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# Coupling Molecular Dynamics to Continuum Computational Fluid Dynamics to simulate Superspreading at the macro-scale

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

# Overview

- Computational Fluid Dynamics (CFD)
  - Model description and results
  - Contact line dynamics essential to superspreading but difficult to model using a continuum

- Molecular Dynamics (MD)
  - Model description and results
  - Limited to nanoscales

- Coupling MD and CFD
  - Types of coupling, techniques and computational framework
  - Coupled droplet spreading

Section 1

# COMPUTATIONAL FLUID DYNAMICS

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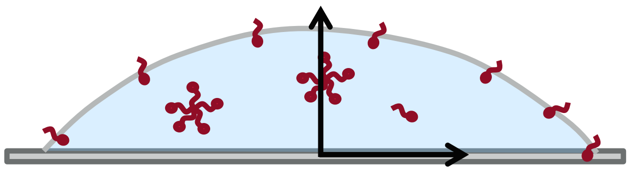
# Computational Fluid Dynamics (CFD)

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

- Incompressible Navier Stokes with the lubrication approximation (H<<L).

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




- 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*

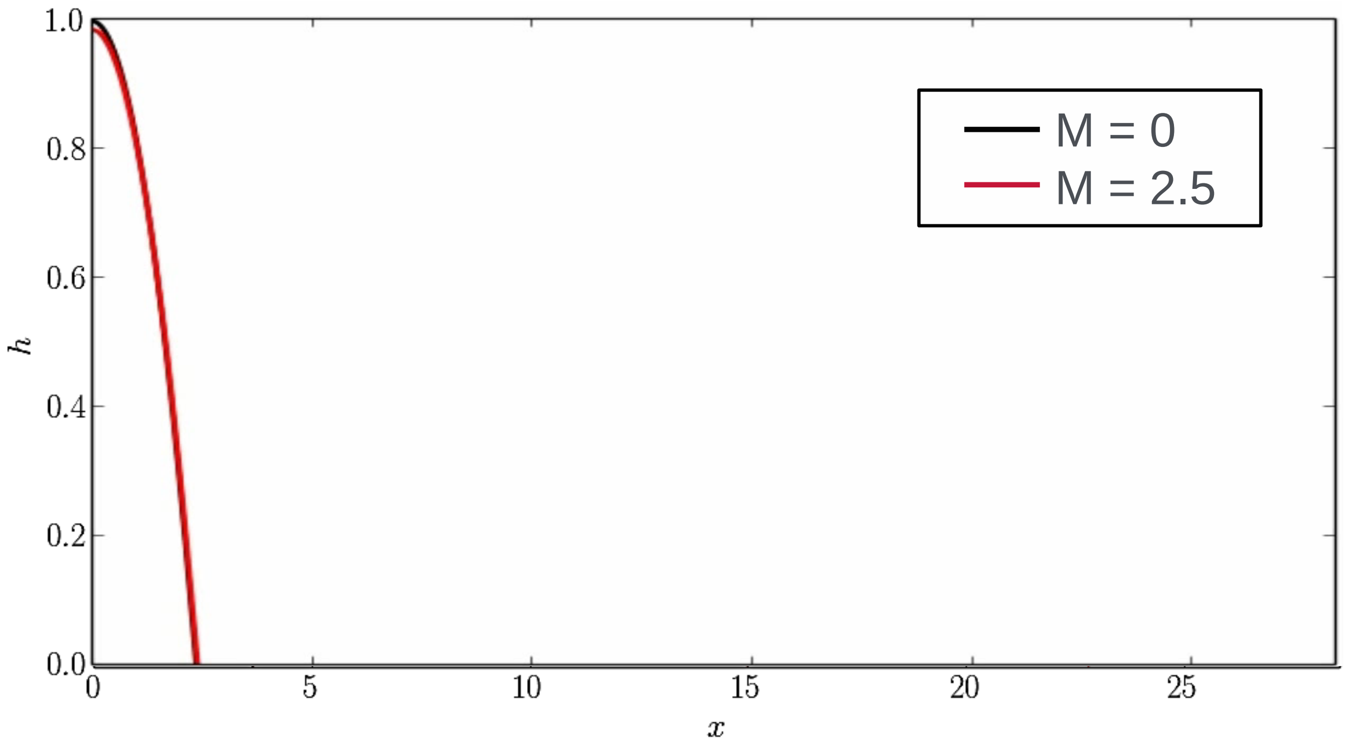
$$\frac{dx_c}{dt} = k(\theta - \theta_a)^n$$

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

# 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

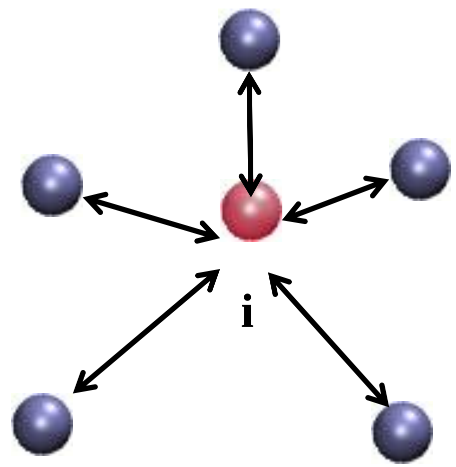
# Molecular Dynamics

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

## 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

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

- 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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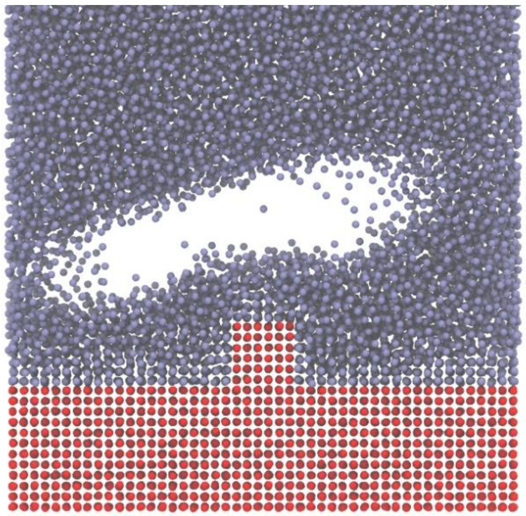
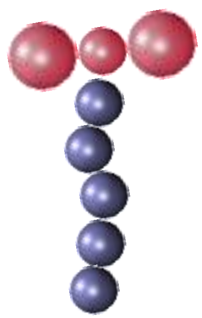
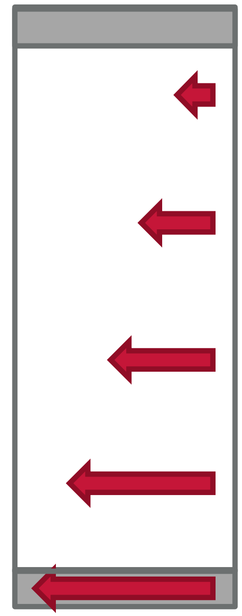
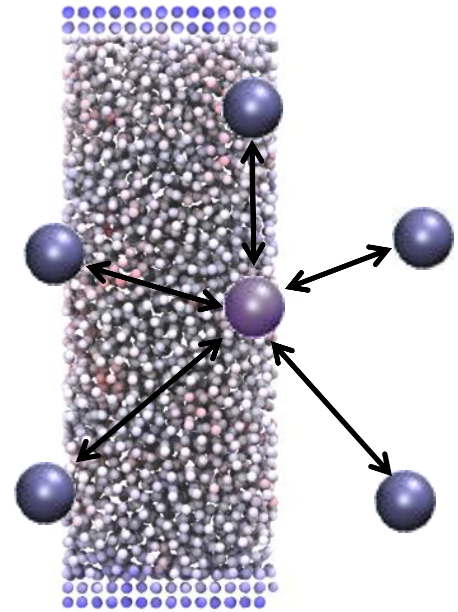
# Molecular Dynamics

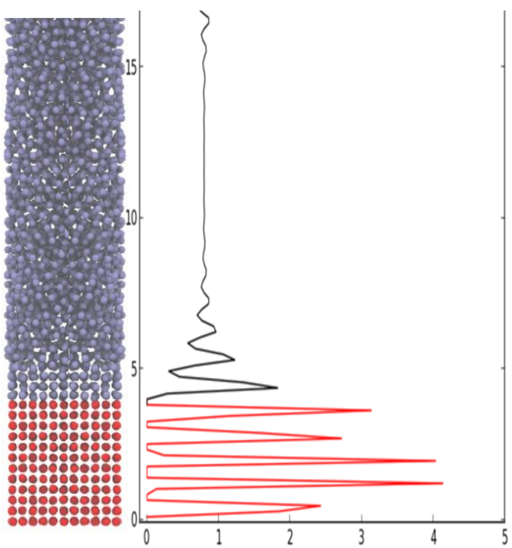


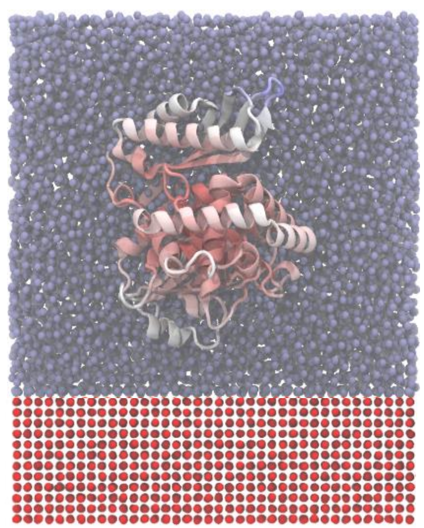
*Superspreading Surfactant, e.g. Silwet-L77*







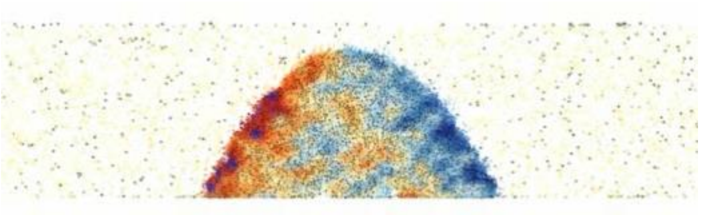


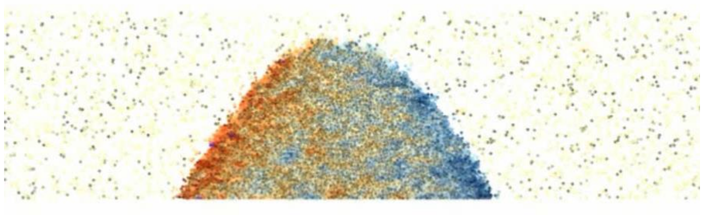
# MD Simulation of Droplets

1) "The superspreading mechanism unveiled via molecular dynamics simulations" by Panagiotis Theodorakis at 1:18 PM, Tuesday, November 25, 2014

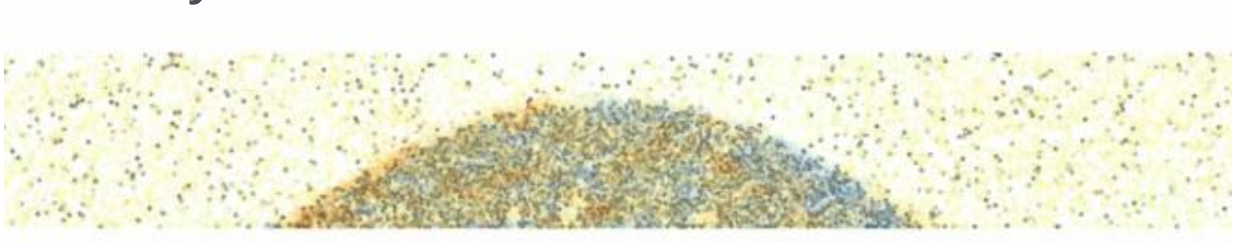
- Low Wettability



- Intermediate Wettability



- High Wettability



- MD with Surfactants by Panos Theodorakis in session **R14** [1)]

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)

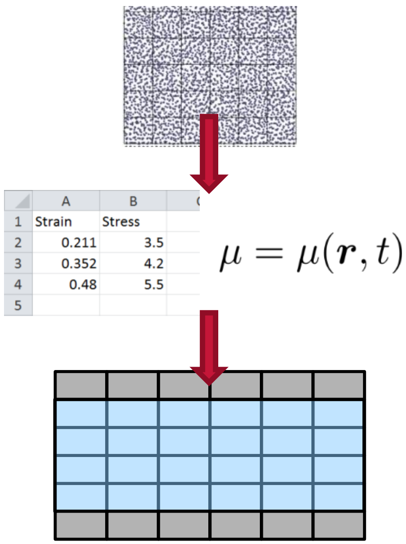
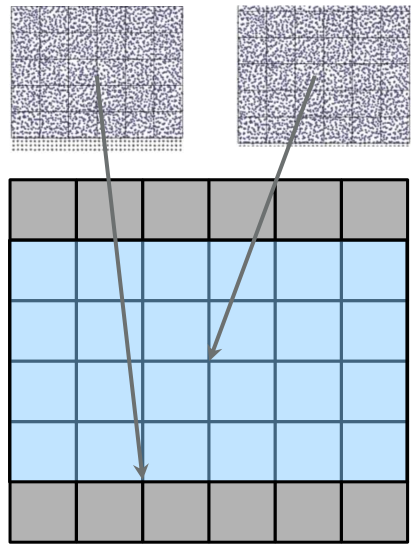



**Table Lookup or Coefficients**

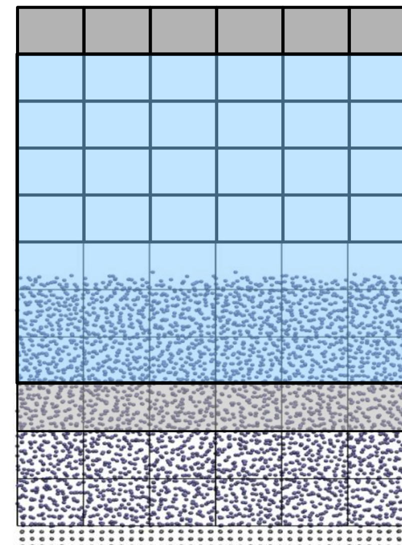
MD parameter study stored in table and CFD uses data



**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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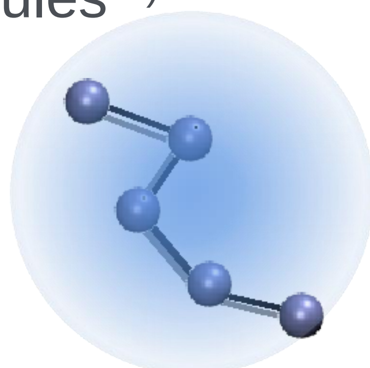
# Coupling Overview

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 - Under Review). 4) Smith, Trevelyan, Anton

Boundary force and insertion of molecules [1)]

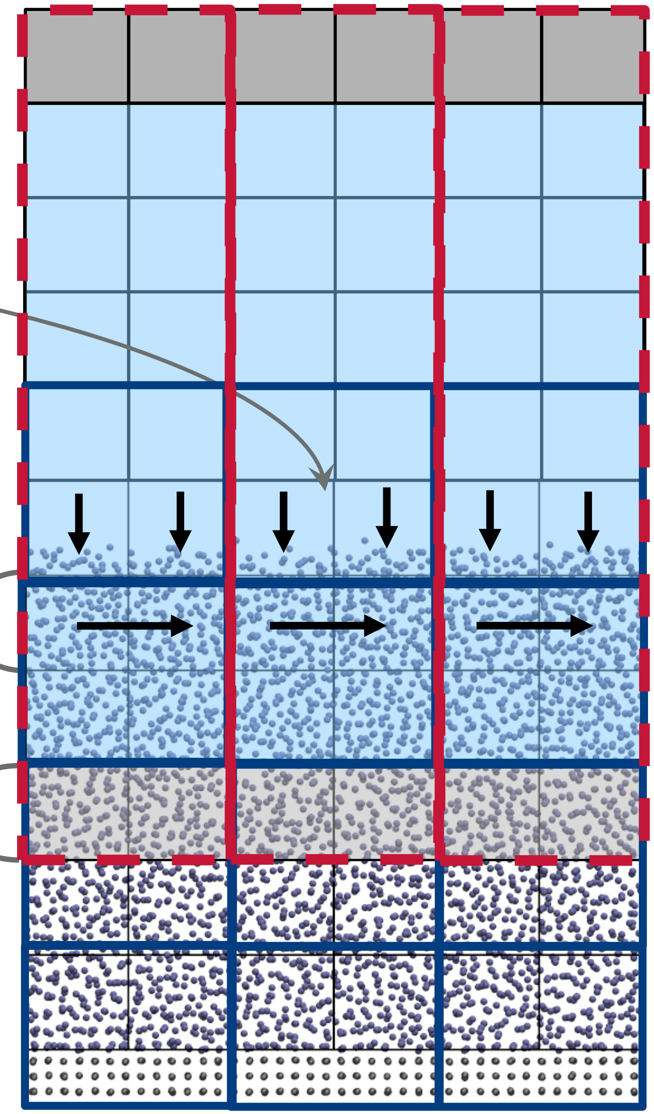


$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{CFD}$$

**CFD→MD** Boundary condition [3)]

$$\int_V \rho \boldsymbol{u} dV = \frac{1}{N} \sum_{i=1}^{N} m_i \boldsymbol{v}_i \vartheta$$

**MD→CFD** Boundary condition [2)]



High performance computers using open source CPL_library (code.google.com/p/cpl-library/) [4)]

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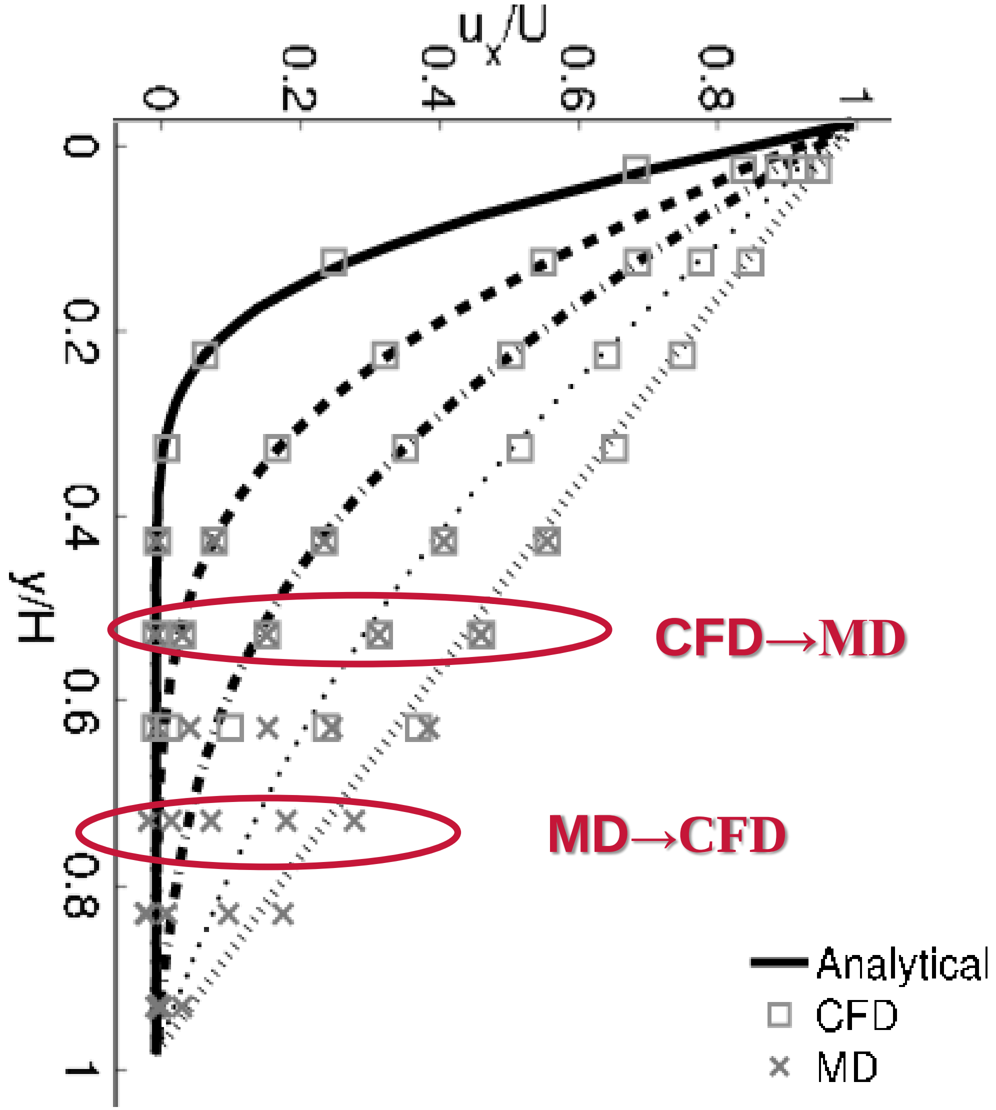
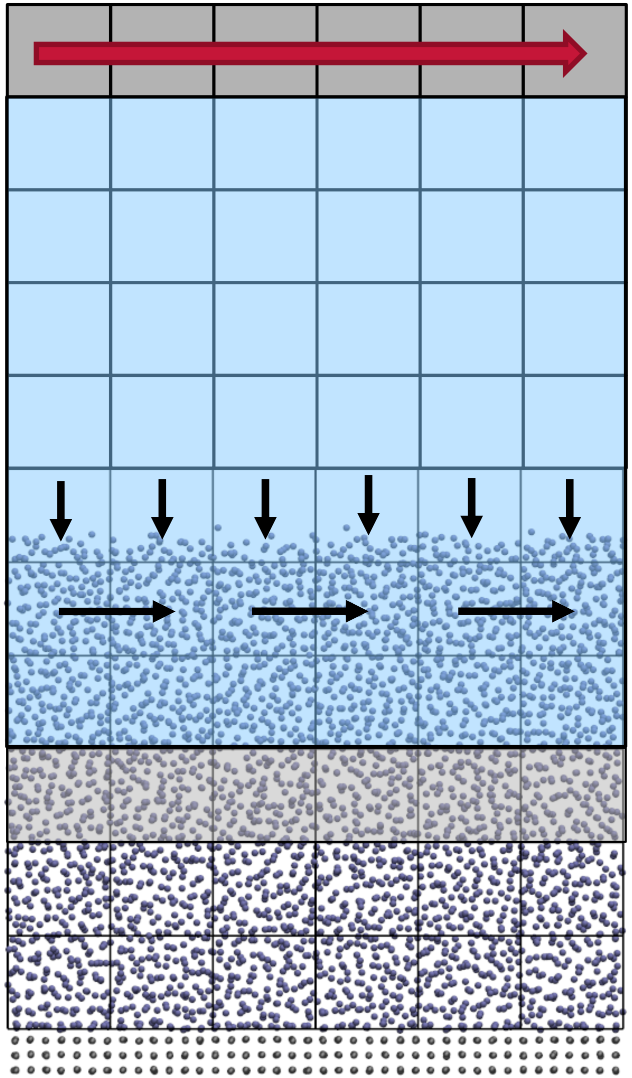
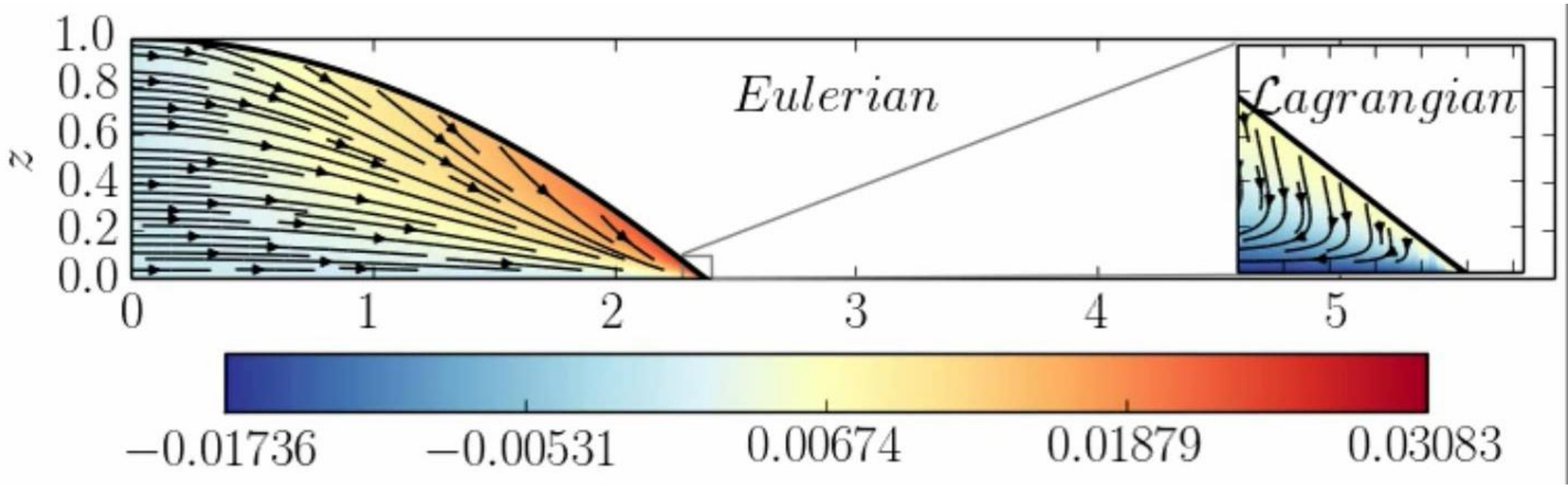
# Coupling Results – Couette Flow

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



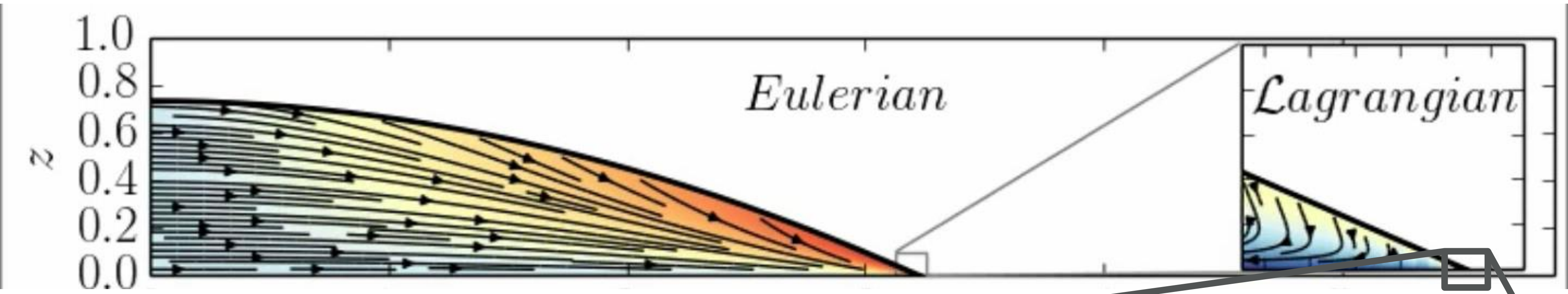



# Coupled Droplet Spreading

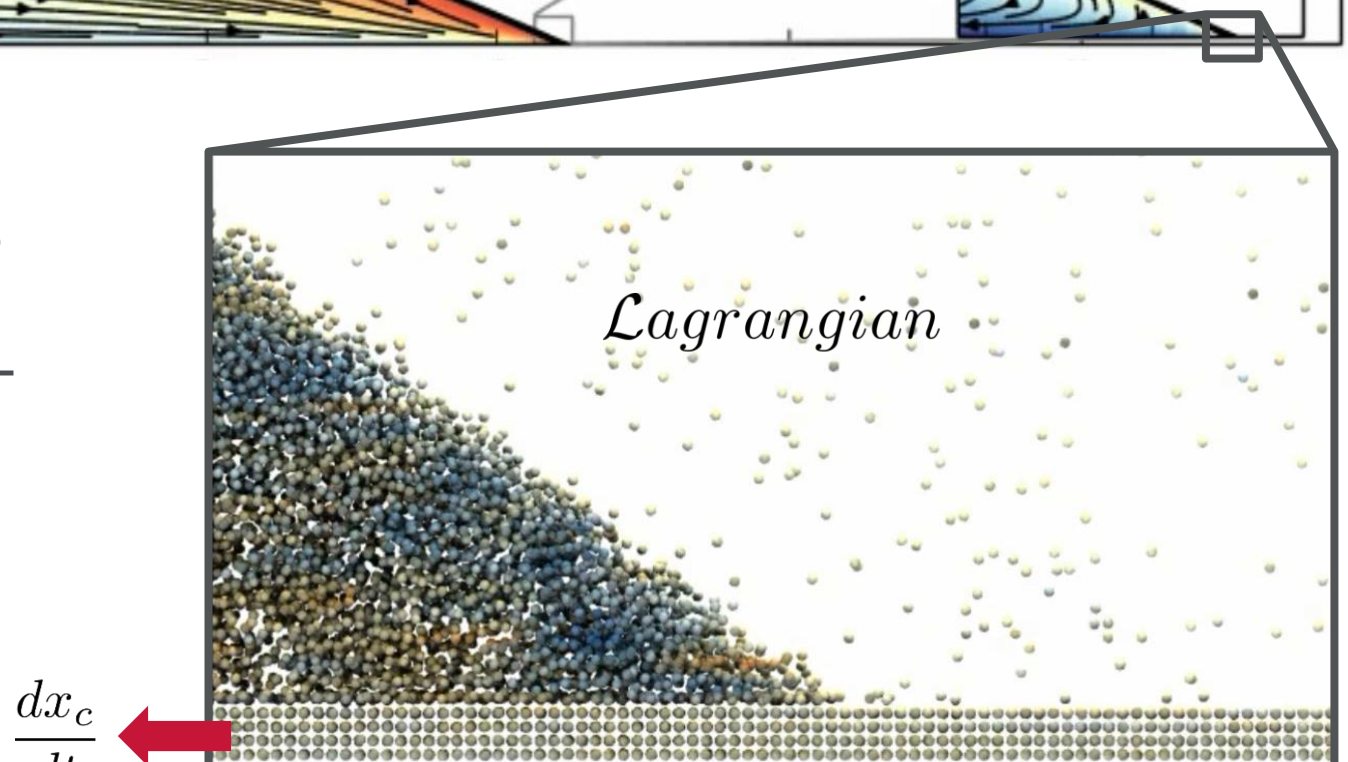


# Coupled Droplet Spreading

1) Thompson and Robbins (1989)
2) Hadjiconstantinou et al (1999)




- Entire contact line region is MD
- Run to a pseudo-steady case[1)]
- Iterative agreement with CFD[2)]



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