couette flow
  - Coupled simulations and constrained dynamics

# Introduction

# Continuum vs. Discrete

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

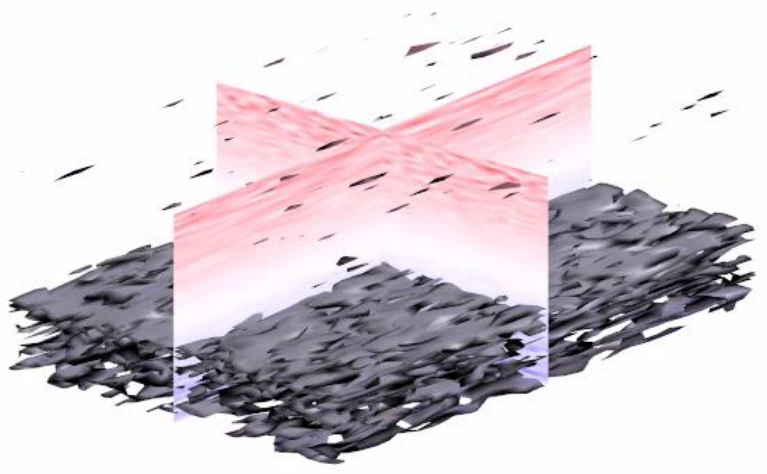
$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \rho \boldsymbol{u}$$

  - 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

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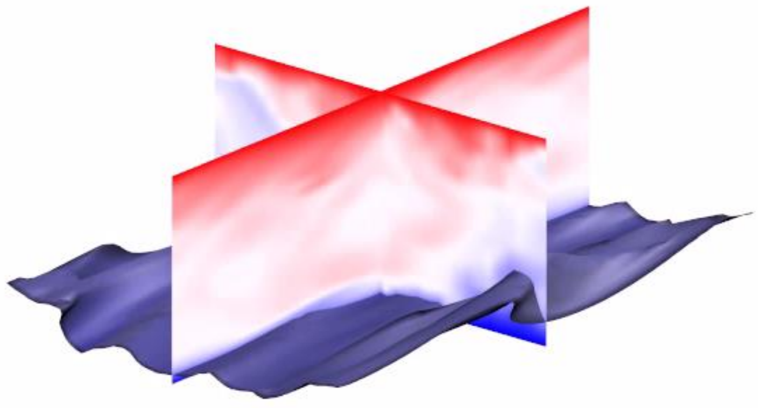
# Continuum vs. Discrete

- **Discrete Molecules in continuous space**
  - Governed by Newton's Law for an N-body system
  - Point particles with pairwise interactions

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

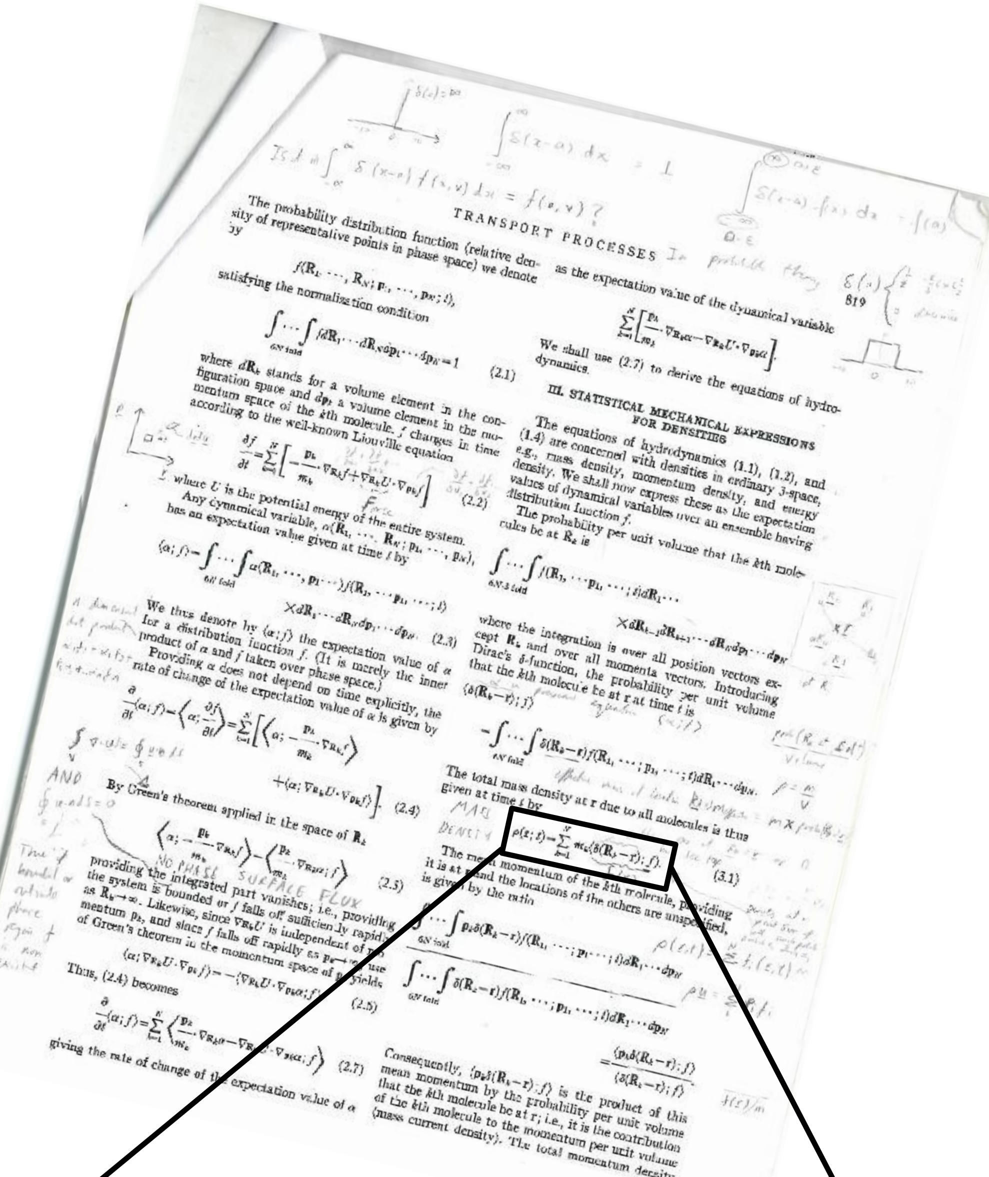
$$\Phi(r_{ij}) = 4\epsilon \left[ \left( \frac{\ell}{r_{ij}} \right)^{12} - \left( \frac{\ell}{r_{ij}} \right)^{6} \right]$$



Molecular Dynamics Simulation of Couette Flow

- **How do we obtain equivalent descriptions?**
  - Both modelled by Newtonian mechanics
  - Linking the discrete and continuous forms

# Irving and Kirkwood (1950)

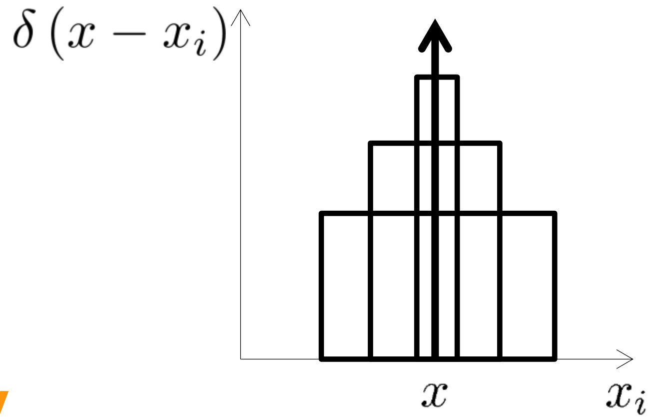




$$\rho(\boldsymbol{r},t)=\sum_{i=1}^{N}\left\langle m_i\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right);f\right\rangle$$

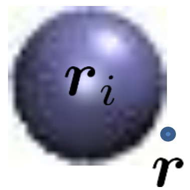
# Selecting Functions

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

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

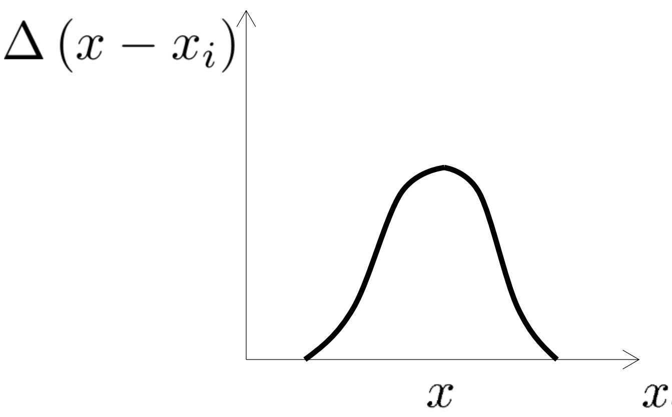



- **In a molecular simulation $\boldsymbol{r}$ is never exactly equal to $\boldsymbol{r}_i$**
  - Other difficulties with the Dirac delta function




- **Relaxed weighting functions**
  - By Hardy(1981), Hoover (2009), Murdoch (2010) and others

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

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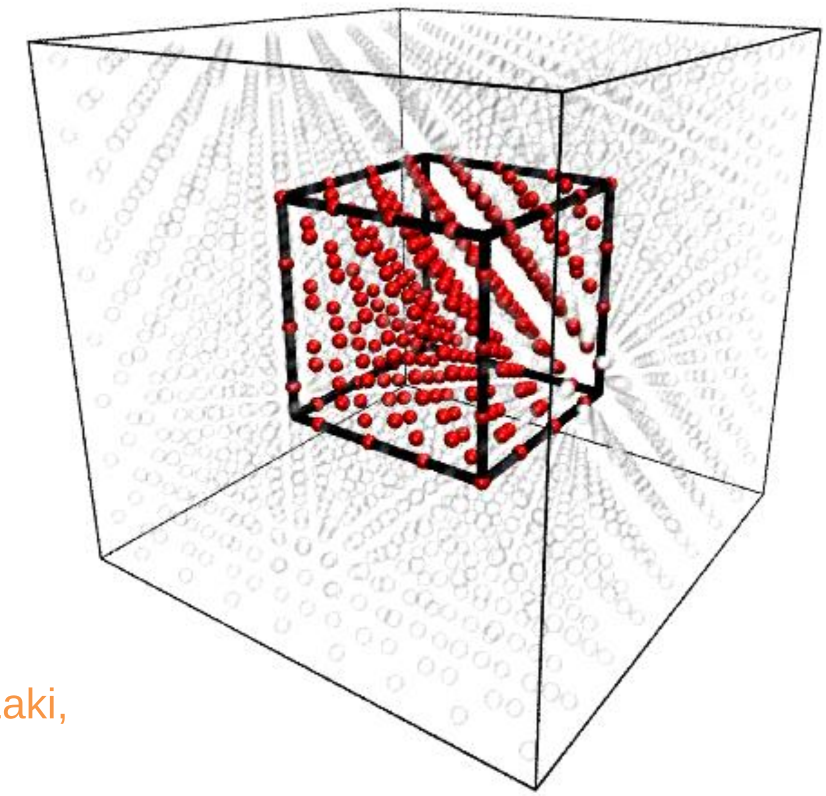
# The Molecular Control Volume

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

# Derivatives yields the Surface Fluxes

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

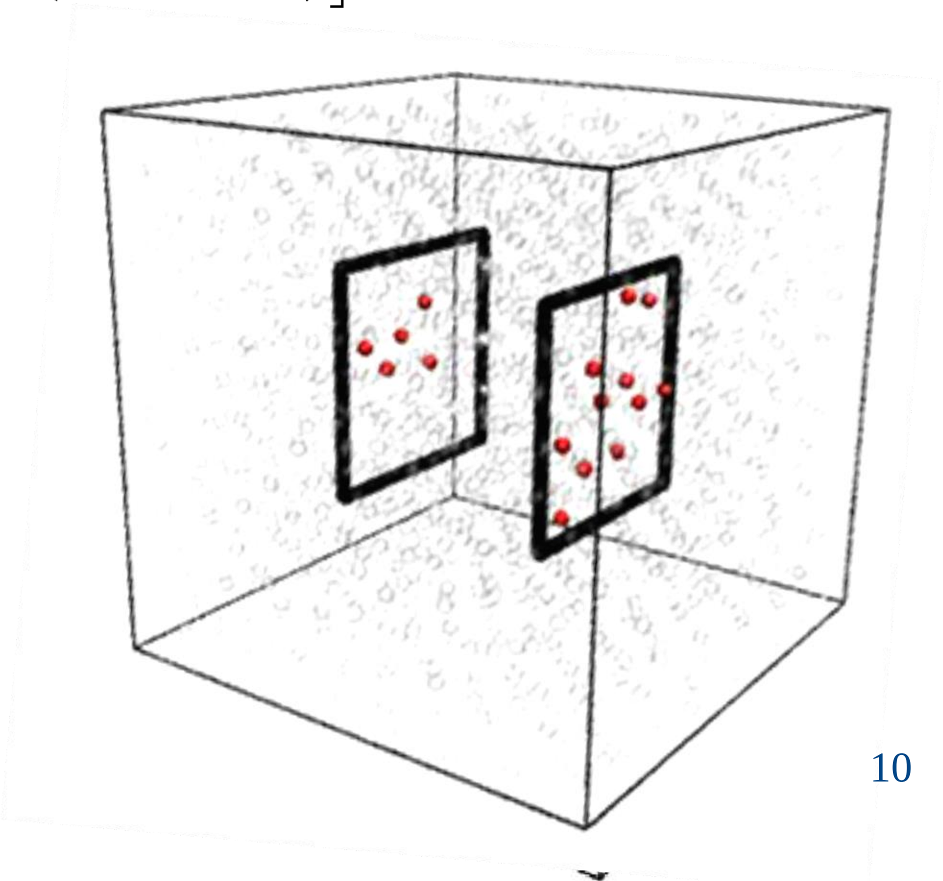
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

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

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

- **Vector form defines six surfaces**

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



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# Applying the Control Volume Function

- **Molecular mass in a control volume**

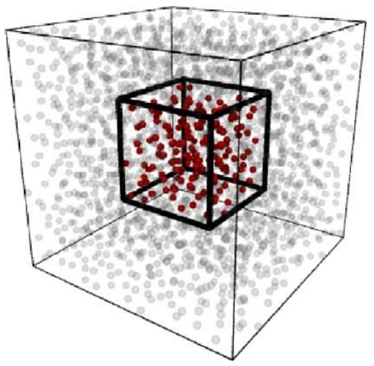
$$\frac{d}{dt}\sum_{i=1}^{N} m_i\vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i \qquad \frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u}\cdot d\mathbf{S}$$

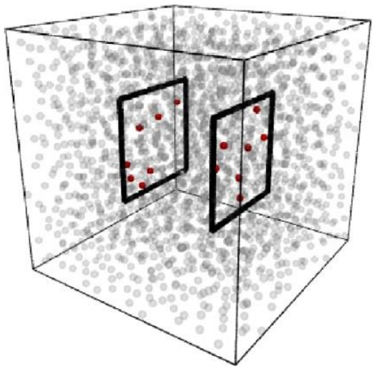
- **Mathematical manipulation yields surface fluxes**

$$\frac{d}{dt}\sum_{i=1}^{N} m_i\vartheta_i = \sum_{i=1}^{N}\left(\vartheta_i \cancel{\frac{d}{dt}m_i} + m_i\frac{d}{dt}\vartheta_i\right)$$

$$= \sum_{i=1}^{N} m_i \frac{d\boldsymbol{r_i}}{dt}\cdot\frac{d}{d\boldsymbol{r_i}}\vartheta_i$$

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

$\frac{d}{dt}$ 

$3\times$ 

# Reynolds' Transport Theorem

- **Mass, momentum and energy equations**

  - Mass Conservation

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

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

  - Momentum Balance

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

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

  - Energy Conservation

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

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

# Reynolds' Transport Theorem

- **Mass, momentum and energy equations**
  - Mass Conservation

$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i \qquad \frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u} \cdot d\mathbf{S}$$

  - Momentum Balance

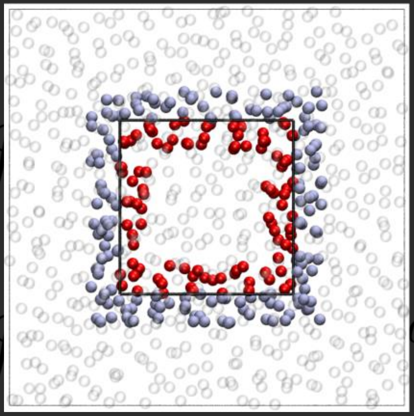
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\vartheta_{ij} \qquad \frac{\partial}{\partial t}\int_V \rho \boldsymbol{u} dV = -\oint_S \rho \boldsymbol{u}\boldsymbol{u} \cdot d\mathbf{S} + \mathbf{F}_{\text{surface}}$$

  - Energy Conservation

$$\frac{d}{dt}\sum_{i=1}^{N} e_i \vartheta_i = -\sum_{i=1}^{N} e_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{i\neq j}^{N} \frac{\mathbf{p}_i}{m_i} \cdot \boldsymbol{f}_{ij}\vartheta_{ij} \qquad \frac{\partial}{\partial t}\int_V \rho \mathcal{E} dV = - \dots - \dots d\mathbf{S}$$

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

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

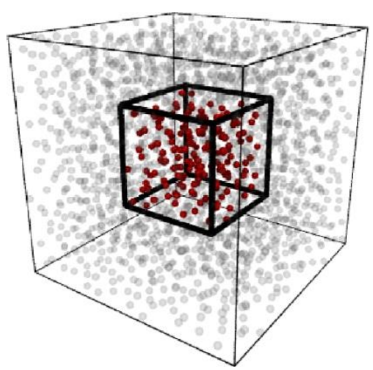
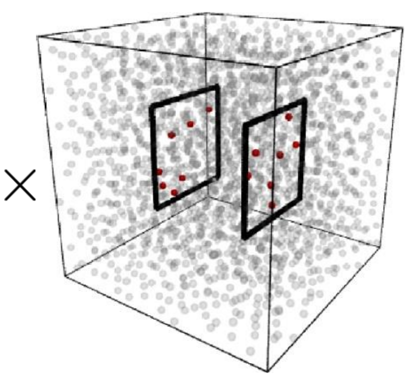
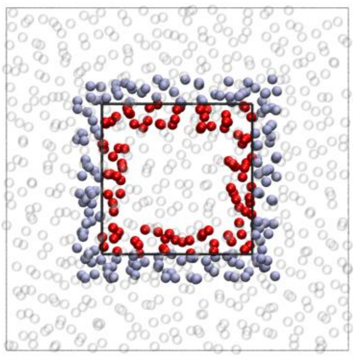


- **This is the IK operator for a CV**

# Testing Momentum Balance

- **Momentum Balance**

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

$\frac{d}{dt}$  $+\ 3\times$  $-$  $= 0$

# Applications

# The Pressure Tensor

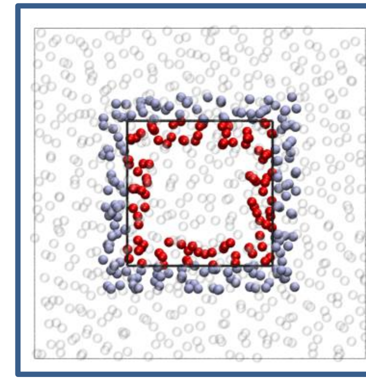
- **Control Volume equations in terms of the pressure tensor**

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

$$-\frac{\partial}{\partial \boldsymbol{r}}\cdot \boxed{\int_V \boldsymbol{\Pi}\, dV}$$

$$\boxed{-\oint_S \boldsymbol{\Pi}\cdot d\boldsymbol{S}}$$

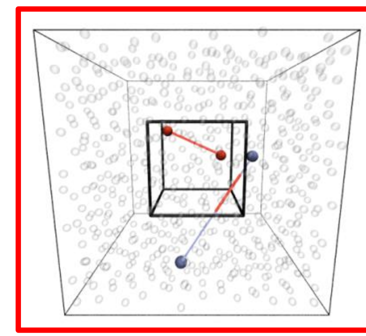
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \boxed{\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\vartheta_{ij}}$$



- **Molecular surface pressure over all 6 surfaces**

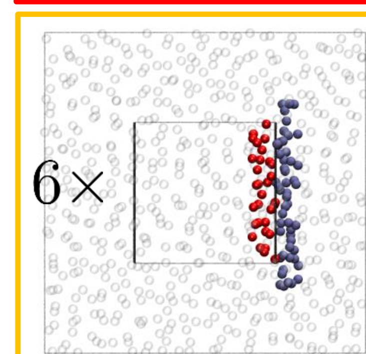
$$\boxed{\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\vartheta_{ij}} = -\frac{\partial}{\partial \boldsymbol{r}}\cdot \boxed{\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\boldsymbol{r}_{ij}\int_0^1 \vartheta_s\, ds}$$

Volume Average
Lutsko (1988) &
Cormier et al (2001)



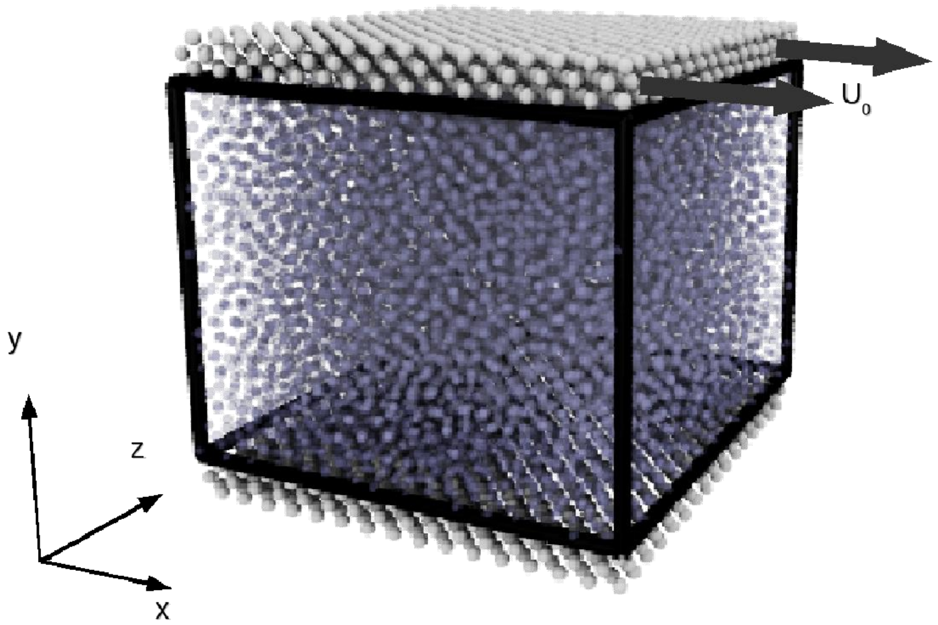
$$= -\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\boldsymbol{r}_{ij}\cdot \int_0^1 \frac{\partial \vartheta_s}{\partial \boldsymbol{r}}\, ds$$

$$= \boxed{-\frac{1}{4}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\underbrace{\left[sgn(r_\alpha^{\pm} - r_{\alpha i}) - sgn(r_\alpha^{\pm} - r_{\alpha j})\right]}_{\text{MOP (Todd et al 1995)}} S_{\alpha ij}^{\pm}}$$



# Unsteady Couette Flow

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

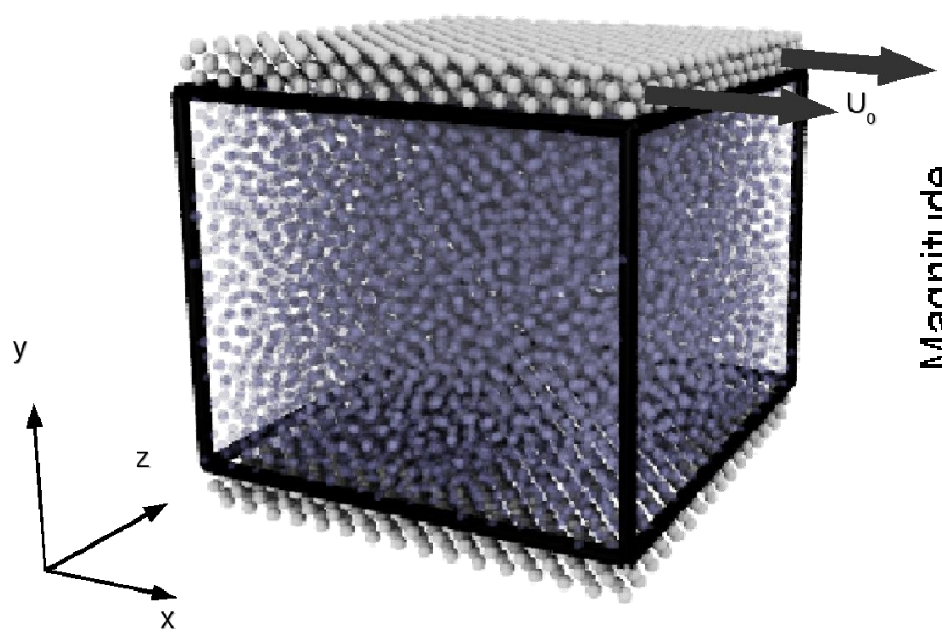


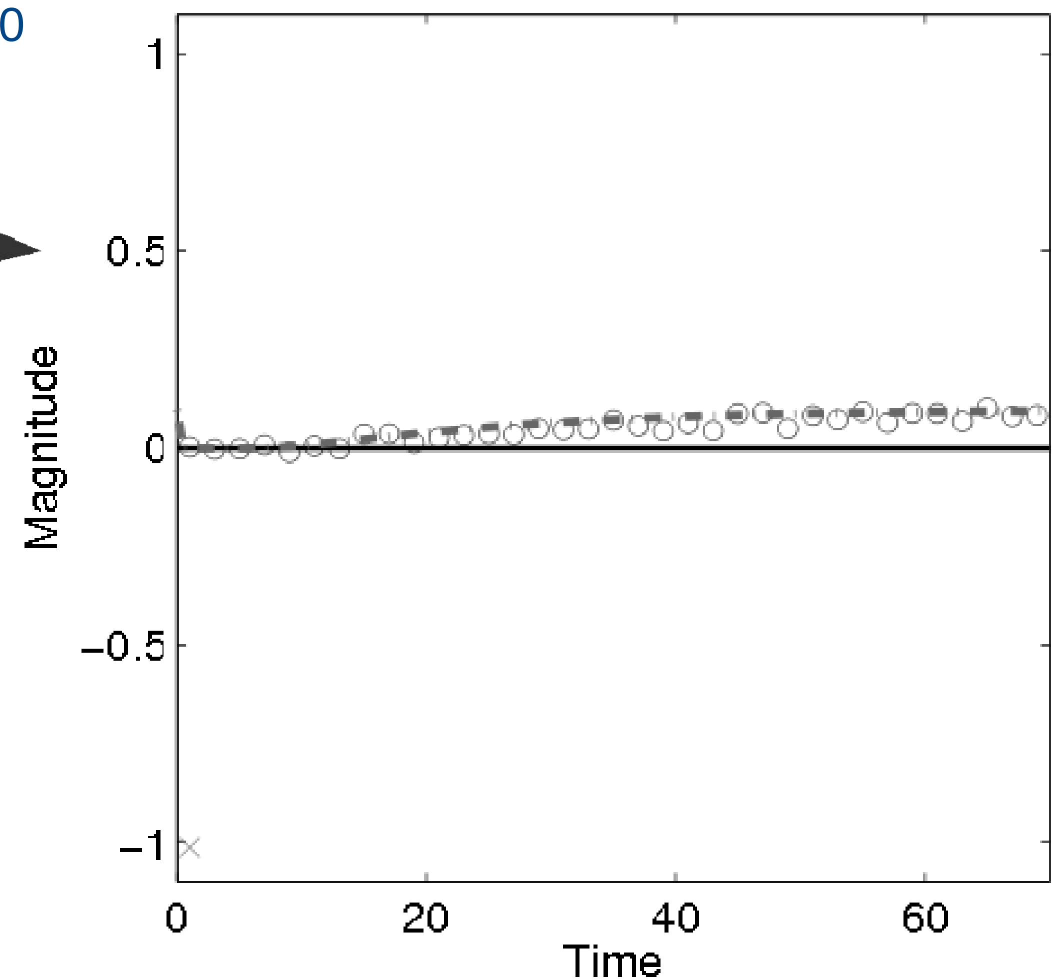
# Unsteady Couette Flow

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

$$-\sum_{i,j}^{N} f_{xij}\, dS^{-}_{yij}$$

$$-\int_{S_f^-} \Pi_{xy}\, dS_f^- .$$



# Unsteady Couette Flow

- **Simulation setup**
  - Starting Couette flow
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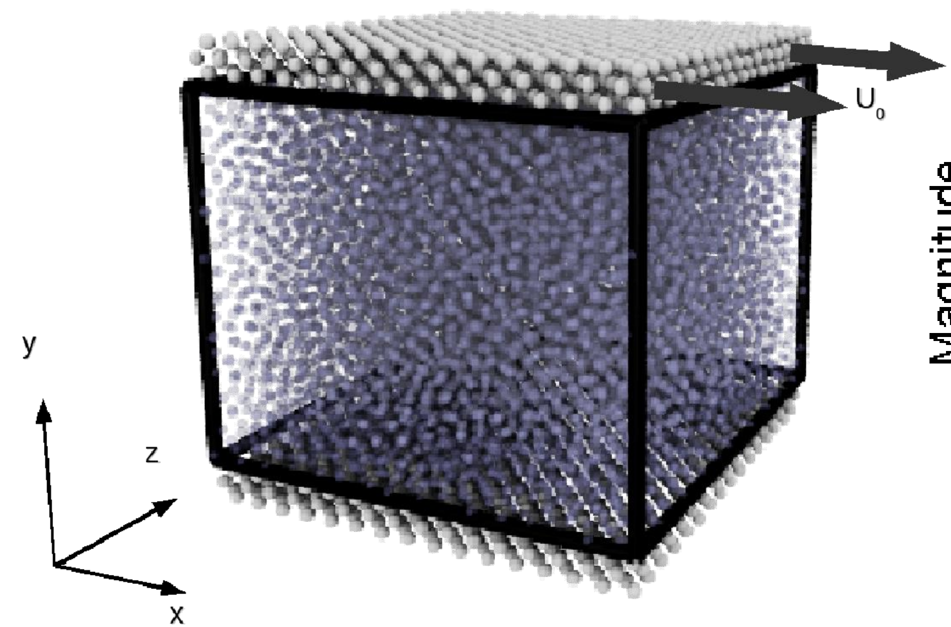
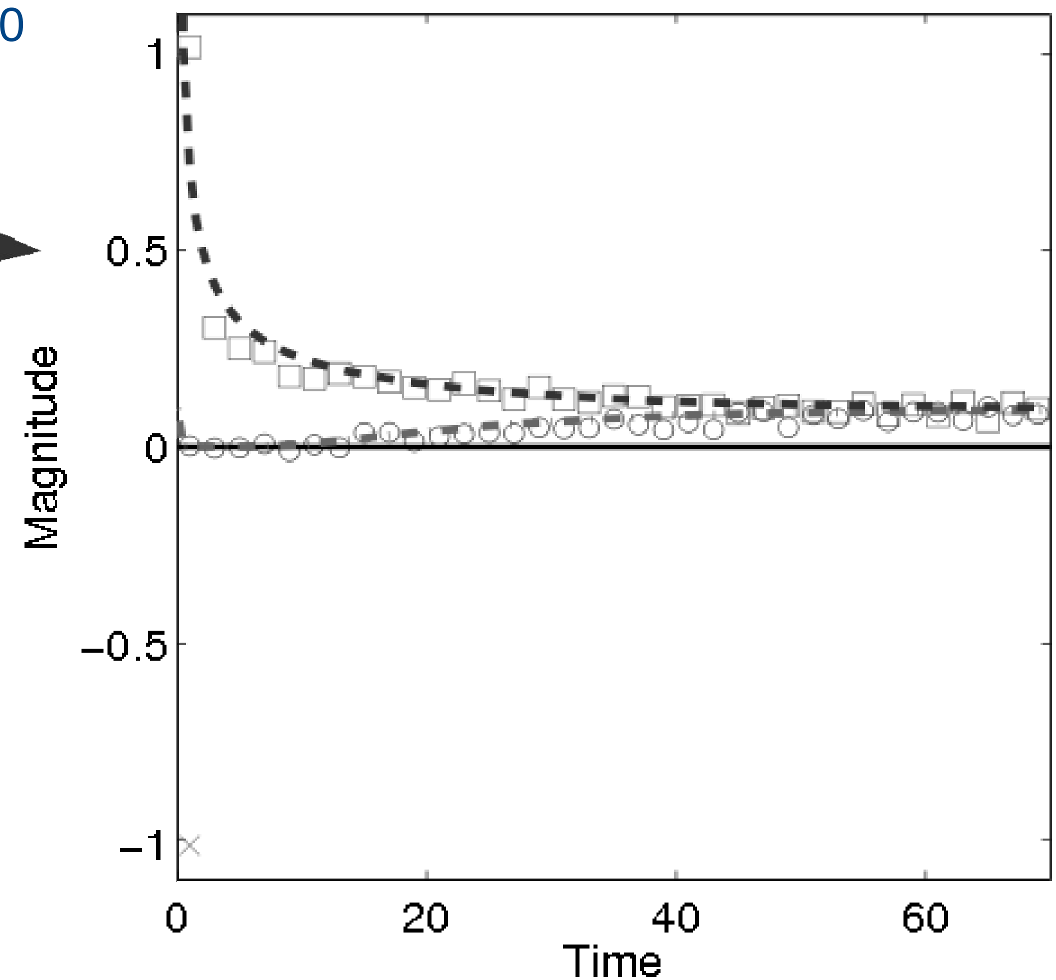
  - Averages are computed over 1000 time steps and 8 realizations

$$= \sum_{i,j}^{N} f_{xij}\, dS^{+}_{yij} - \sum_{i,j}^{N} f_{xij}\, dS^{-}_{yij}$$

$$= \int_{S_f^+} \Pi_{xy}\, dS_f^{+} - \int_{S_f^-} \Pi_{xy}\, dS_f^{-} .$$



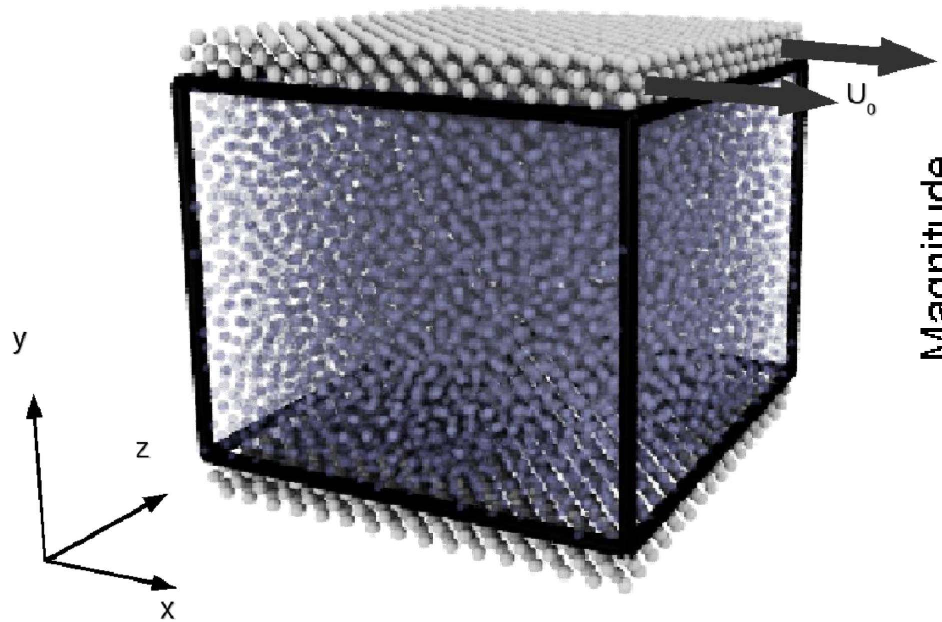



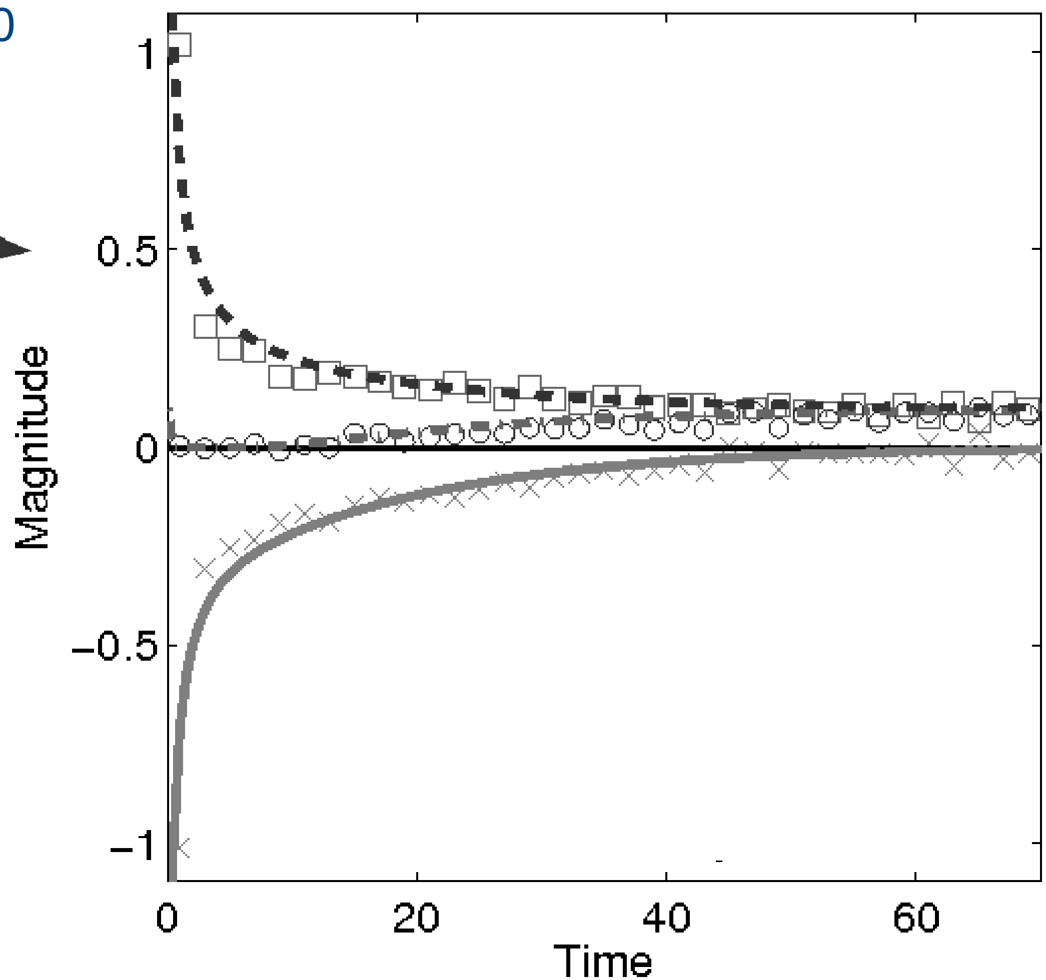
# Unsteady Couette Flow

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

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

$$\frac{\partial}{\partial t}\int_V \rho u_x dV = \int_{S_f^+} \Pi_{xy} dS_f^{+} - \int_{S_f^-} \Pi_{xy} dS_f^{-}.$$



# Control Volume Coupling

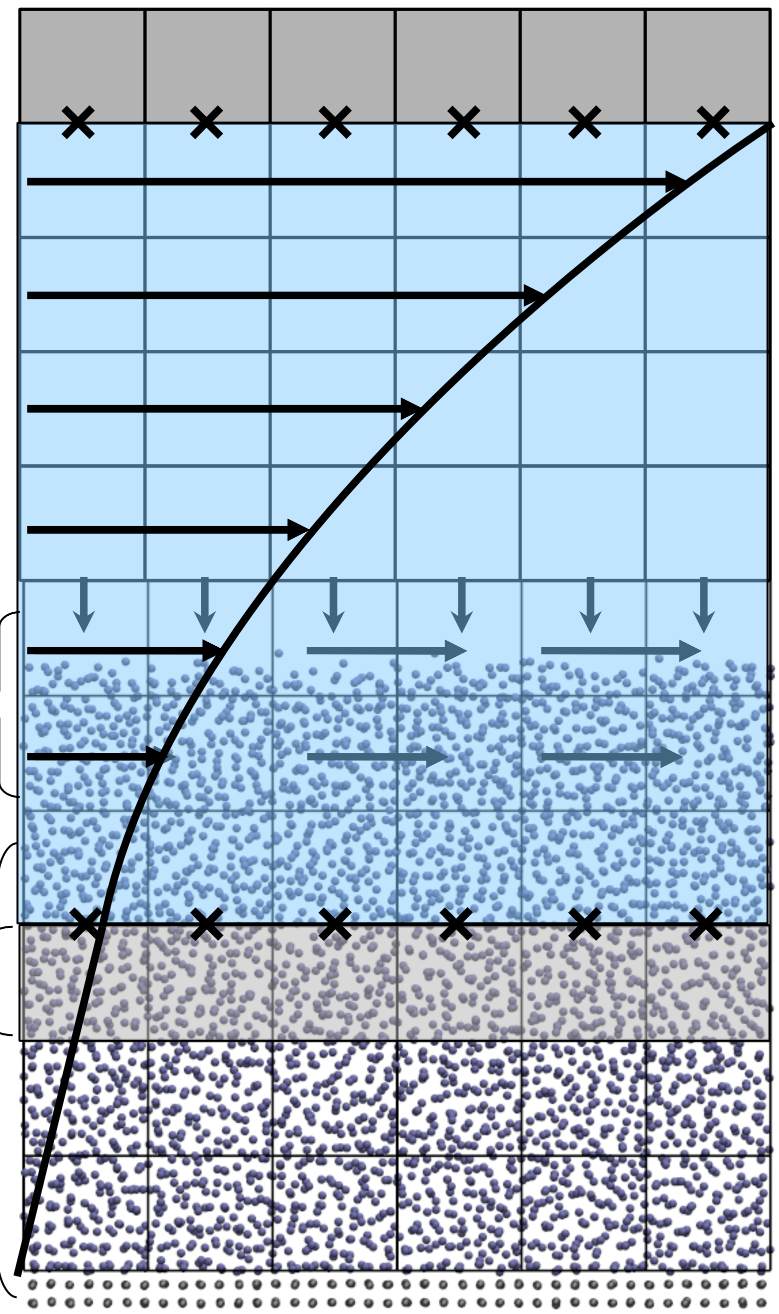
- **Molecular Equations**

Gauss Principle of Least Constraint with

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

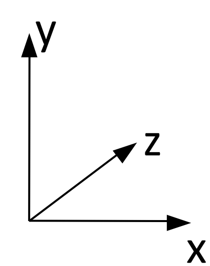
$$\sum_{i=1}^{N} m_i \boldsymbol{v}_i \vartheta_i$$

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



$$\rho u = \rho U_0$$

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




- **Continuum Equations**

O'Connell and Thompson, (1995).

# Summary

- **Reformulated the Irving and Kirkwood (1950) equations in terms of a control volume**
  - Compared to the continuum Control Volume equations – not pointwise so the Dirac delta function is replaced by the CV function
  - The CV function is mathematically and computational well defined and applicable to any discrete system
- **Derivation of discrete CV equations**
  - Not an approximation of the Dirac delta but an integration over a volume
  - Exactly conservative equations derived for mass, momentum and energy
- **Applications**
  - Provides insight into the pressure tensors and link them to time evolution
  - Arbitrary CV shapes and exact conservation can be exploited
  - Can be used in the derivation of localised constraint algorithms using minimisation principles (e.g. Gauss' Least Constraint)

# References

- **References**

J. H. Irving and J. G. Kirkwood, J. Chemical. Phys. 18(6), 817 (1950).
R.J. Hardy J. Chem. Phys. 76, 1 (1998)
P. Schofield and J. R. Henderson, Proc. R. Soc. London A 379, 231 (1982).
J. F. Lutsko, J. Appl. Phys 64(3), 1152 (1988)
S. T. O'Connell and P. A. Thompson, Phys. Rev. E 52, R5792 (1995).
B. D. Todd, D. J. Evans, and P. J. Daivis, Physical Review E 52(2), 1627 (1995).
J. Cormier, J. Rickman, and T. Delph, J. Appl. Phys 89-1, 99 (2001).
M. Han and J. Lee, Phys. Rev. E 70, 061205 (2004).
Wm. G. Hoover, C. G. Hoover Phys. Rev. E 80 011128 (2009)
A. I. Murdoch, J. Elast. 100, 33 (2010).
D. M. Heyes, E. R. Smith, D. Dini, T. A. Zaki J. Chemical Phys. 135, 024512 (2011)
E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

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  - Professor David Heyes
  - Dr Daniele Dini
  - Dr Tamer Zaki

**Thank you for listening**

**Any Questions?**

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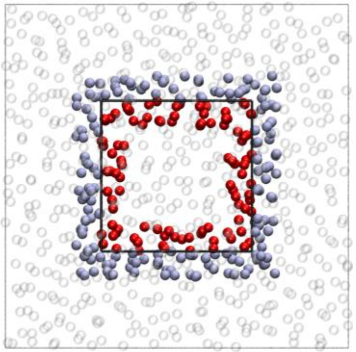
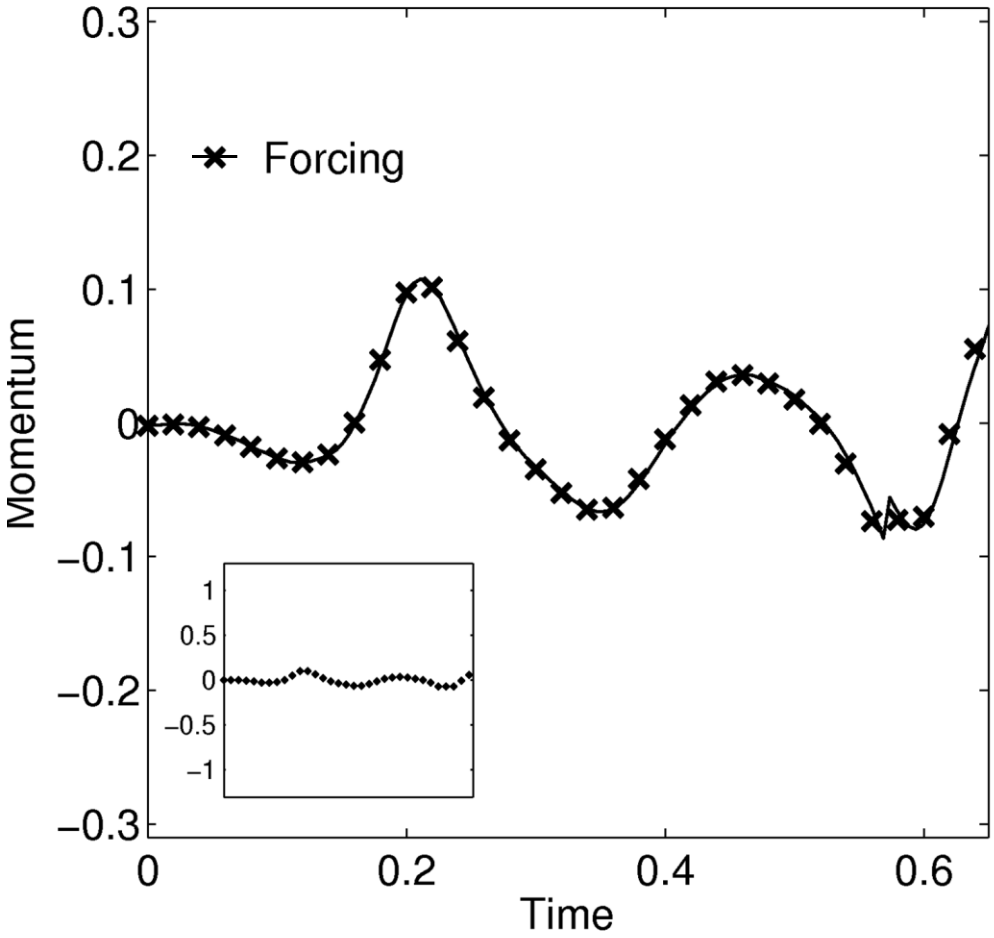
# Extra Material

# Testing Momentum Balance

- **Momentum Balance**

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



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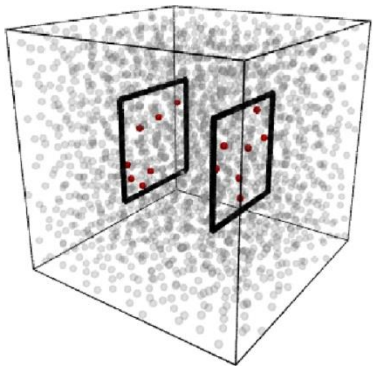
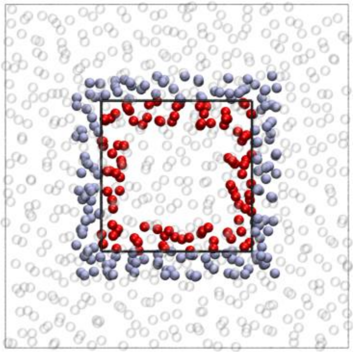
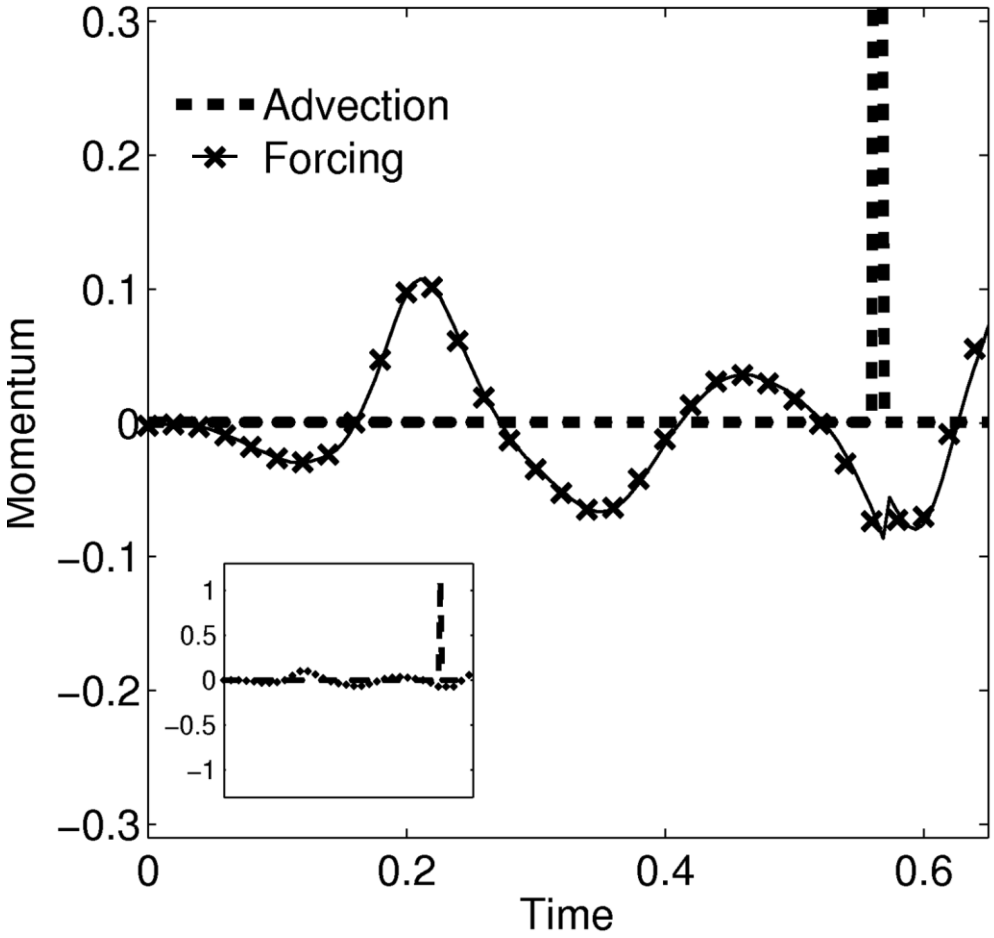
# Testing Momentum Balance

- **Momentum Balance**

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





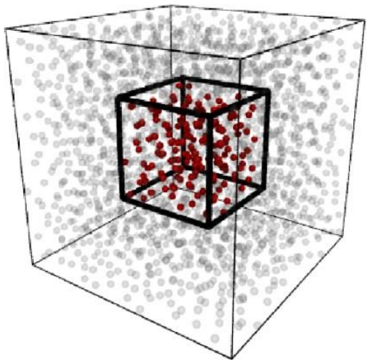


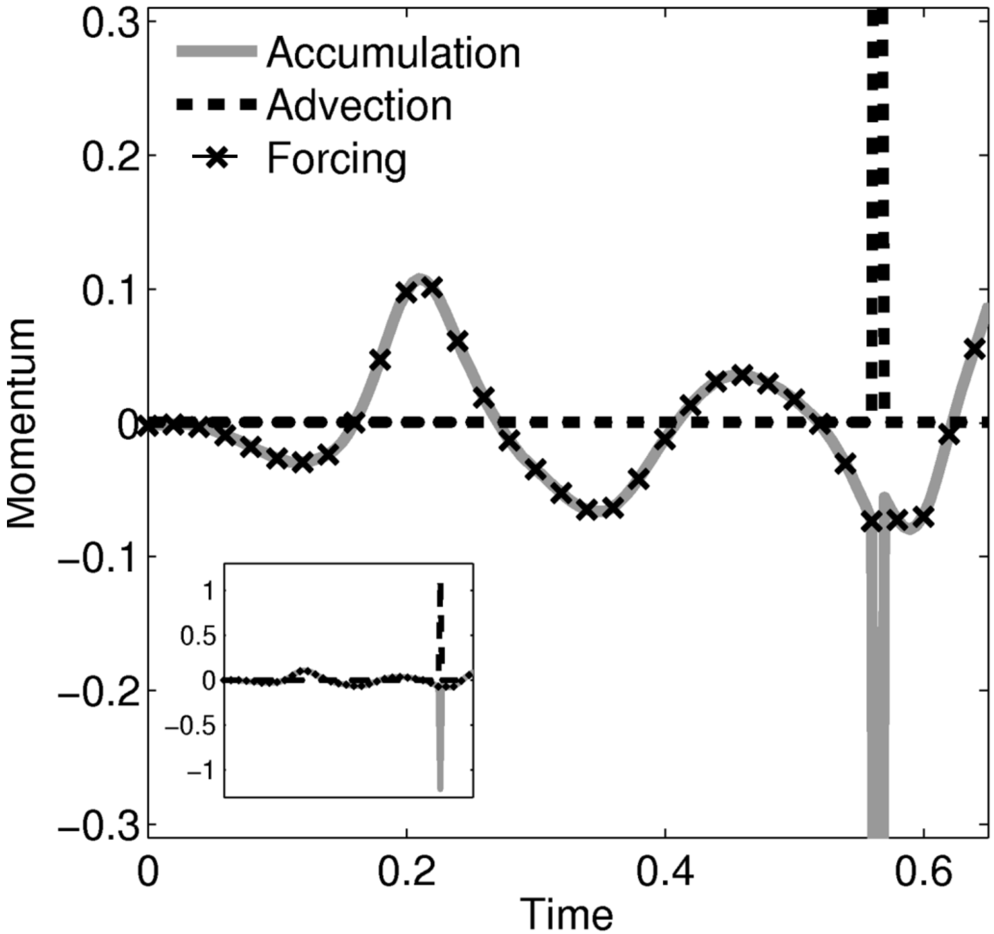
# Testing Momentum Balance

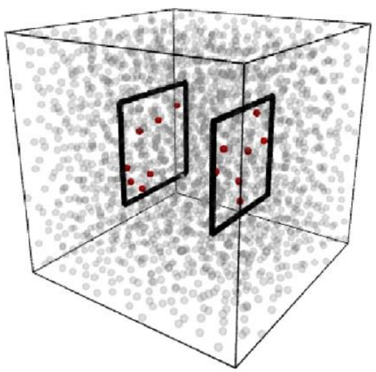
- **Momentum Balance**

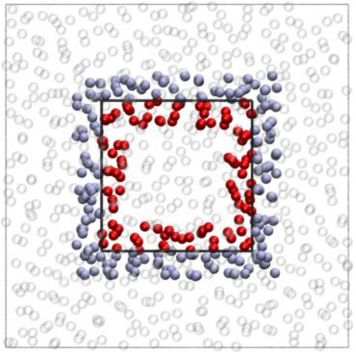
$$\underbrace{\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\textit{Accumulation}} = \underbrace{-\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\boldsymbol{S}_i}_{\textit{Advection}} + \underbrace{\sum_{i=1}^{N}\sum_{j\neq i}^{N} \mathbf{f}_{ij}\vartheta_{ij}}_{\textit{Forcing}}$$

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







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# Control Volume Function (revisited)

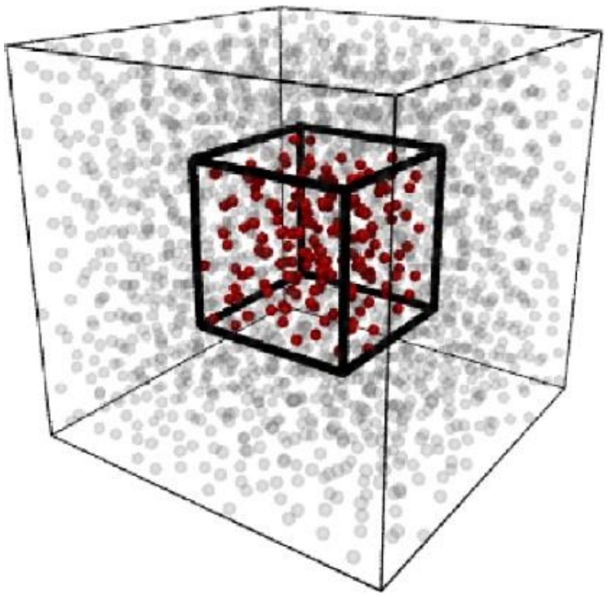
- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

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

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

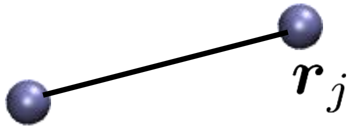
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

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



- **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)

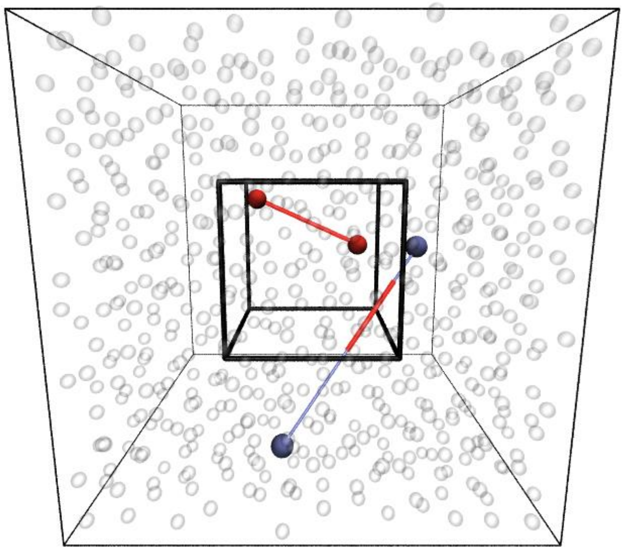
- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

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

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

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

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



- **Length of interaction inside the CV**

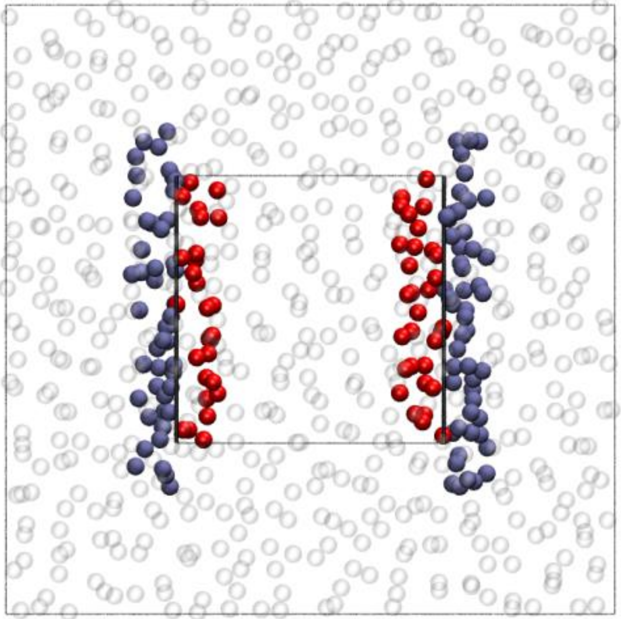
$$\ell_{ij} = \int_0^1 \vartheta_s ds$$

# 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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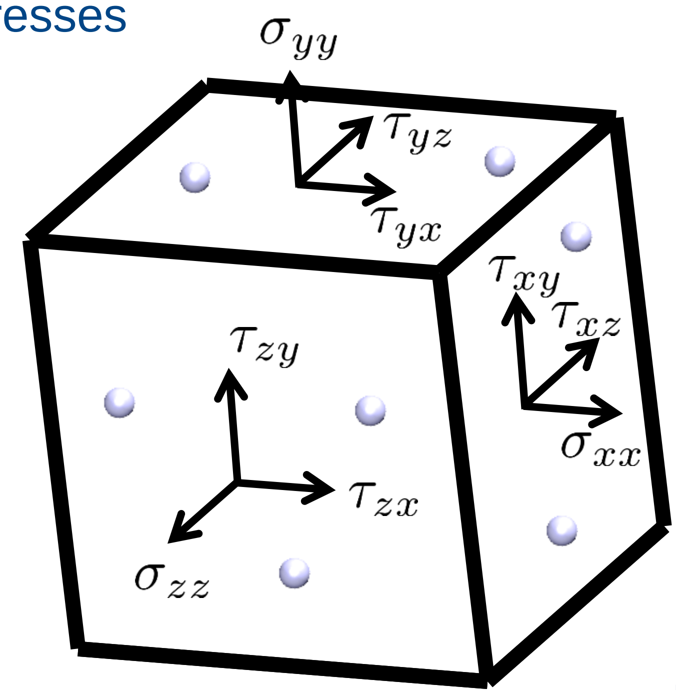
# More on the Pressure Tensor

- **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



# 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

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

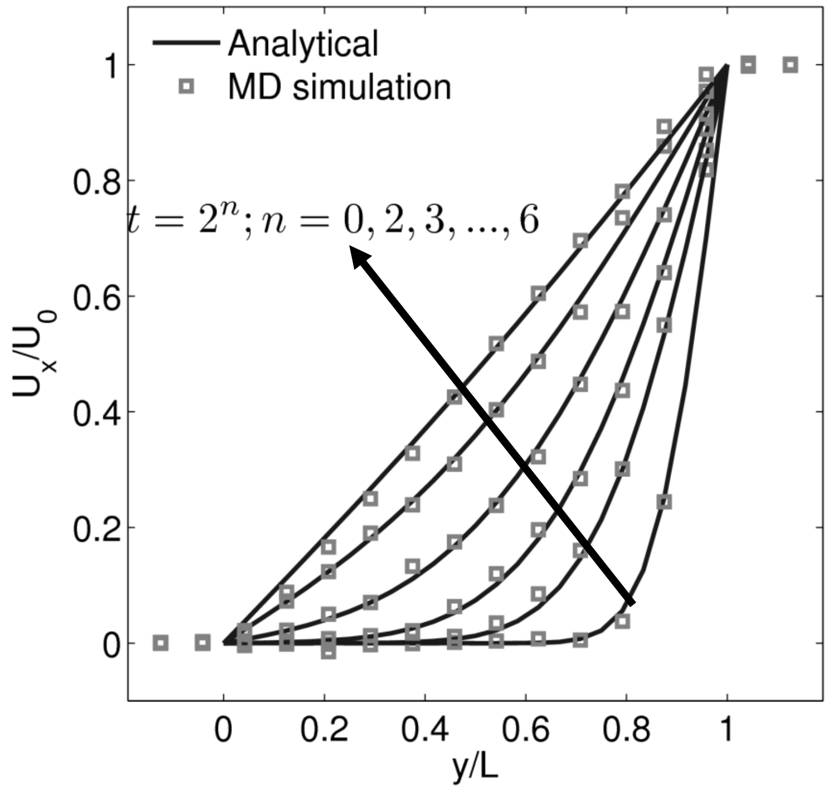
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \left(\mathbf{v}_i + \overline{\boldsymbol{u}}\right) \cdot d\boldsymbol{S}_i$$

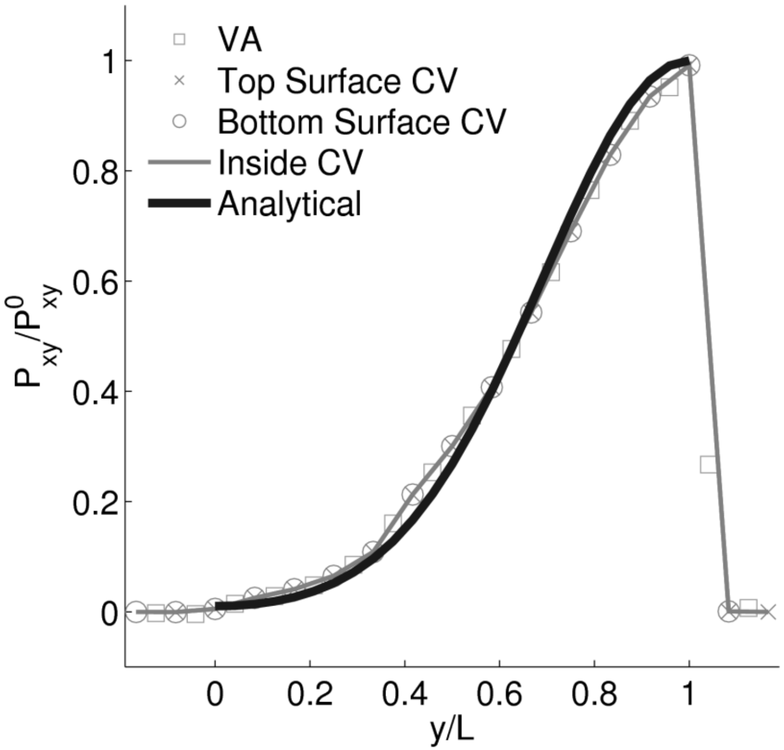
$$\frac{d}{dt}\int_V \rho dV = \oint_S \rho \left(\boldsymbol{u} - \overline{\boldsymbol{u}}\right) \cdot d\boldsymbol{S}$$

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

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

# Continuum Analytical Couette Flow




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

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

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

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# Unsteady Couette Flow

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

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

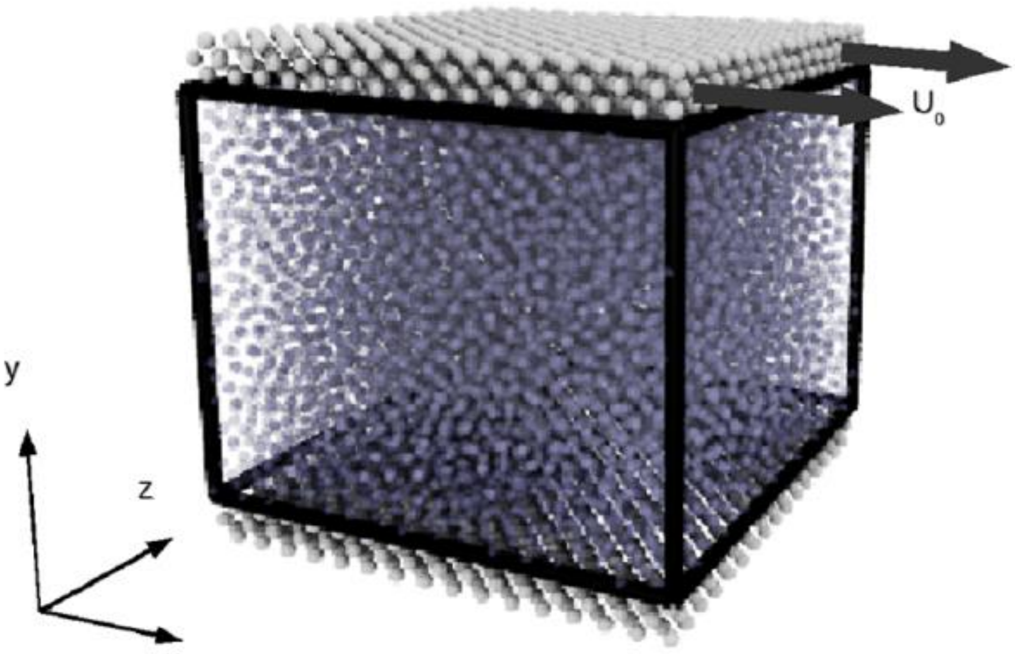
  - Solve the 1D unsteady diffusion equation.

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

  - 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

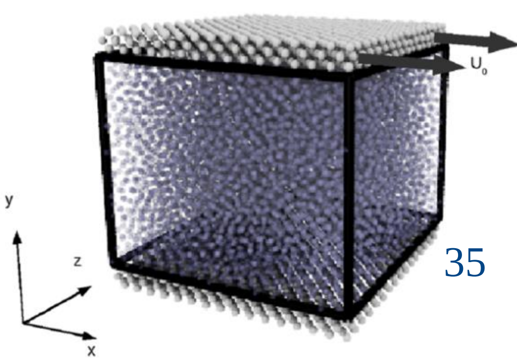
- Discrete form of the Momentum balance equation

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

- Simplifies for a single control volume

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

- Fixed bottom wall, sliding top wall with both thermostatted

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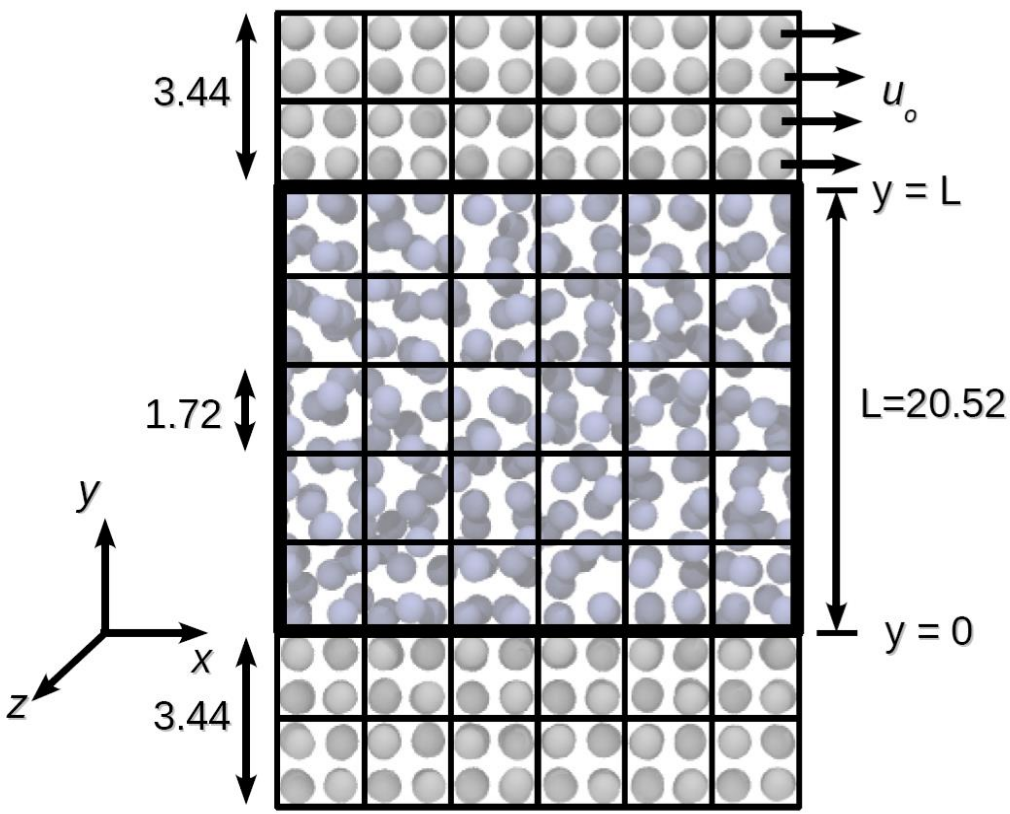
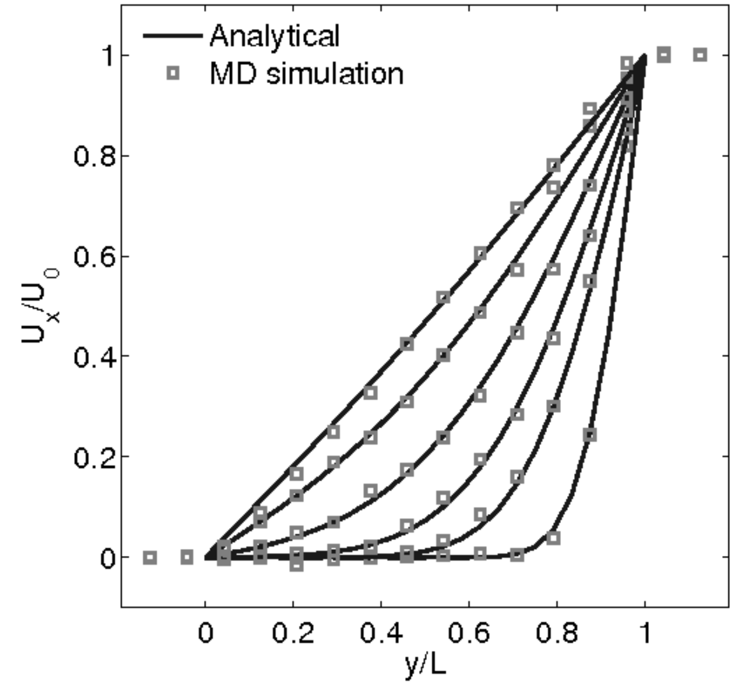
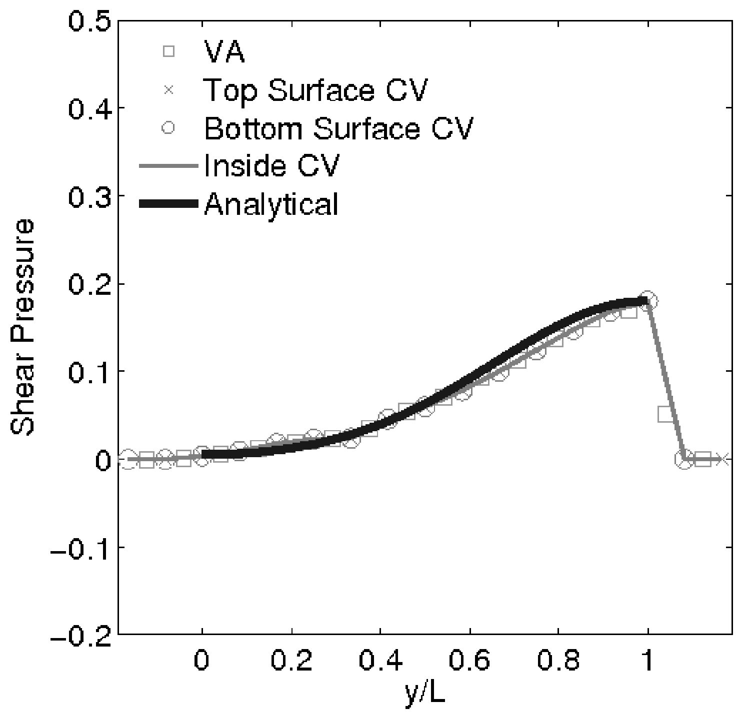
# Unsteady Couette Flow

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

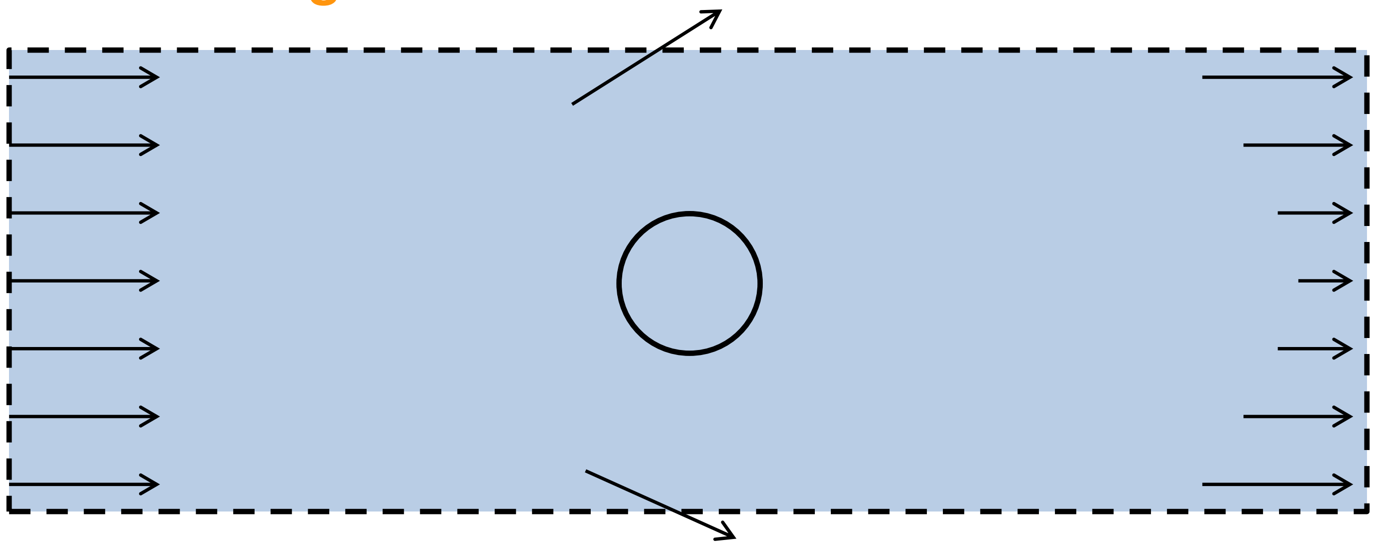


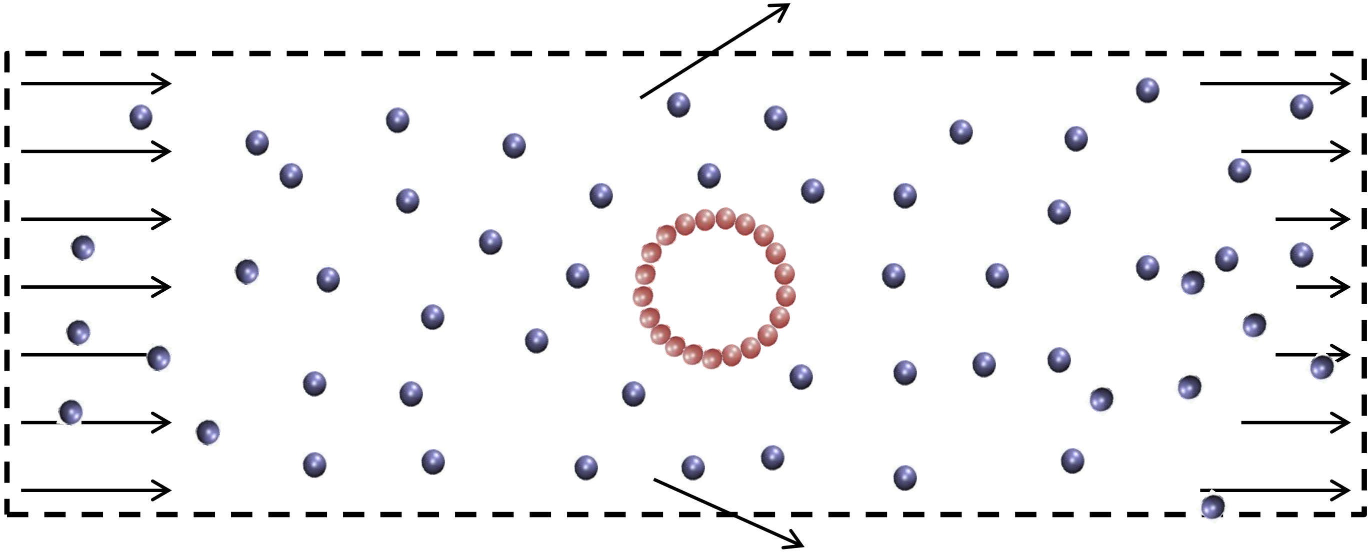



# Flow past a cylinder

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

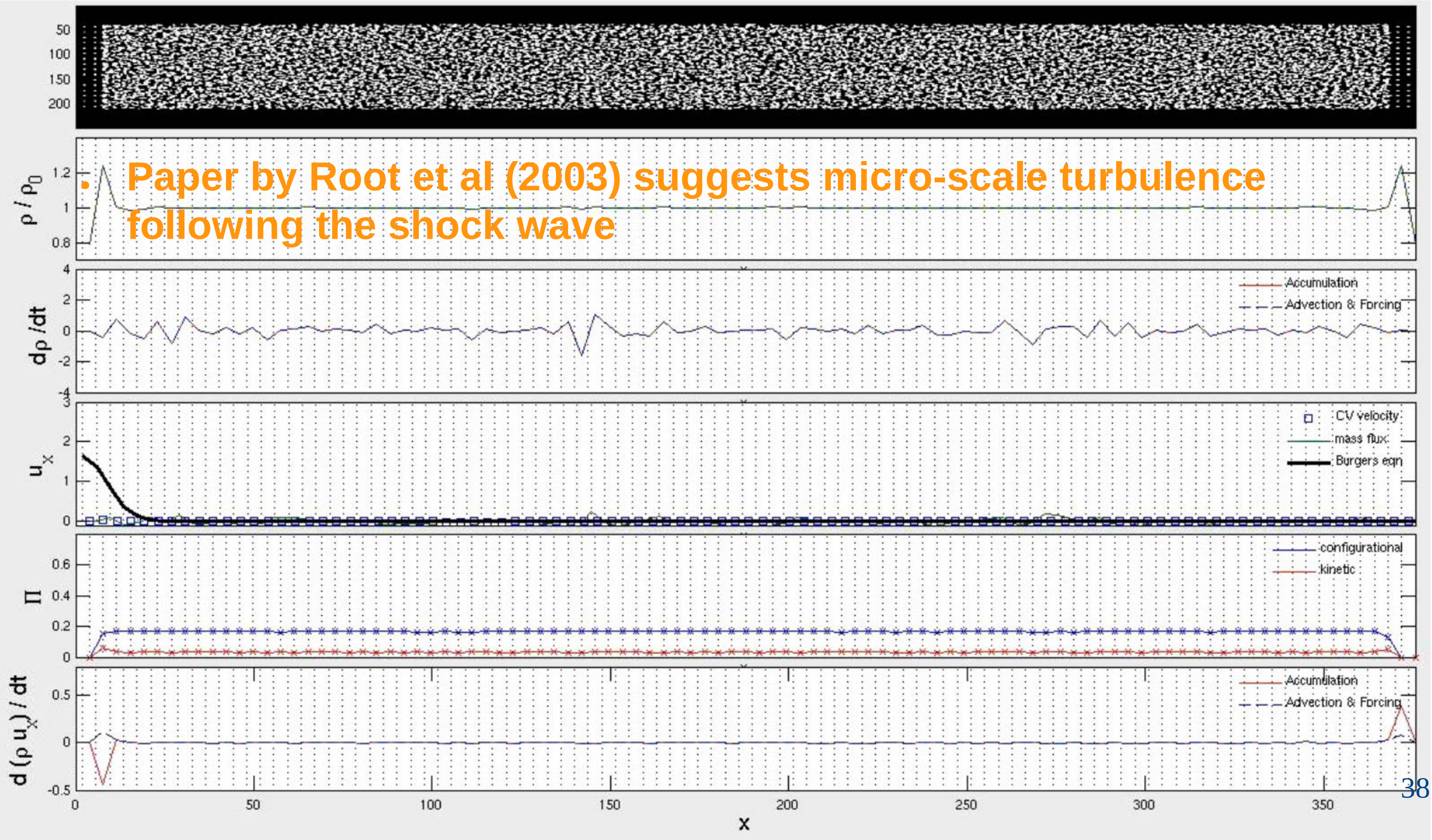


- Drag over a Carbon Nano-tube can be determined



# Shockwaves

- Current work on application of control volume theory

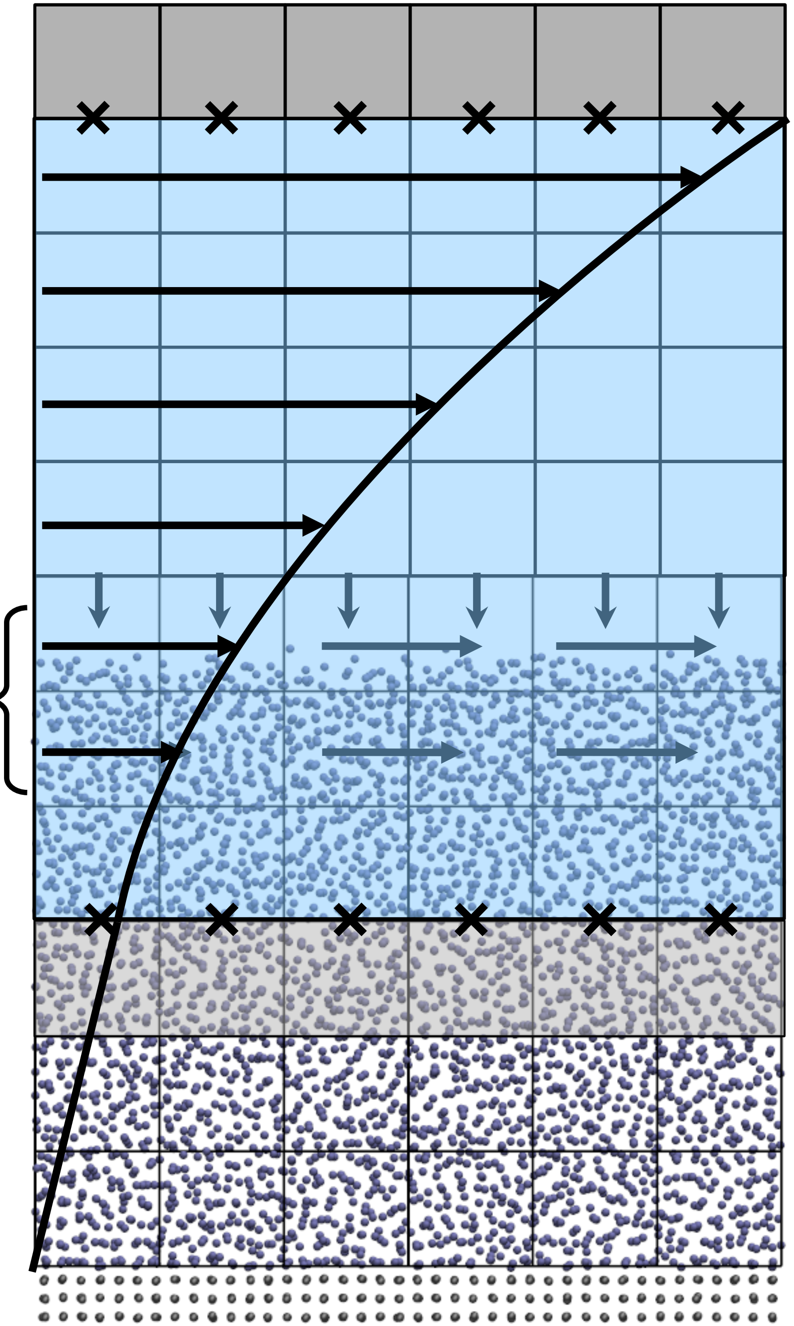



- Paper by Root et al (2003) suggests micro-scale turbulence following the shock wave

# Constrained dynamics for coupling

# Control Volume Coupling

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



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

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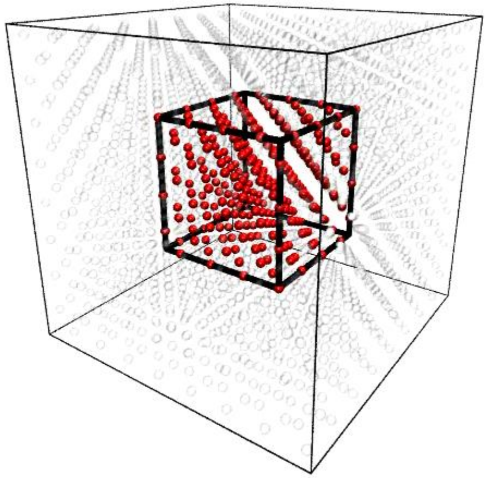
# Constrained Control Volume

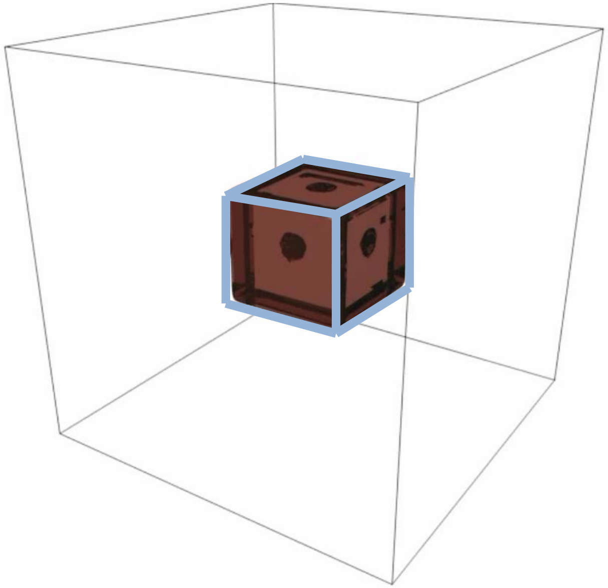
- **We want to apply a constraint of the form**
  - Control Volume momentum in both domains fixed to the same value

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



- **The molecular Control Volume is given by**

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



# Constrained Control Volume

- **We want to apply a constraint of the form**
  - Control Volume momentum in both domains fixed to the same value

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

- **Several methods for doing this**
  - Principle of Least Action (subject to constraint)

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

  - Gauss' Principle of Least Action

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

  - Extra terms in the Hamiltonian?

$$\mathcal{H}_c = \mathcal{H} + \boldsymbol{\lambda} \cdot \boldsymbol{g}$$

# Principle of least action

- **If the constraint is semi-holonomic, i.e.**
  - The constraint ‘g’ can be integrated
  - Alternatively/equivalently the constraint satisfies the condition (Flannery 2004)

$$\frac{d}{dt}\frac{\partial g}{\partial \dot{q}_i} - \frac{\partial g}{\partial q_i} = 0$$

- **The result is the Euler-Lagrange equation is applicable in the form**
  - Lagrangian in constrained form
  - Resulting equation is equivalent to the one obtained from Gauss’ principle

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

# Resulting equations

- **Can be written in terms of the peculiar momentum**

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

- **To give equations in the form**

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

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

# Combining the equations

- **Differentiating q dot and inserting into the other**

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

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

- **Give the following equation – equivalent to one obtained by Gauss principle of Least constraint**

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

# Questions

- Is energy conserved by this semi-holonomic constraint? How can we prove this?
- This is a differential constraint – it doesn't seem to work in practice. Is this a mistake?
- Should we instead try to constrain the mass?
- Localisation of SLLOD possible?
- Nose Hoover style constraint possible – is this preferable?