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A Langevin model for the Dynamic Contact Angle Parameterised Using Molecular Dynamics

APS 2016

2:57 PM–3:10PM

By

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In collaboration with,

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and Omar Matar

APS | DFD 16

Division of Fluid Dynamics

Portland, Oregon | November 20 -22

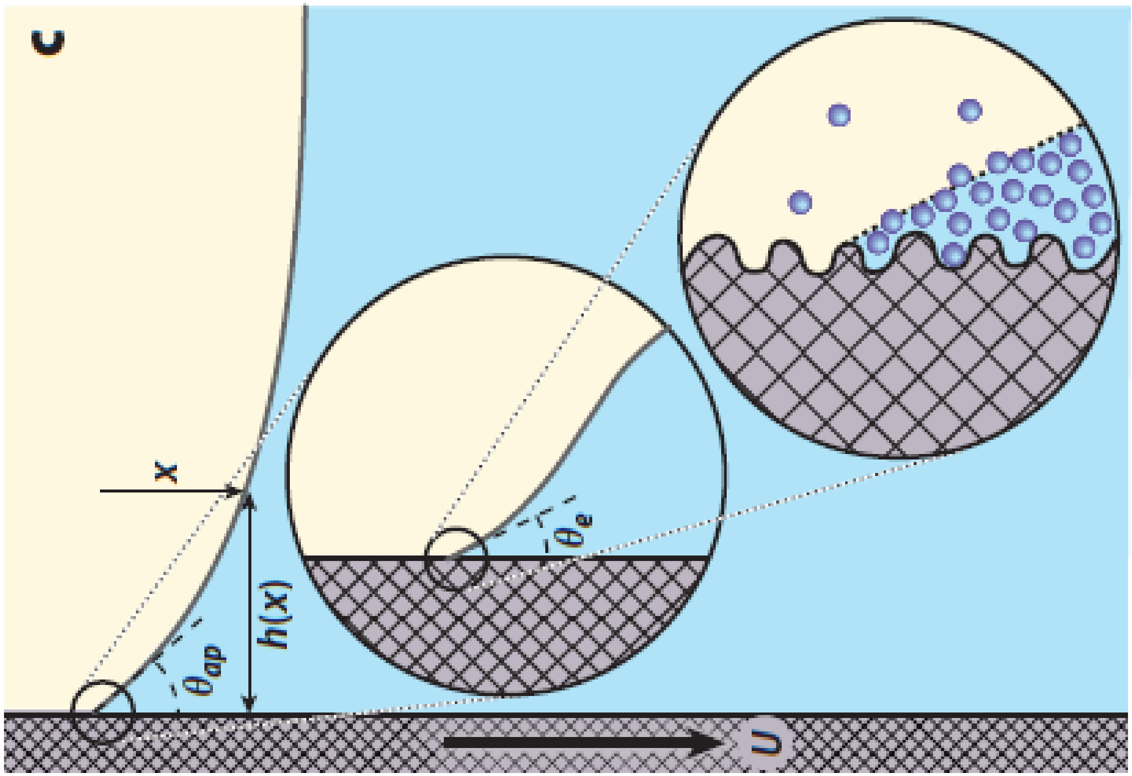
APS physics

EPSRC

Pioneering research and skills

Determining the Contact angle

- Molecular simulation provides insight into contact line dynamics



Snoeijer, Andreotti (2013) Annual Rev Fluid Mech 45:269–92

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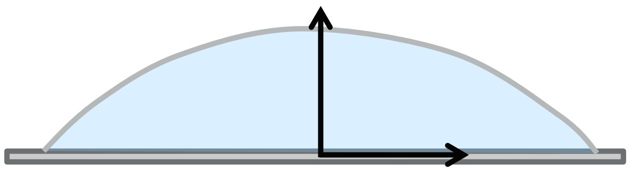
Computational Fluid Dynamics (CFD)

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

$$P = -\left(\frac{H}{L}\right)^2 \frac{\partial^2 h}{\partial x^2}\sigma_l \qquad \frac{\partial h}{\partial t} + u\frac{\partial h}{\partial x} = w \qquad \frac{\partial u}{\partial z} = 0 \qquad z = h$$

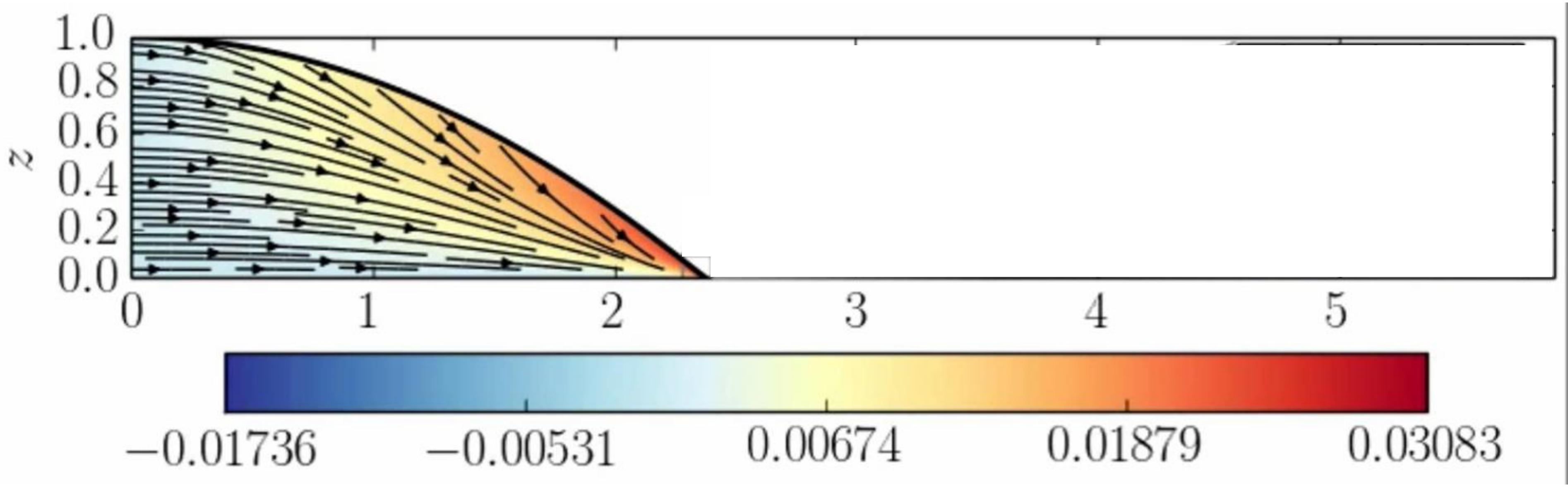
$$u = \beta\frac{\partial u}{\partial z} \qquad w = 0 \qquad z = 0$$

- *Contact line evolution is modelled by an empirical law*

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

1) Thompson and Robbins (1989)

Coupled Droplet Spreading and MD



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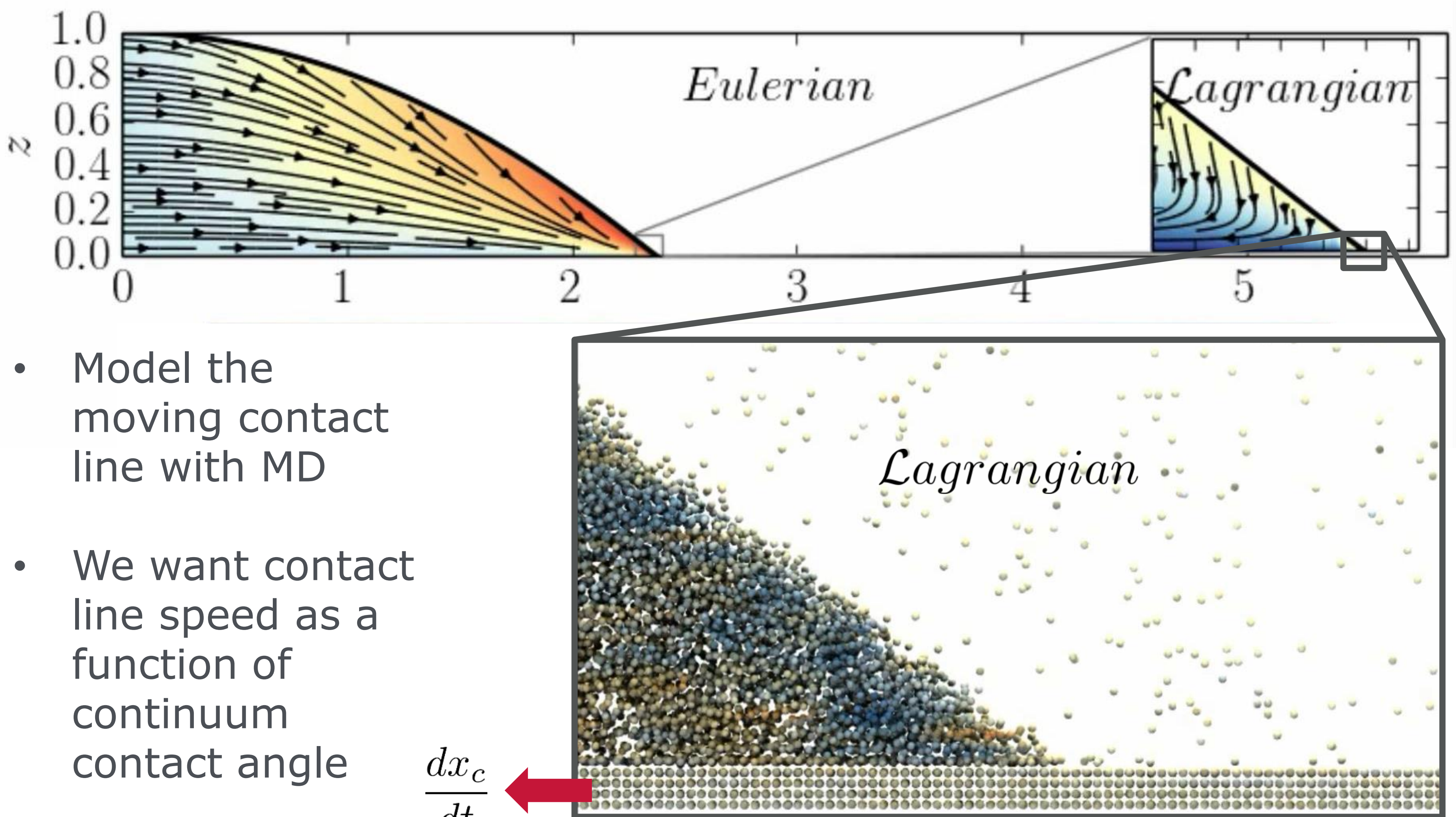
Coupled Droplet Spreading and MD



- Model the moving contact line with MD

- We want contact line speed as a function of continuum contact angle

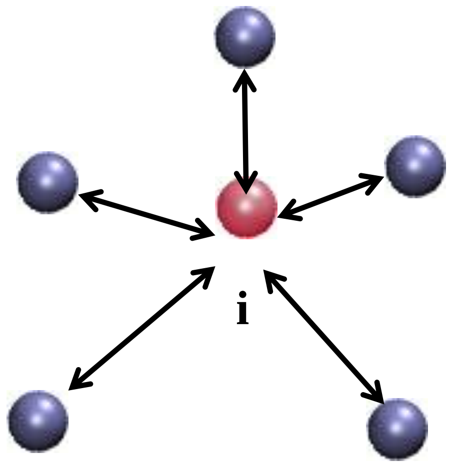
$$\frac{dx_c}{dt}$$

Molecular Dynamics

Discrete molecules in continuous space

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

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



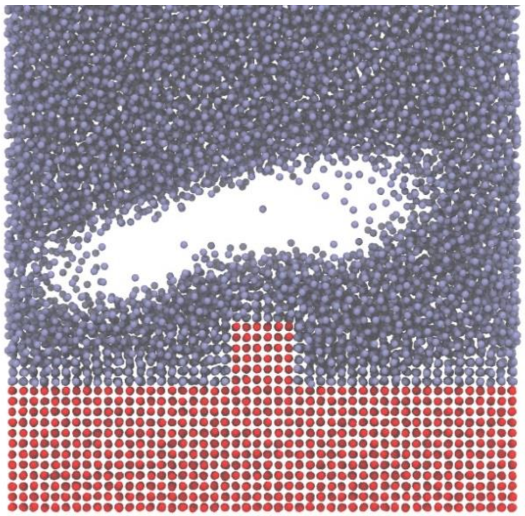
Acceleration obtained from forces

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

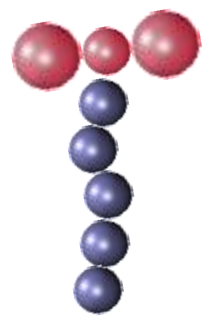
$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i \neq j}^{N} \boldsymbol{f}_{ij}$$

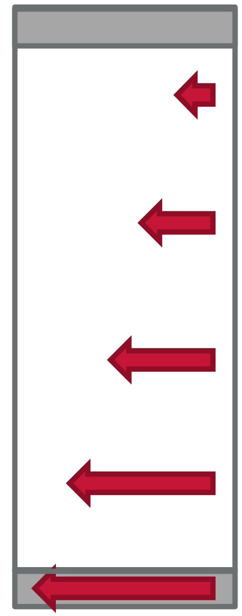
$$\Phi(r_{ij}) = 4\epsilon \left[\left(\frac{\ell}{r_{ij}} \right)^{12} - \left(\frac{\ell}{r_{ij}} \right)^{6} \right]$$

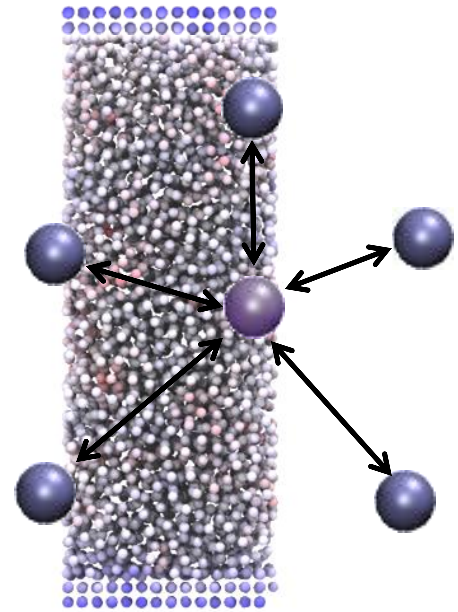
Molecular Dynamics

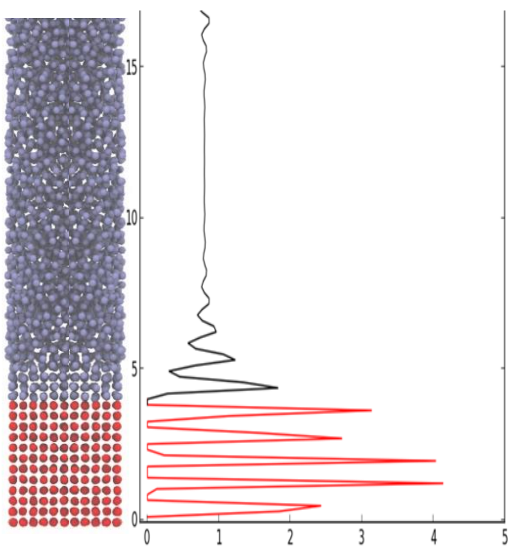


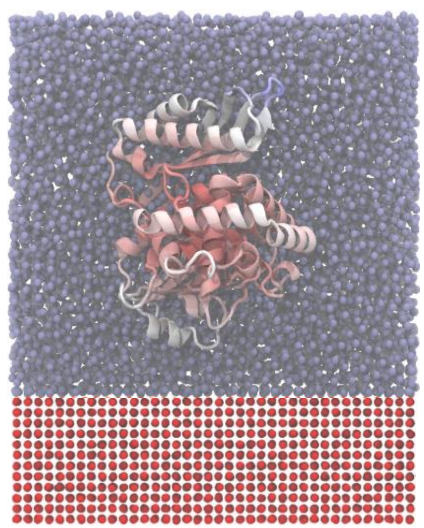
Superspreading Surfactant, e.g. Silwet-L77





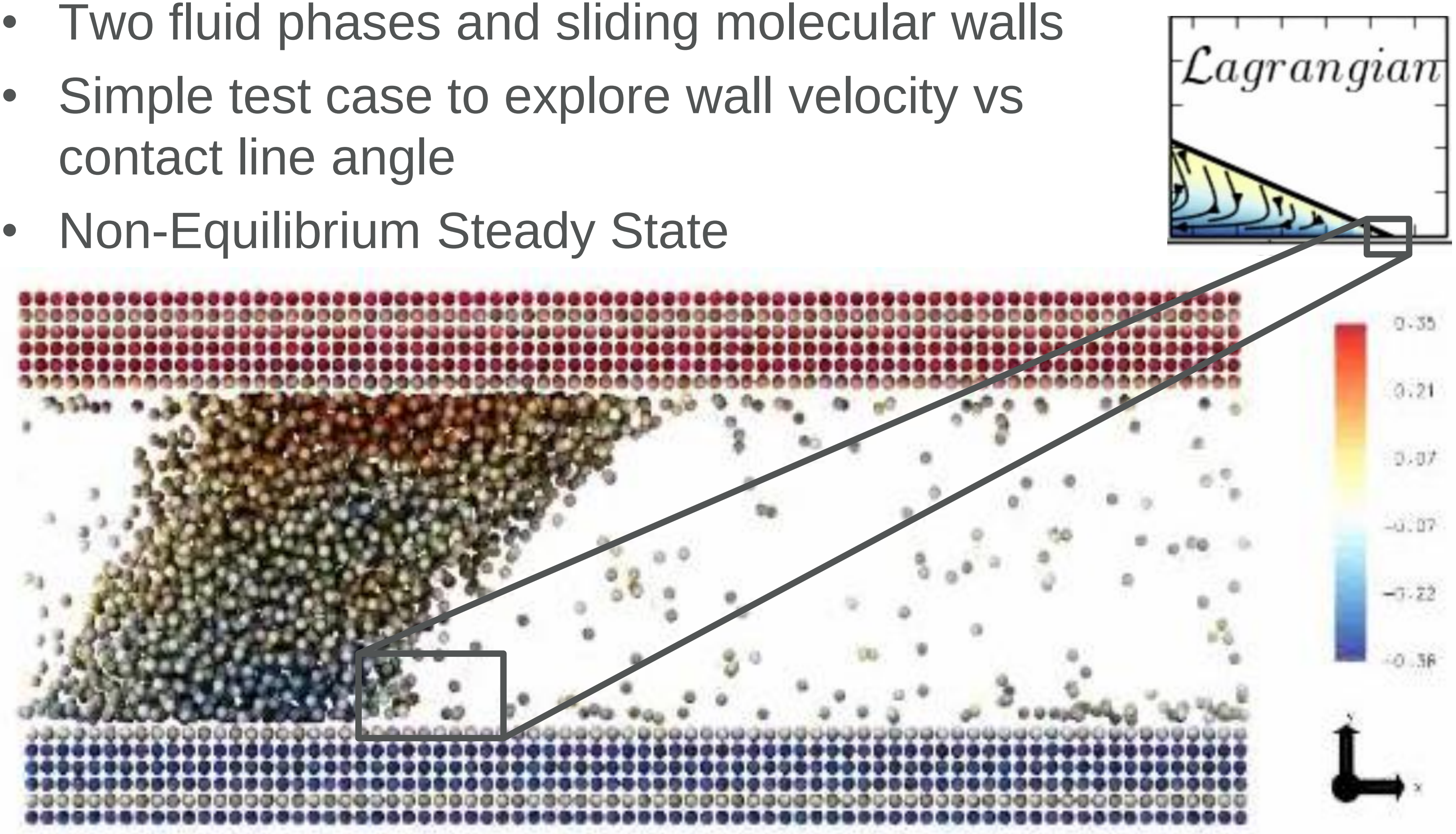






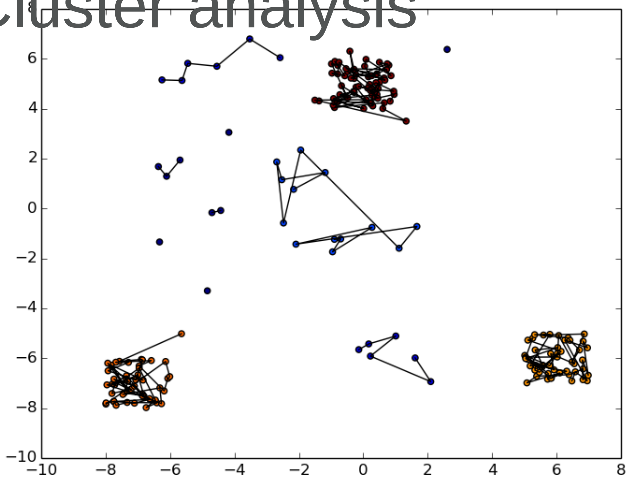
Two phase version closer to experimental reality

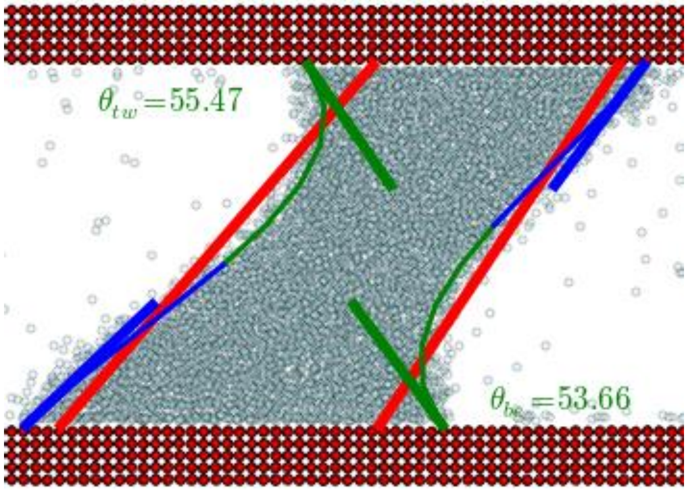
- Two fluid phases and sliding molecular walls
- Simple test case to explore wall velocity vs contact line angle
- Non-Equilibrium Steady State



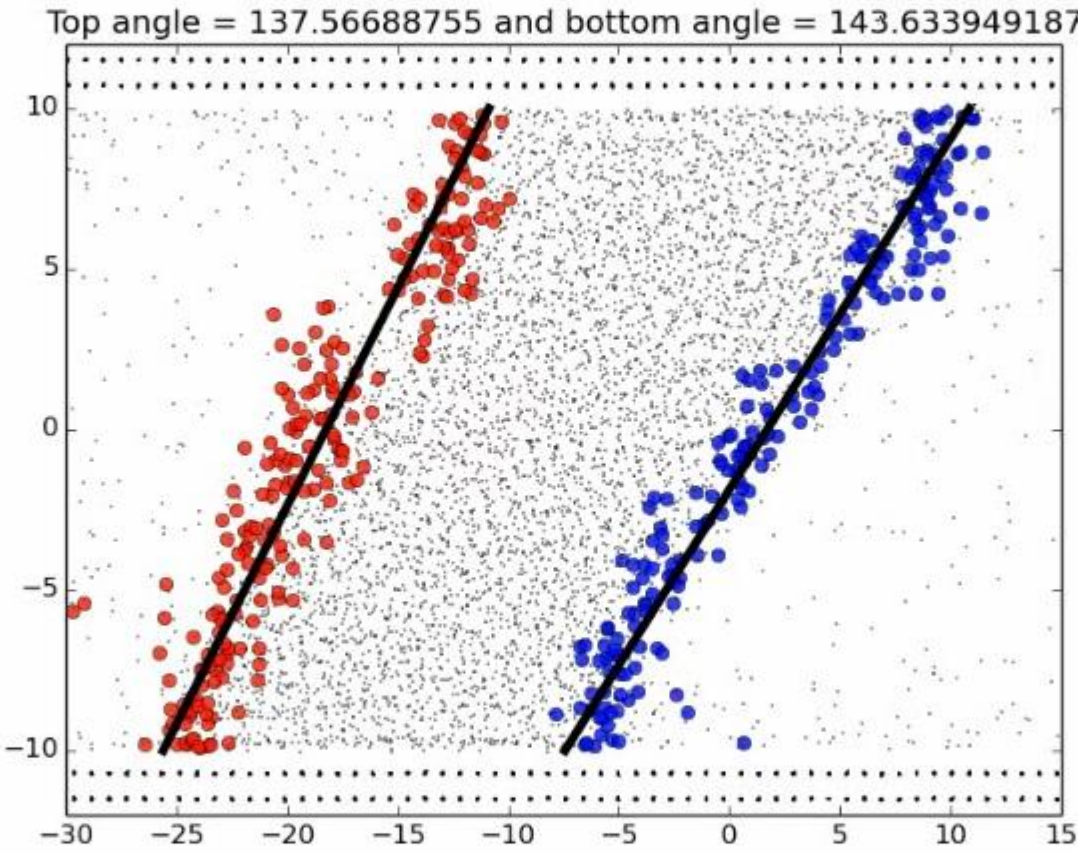
Cluster analysis and surface fitting

- Cluster analysis



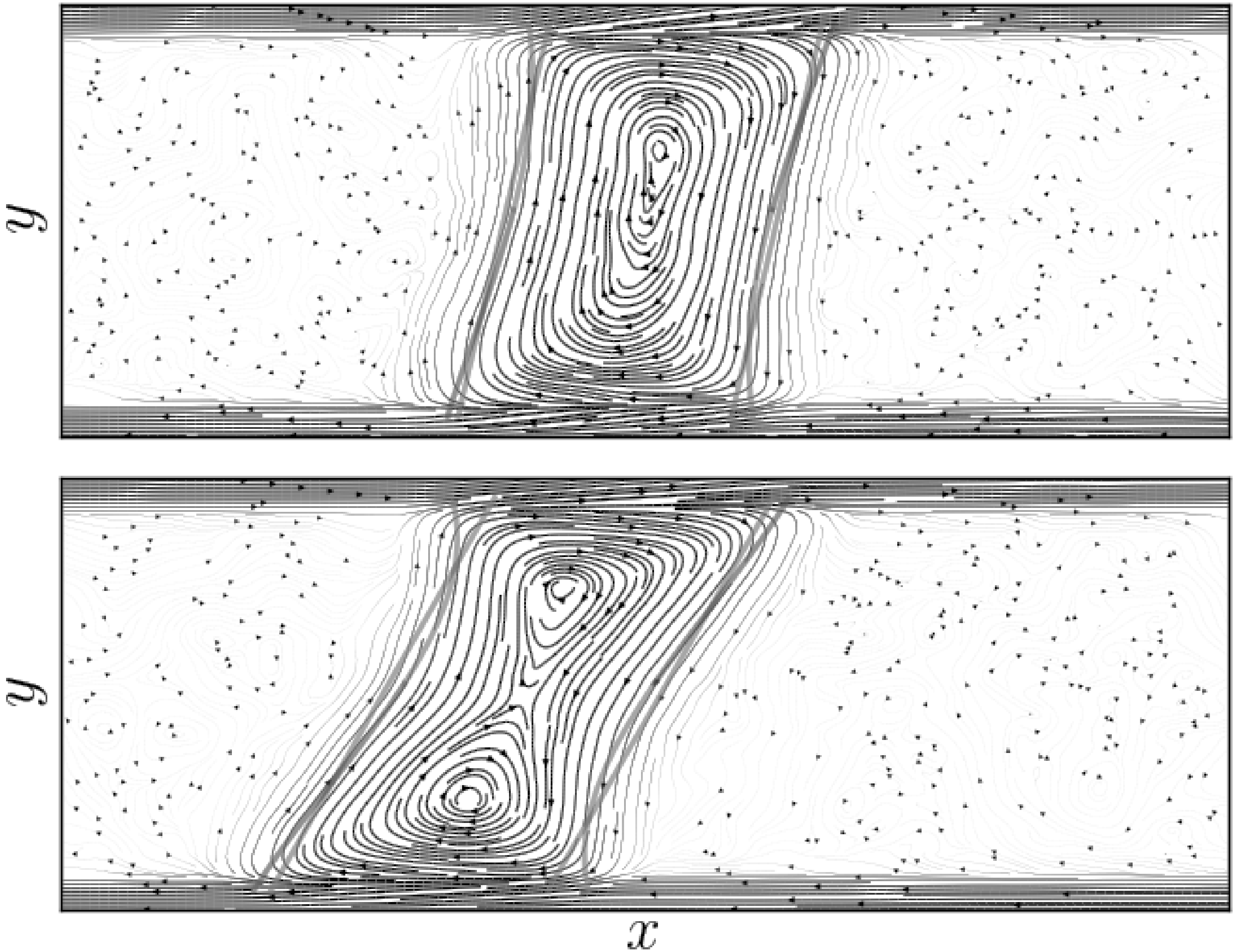


- Finding the fluid-liquid interface



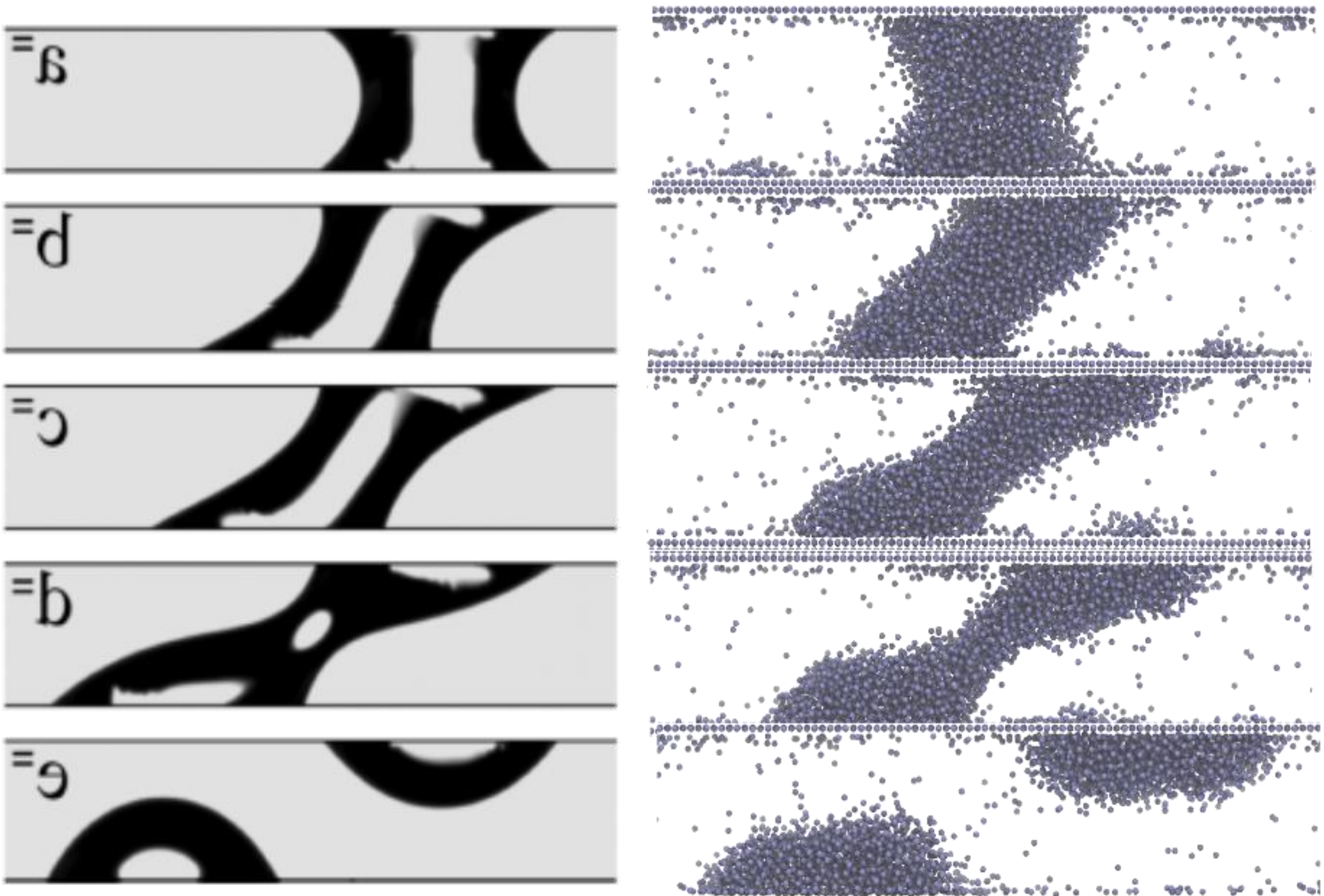
Linear, Advancing, Receding

Streamlines

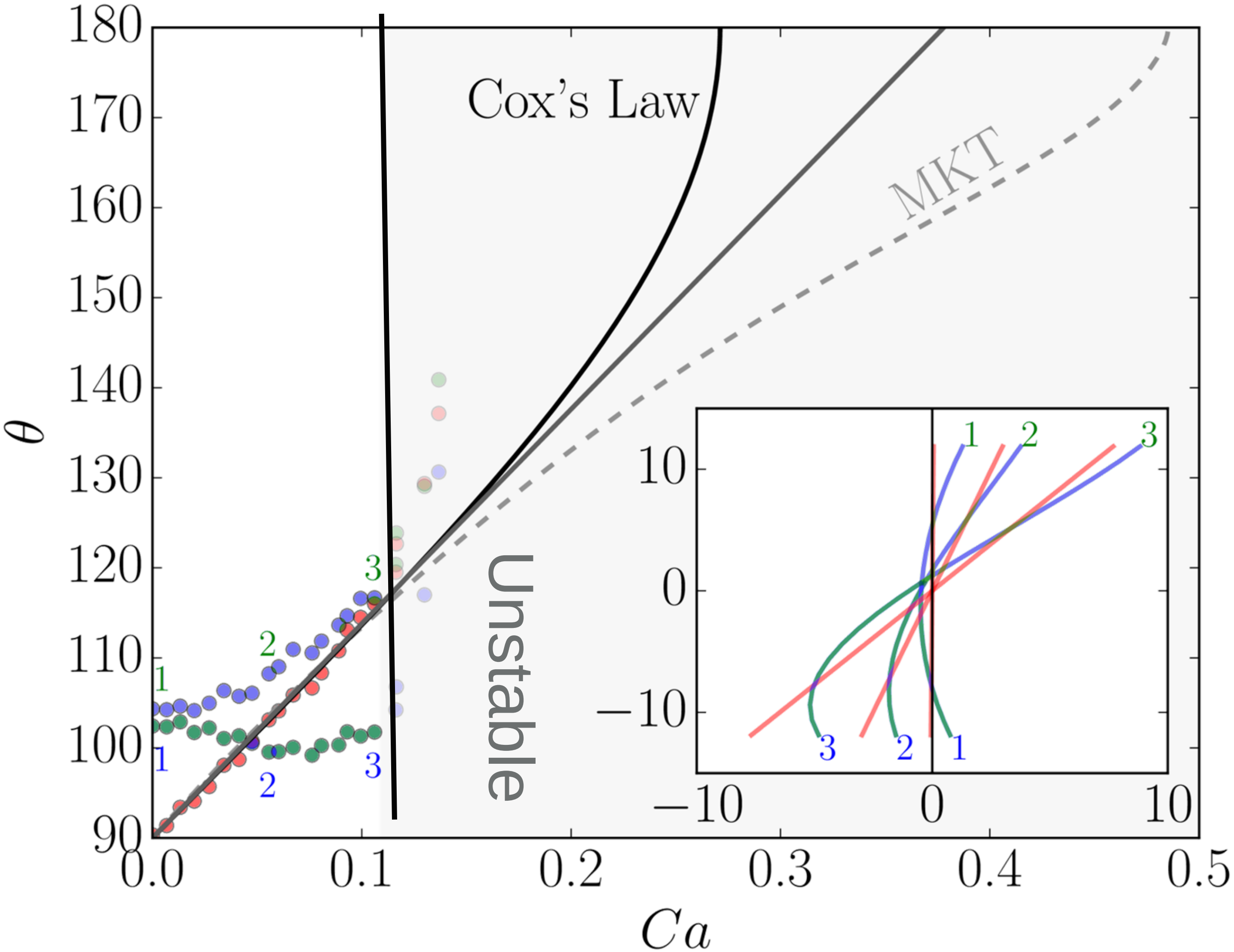


Droplet Breakdown

L. Wang, T. J. McCarthy (2013) Shear Distortion and Failure of Capillary Bridges. Wetting Information Beyond Contact Angle Analysis Langmuir 29, 7776–7781



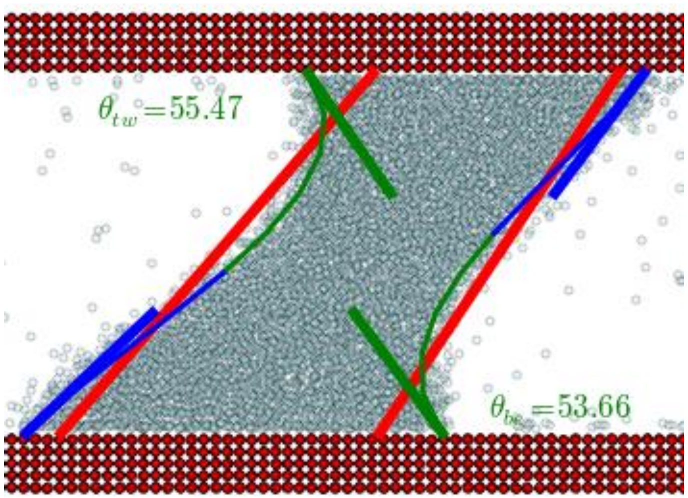
Contact angles vs sliding velocity

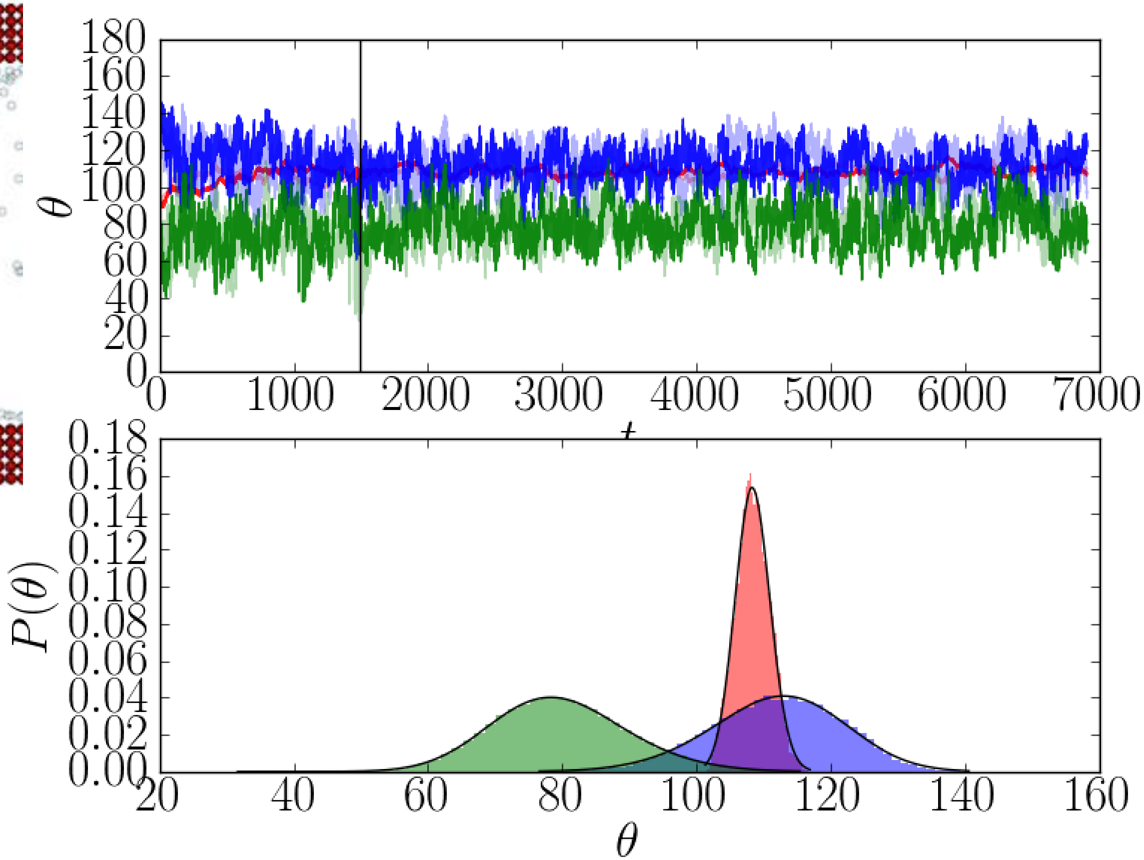


- Linear
- Advancing
- Receding

Time Evolution of Contact Angle

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



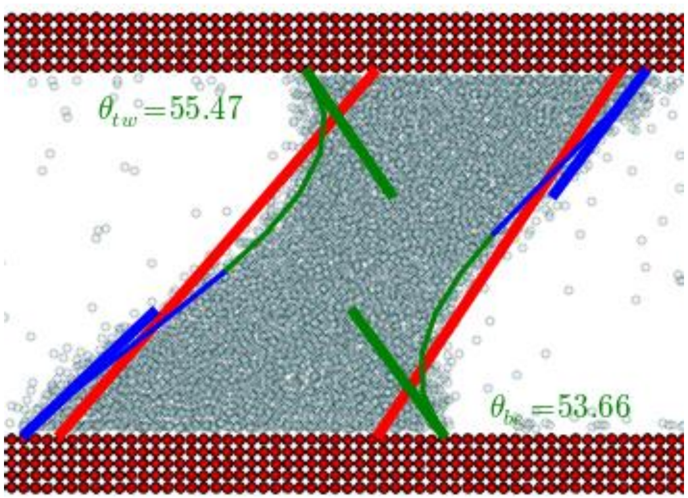


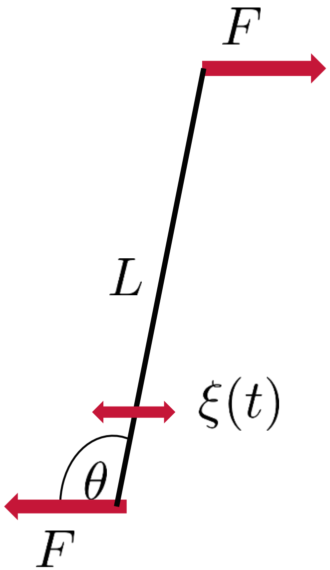
- Probability density function of angle shows range of micro-scale behaviour

- Linear, Advancing and Receding angles

Building this into the Continuum Model

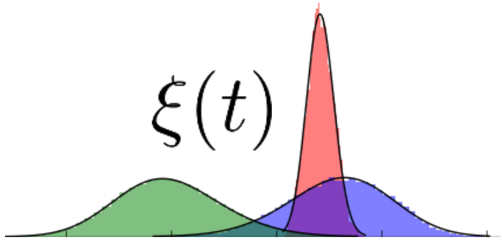
- Model the movement of the contact line as a torsional





string mass system + a random noise term

$$I\ddot{\theta} + \Gamma\dot{\theta} + k\theta - \xi = \mathcal{T}$$



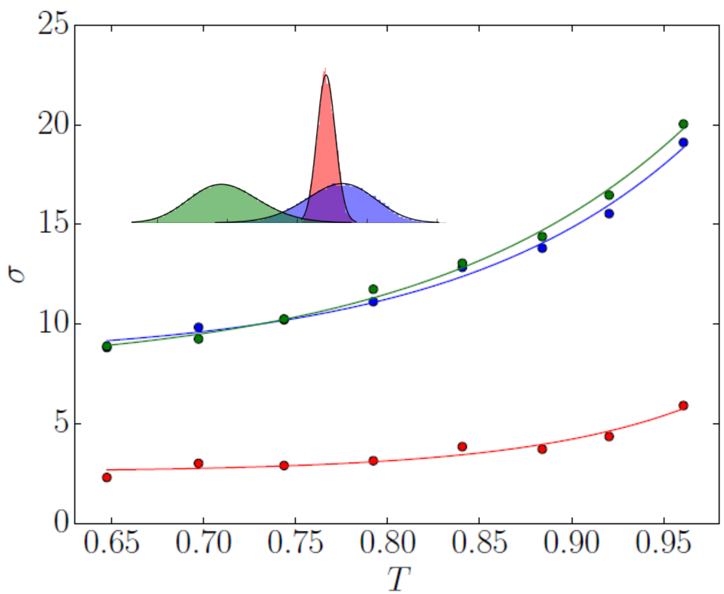
- Torque $\mathcal{T} = F \times L$ approximately equal to wall sliding

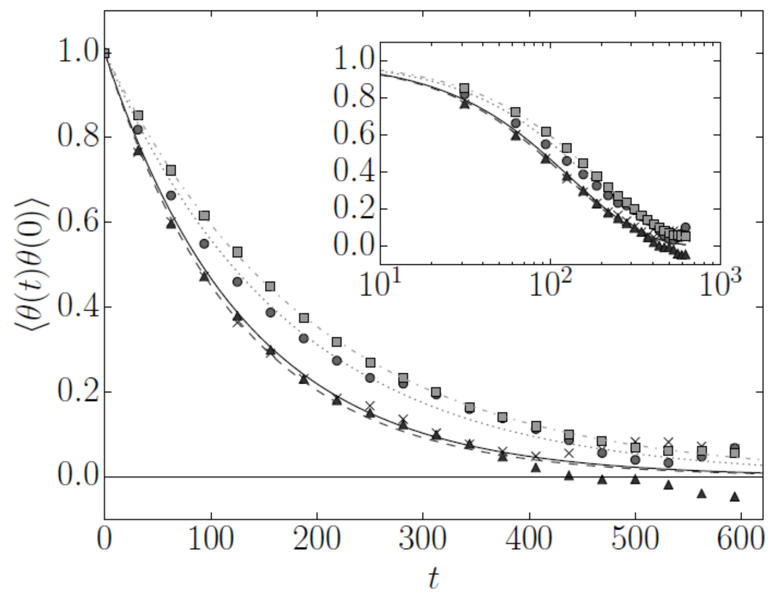
Building this into the Continuum Model

- In the limit overdamped limit we get the Langevin Equation

$$\dot{\theta} + \frac{k}{\Gamma}\left[\theta - \langle\theta\rangle\right] - \frac{1}{\Gamma}\xi(t) = 0 \text{ where } \langle \xi(t)\xi(t')\rangle = C\delta(t-t'),$$

- Coefficients parameterised using
  - Standard deviation - function of temperature but velocity independent
  - Autocorrelation - roughly velocity and temperature independent.





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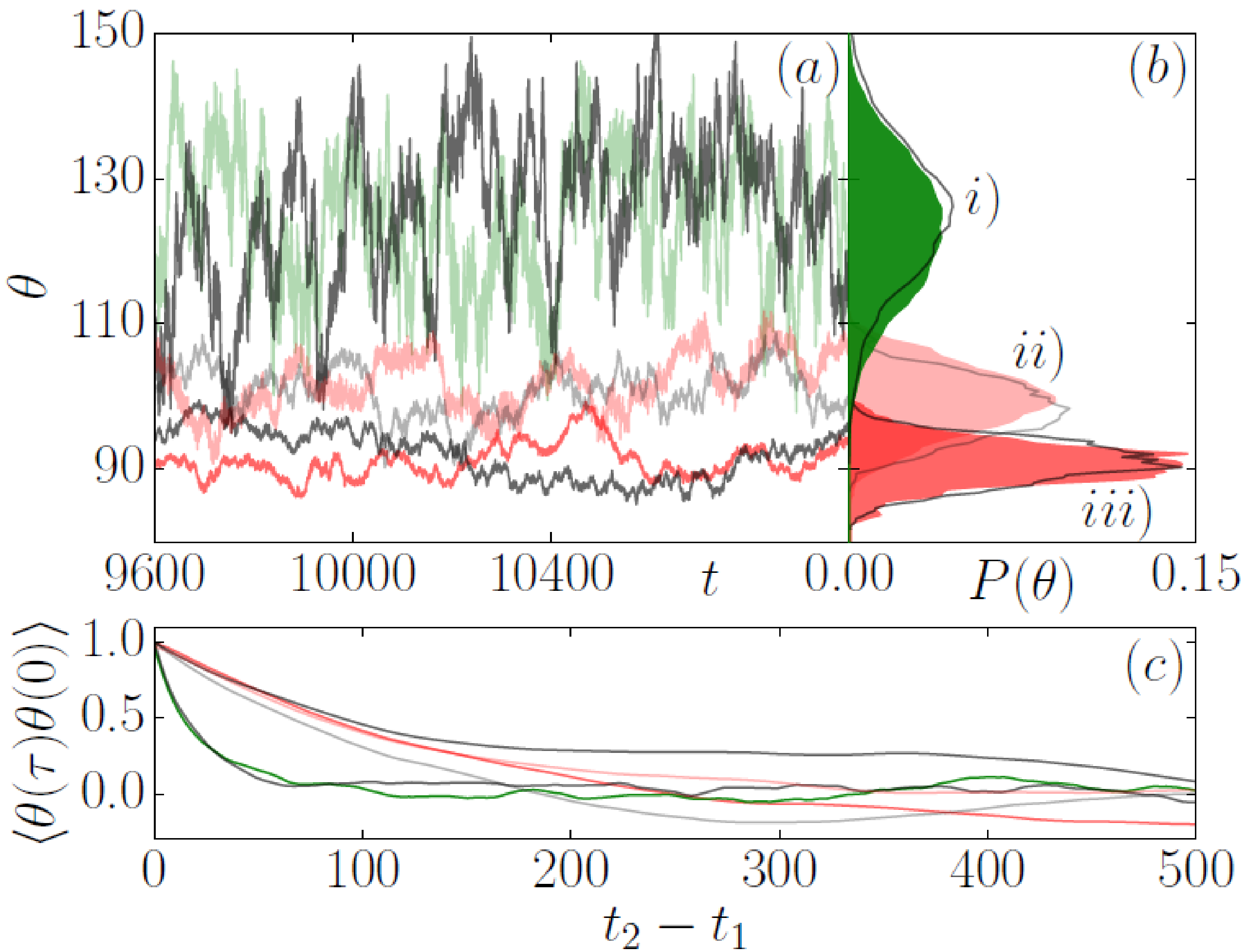
Results of the model



- *i)* Advancing angle for stationary case
- *ii)* Linear angle sliding at U=0.02
- *iii)* Linear angle sliding at U=0.0025
- Black lines Langevin model

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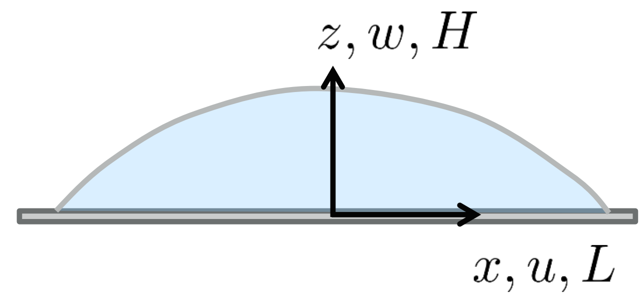

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- *Contact line evolution is modelled by an empirical law*

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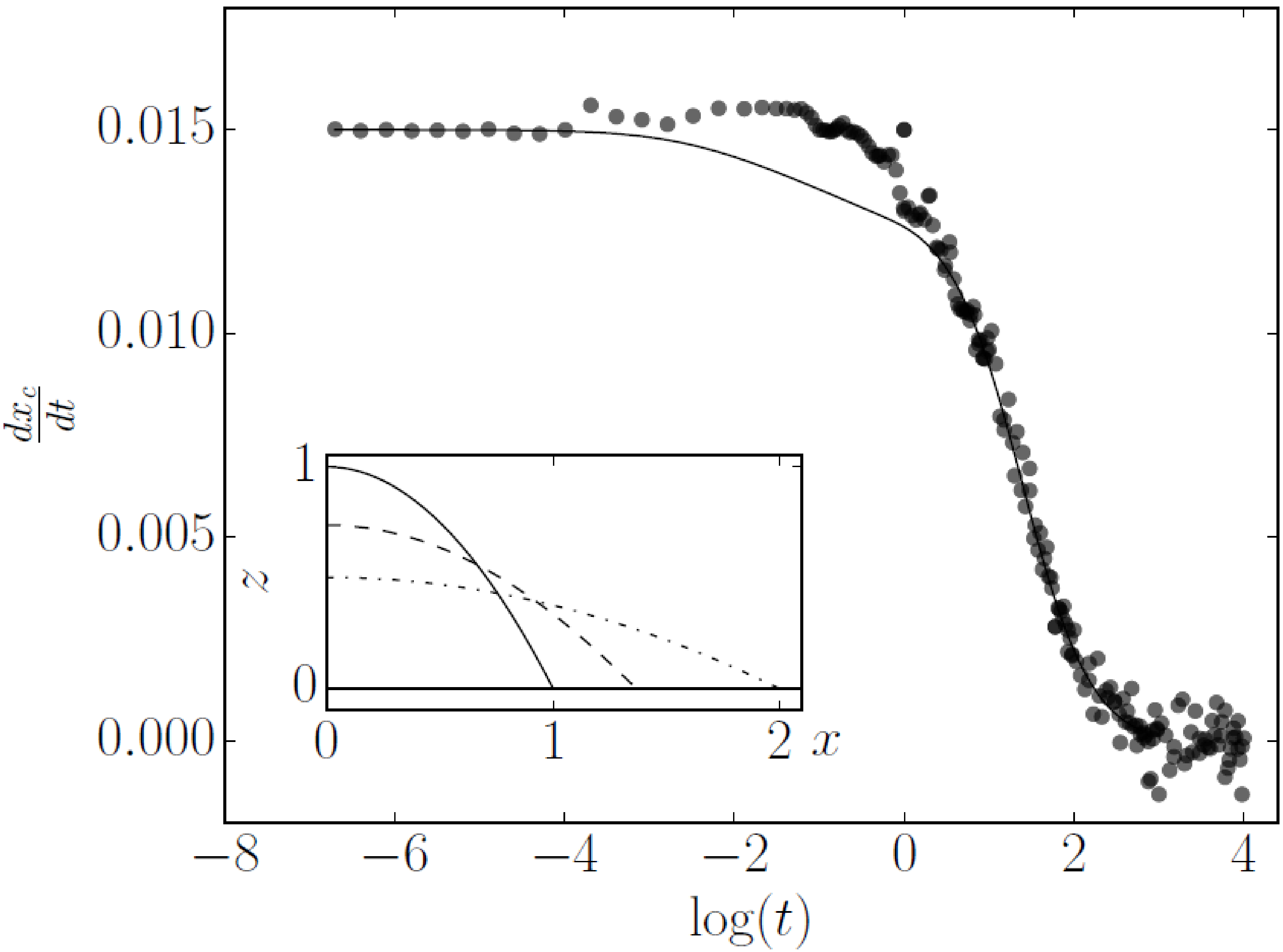
- *Evolution of contact line includes molecular fluctuations*

$$\theta^{t+1} = \theta^t - \frac{k\Delta t}{\Gamma}\left[\theta^t - \langle\theta\rangle\right] + \xi\frac{\sqrt{C\Delta t}}{\Gamma}$$

Molecular contact angle in continuum model



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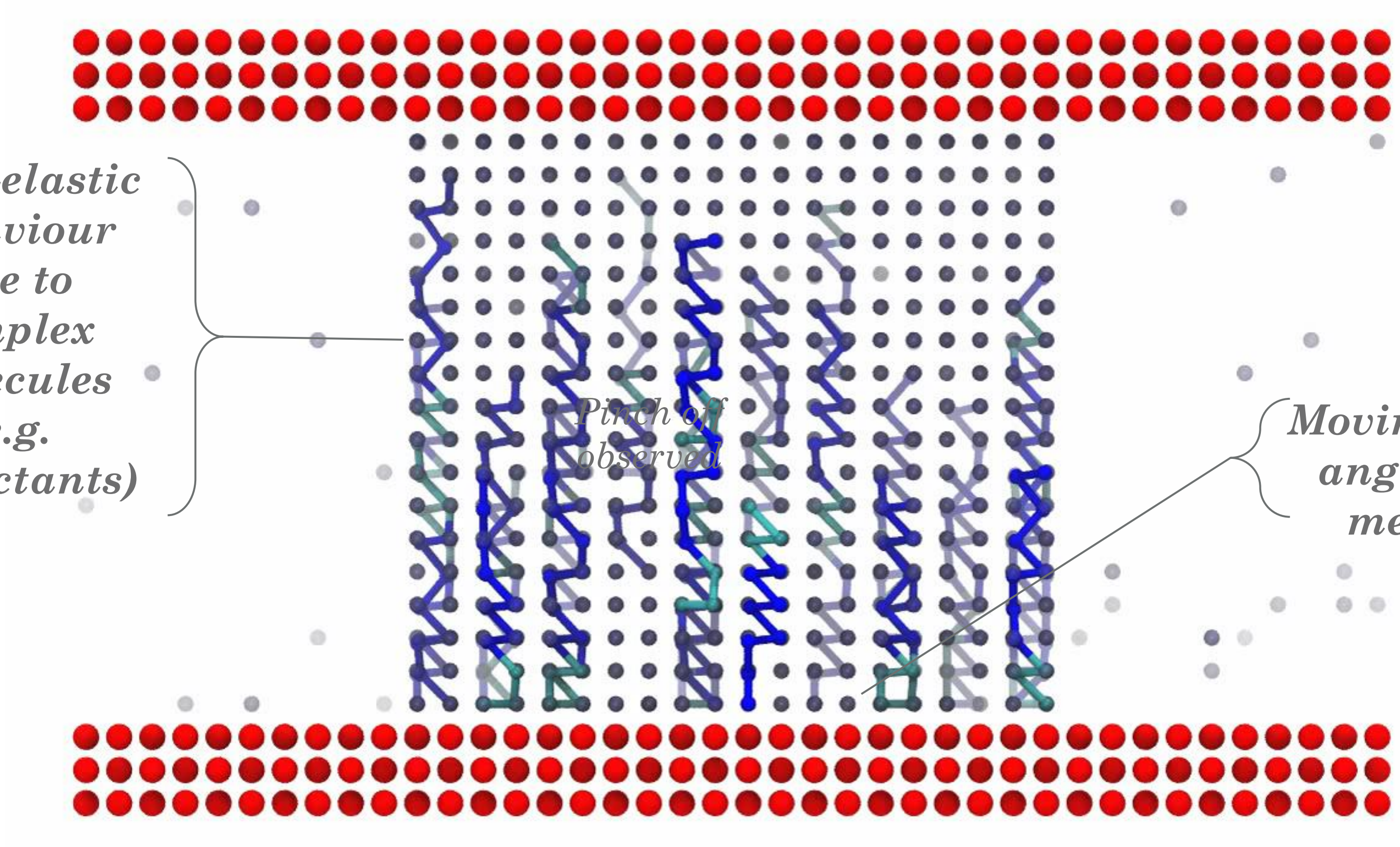
Application of this Work

Visco-elastic behaviour due to complex molecules (e.g. surfactants)



Moving contact angle can be measured

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Summary

- Molecular Dynamics (MD) is used to study the relationship between contact angle and wall sliding speed
- The mean contact angle and fluctuations are explored
- A Langevin model is be used to reproduce key MD detail
- Molecular detail can be incorporated into a CFD model using the Langevin equation, tuned using MD.