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Coupled Molecular Dynamics and Continuum Modelling of Super-Spreading Surfactants ICIAM 2015

By

Edward Smith,

In collaboration with Panagiotis Theodorakis, Erich Muller, Richard Craster and Omar Matar

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Overview

- Computational Fluid Dynamics (CFD)
  - Model description and results
  - Contact line dynamics essential to superspreading
  - Difficult to model using a continuum
- Molecular Dynamics (MD)
  - Model description and results
  - Advantages for modelling of droplets and surfactants
  - Limited to nanoscales
- Coupling MD and CFD
  - Types of coupling, techniques and computational framework
  - Coupled droplet spreading
  - Future work

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Motivation

- Control of wetting processes is of great importance to many industries
  - Coating and spraying
  - Pesticide spreading on waxy leaves
  - Biomedical applications e.g. Surfactant replacement therapy

- Surfactants reduce surface tension and change wetting
- Certain substances show super-spreading
  - The mechanism is poorly understood and therefore difficult to model accurately
  - Empirical models typically employed
  - Would be of great benefit to many industries to improve the modelling methodology

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Section 1

COMPUTATIONAL FLUID DYNAMICS

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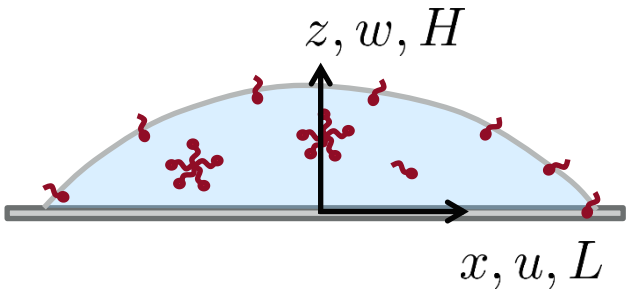
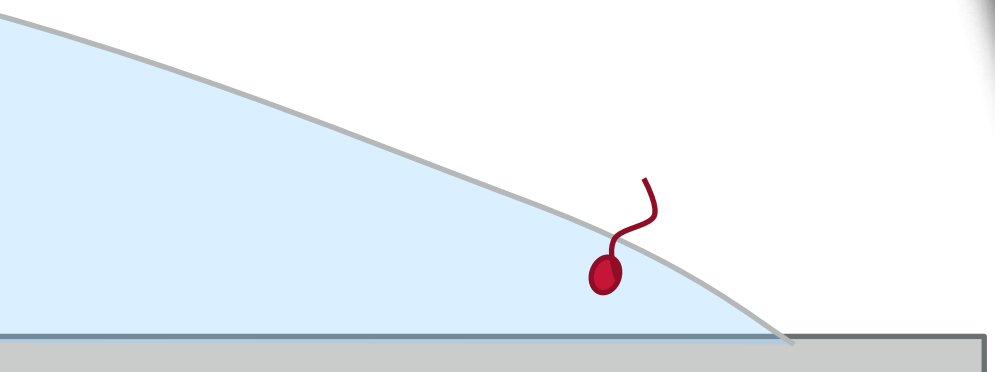
Computational Fluid Dynamics (CFD)

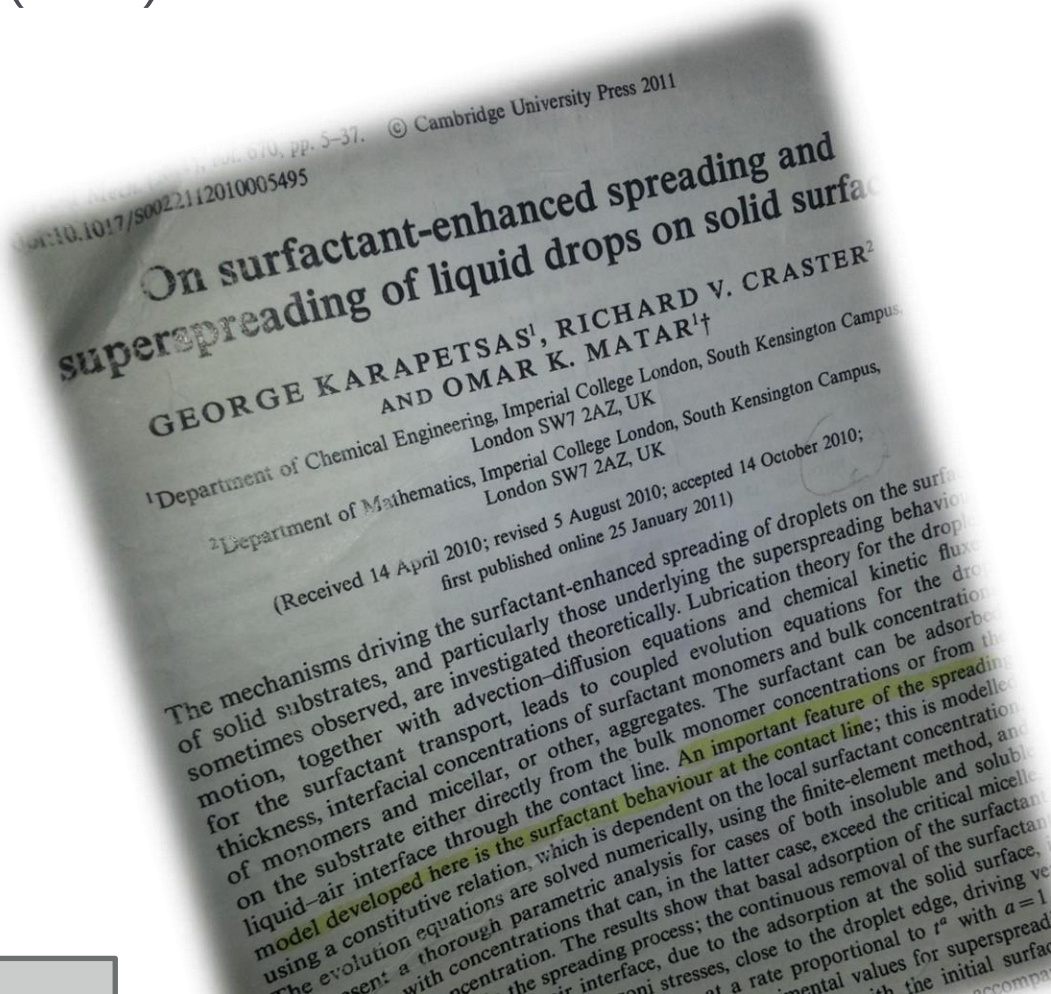
1) G. Karapetsas, R. Craster & O. Matar, JFM, 2011

- Starting from thin film equation based model of Karapetsas, Craster and Matar (2011)



- *Includes a mechanism for deposition of surfactant at contact line*





doi:10.1017/S0022112010005495

On surfactant-enhanced spreading and superspreading of liquid drops on solid surfa

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The mechanisms driving the surfactant-enhanced spreading of droplets on the surfa of solid substrates, and particularly those underlying the superspreading behavio sometimes observed, are investigated theoretically. Lubrication theory for the drop motion, together with advection–diffusion equations and chemical kinetic flux for the surfactant transport, leads to coupled evolution equations for the dro thickness, interfacial concentrations of surfactant monomers and bulk concentration of monomers and micellar, or other, aggregates. The surfactant can be adsorbe on the substrate either directly from the bulk monomer concentrations or from th liquid–air interface through the contact line. An important feature of the spreadi model developed here is the surfactant behaviour at the contact line; this is modelle using a constitutive relation, which is dependent on the local surfactant concentration evolution equations are solved numerically, using the finite-element method, and sent a thorough parametric analysis for cases of both insoluble and solubl with concentrations that can, in the latter case, exceed the critical micelle centration. The results show that basal adsorption of the surfactan the spreading process; the continuous removal of the surfactan ir interface, due to the adsorption at the solid surface, ni stresses, close to the droplet edge, driving ve at a rate proportional to t^a with $a = 1$ mental values for superspread ith the initial surfac accompa

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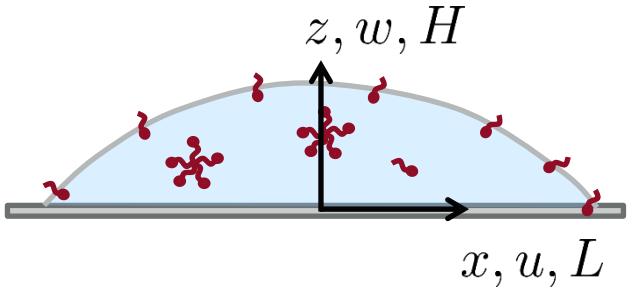
Computational Fluid Dynamics (CFD)

1) G. Karapetsas, R. Craster & O. Matar, JFM, 2011

- Incompressible Navier Stokes with the thin-film approximation.

$$\frac{\partial P}{\partial x} = \frac{\partial^2 u}{\partial z^2} \qquad \frac{\partial P}{\partial z} = 0 \qquad \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$$



- With boundary conditions

$$P = -\left(\frac{H}{L}\right)^2 \frac{\partial^2 h}{\partial x^2}\left(\sigma_l + \frac{1}{\Sigma_l}\right) \qquad \frac{\partial h}{\partial t} + u\frac{\partial h}{\partial x} = w \qquad \frac{\partial u}{\partial z} = \frac{\partial \sigma_l}{\partial x} \qquad z = h$$

$$u = \beta\frac{\partial u}{\partial z} \qquad w = 0 \qquad z = 0$$

- *Surfactant modelled by advection-diffusion equations with empirical sorption processes - coupled to the dynamics through surface tension*
- *Contact line evolution is modelled by an empirical law*

$$\frac{dx_c}{dt} = k(\theta - \theta_a)^n$$

- *The angle coupled to surfactant absorption at the contact line is essential*[1)]

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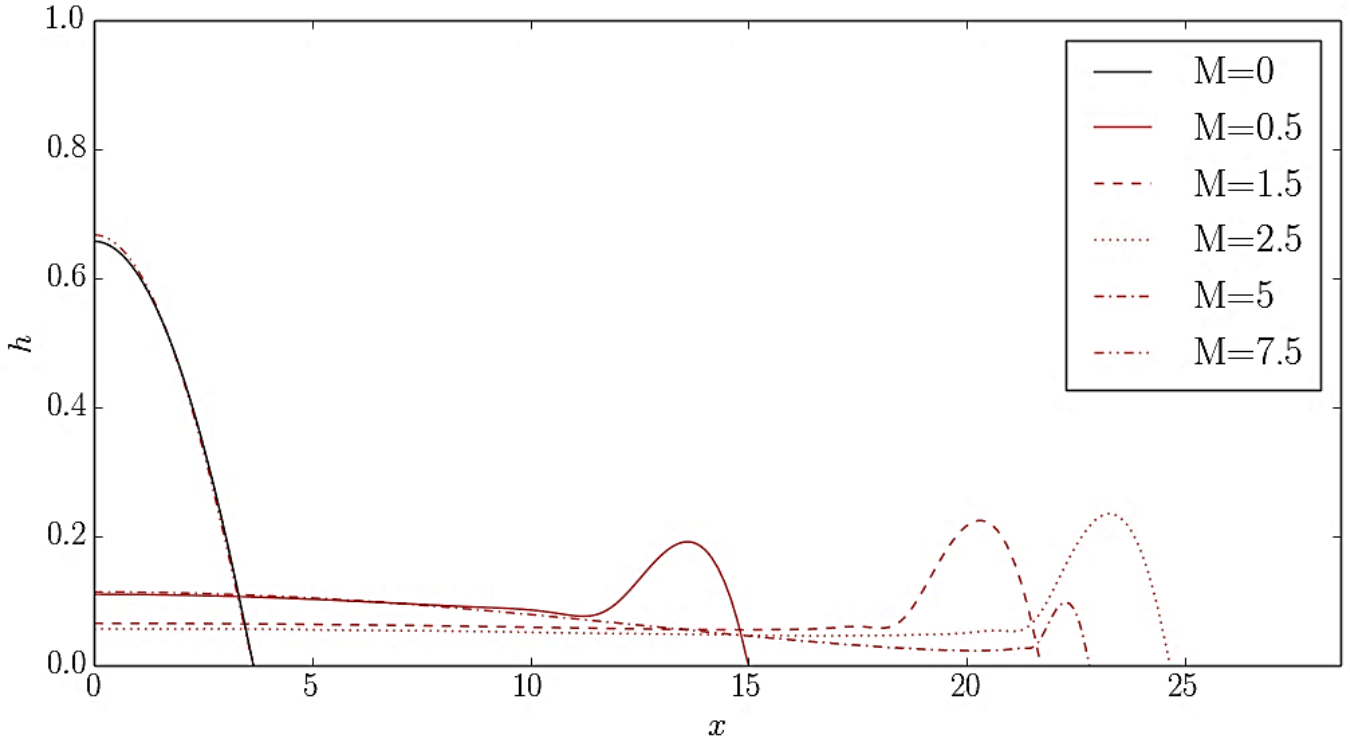
CFD Results

1) G. Karapetsas, R. Craster & O. Matar, JFM, 2011

- Coupled equations are solved using the finite elements method[1)]



- Droplet behaviour changed by adjusting the surface tension
- Surfactant deposition at the contact line behaviour is key –

Can we improve the contact line model?

Section 2

MOLECULAR DYNAMICS

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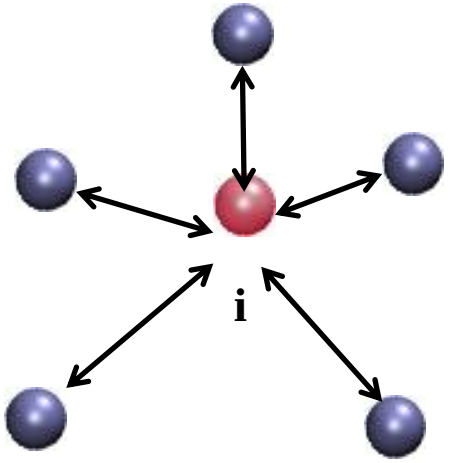
1) *Statistical Associated Field Theory*
2) *Müller & Jackson (2014)*

Molecular Dynamics

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

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

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

- SAFT[1] using the γ-Mie[2] potential

$$\Phi(r_{ij}) = 4C\epsilon_{ij}\left[\left(\frac{\ell_{ij}}{r_{ij}}\right)^{\lambda_r} - \left(\frac{\ell_{ij}}{r_{ij}}\right)^{\lambda_a}\right]$$

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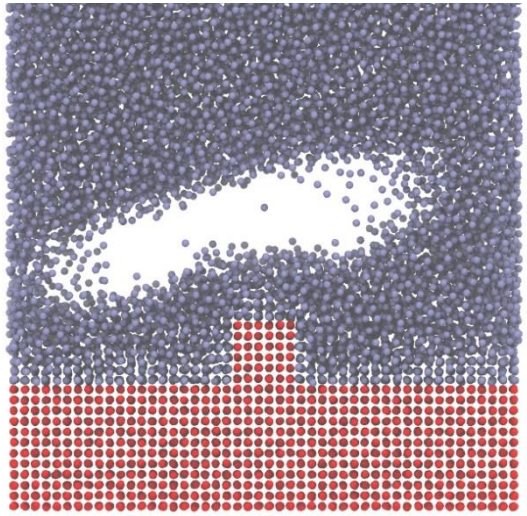
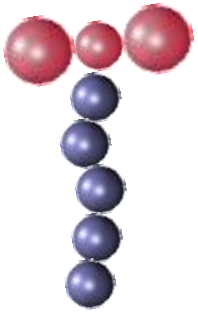
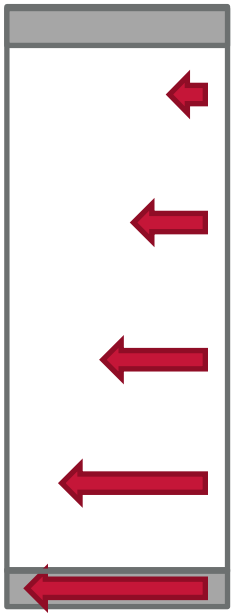
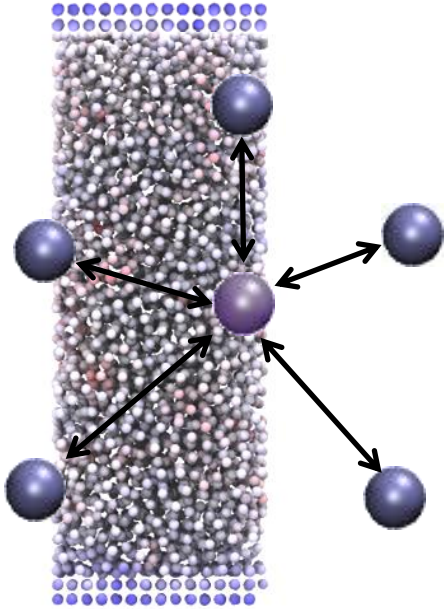
Molecular Dynamics

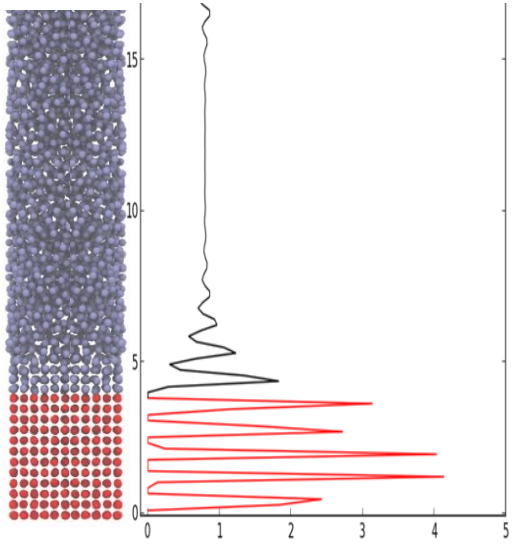


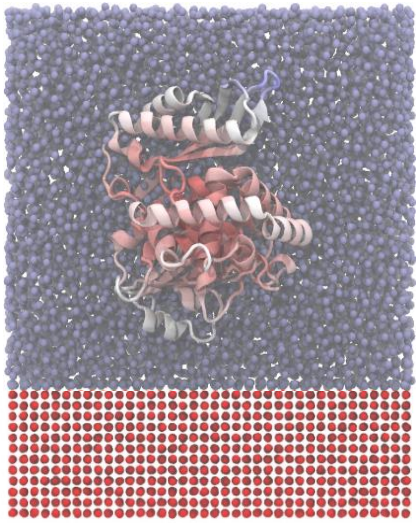
Superspreading Surfactant, e.g. Silwet-L77











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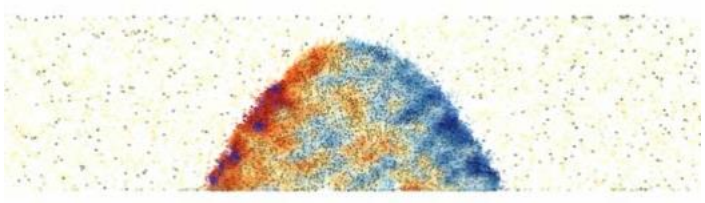
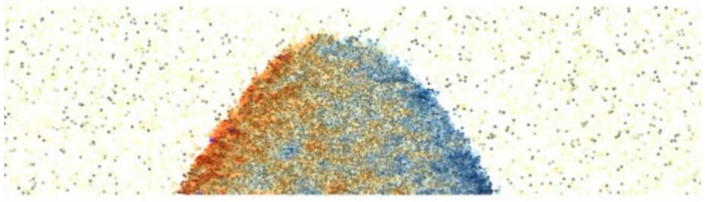
MD Simulation of Droplets

- Low Wettability



- Intermediate Wettability



- High Wettability

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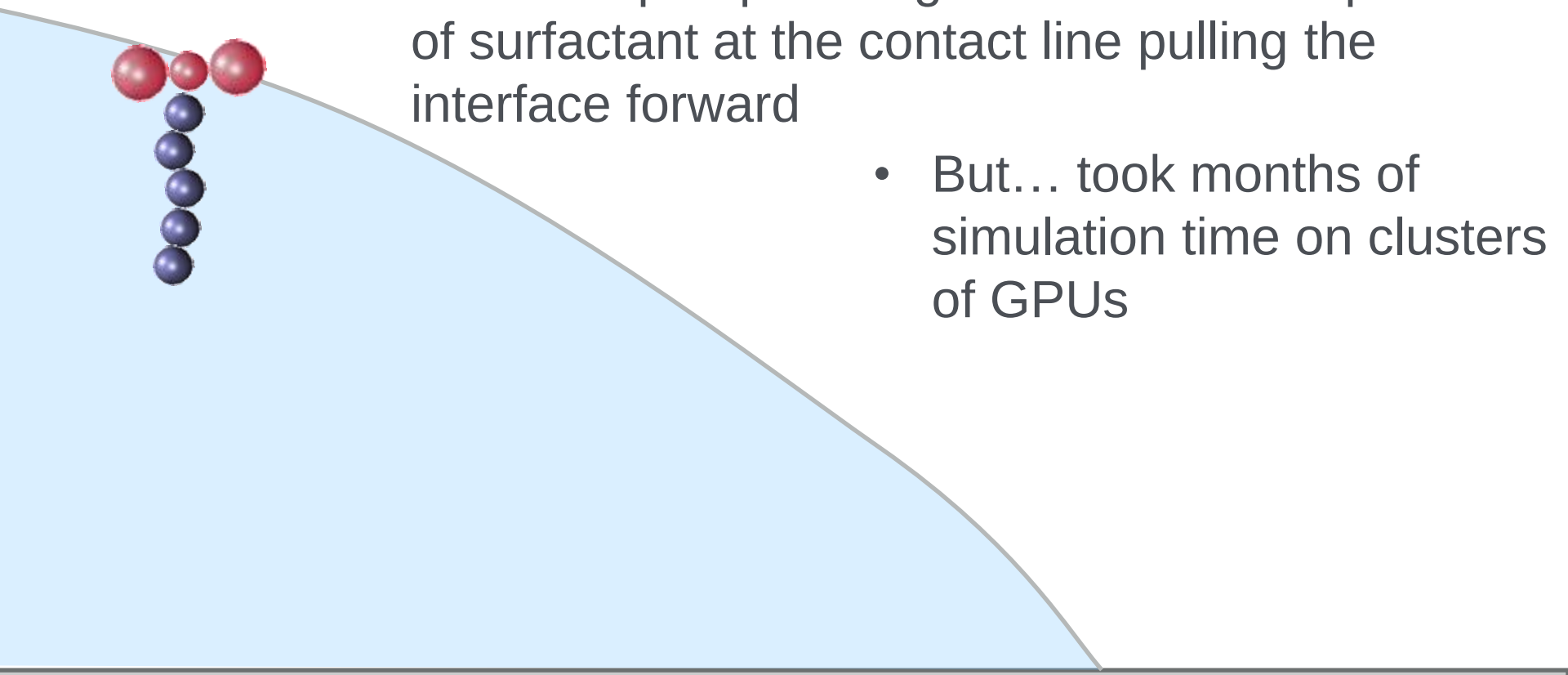
Surfactant mechanism

1) Theodorakis PE, Mueller EA, Craster RV, Matar O, 2015, Superspreading: Mechanisms and Molecular Design,*Langmuir*, Vol: 31, Pages: 2304

- Molecular Dynamics (SAFT) with Surfactants by Panos Theodorakis et al [1)]
- Shows superspreading occurs due to deposition of surfactant at the contact line pulling the interface forward
  - But… took months of simulation time on clusters of GPUs



Section 3

COUPLING

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Coupling Overview

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 and Coveney, (2003)

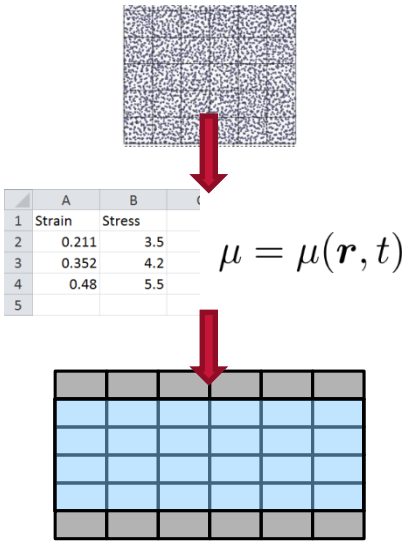
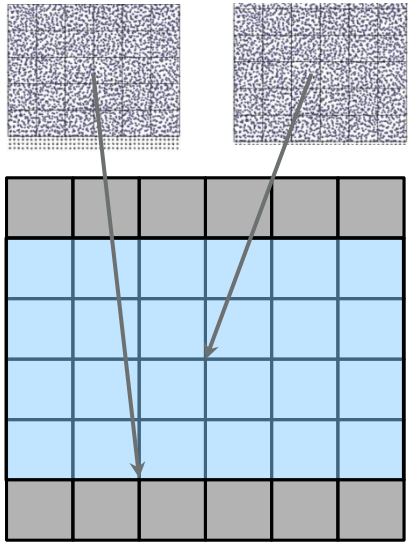


Table Lookup or Coefficients

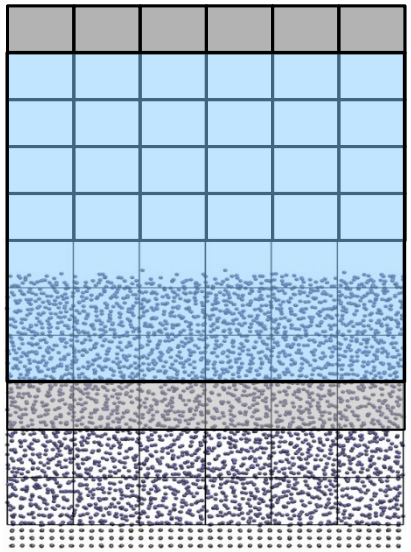
MD parameter study stored in table and CFD uses data



Embedded Models

MD – embedded in a CFD simulation

Used for Non-Newtonian effects [1)]



Domain Decomposition

MD –CFD linked along an interface

Local features e.g. contact line [2)]

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Coupling Overview

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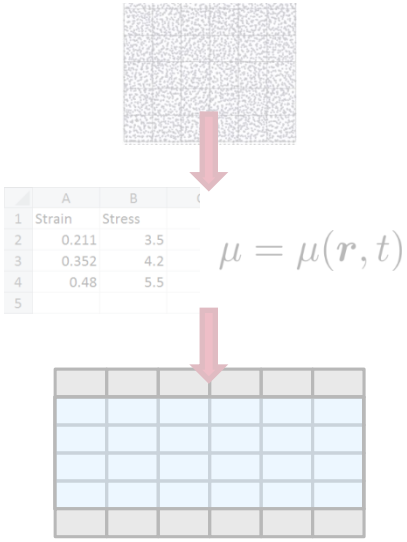

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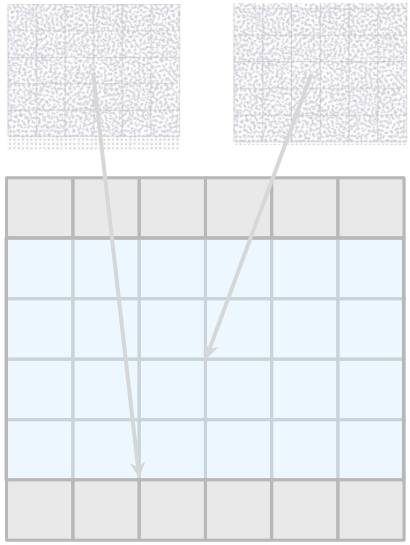

Embedded Models

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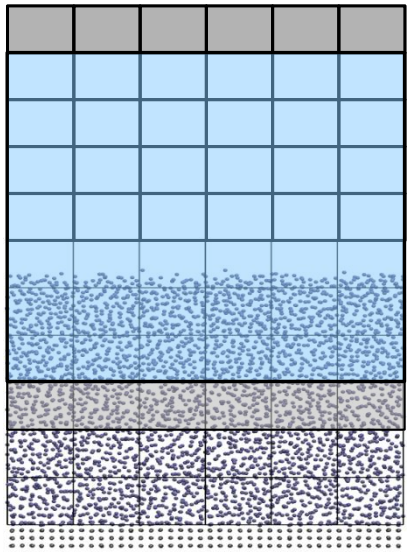


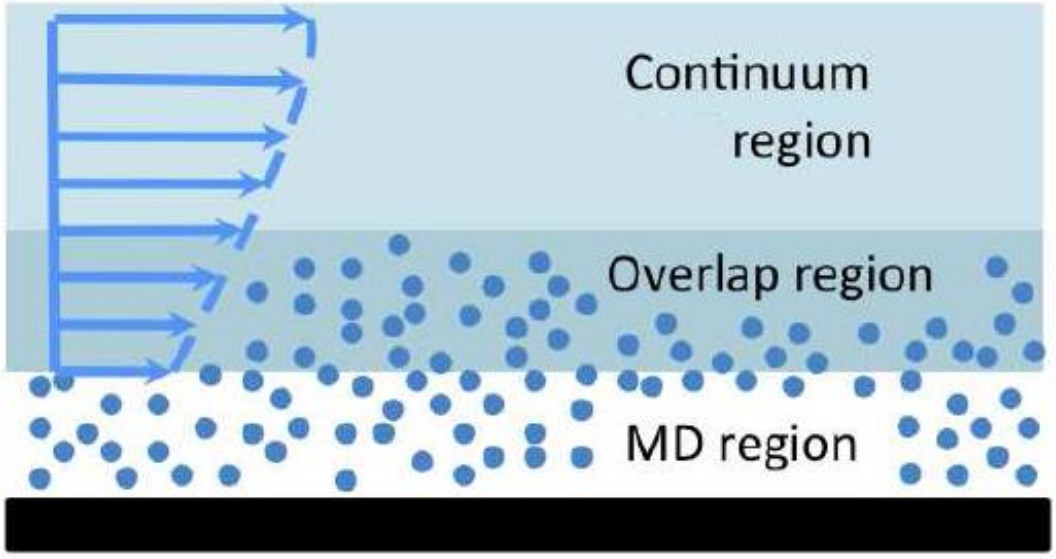
Domain Decomposition

MD –CFD linked along an interface

Local features e.g. contact line [2)]

CFD and MD

- Connect the two descriptions of matter
  - Continuum only region – majority of the spatial domain
  - Overlap of arbitrary size – for purely numerical reasons
  - Molecular only region – required where molecular effects are important



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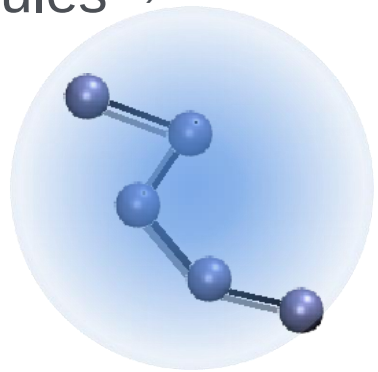
Coupling Overview

Review 1-3): Mohammed & Mohammed (2009). 1) Delgado-Buscalioni & Coveney (2003): USHER. 2) Smith, Dini, Heyes, Zaki PRE (2012). 3) Constraints of O'connell et al (1995), Nie et al (2004), Flekkoy et al (2000) unified in Smith, Dini, Heyes, Zaki JCP (2014).

Boundary force and insertion of molecules [1)]



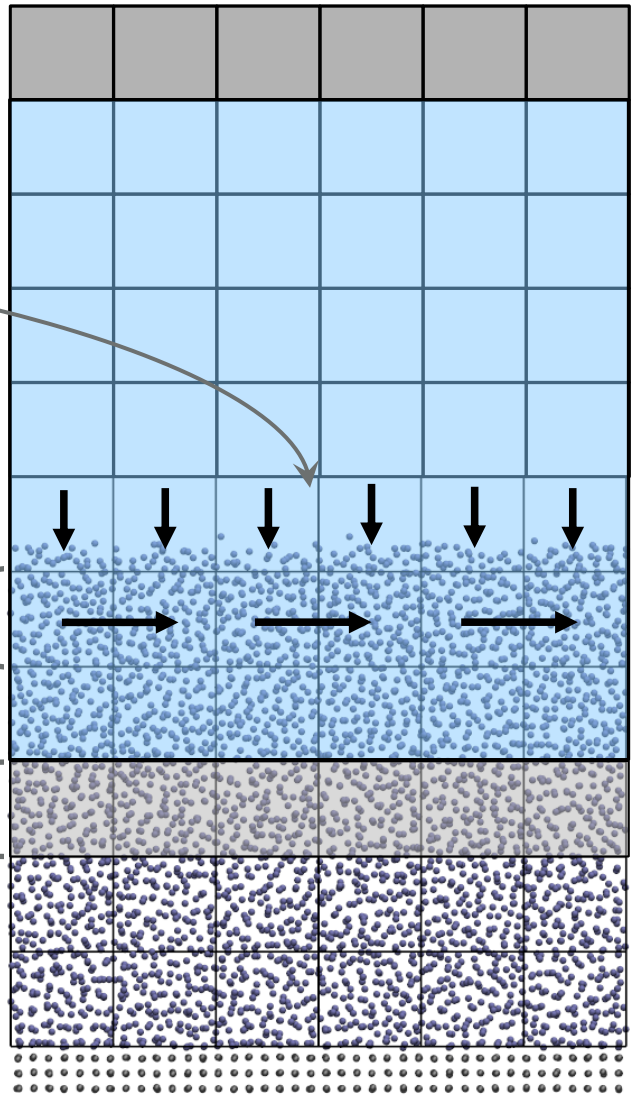
$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{CFD}$$

$$\rho \boldsymbol{u} = \frac{1}{N} \sum_{i \in S} \boldsymbol{p}_i$$

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

CFD→MD Boundary condition [3)]

MD→CFD Boundary condition [2)]



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Control Volume Functional

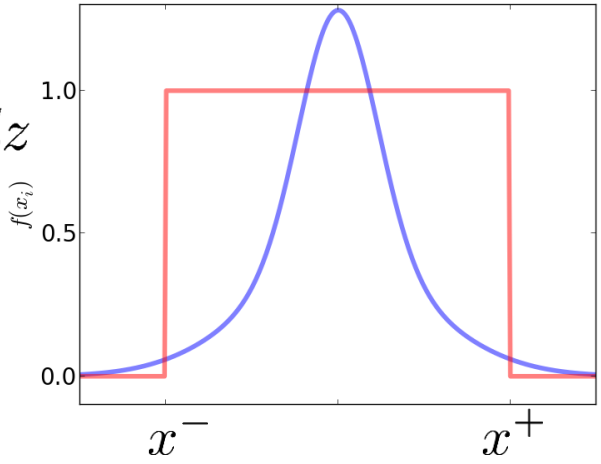
- The Control volume function is the integral of the Dirac delta function in 3 dimensions

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

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

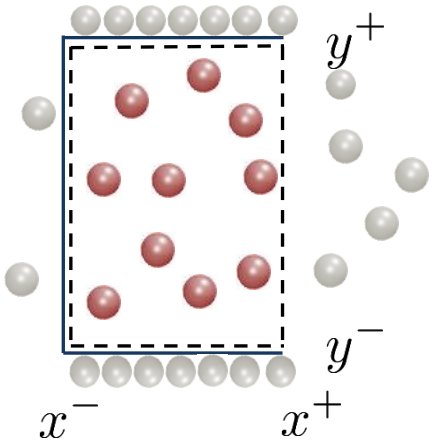
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

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



- Or in words

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



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Derivatives yields the Surface Fluxes

- Taking the Derivative of the CV function

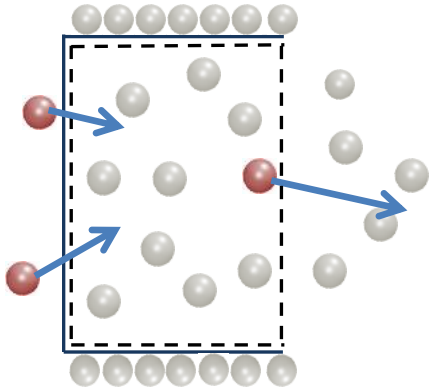
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

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



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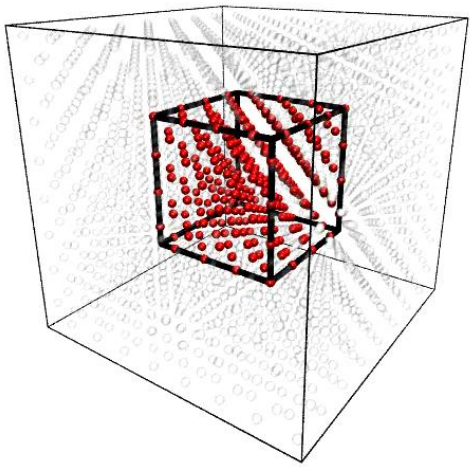
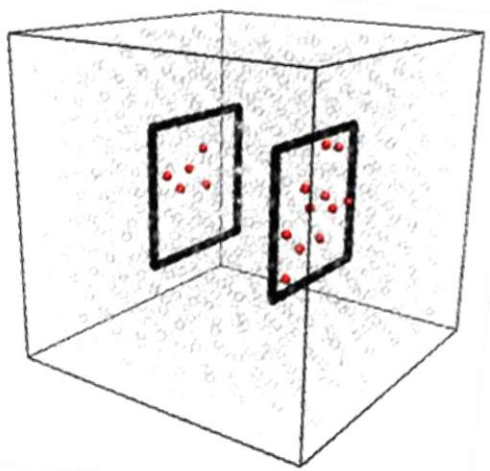
Control Volume (CV) Formulation

- *Extends the control volume concept to molecular dynamics*
  - *Same mathematically weak descriptions for continuum and discrete*
  - *Well defined functional can be mathematically manipulated*



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

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



- *Any arbitrary volume can be specified*
  - *A cuboid is best suited to couple to CFD (3D boxcar function)**
  - *Recently applied to a spherical control volume †*

* E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

† D.M. Heyes, E.R. Smith, D. Dini, T.A. Zaki, J. Chem. Phys 140, 054506 (2014)

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1) Irving and Kirkwood (1950) J Chem. Phys. 15,6

Applying the Control Volume Function

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

- **Process of Irving and Kirkwood (1950) [1)]**

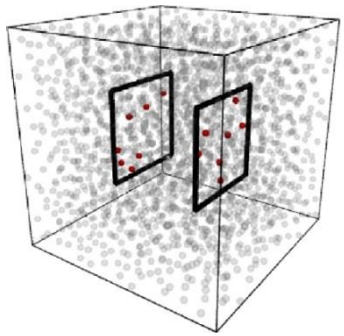
$$\frac{\partial}{\partial t}\left\langle \alpha;f\right\rangle = \sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i}{m_i}\cdot\frac{\partial\alpha}{\partial\boldsymbol{r}_i} - \boldsymbol{F}_i\cdot\frac{\partial\alpha}{\partial\boldsymbol{p}_i};f\right\rangle \qquad \alpha = \sum_{i=1}^{N} m_i\vartheta_i$$

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

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

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

$3\times$



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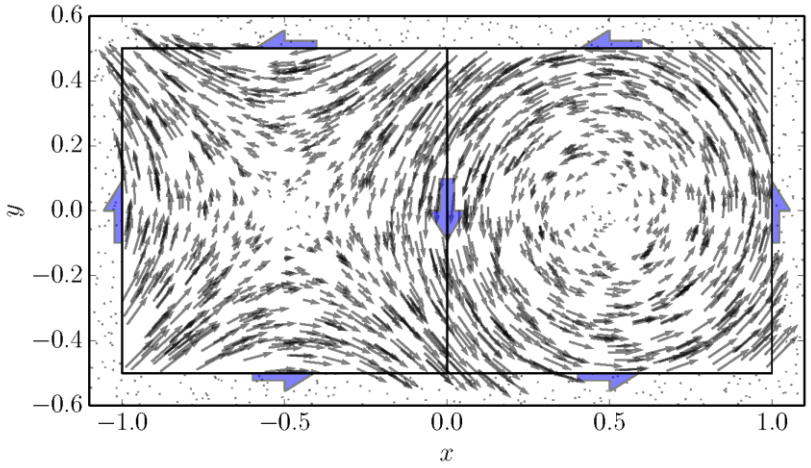
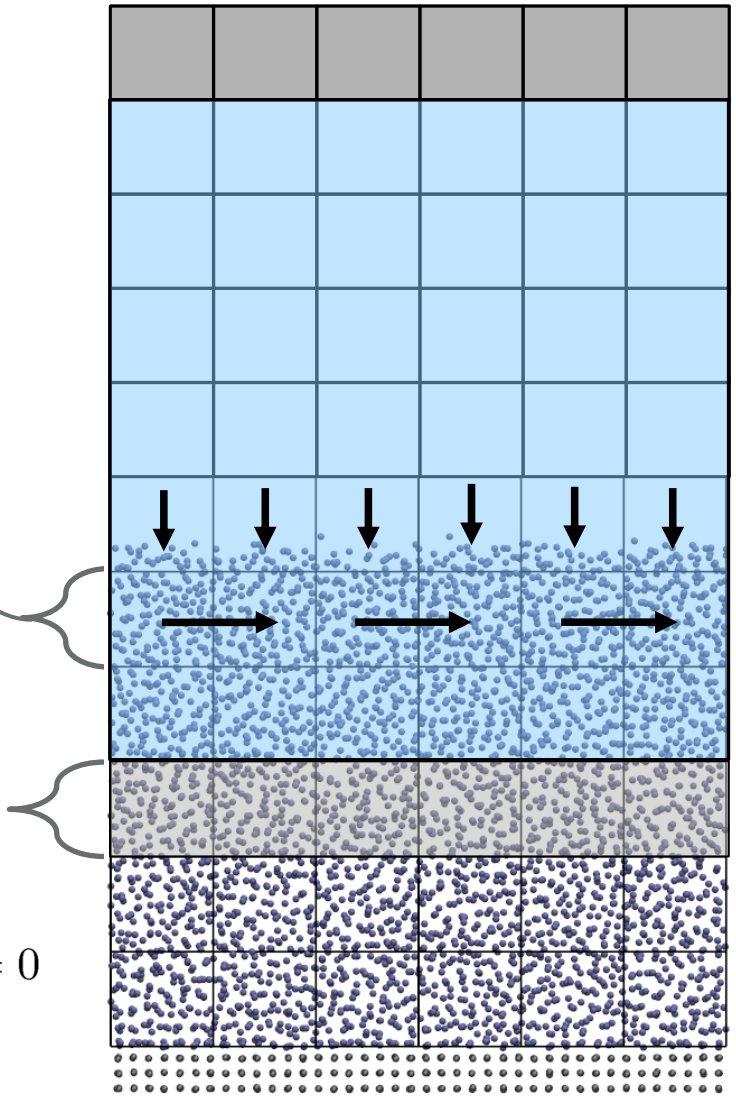
1) Smith, Dini, Heyes, Zaki PRE (2012).
2) Smith, Dini, Heyes, Zaki JCP (2014).

Coupling Theoretical Development

Apply a constraint to a local volume [2)]



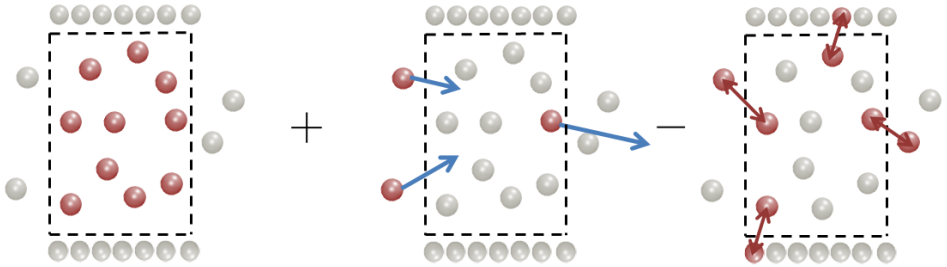
$\boldsymbol{F}_i^{CFD}$



Write both in the weak formulation[1)]

$$\frac{\partial}{\partial t}\int_V \rho \boldsymbol{u} dV + \oint_S \rho \boldsymbol{u}\boldsymbol{u} - \mathbf{F}_{\text{surface}} = 0$$

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



$$= 0$$

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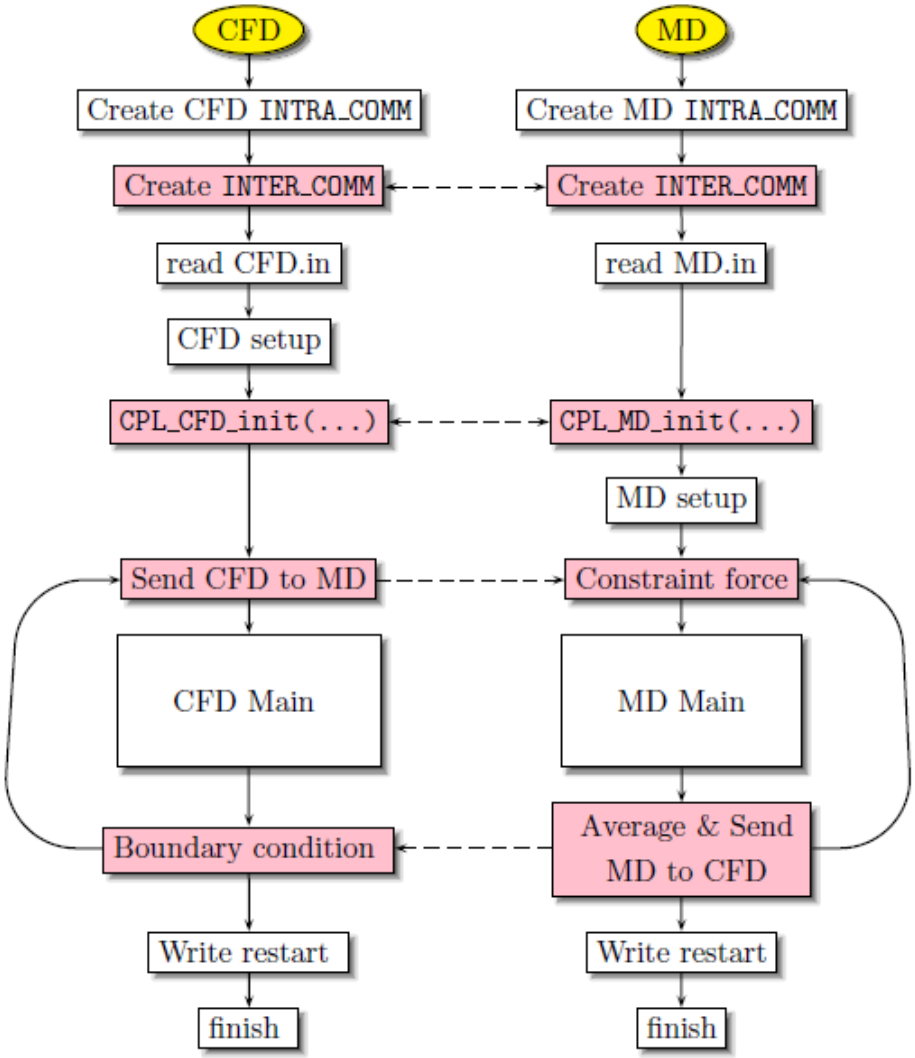
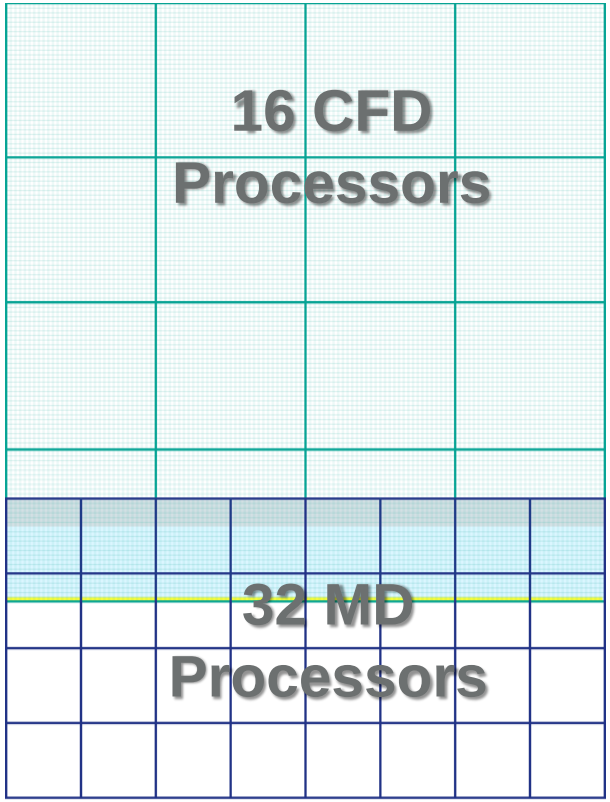
Coupling Computational Framework – *cpl-library*



Open source (www.cpl-library.org)

mpiexec –n 32./md.exe : -n 16 ./cfd.exe



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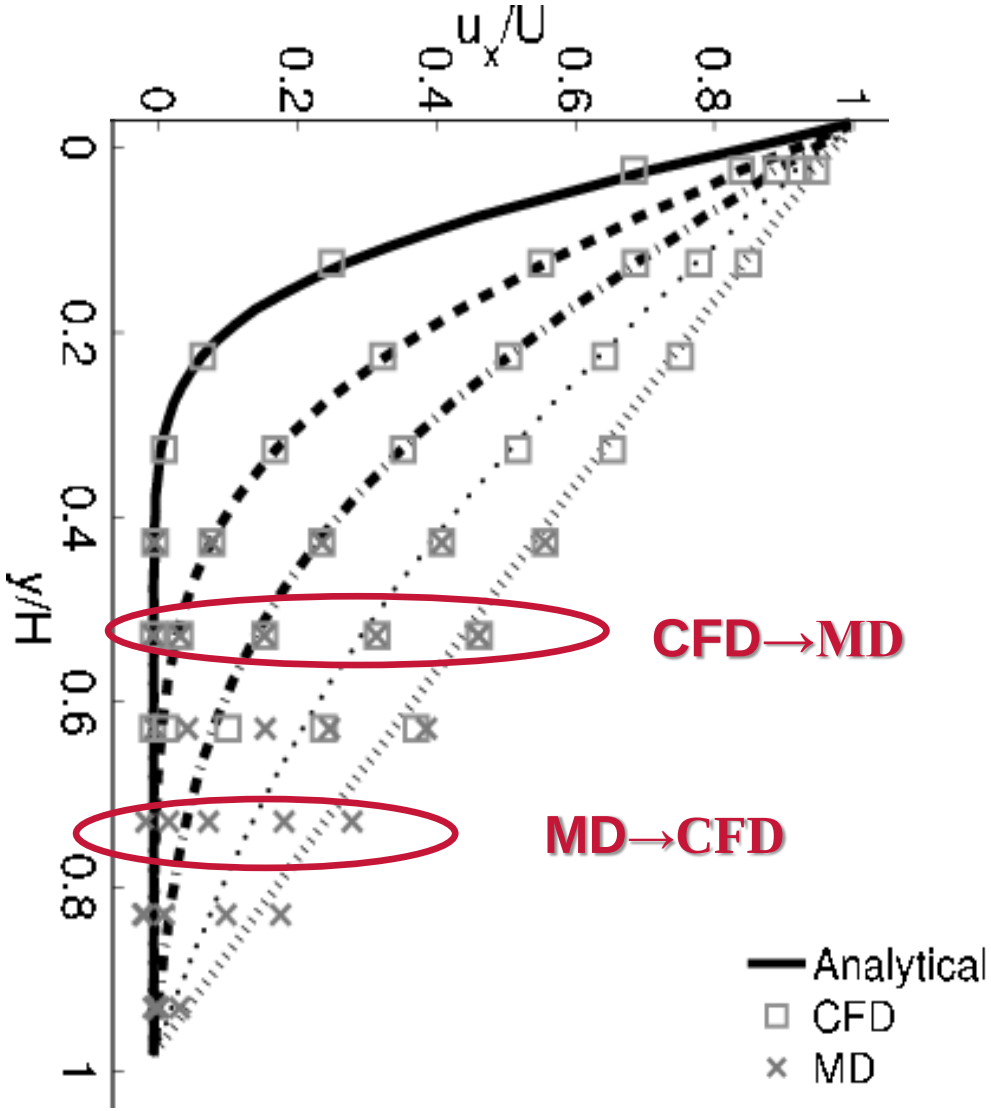
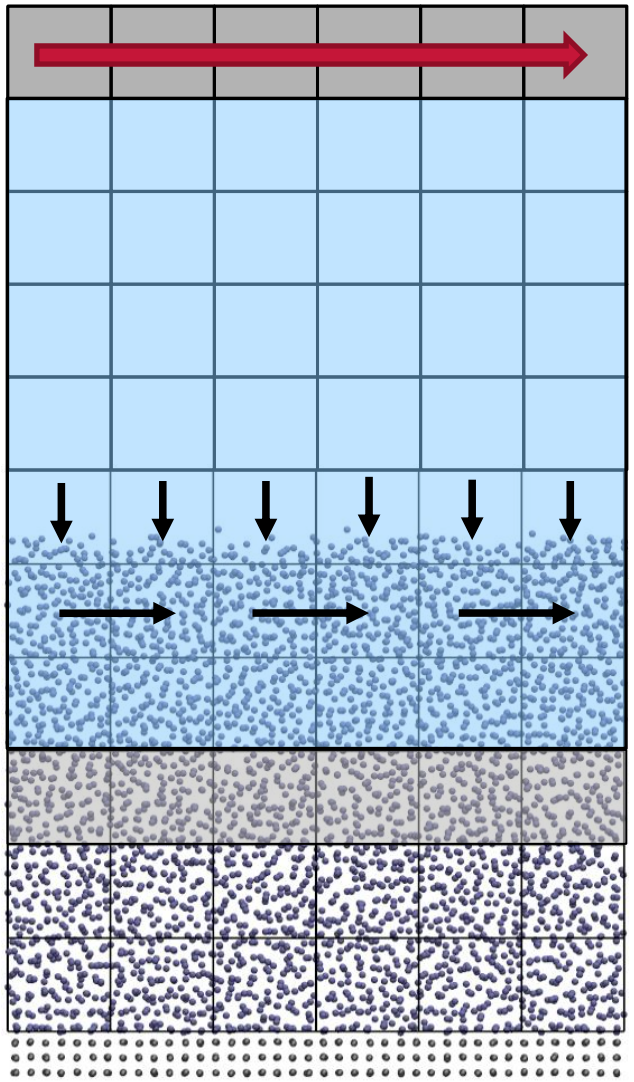
Coupling Results – Couette Flow

1) Case originally by Nie et al (2004) used in Smith, Dini, Heyes, Zaki (Under Review JCP)





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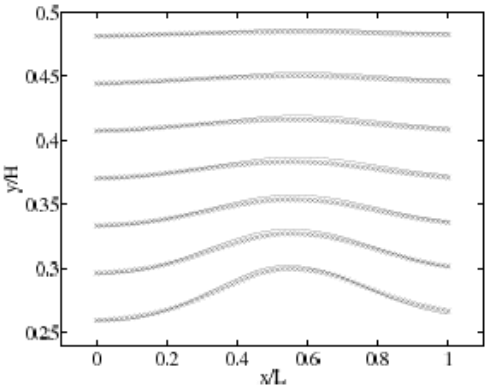
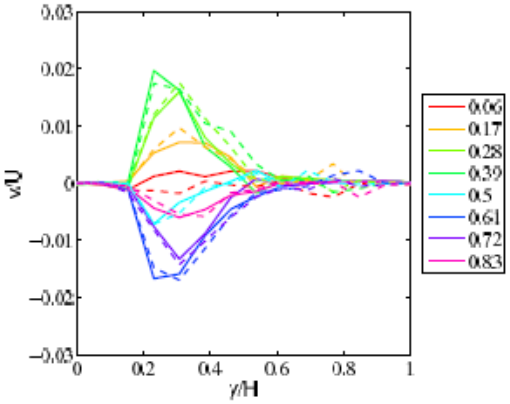
Coupling Results – Wall textures

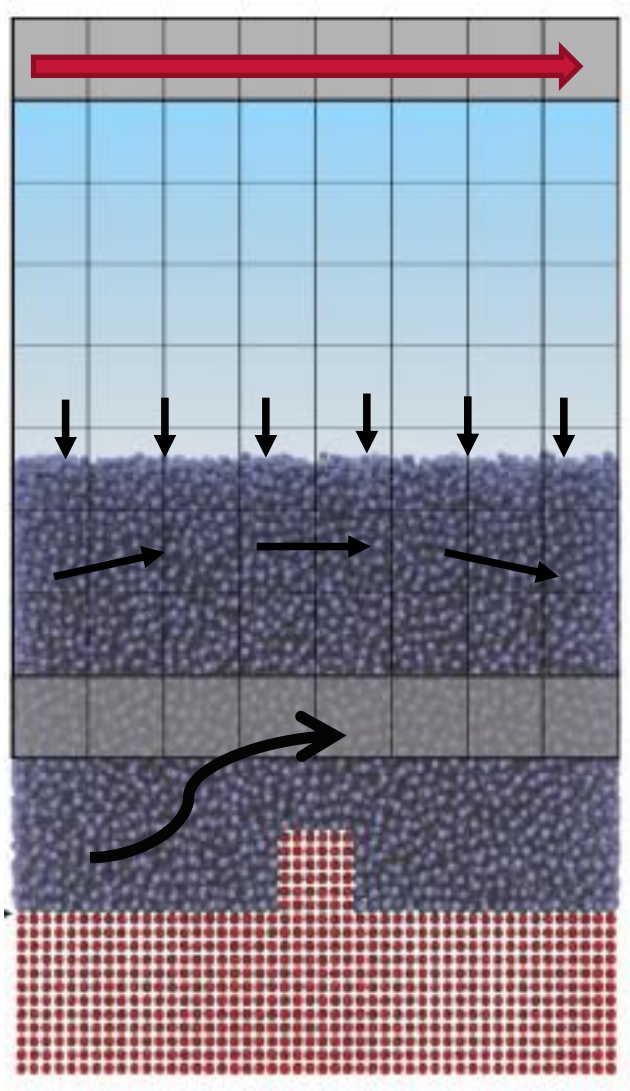
- Molecular scale surface texture
  - Explicitly modelled using molecular posts
  - Impacts flow in CFD simulation



(a) Streamlines: CPL (×) vs all MD (—)



(b) Velocity v : CPL (—) vs all MD (- -)



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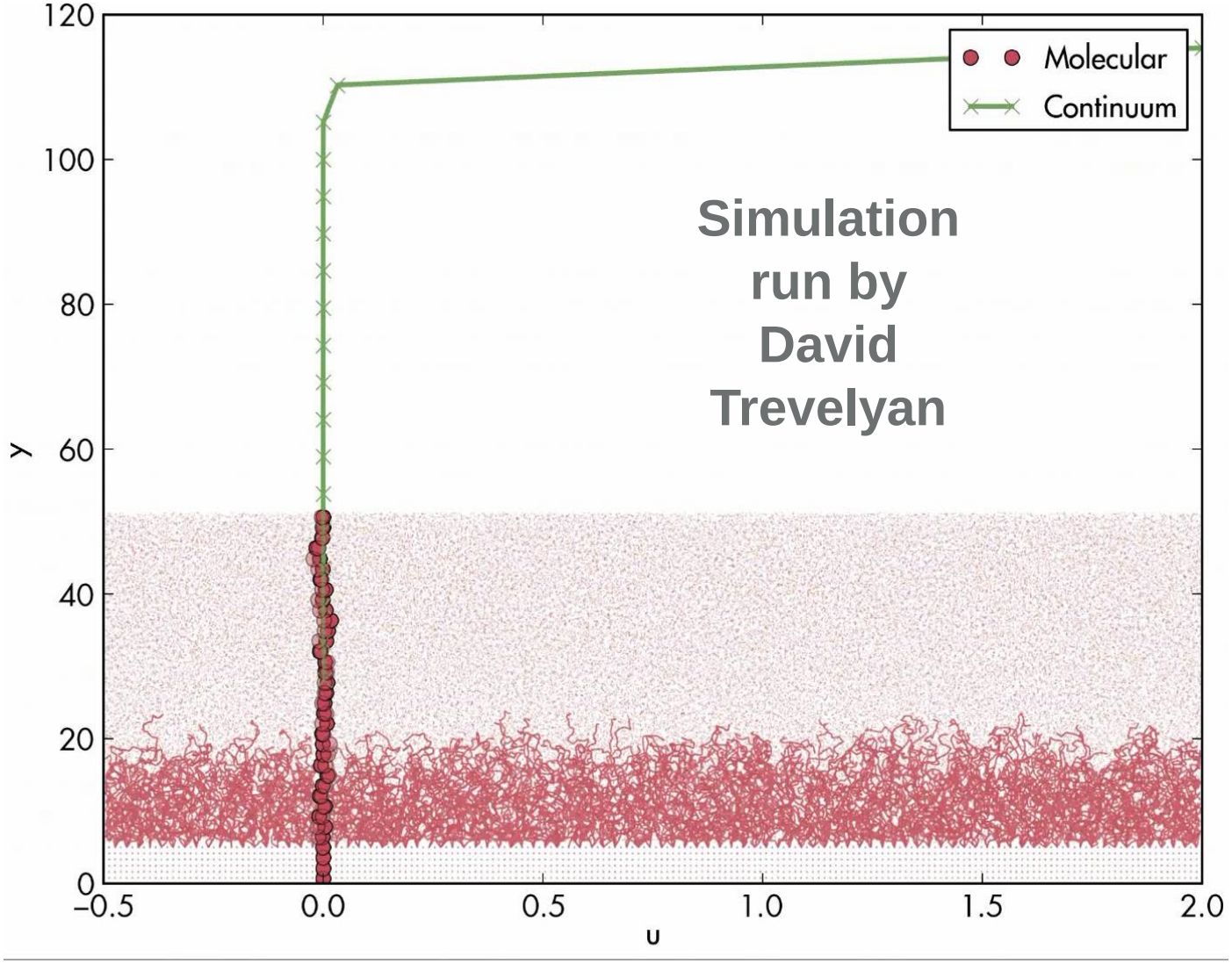
Coupling Results – Polymer Brushes



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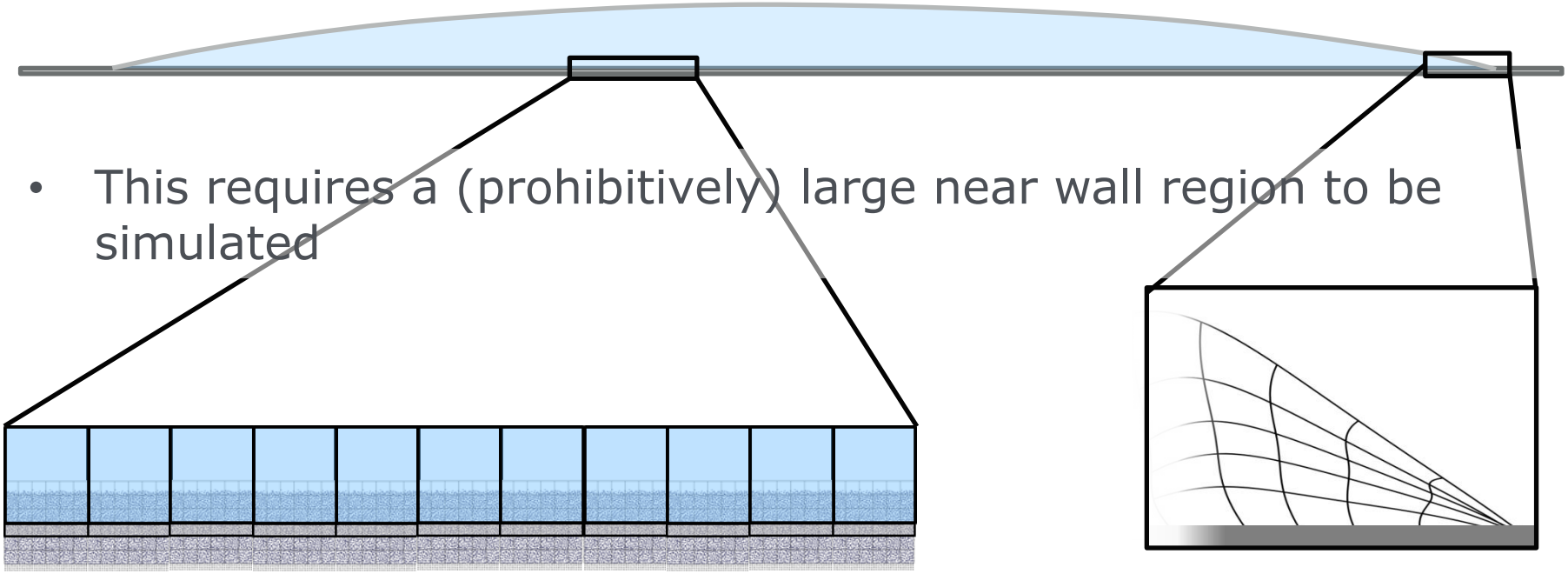
Droplet Modelling

- Thin film equations assumes a large length to height ratio



- This requires a (prohibitively) large near wall region to be simulated
- Especially when only the contact line dynamics are of interest
  - Stretched grid and moving interface are complex to model

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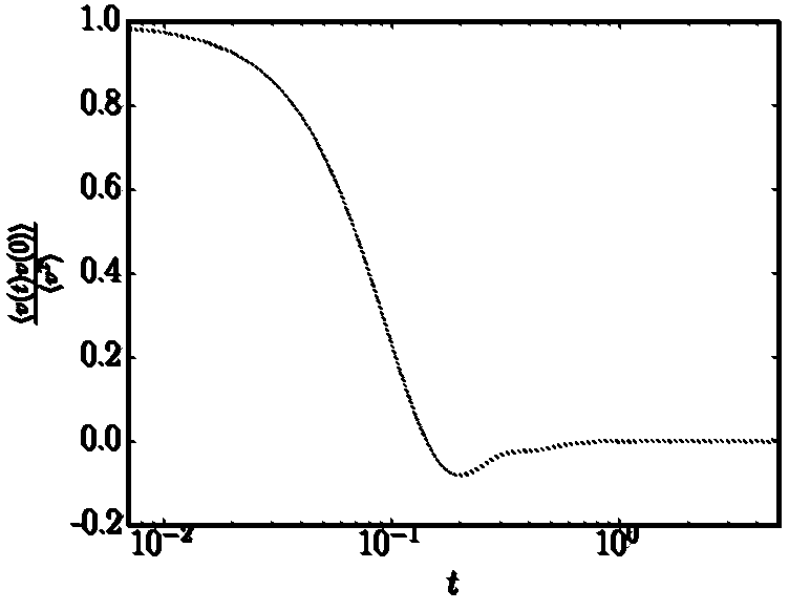
The Thin Film Equations Coupled in Domain Decomposition

- Domain decomposition links both systems directly
  - Molecular dynamics

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

$$\oint_S \boldsymbol{\Pi}\cdot d\mathbf{S} = \underbrace{\sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{m_i}\cdot d\mathbf{S}_i\right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left\langle \boldsymbol{f}_{ij}\mathbf{n}\cdot d\mathbf{S}_{ij}\right\rangle}_{\text{Configurational}}$$



  - CFD using thin-film assumptions

$$\frac{\partial P}{\partial x} = \frac{\partial^2 u}{\partial z^2} \qquad \frac{\partial P}{\partial z} = 0$$

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$$

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Coupling Overview

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 and Coveney, (2003)

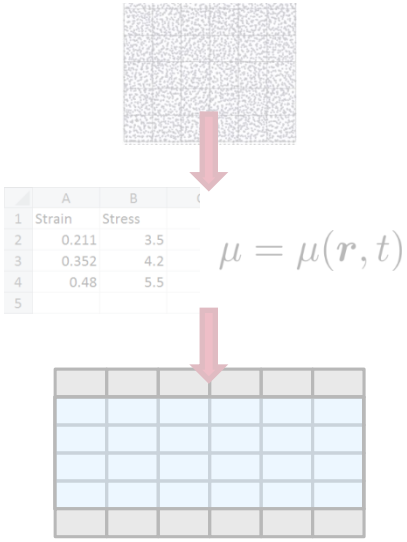
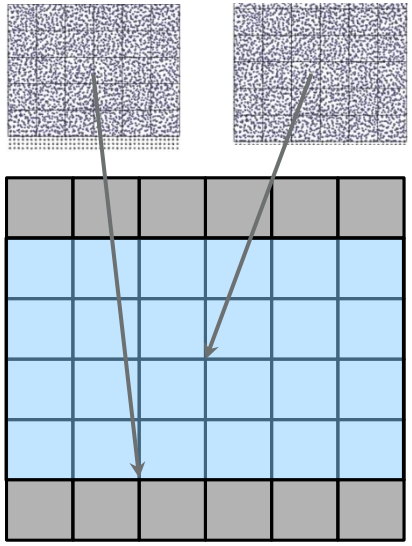


Table Lookup or Coefficients

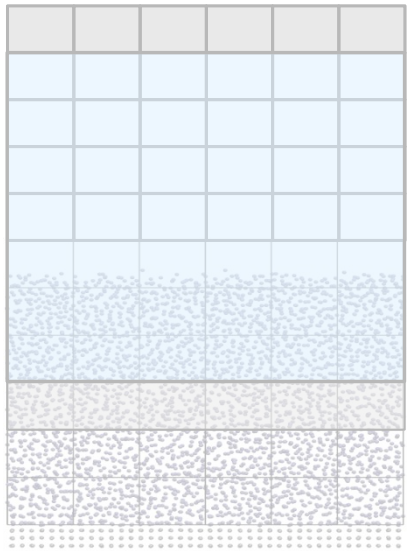
MD parameter study stored in table and CFD uses data



Embedded Models

MD – embedded in a CFD simulation

Used for Non-Newtonian effects [1)]



Domain Decomposition

MD –CFD linked along an interface

Local features e.g. contact line [2)]

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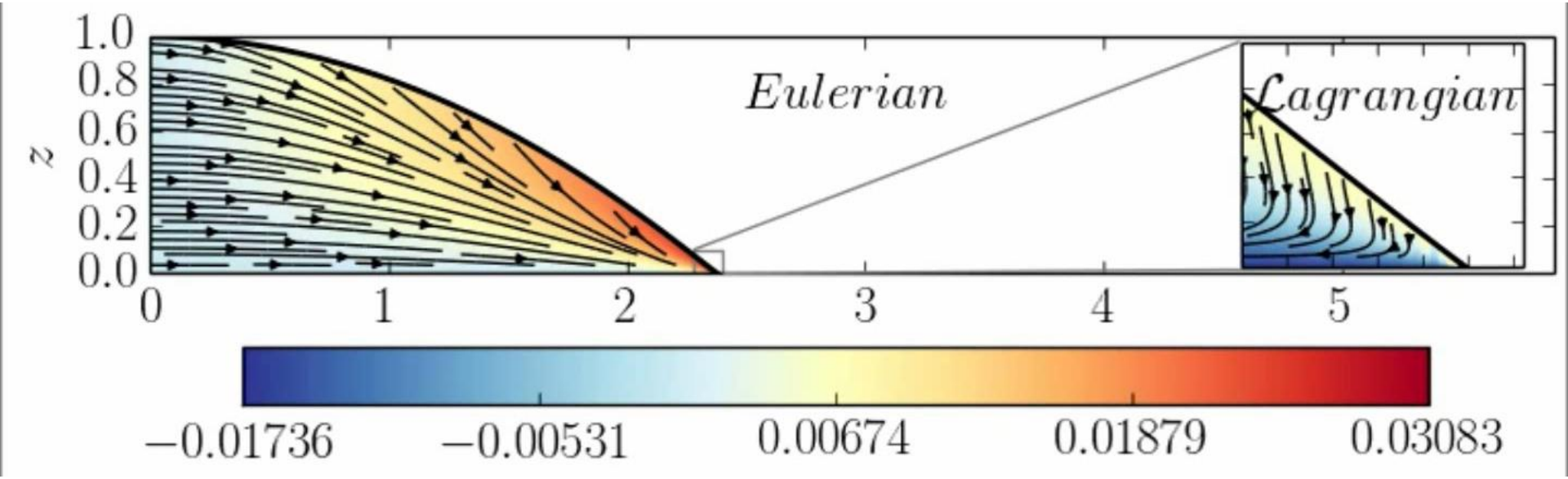
Coupled Droplet Spreading



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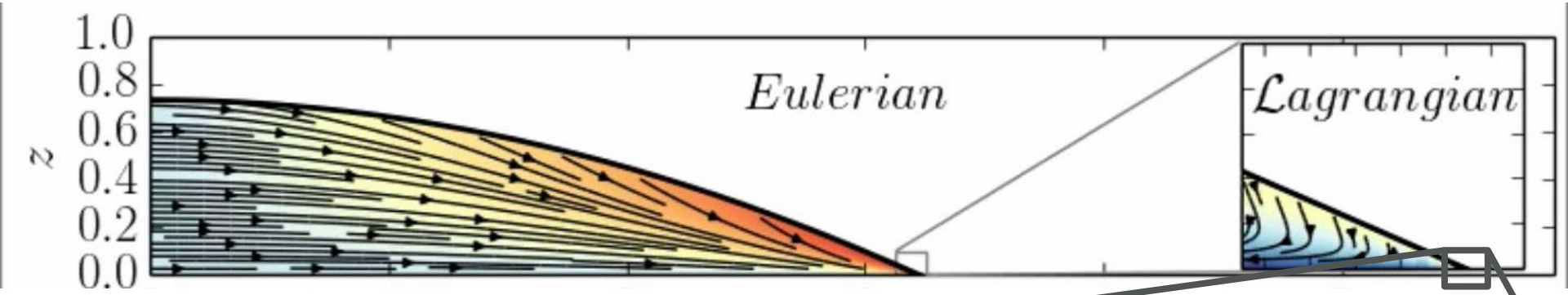
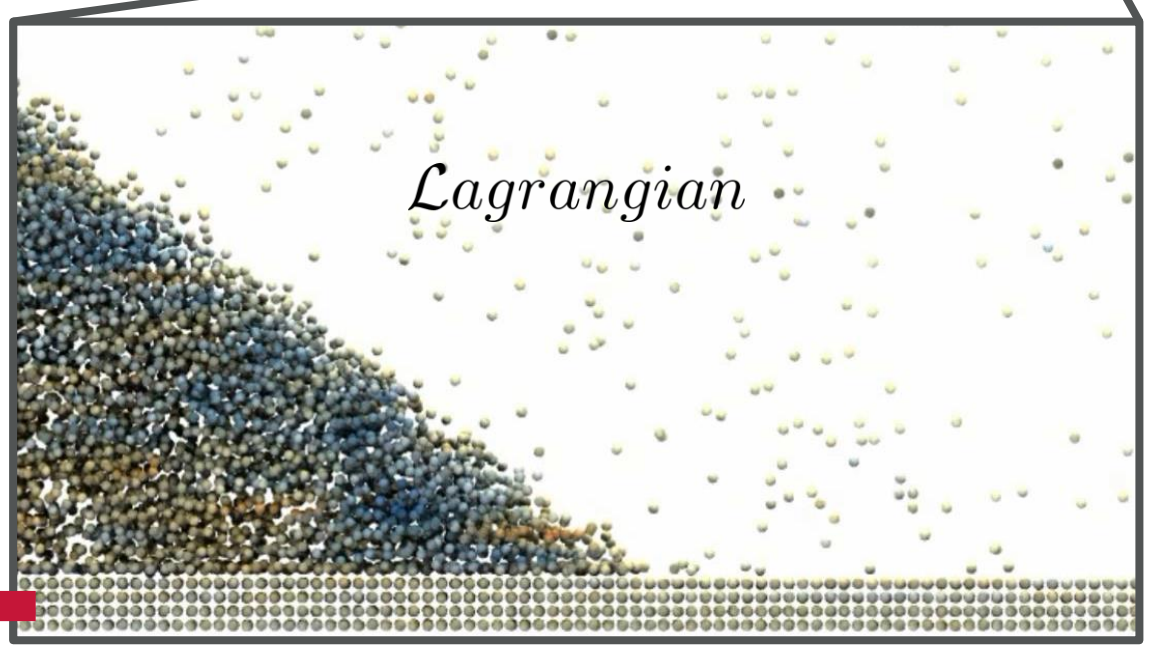
1) Thompson and Robbins (1989)

Coupled Droplet Spreading



- Model just the moving contact line with MD
- Iterate until convergence between models



$$\frac{dx_c}{dt}$$

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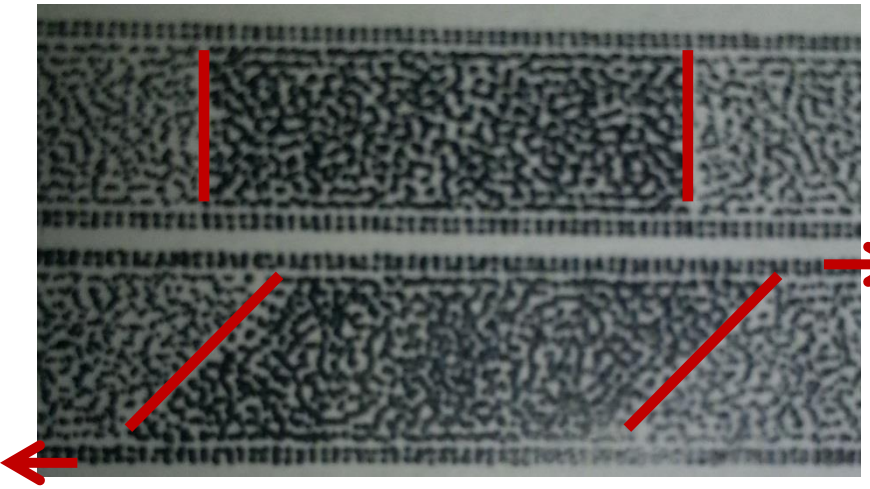
A Better way of Getting the Contact Angle

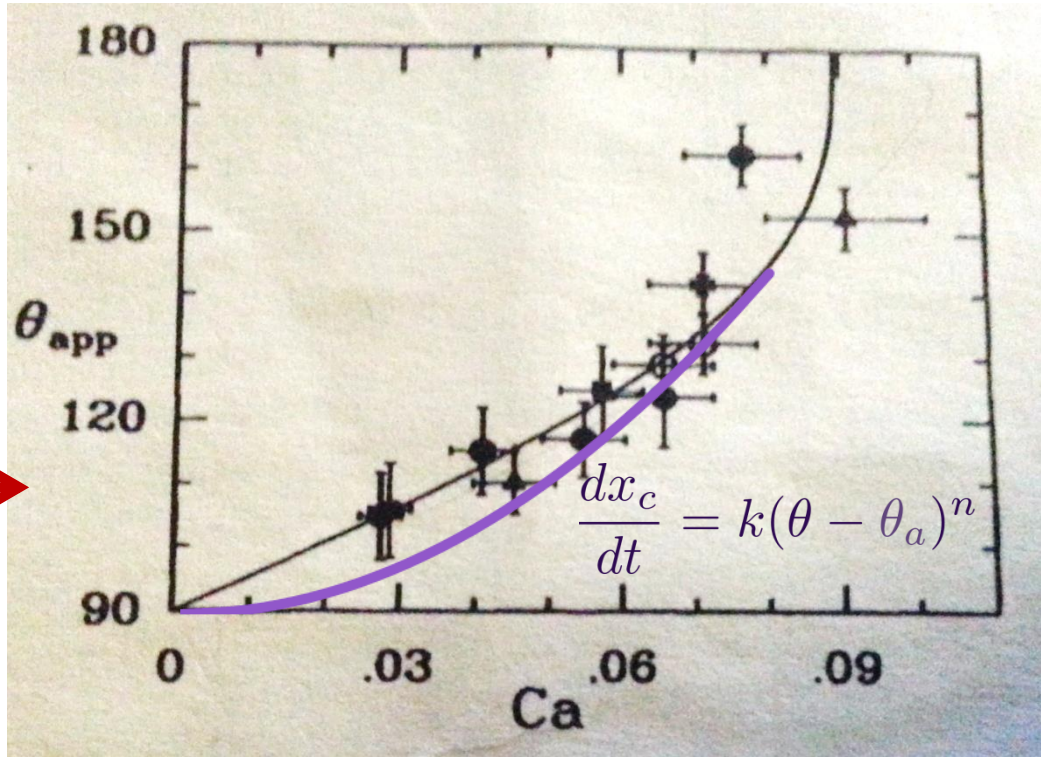
VOLUME 63, NUMBER 7 PHYSICAL REVIEW LETTERS 14 AUGUST 1989

Simulations of Contact-Line Motion: Slip and the Dynamic Contact Angle

Peter A. Thompson and Mark O. Robbins
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 7 February 1989)

- Reproduces Cox's Law





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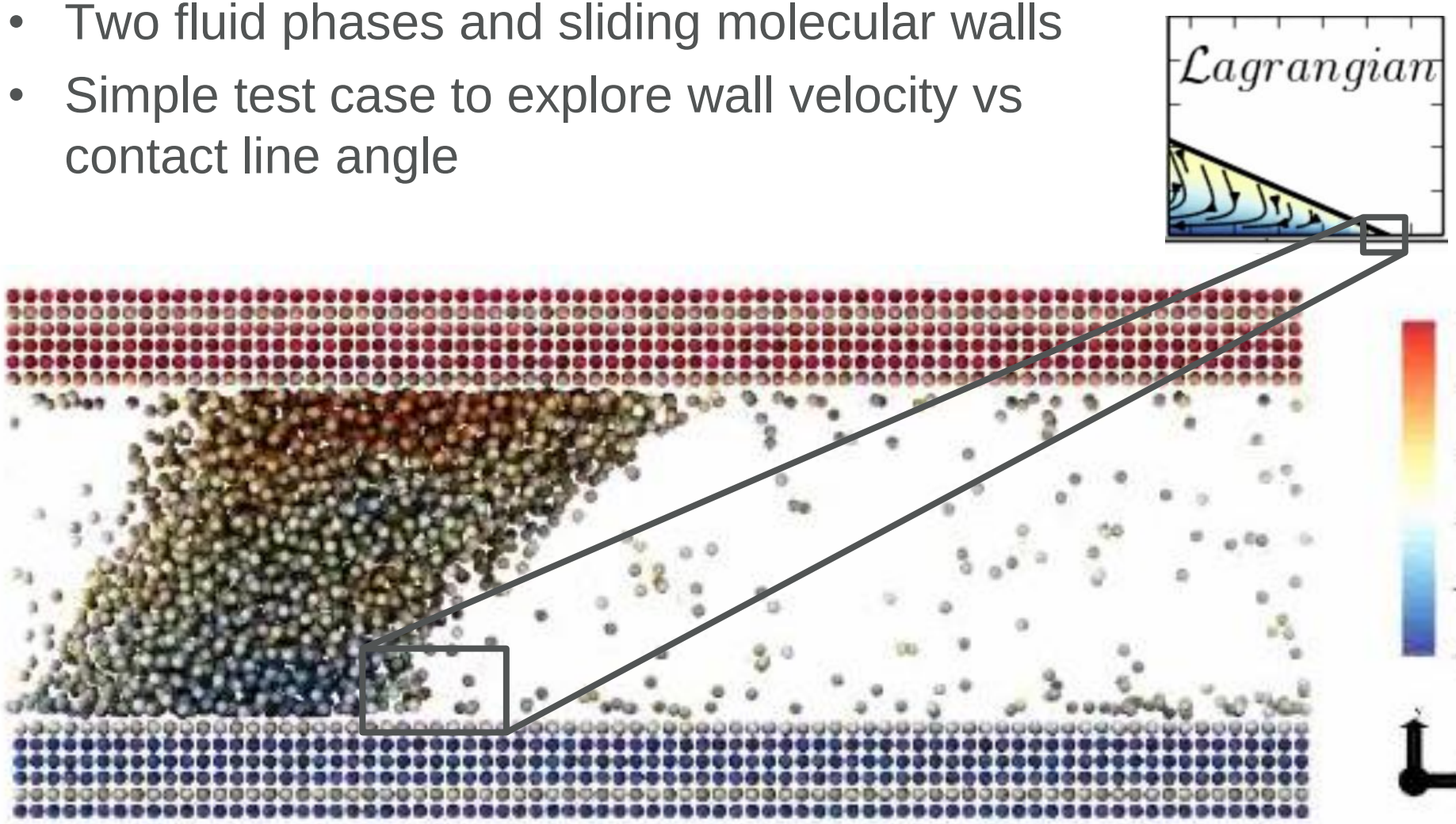
Two phase version closer to experimental reality

- Two fluid phases and sliding molecular walls
- Simple test case to explore wall velocity vs contact line angle



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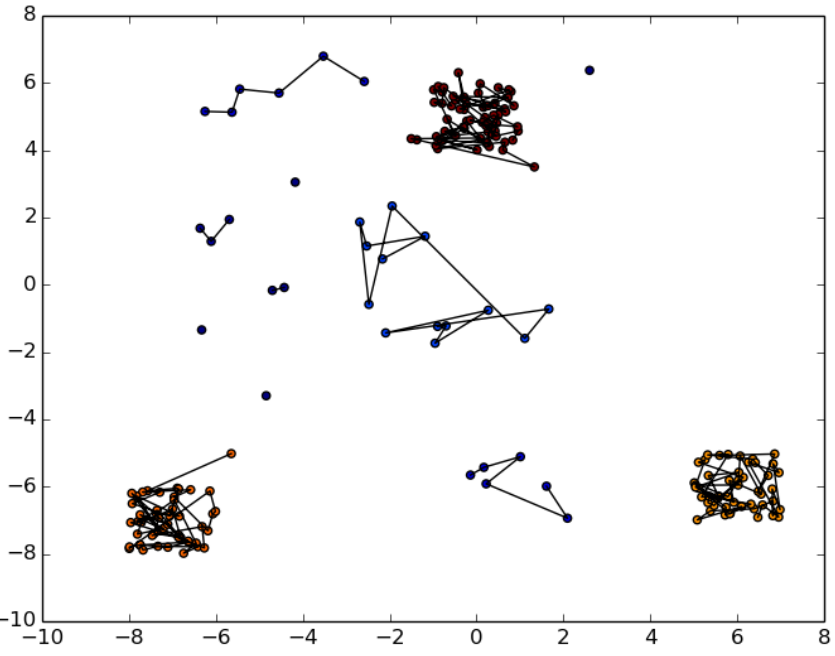
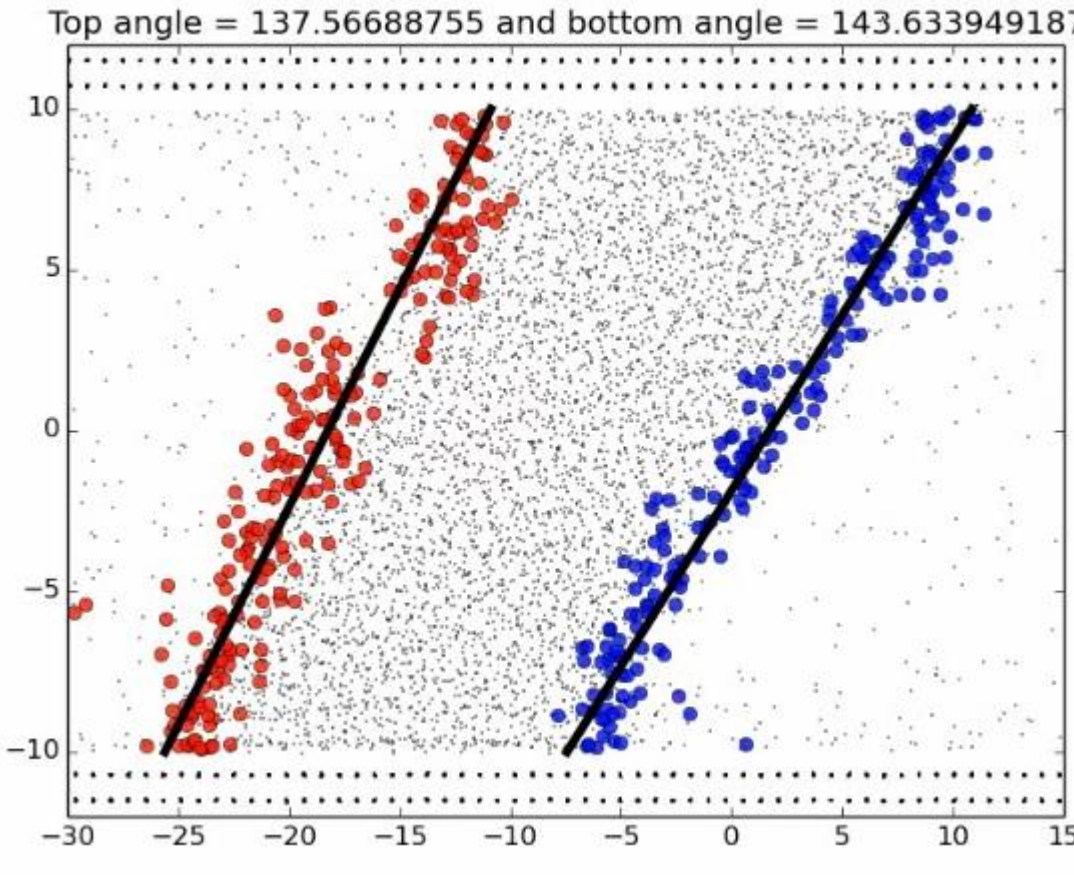
Cluster analysis and surface fitting to give theta



- Cluster analysis

- Finding the fluid-liquid interface



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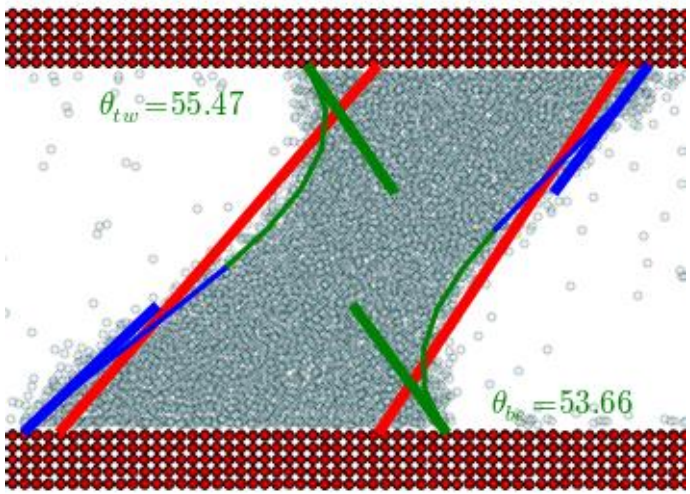
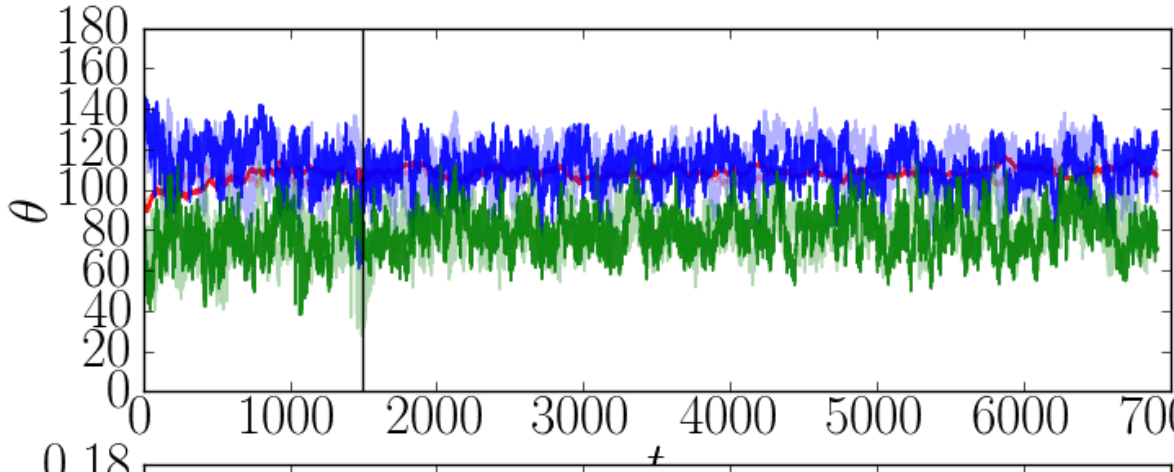
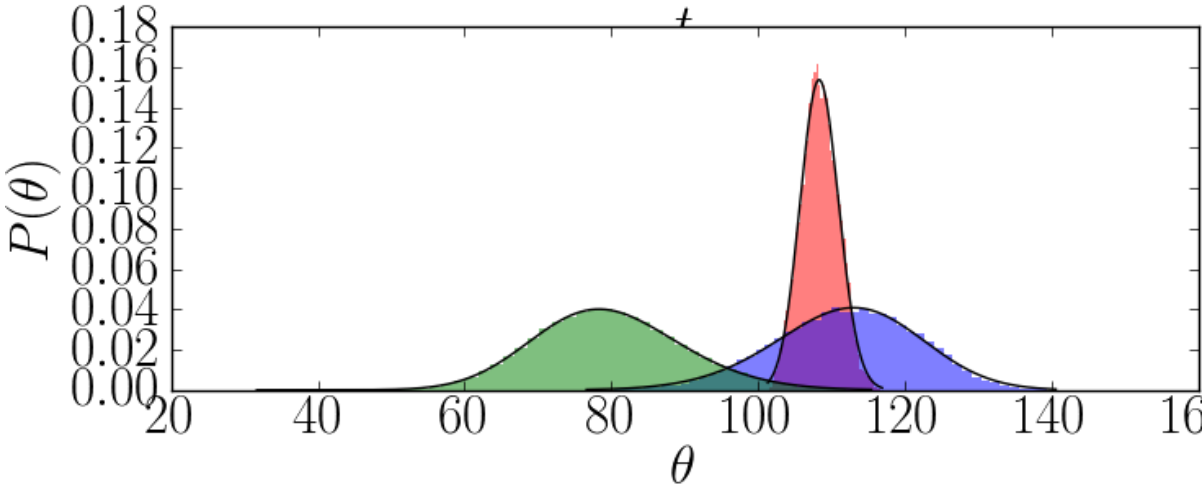
Time Evolution of Contact Angle

- Plot evolution of various contact angles as a function of time





- Probability density function of angle shows range of micro-scale behaviour



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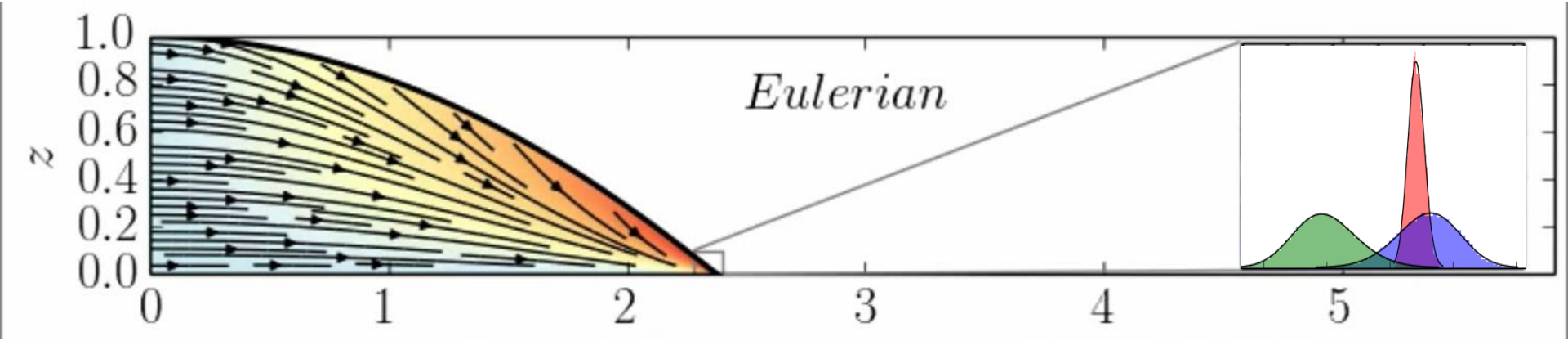
Building this into the Continuum Model



- Speed of contact line can be chosen from the molecular PDF with the appropriate speed in a simple fluid model

$$\frac{dx_c}{dt} = k(\theta - \theta_a)^n$$

- The more complex surfactant case requires simulations to be run dynamically for current surfactant concentration

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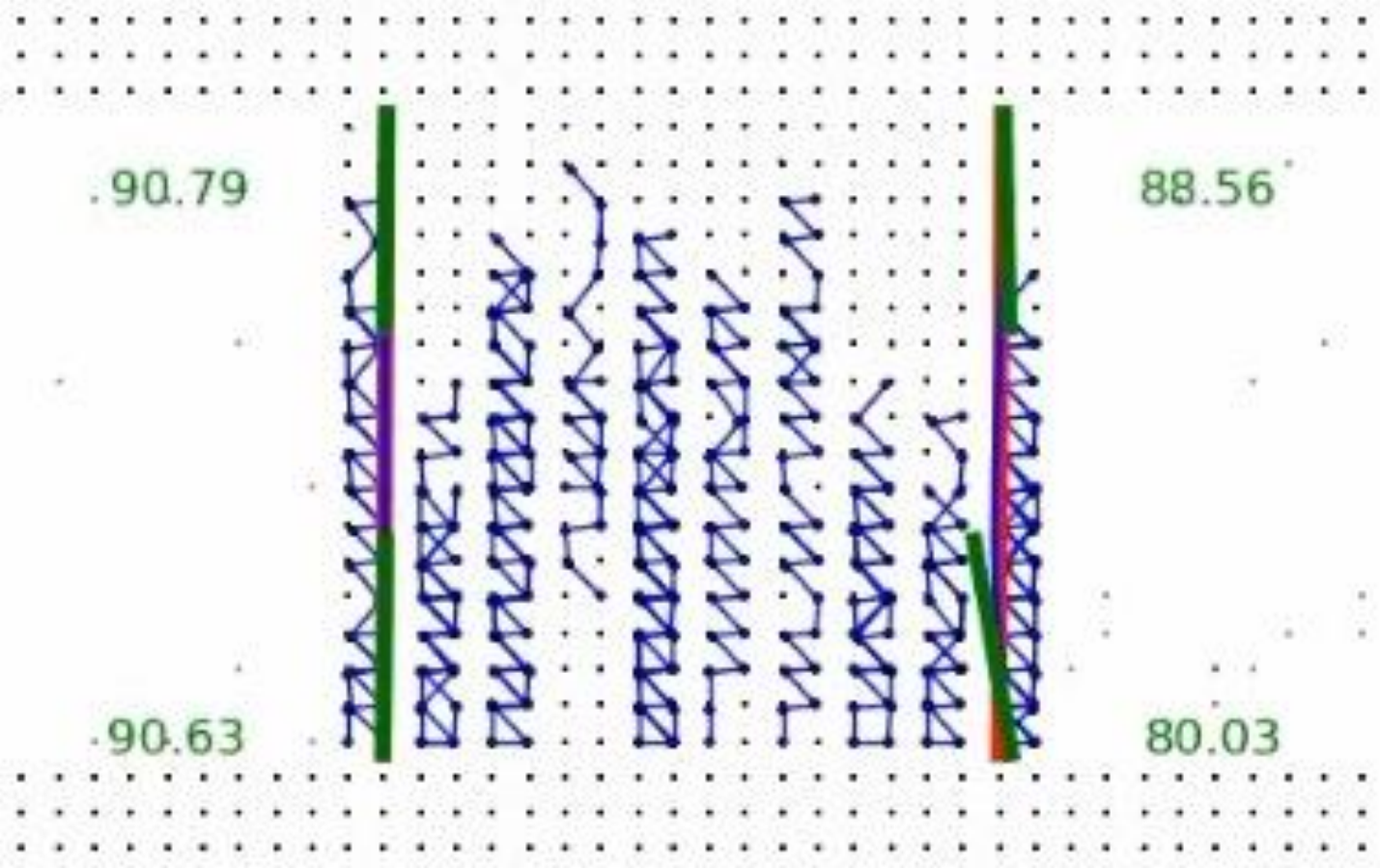
Surfactant Spreading More Complex

- Surfactant concentration impacts contact angle
  - Includes mechanism for deposition at contact line



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Conclusions and Future Aims

- Thin film equations with surfactant deposition at the contact line reproduce superspreading
- Molecular dynamics models surfactant deposition at the contact line, multiple phases and wall-fluid interactions
- We want to combine both in a single model
  - For simple cases, probability density functions of molecular detail
  - For surfactant simulations the references solutions are run on the fly based on surfactant concentration
  - Longer term domain decomposition using a CV based grid and a more detailed continuum model
- Choice of methodology depends on phenomenon of interest
  - molecular modelling represents an improvement on empirical models.

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Summary

- Computational Fluid Dynamics (CFD)
  - Model description and results
  - Contact line dynamics essential to superspreading
  - Difficult to model using a continuum
- Molecular Dynamics (MD)
  - Model description and results
  - Advantages for modelling of droplets and surfactants
  - Limited to nanoscales
- Coupling MD and CFD
  - Types of coupling, techniques and computational framework
  - Coupled droplet spreading
  - Future work

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Acknowledgements

- Current work funded by EPSRC Grant number EP/J010502/1
- Working with Erich Muller, Richard Craster and Omar Matar
- Coupling theory work with David Heyes, Daniele Dini and Tamer Zaki
- Open source cpl-library developed with David Trevelyan and Lucian Anton
- Funding by an EPSRC DTA in Mechanical Engineering at Imperial College and one year funded by an EPSRC postdoctoral prize fellowship

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Control Volume Function (revisited)

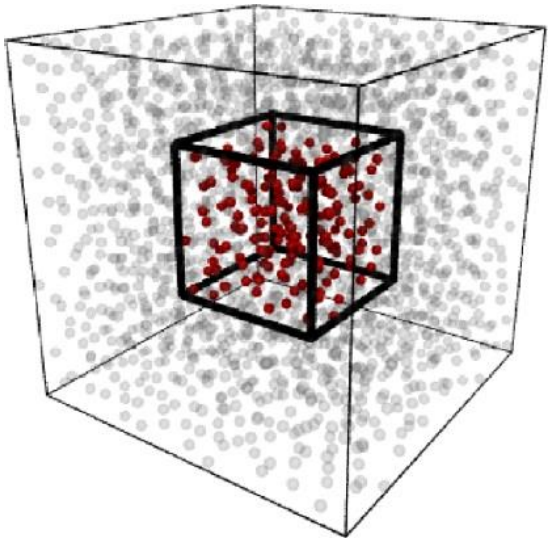
- The Control volume function is the integral of the Dirac delta function in 3 dimensions

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

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

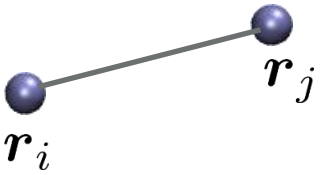
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

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



- Replace molecular position with for a line

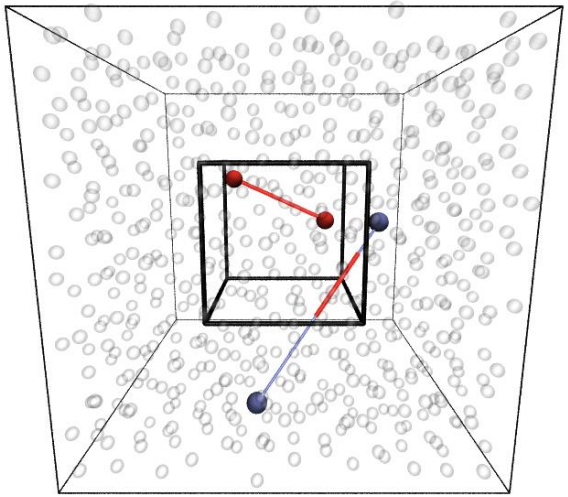
$$\boldsymbol{r}_i \rightarrow \boldsymbol{r}_i - s\boldsymbol{r}_{ij}$$



Control Volume Function (revisited)

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

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



- Length of interaction inside the CV

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

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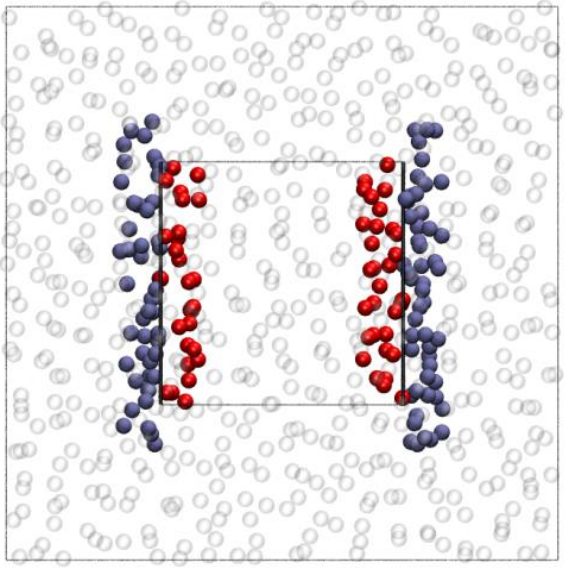
Derivatives Yield the Surface Forces

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

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

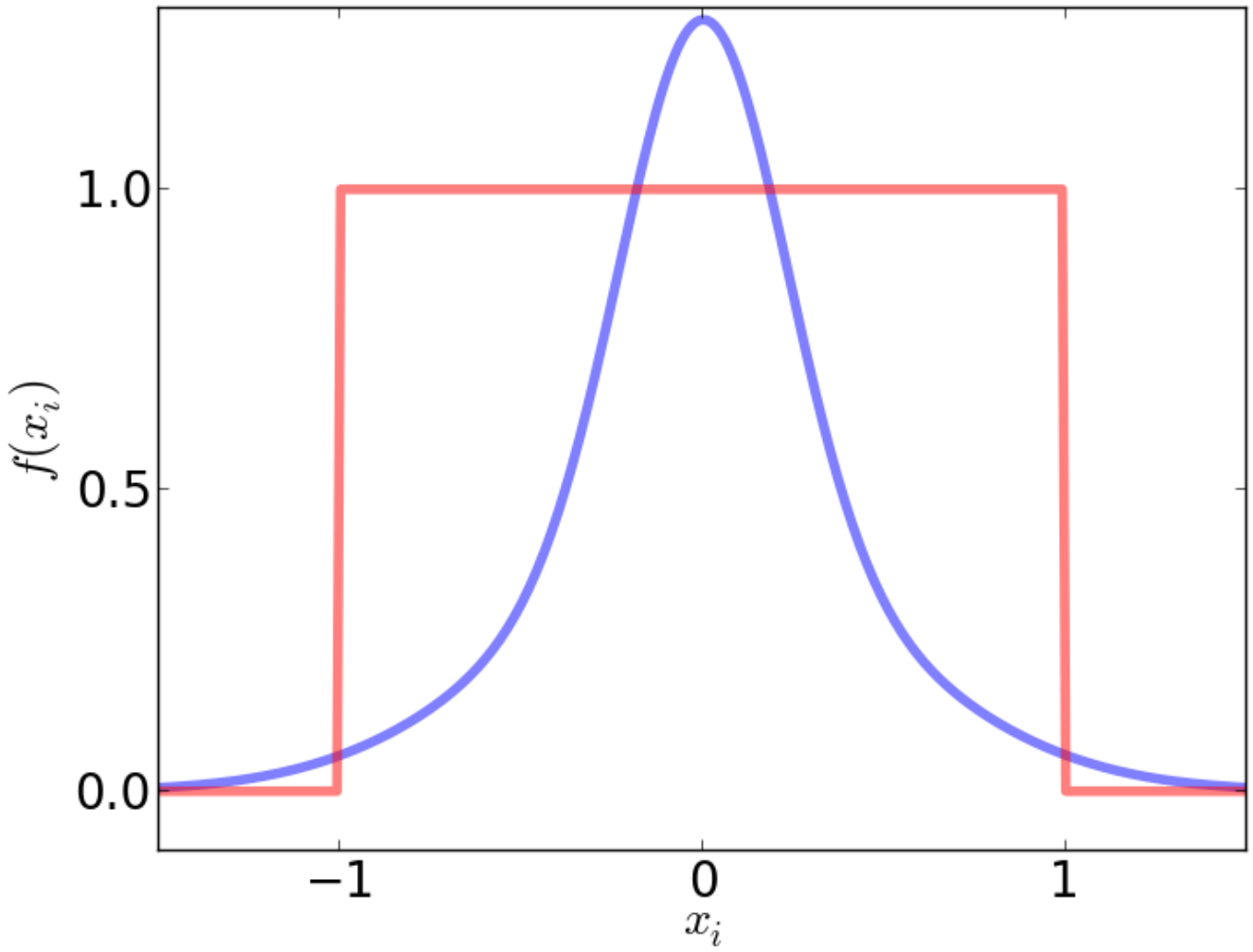


- **Surface fluxes over the top and surface**

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

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

Gaussian Kernel vs Heavisides



Applying the Control Volume Function

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

- **Simple mathematical operations using the control volume function**

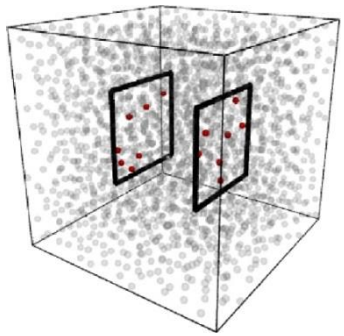
$$\frac{\partial}{\partial t}\left\langle \alpha; f\right\rangle = \sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i}{m_i}\cdot\frac{\partial\alpha}{\partial \boldsymbol{r}_i} - \boldsymbol{F}_i\cdot\frac{\partial\alpha}{\partial \boldsymbol{p}_i}; f\right\rangle \qquad \alpha = \sum_{i=1}^{N} m_i\vartheta_i$$

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

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

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

$3\times$



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Reynolds' Transport Theorem

- 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

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

- 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

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

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

- Energy Conservation

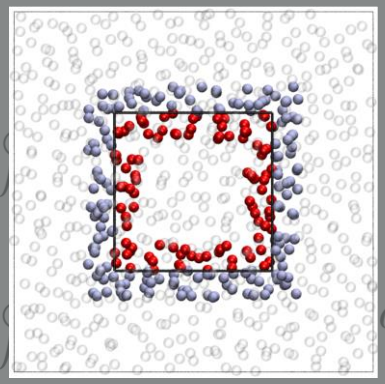
$$\frac{d}{dt}\sum_{i=1}^{N} e_i \vartheta_i = -\sum_{i=1}^{N} e_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{i\neq j} \frac{\mathbf{p}_i}{m_i} \boldsymbol{f}_{ij} \vartheta_{ij}$$

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

- **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**



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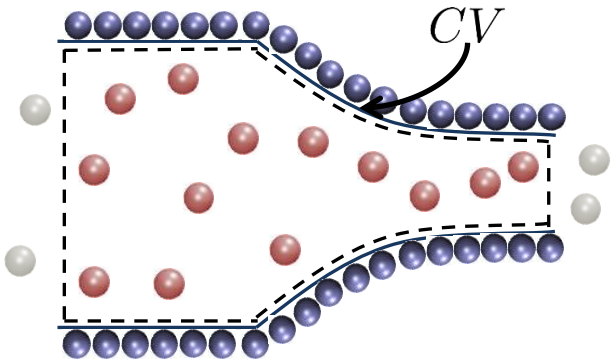
The Molecular Equations in CV Form

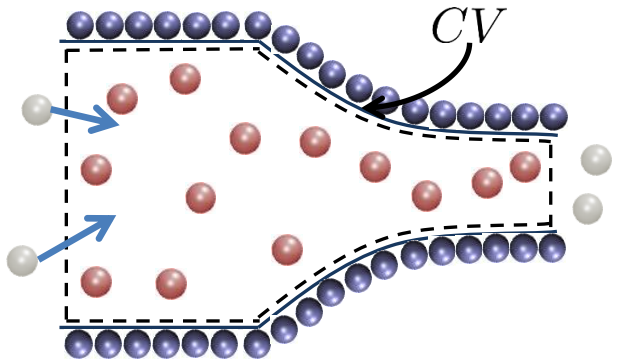
- *The Control Volume is a purely conceptual closed surface used to analyse fluid flow*



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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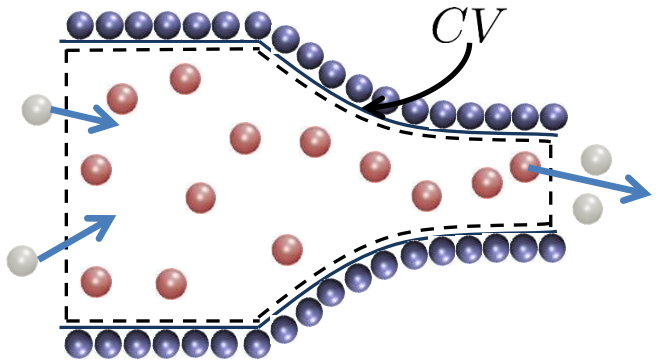
The Molecular Equations in CV Form

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

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



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

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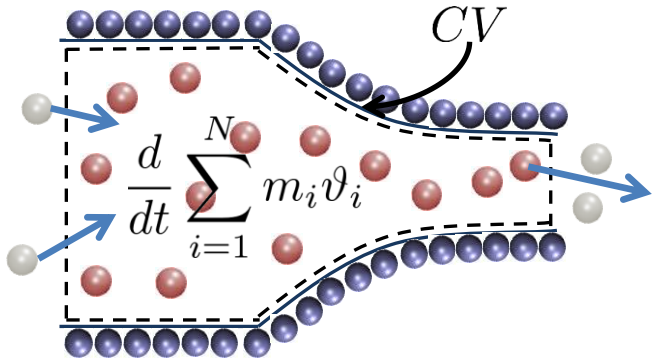
The Molecular Equations in CV Form

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

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



- *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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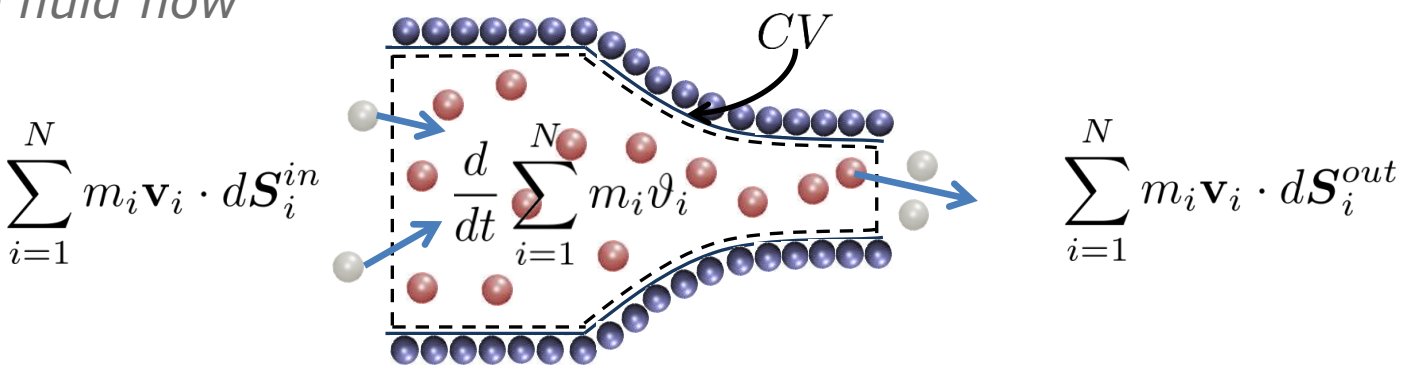
The Molecular Equations in CV Form

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



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

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

  - *Momentum Balance*

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

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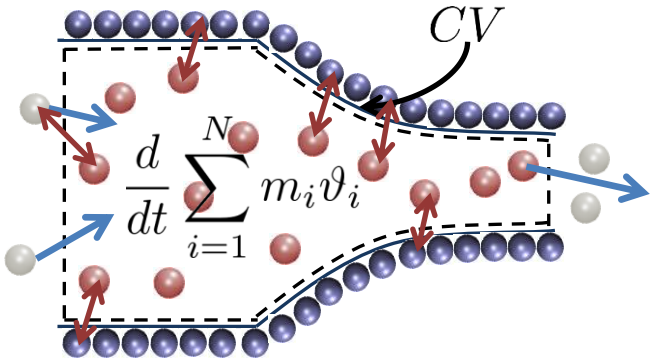
1) Irving and Kirkwood (1950) J Chem. Phys. 15,6

The Molecular Equations in CV Form

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

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



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

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

$$\int_V \ldots dV \;\Leftrightarrow\; \lim_{V\to 0}$$

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

  - *Momentum Balance*

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

$$\Leftrightarrow$$

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

- Continuum equations[1)]

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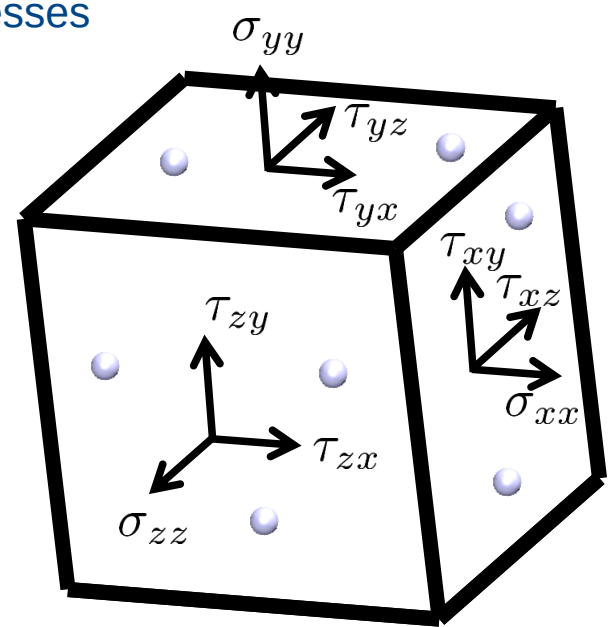
More on the Pressure Tensor

- **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

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

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

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

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

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