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A Decomposition of Droplet Simulation Using Molecular Dynamics

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Panos Theodorakis, Richard Craster and Omar Matar

11:20-11:40

18/09/19

Molecular Dynamics

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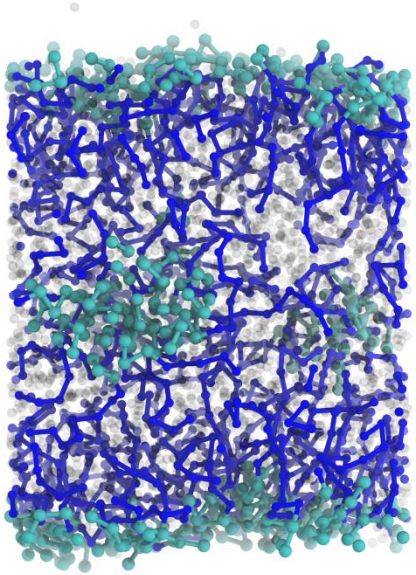

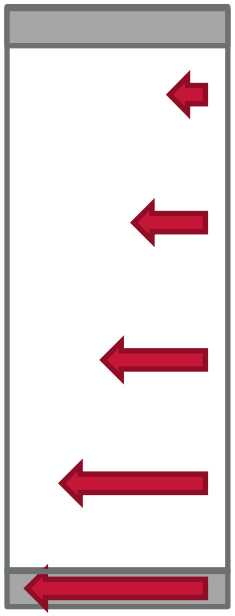

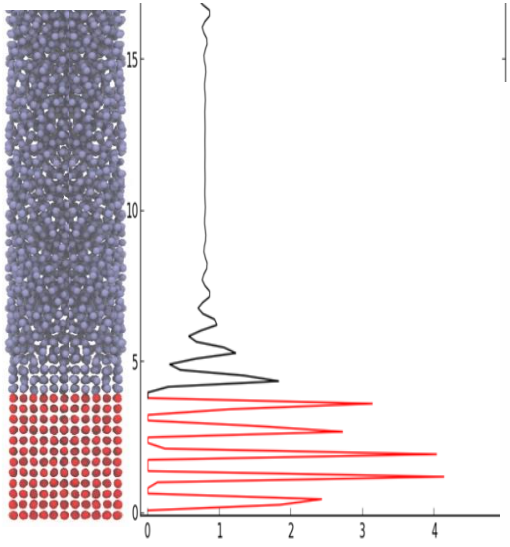

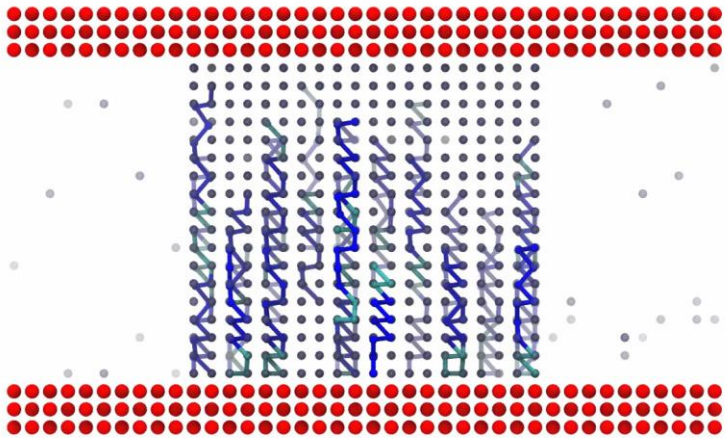

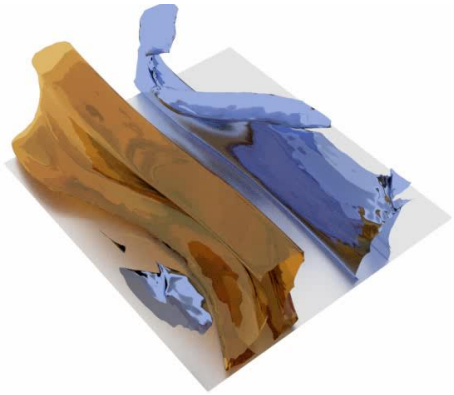

Molecular Dynamics

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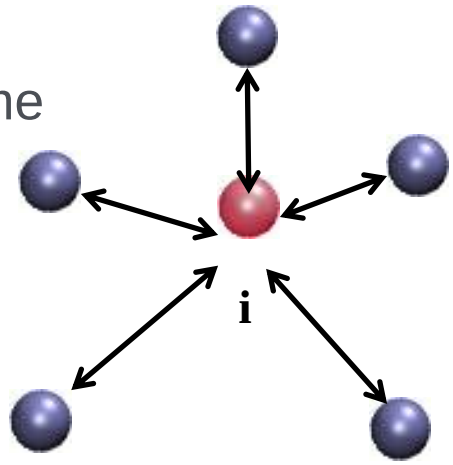
Discrete molecules in continuous space

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

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



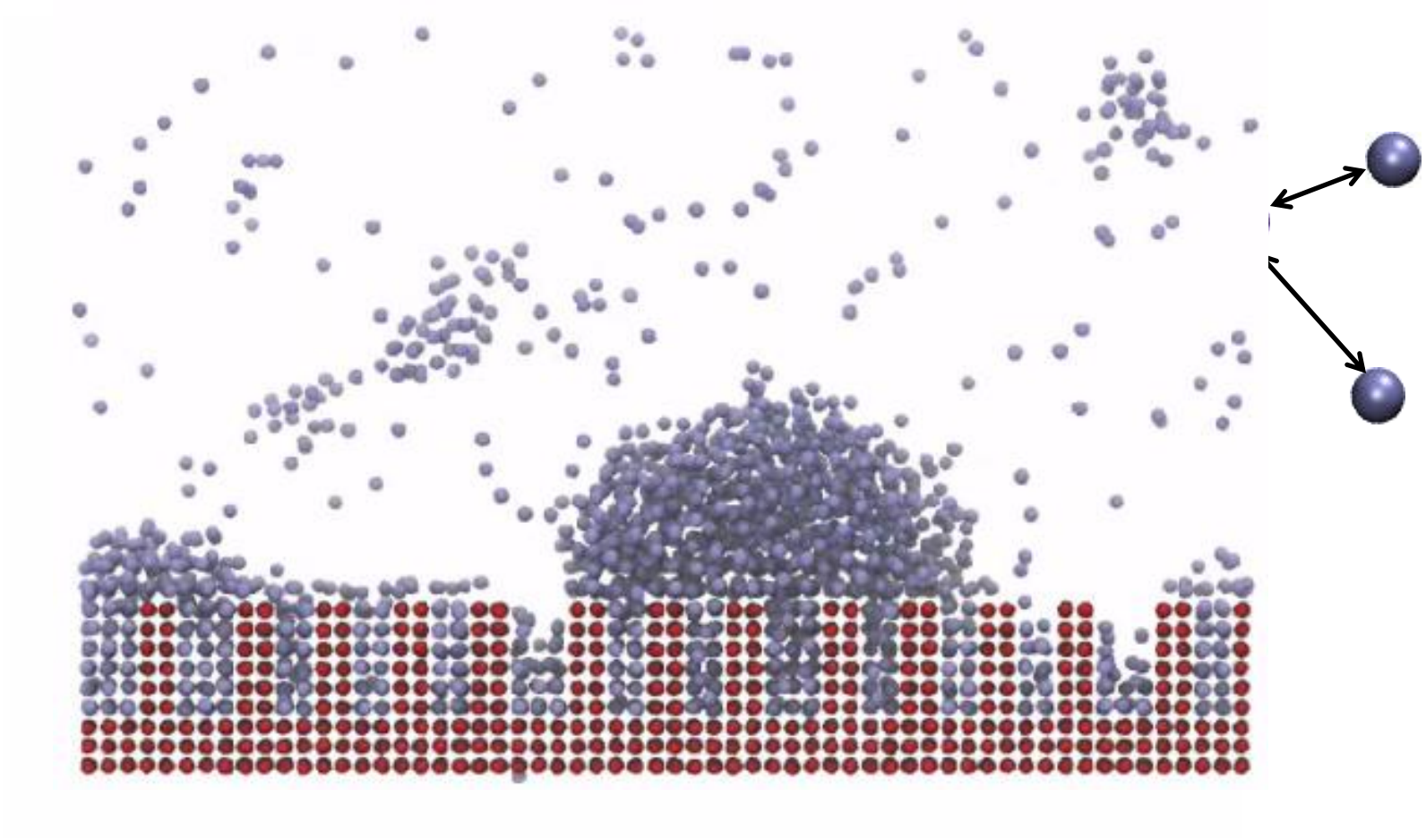
Acceleration obtained from forces

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

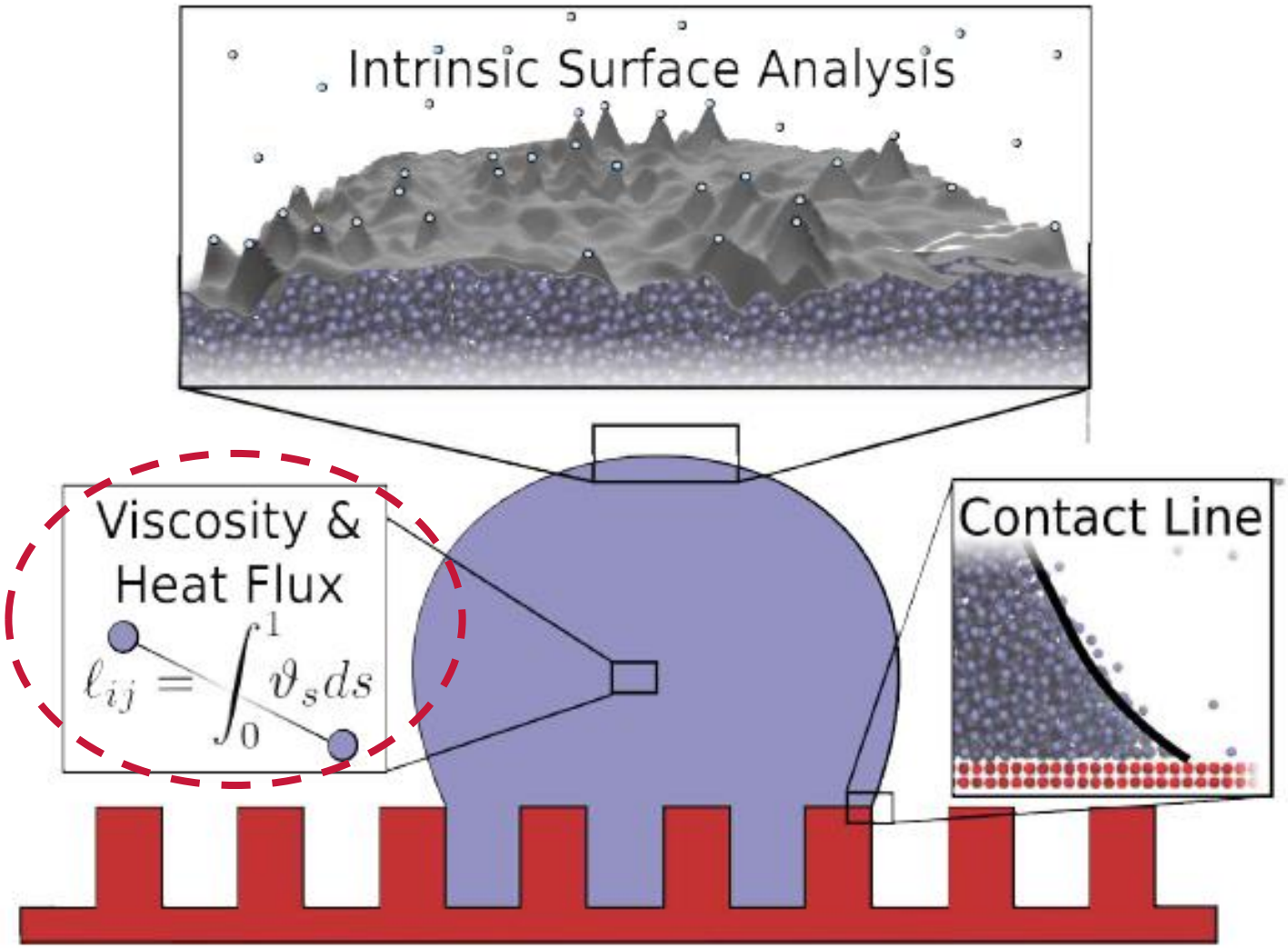
$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i \neq j}^{N} \boldsymbol{f}_{ij} = \sum_{i \neq j}^{N} \boldsymbol{\nabla} \Phi_{ij}$$

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

Molecular Dynamics



Overview


Intrinsic Surface Analysis
Viscosity &
Heat Flux
$\ell_{ij} = \int_0^1 \vartheta_s ds$
Contact Line

Linking Molecular and Continuum

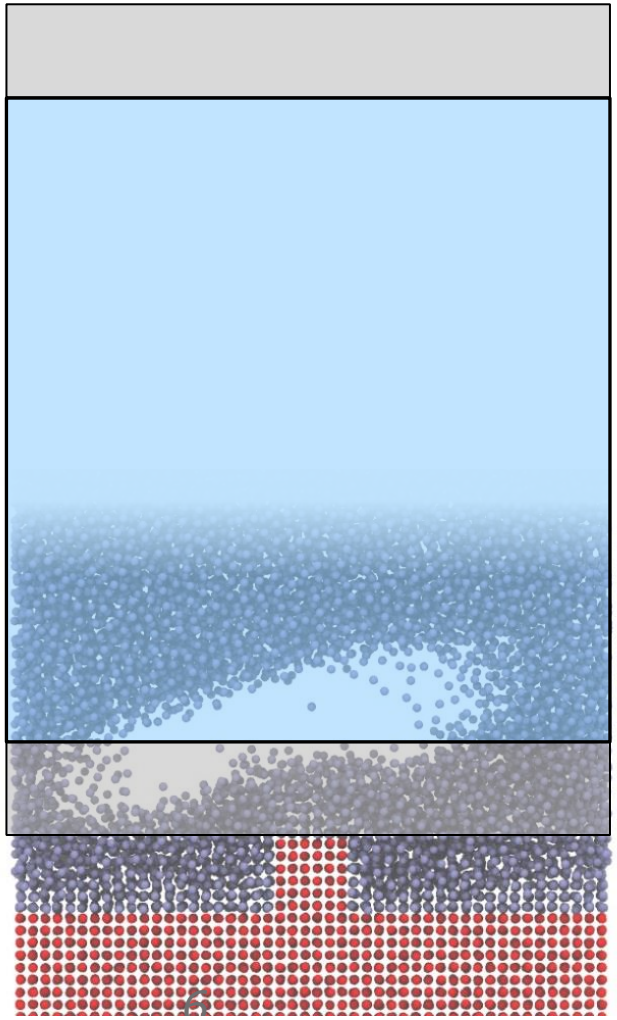
- Assumes continuous fields

$$\frac{\partial}{\partial t}\rho \boldsymbol{u} + \boldsymbol{\nabla} \cdot \rho \boldsymbol{u}\boldsymbol{u} = \boldsymbol{\nabla} \cdot \boldsymbol{\Pi} \quad \text{and } \mu, \lambda, \ldots$$

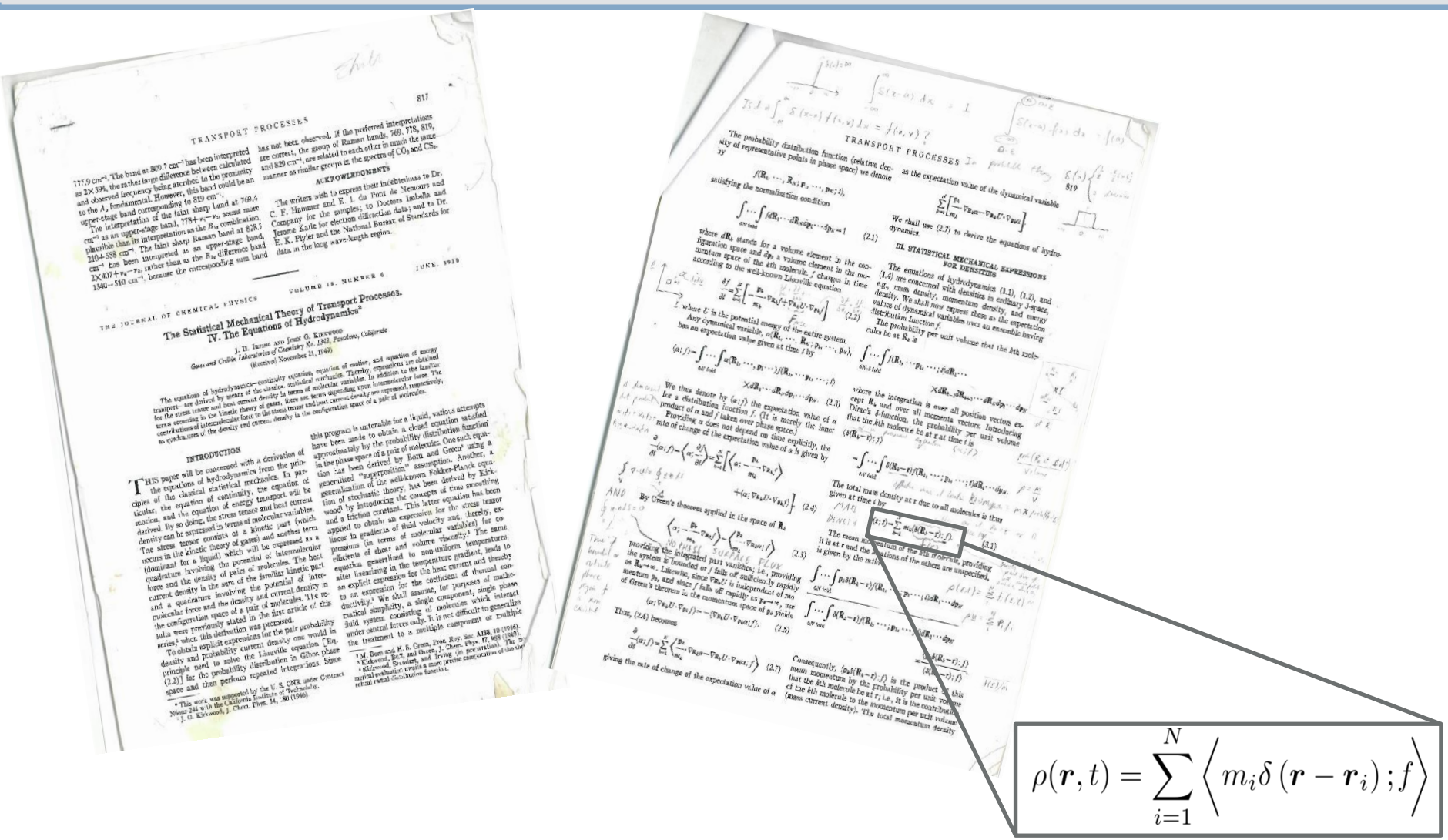
How do we get continuum values from the molecular system?

- Discrete molecules

$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i \text{ for all i in N}$$



Irving and Kirkwood (1950)



Irving and Kirkwood (1950)

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*Continuum density field valid at any point, **r**, in space*

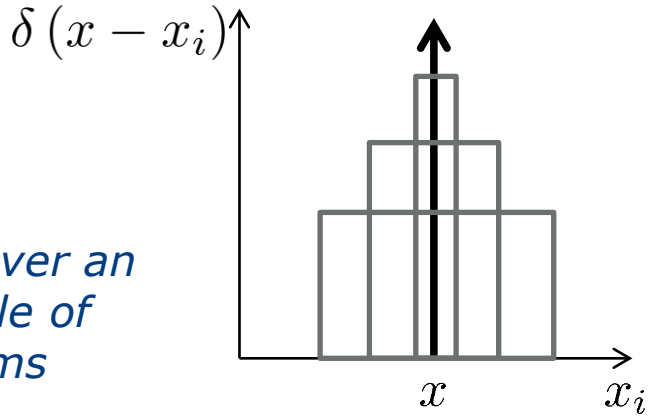
Mass of each molecule

Average over an ensemble of systems

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

Sum over all molecules

*Delta function is only non-zero if molecule i's position $\boldsymbol{r}_i$ is exactly at **r***



The Dirac delta infinitely high, infinitely thin peak. Formally equivalent to the continuum differential formulation
BUT
No molecule is ever exactly at a point

The Control Volume (Weak) Form

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- The “weak formulation” expressed the equations in integrated form

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

- Integrating the Dirac delta function exactly provides a combination of Heaviside functions
  - » Instantaneous description
  - » Direct link between macro and micro description
  - » Exactly conservative

The Control Volume Functional

- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

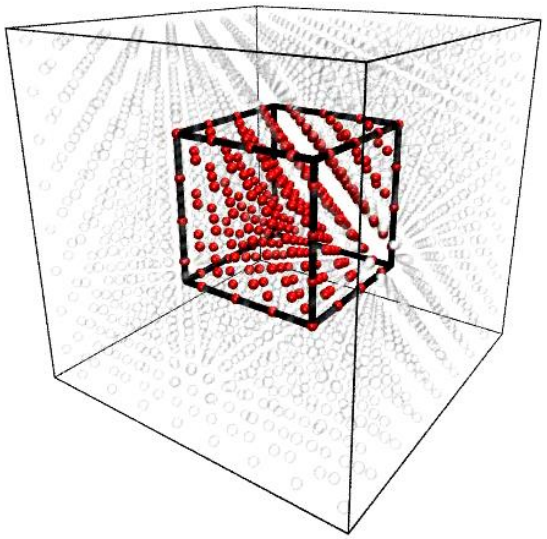
$$= \left[H(x^+ - x_i) - H(x^- - x_i)\right]$$

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

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

- In words

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



Derivative yields surface fluxes (Method of Planes)

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- Taking the derivative gives flux over the surface of the cube

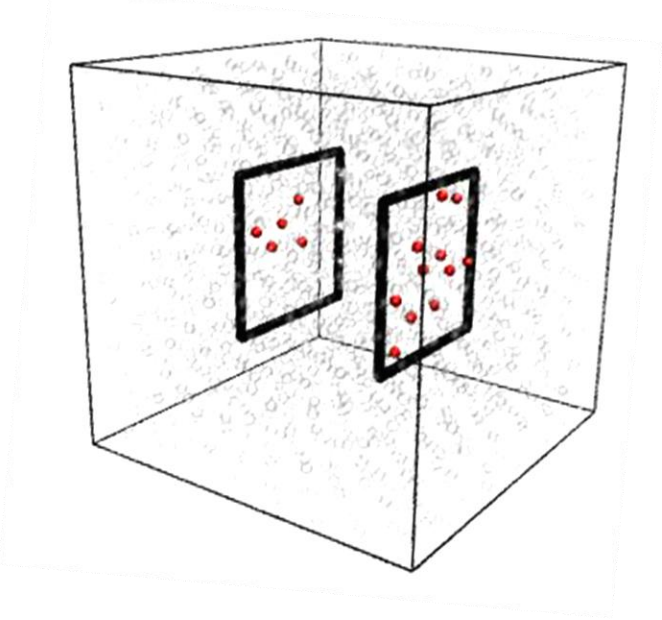
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

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



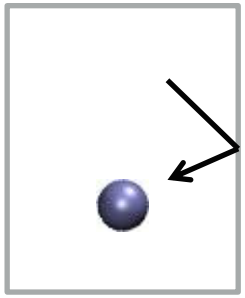
Pressure (Stress) in an MD Simulation

- Pressure definition in a dense molecular system
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

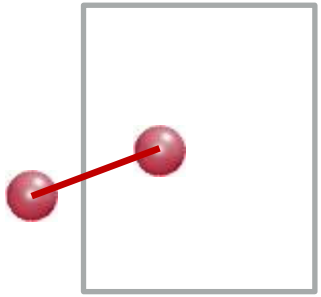
$$\Pi_{xy} = \underbrace{\sum_{i=1}^{N} \left\langle m_i c_{xi} c_{yi} dS_{ix} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left\langle f_{xij} r_{yij} dS_{ijx} \right\rangle}_{\text{Configurational}}$$

Kinetic theory part

Momentum due to average of molecules crossing a plane and returning



$$\boldsymbol{c}_i = \dot{\boldsymbol{r}}_i - \boldsymbol{u}$$



Configurational part

Inter-molecular bonds act like the stress in a stretched spring

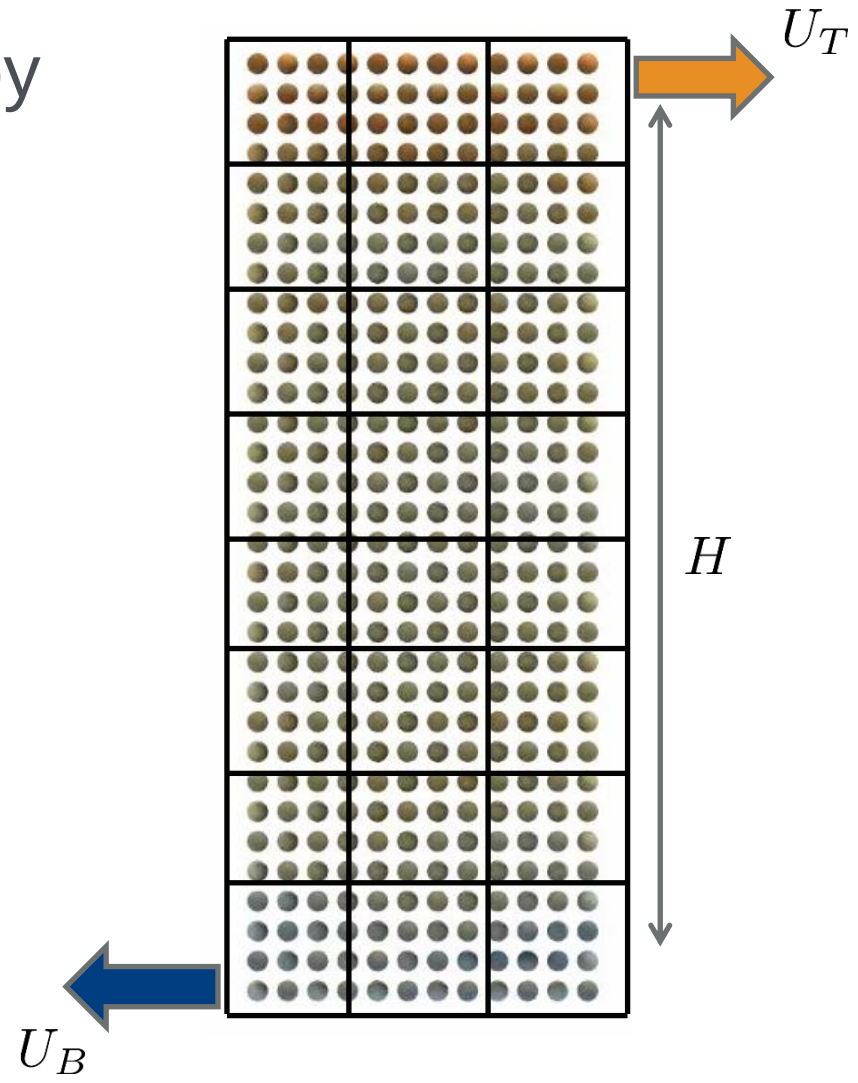
Newton's Law of Viscosity

- Shear flow Π_{xy} driven by sliding walls

$$\frac{\partial u}{\partial y} \approx \frac{U_T - U_B}{H}$$

- Viscosity from stress divided by strain

$$\mu = -\frac{\Pi_{xy}}{\partial u / \partial y}$$



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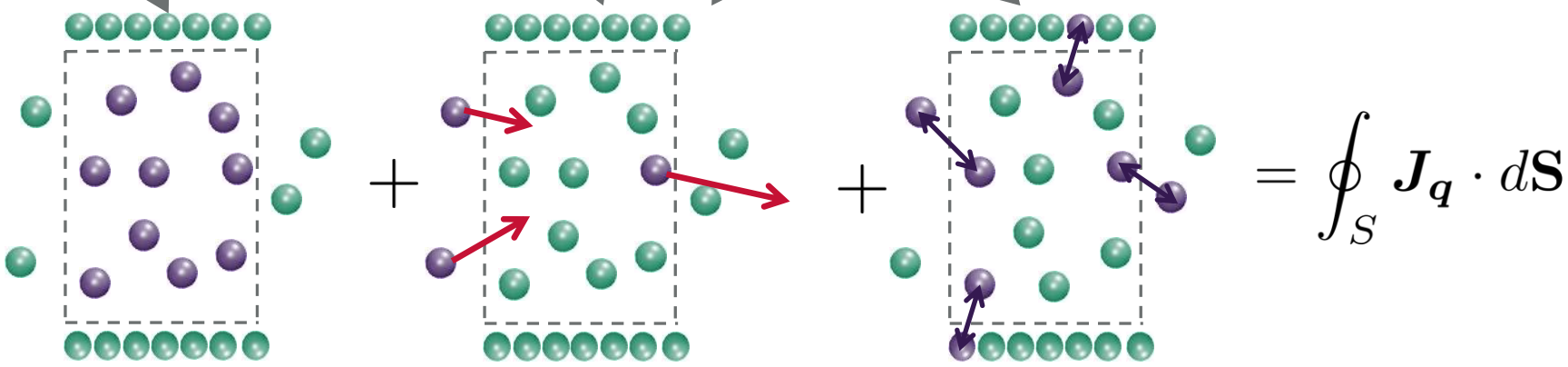
Heat Flux in an MD Simulation

- Heat flux is left over after counting all other terms

$$\underbrace{\int_V \frac{\partial}{\partial t}\rho\mathcal{E}dV}_{Unsteady} + \oint_S \Big[\underbrace{\rho\mathcal{E}\boldsymbol{u}}_{\text{Advection}} + \underbrace{\boldsymbol{\Pi}\cdot\boldsymbol{u}}_{\text{Stress Work}}\Big]\cdot d\mathbf{S} = -\underbrace{\oint_S \boldsymbol{J_q}\cdot d\mathbf{S}}_{\text{Heat Flux}}$$



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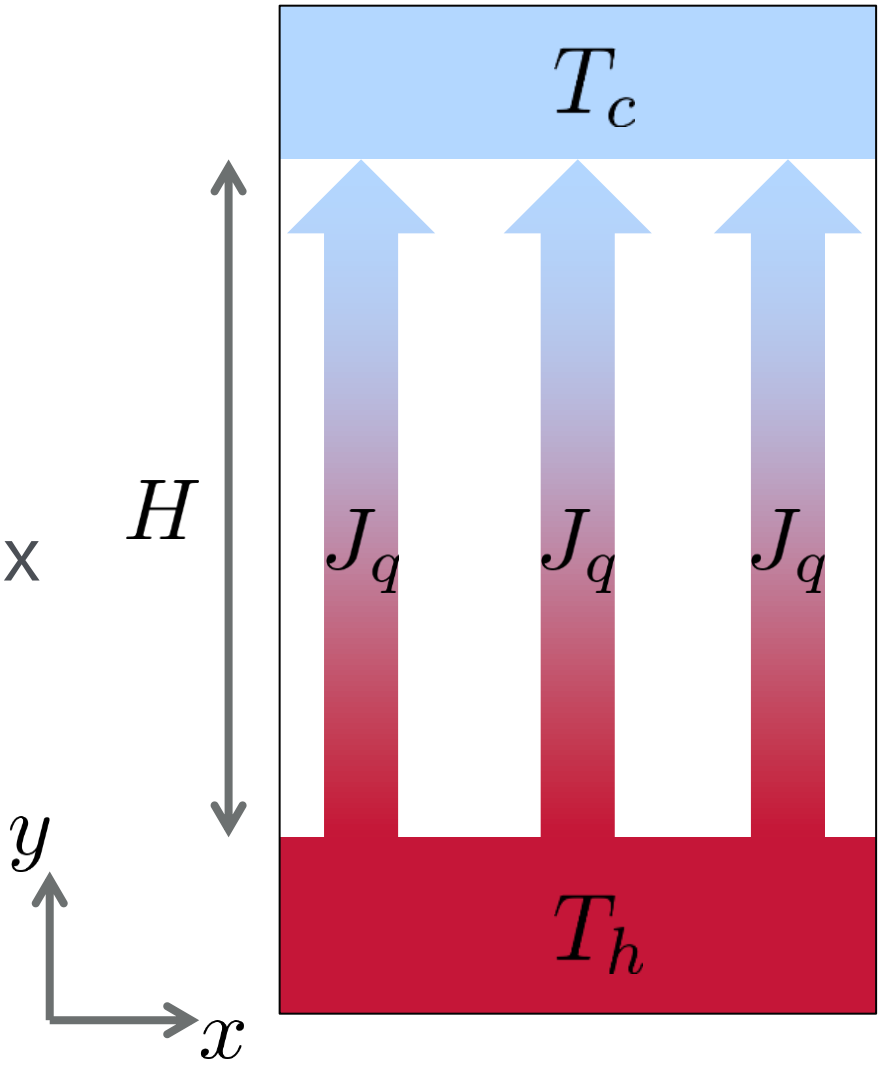
Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

$$\frac{\partial T}{\partial y} \approx \frac{T_c - T_h}{H}$$

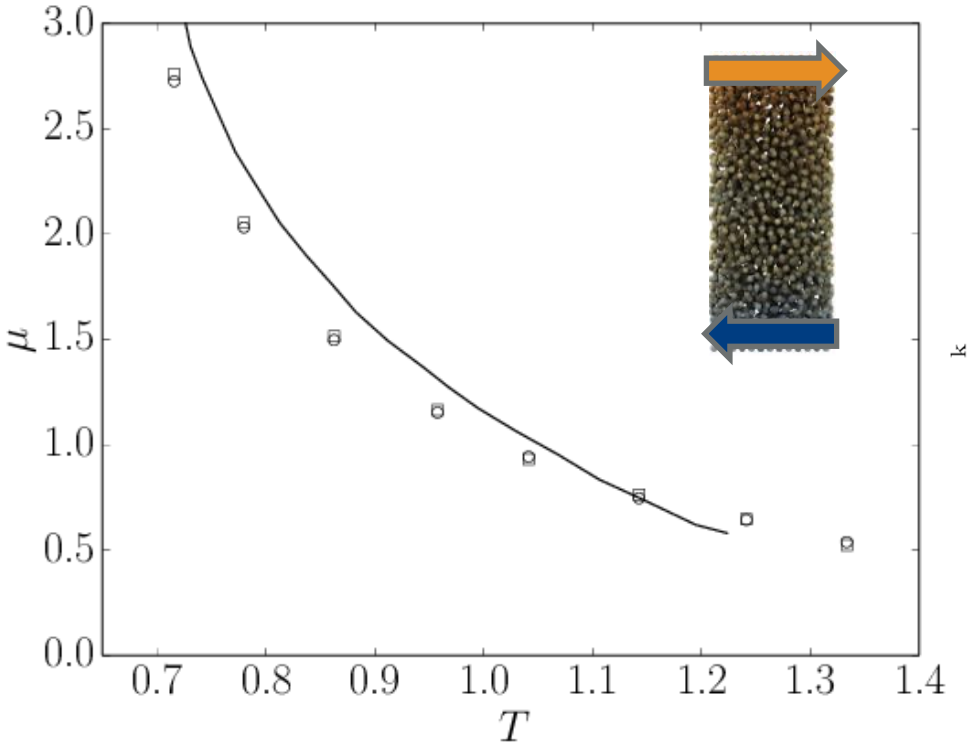
- Coefficient from heat flux divided by temperature gradient

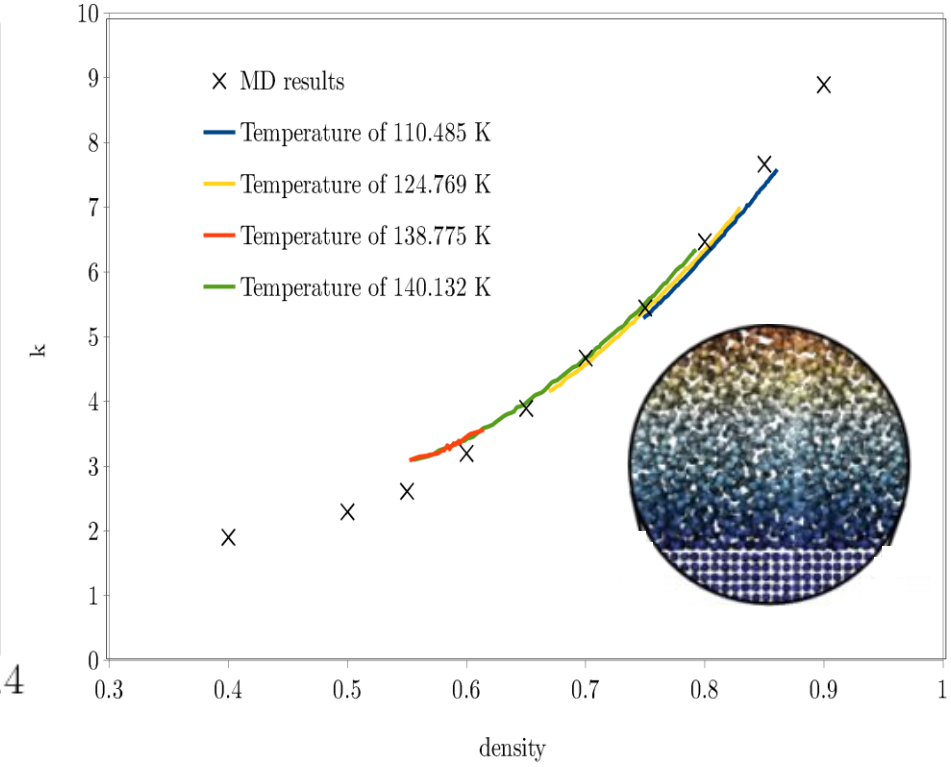
$$\lambda = -\frac{J_q}{\partial T / \partial y}$$



Validation Against Experiments

- Outputs of the simulation match experiments, shown here for liquid Argon





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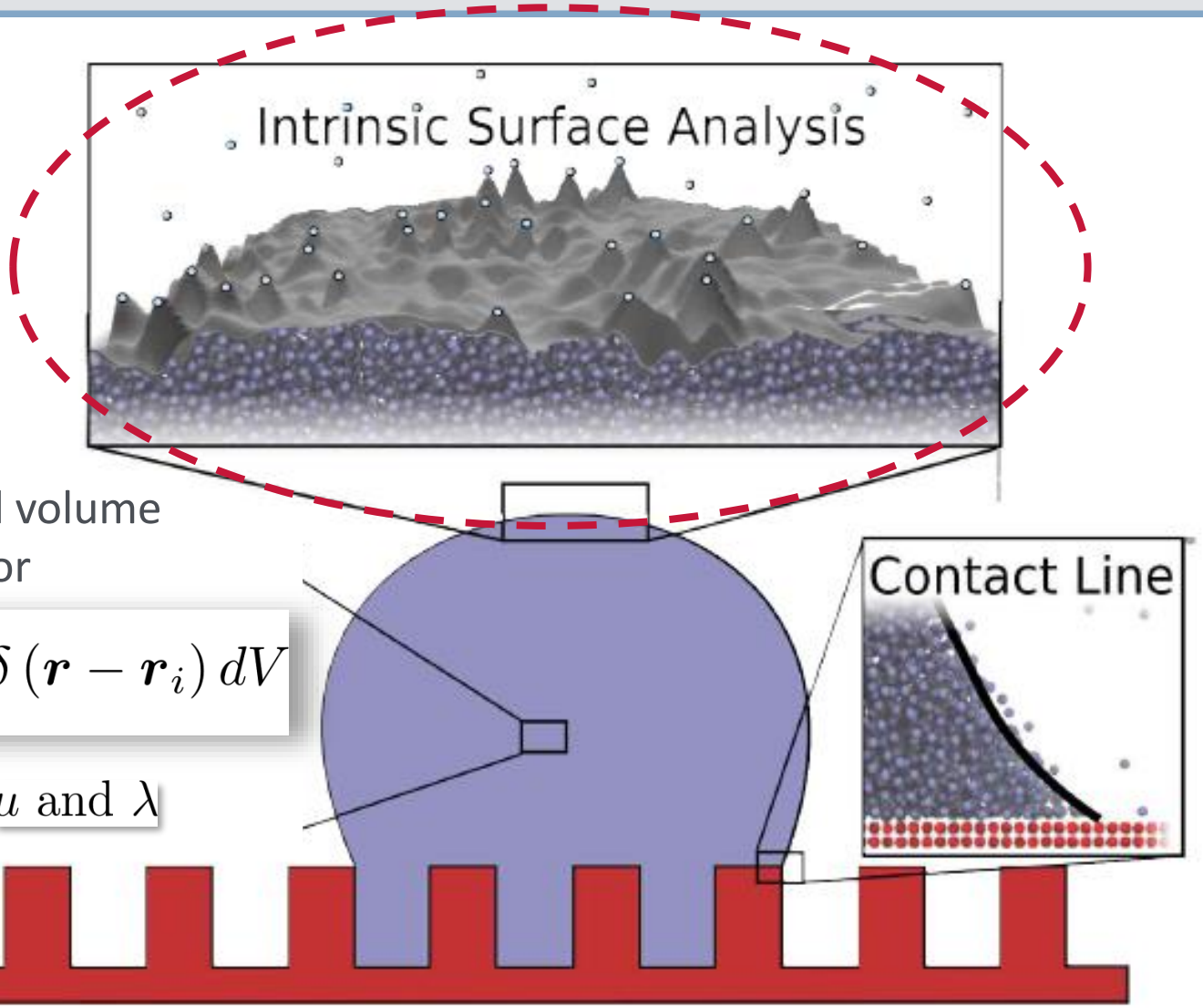


Control volume operator

$$\vartheta = \int_V \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

gets μ and λ

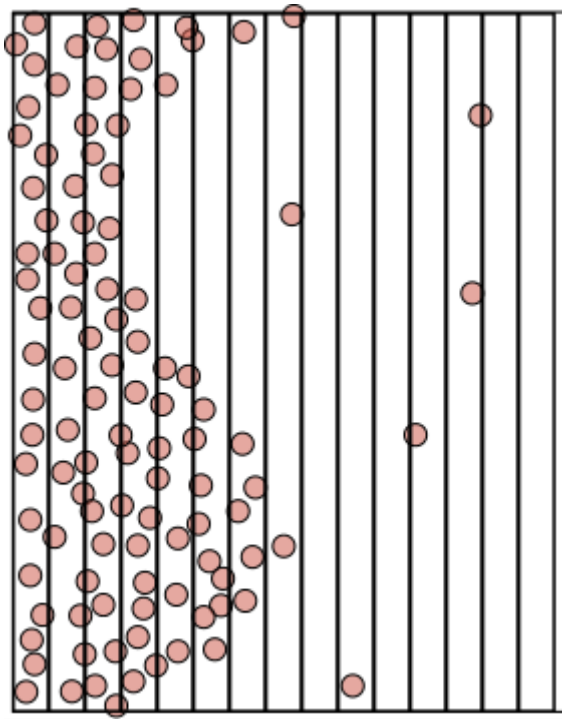
Getting Quantities Near an Interface

- Density in a cubic control volume

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

$$= \sum_{i=1}^{N} m_i \left[H\left(x^+ - x_i\right) - H\left(x^- - x_i\right)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Assume a periodic domain in y and z



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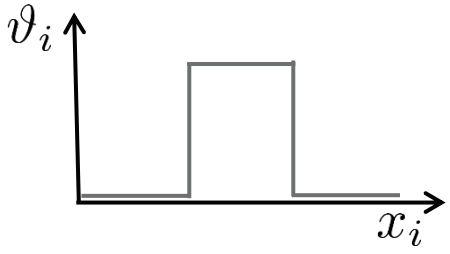
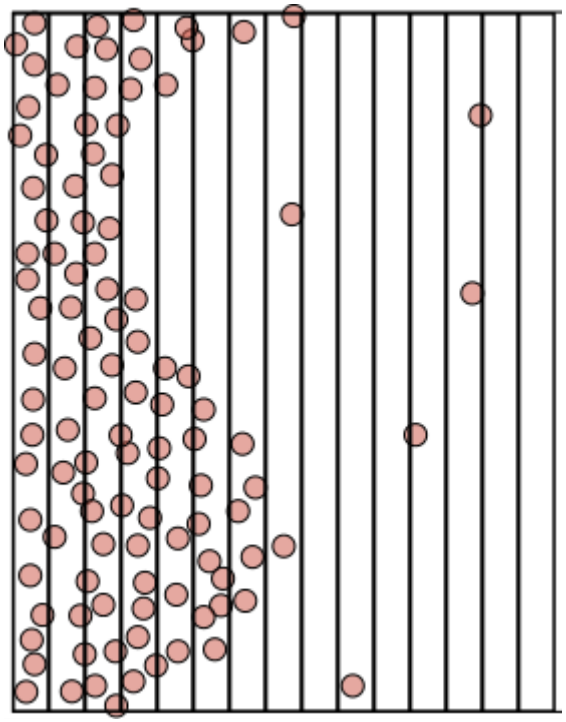
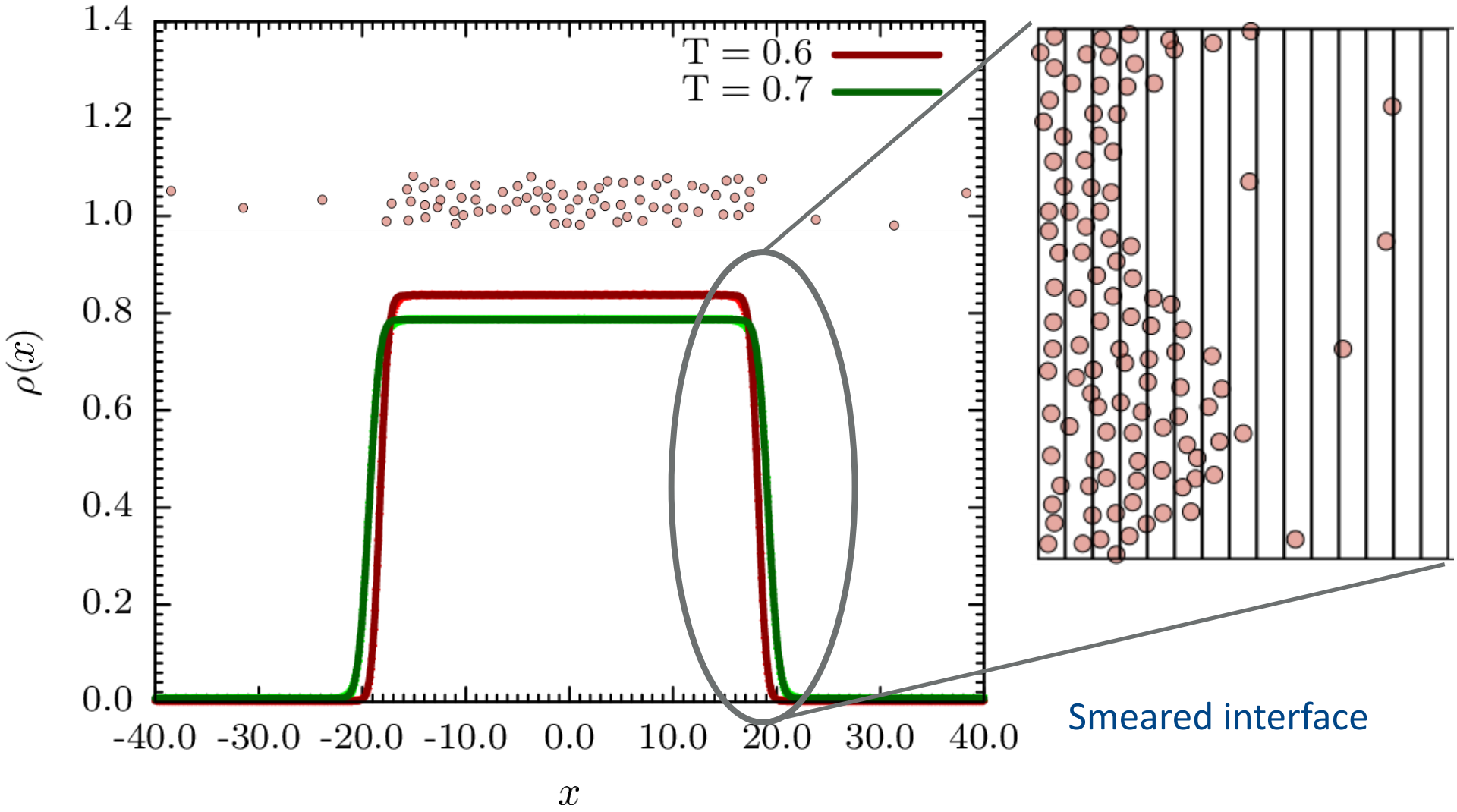




- Top hat function selects molecules inside a volume. Domain is therefore split into uniform bins in x

Results for Density



Smeared interface

Cluster analysis and surface fitting

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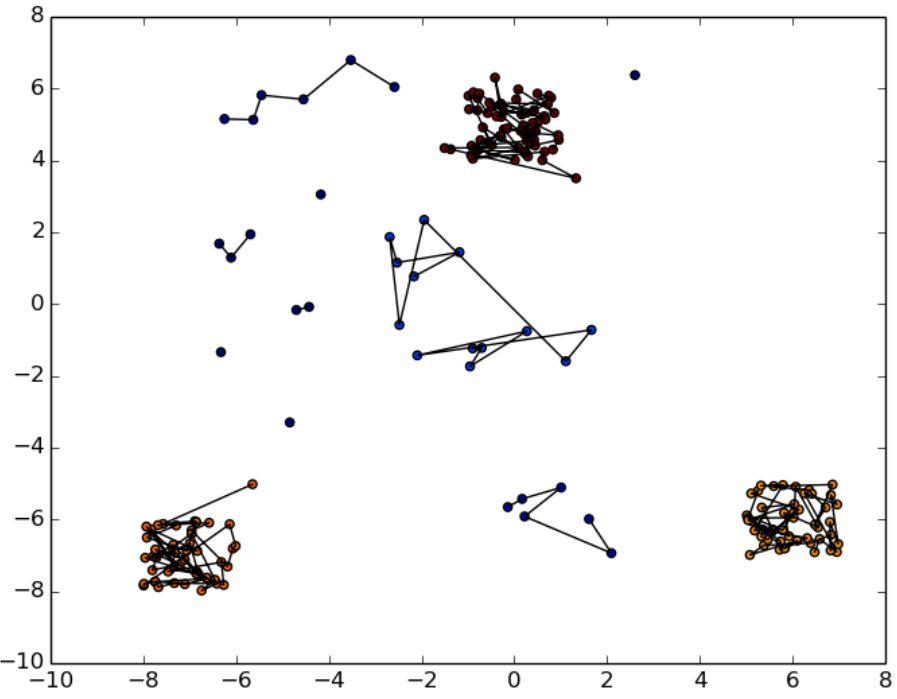
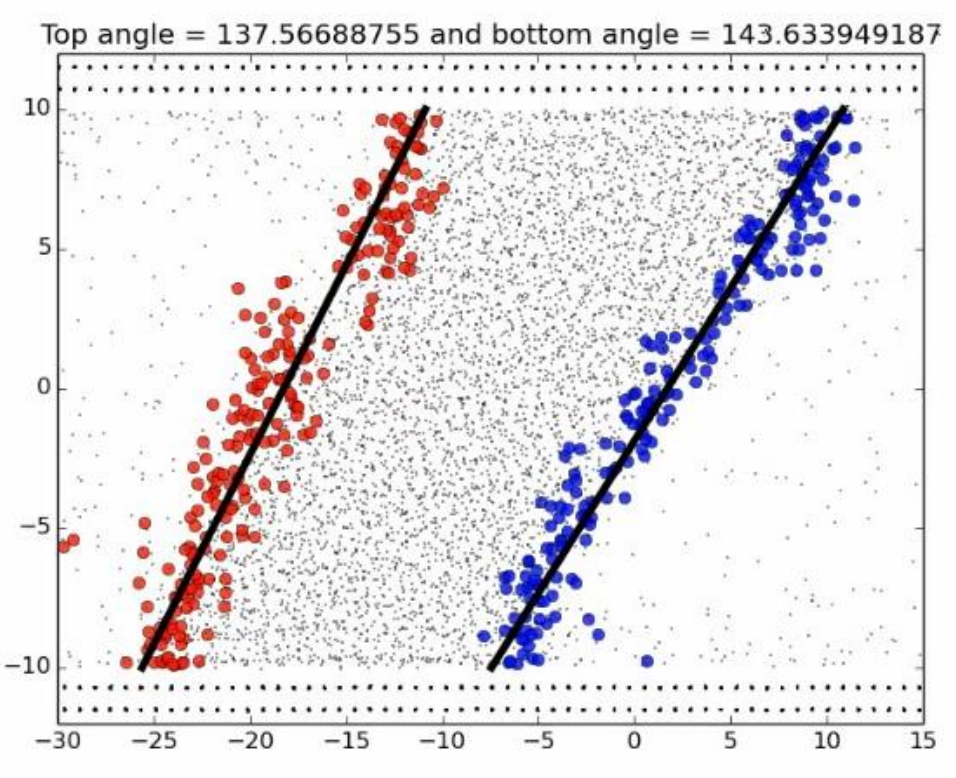
Cluster analysis

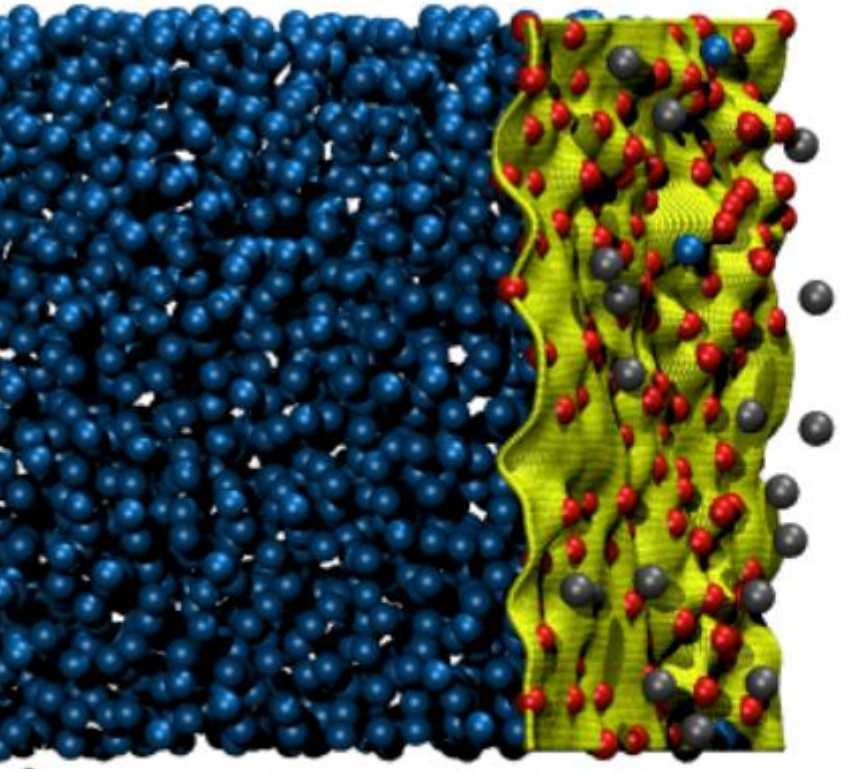


Finding the fluid-liquid interface



Intrinsic surface

- Choose a function which can fit down to intermolecular spacing



$$W = \frac{1}{2}\sum_{i=1}^{N_s}\left(x_i - \xi(y,z)\right)^2 + \lambda C$$

$$\xi(y,z) = \sum_{\mu,\nu} a_{\mu\nu} f_\mu(x) f_\nu(y)$$

Function of sines and cosines

Chacon & Tarazona (2003) PRL 91, 166103

An Intrinsic Control Volume Functional

- Integral between moving intrinsic surfaces

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

$$= \left[H\left(x^+ + \xi(y_i, z_i) - x_i\right) - H\left(x^- + \xi(y_i, z_i) - x_i\right)\right]$$

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

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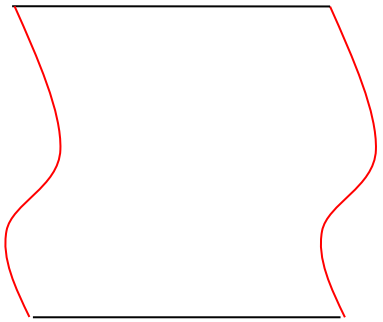

- In words

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

An Intrinsic Control Volume Functional

- Assume a periodic domain in y and z with a surface which is equal at the top and bottom (correct as sines and cosines)

$$\vartheta_i = \left[H\left(x^+ + \xi(y_i, z_i) - x_i\right) - H\left(x^- + \xi(y_i, z_i) - x_i\right)\right]$$

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

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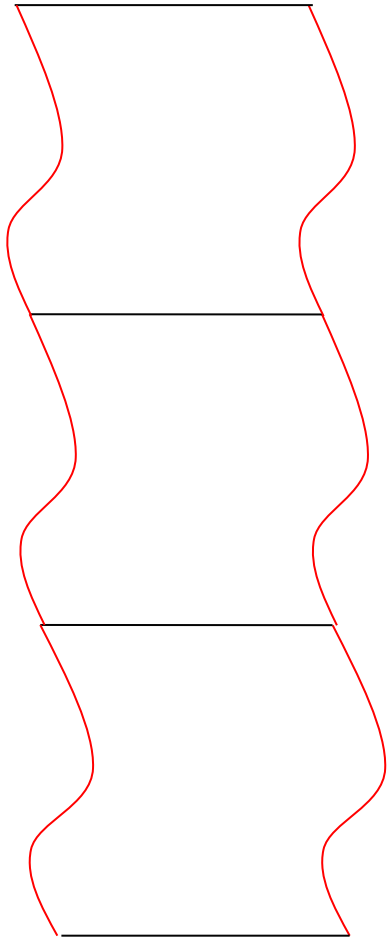

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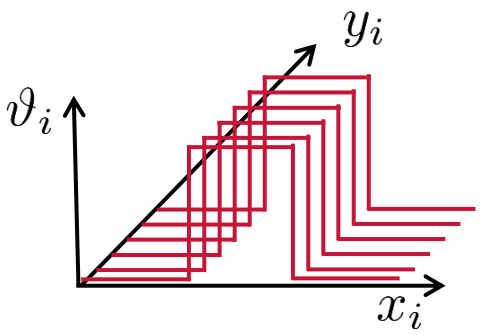
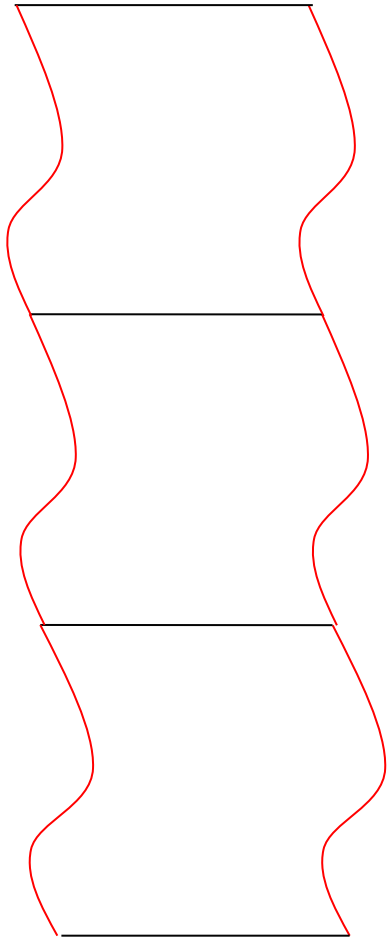


- Top hat functions (varying with y) select molecules inside a volume.



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Braga C. et al **2018** J. Chem. Phys 149, 044705

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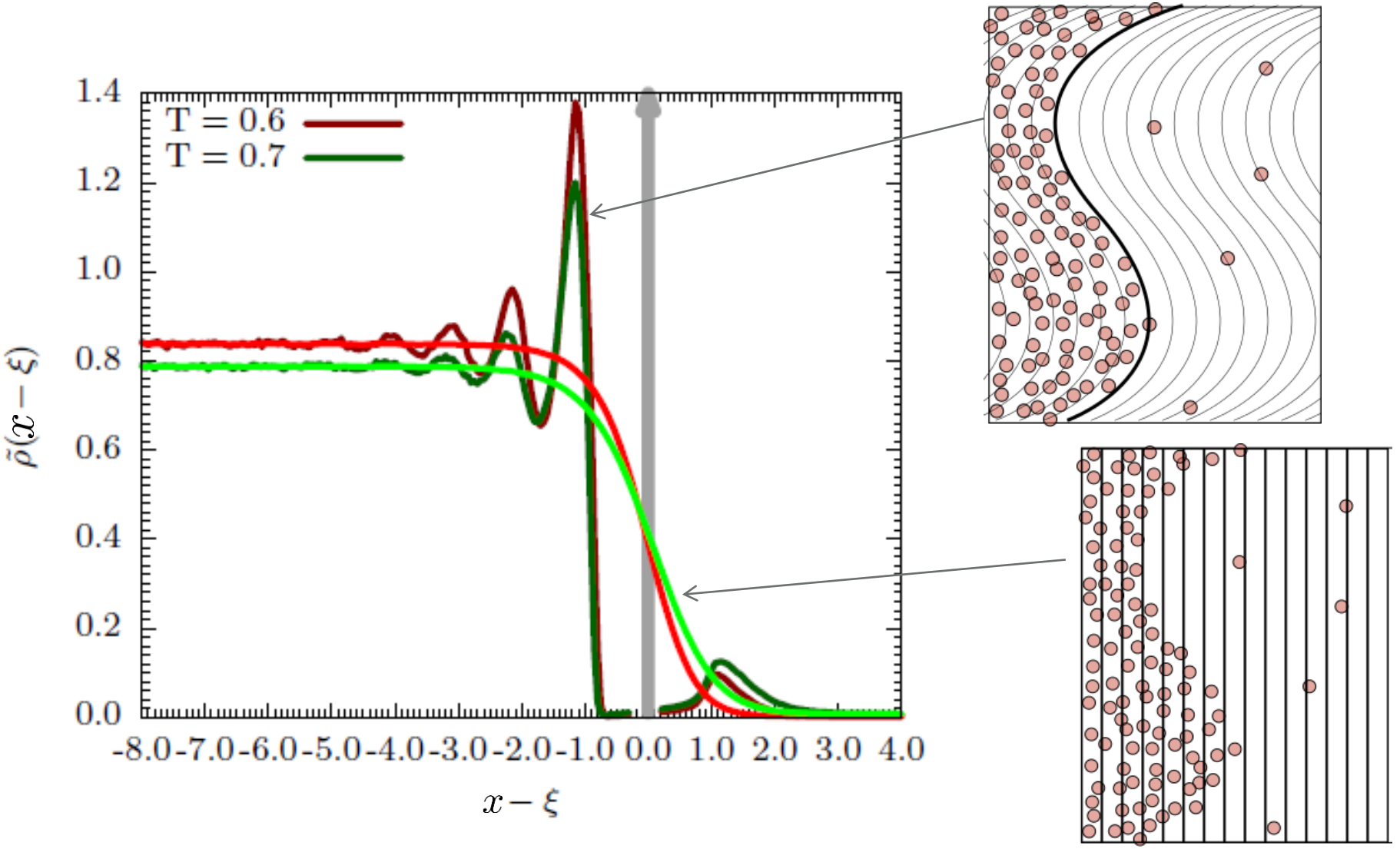
Results for Density



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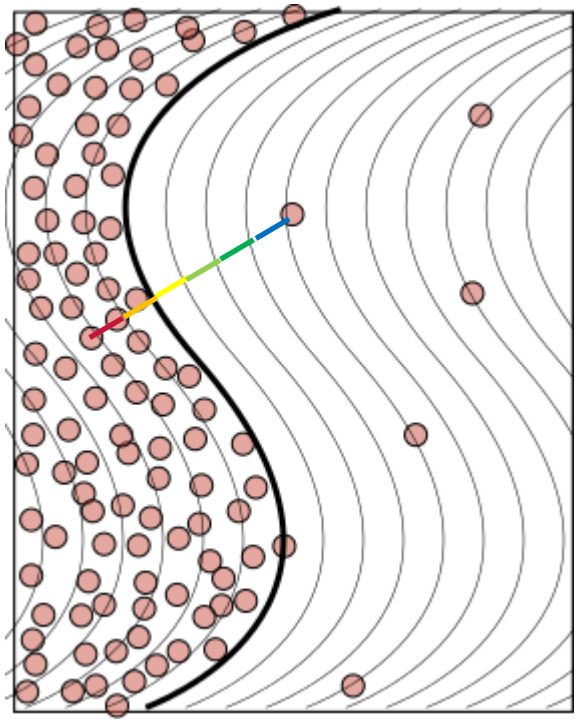
Applied to Stress

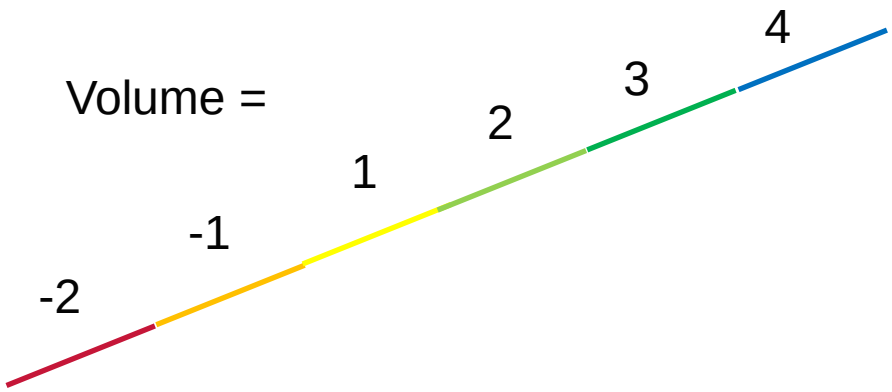
- Stress in a control volume based on the intrinsic surface

$$\int_V \tilde{\mathbf{\Pi}}^c dV = \sum_{i,j}^{N} \boldsymbol{f}_{ij} \boldsymbol{r}_{ij} \int_0^1 \vartheta_s ds$$

$$\vartheta_s = [\ H(x^+ + \xi(y_s, z_s) - x_s) - H(x^- + \xi(y_s, z_s) - x_s)]$$



- Line of interaction split over every volume it passes through (shown here by colour)



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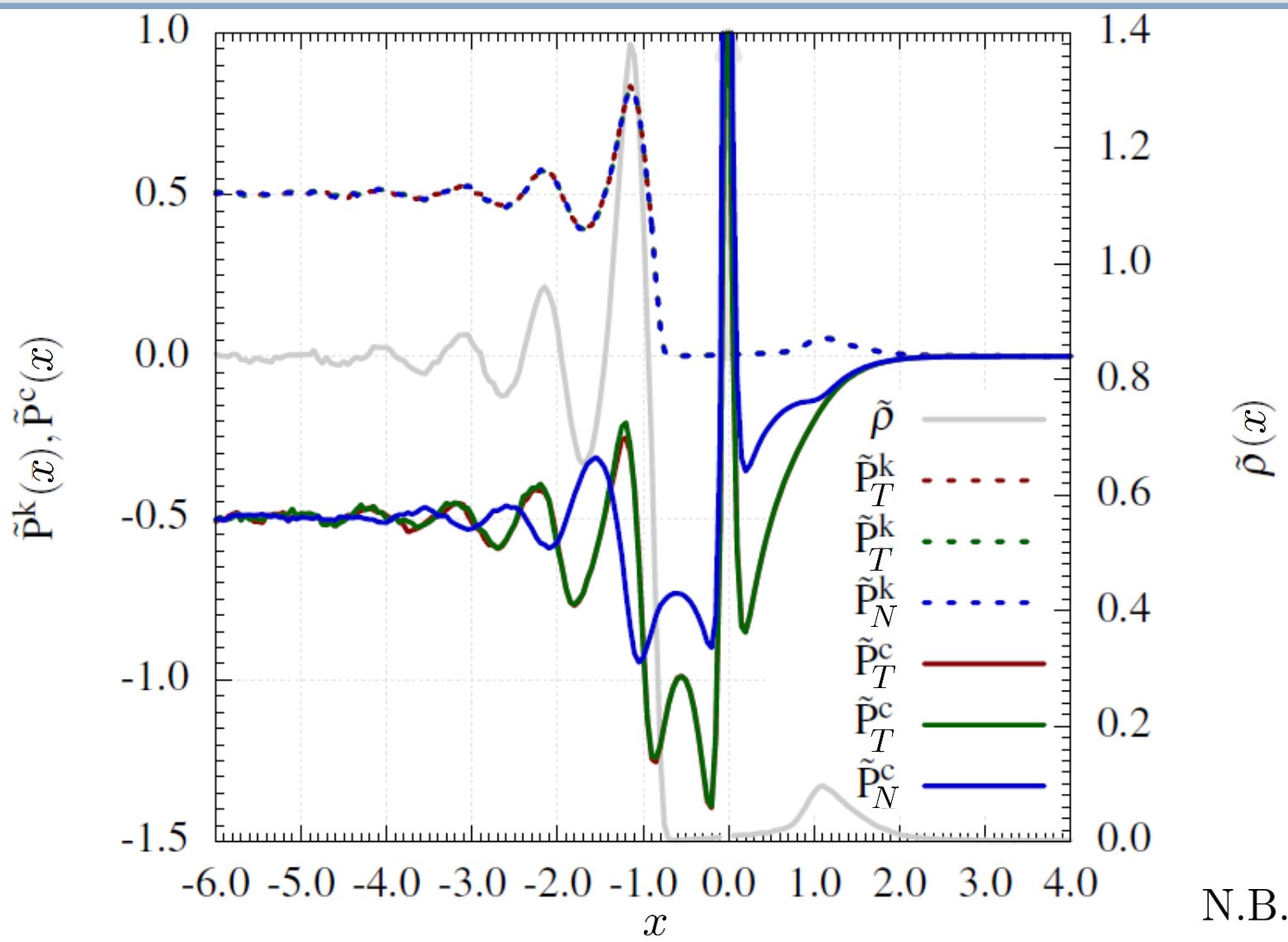
Results for Stress



N.B. $\Pi \equiv P$

$$\gamma = \int_{-\infty}^{x} [\Pi_N - \Pi_T]\, dx$$

Results for Surface Tension

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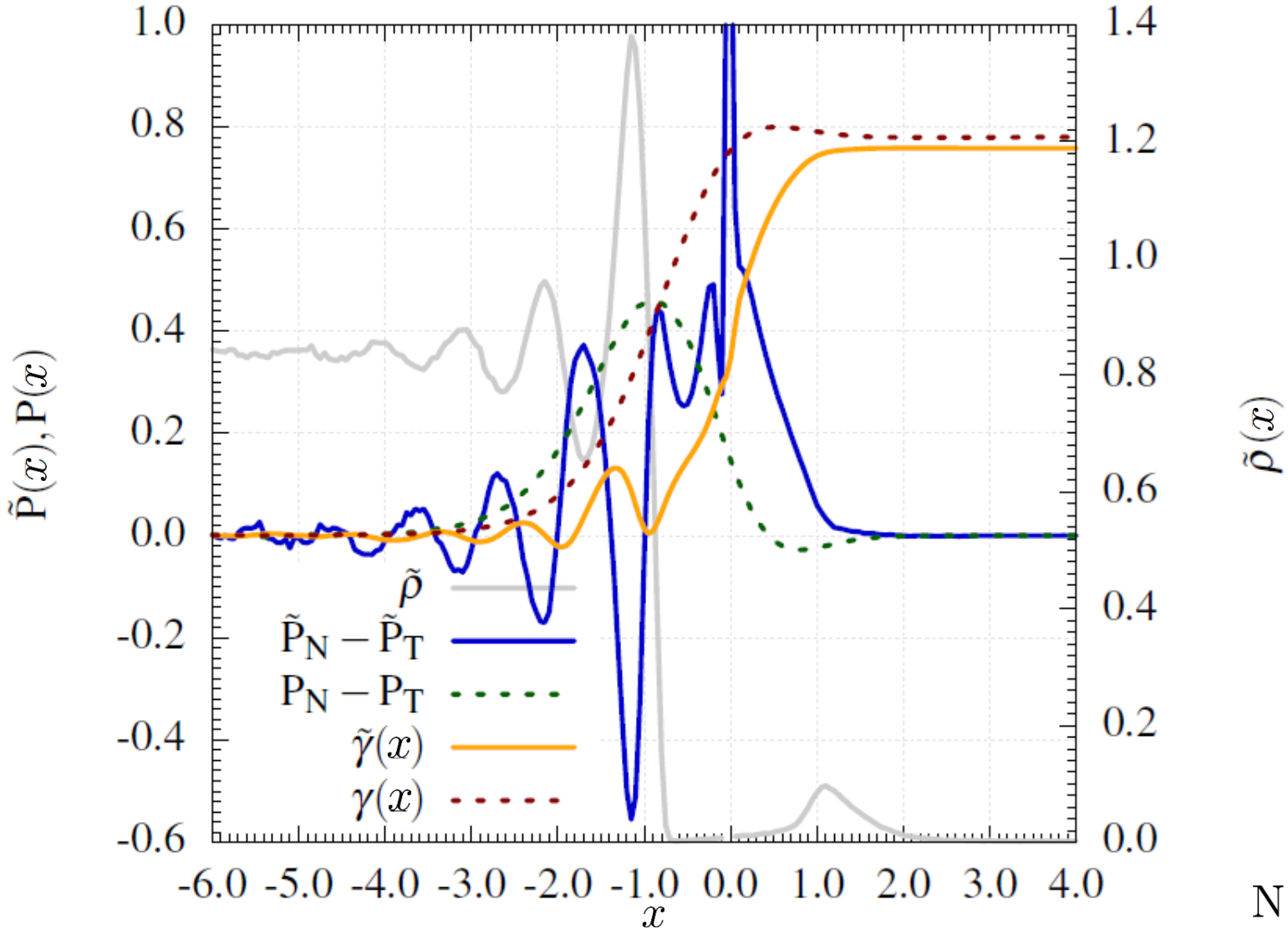
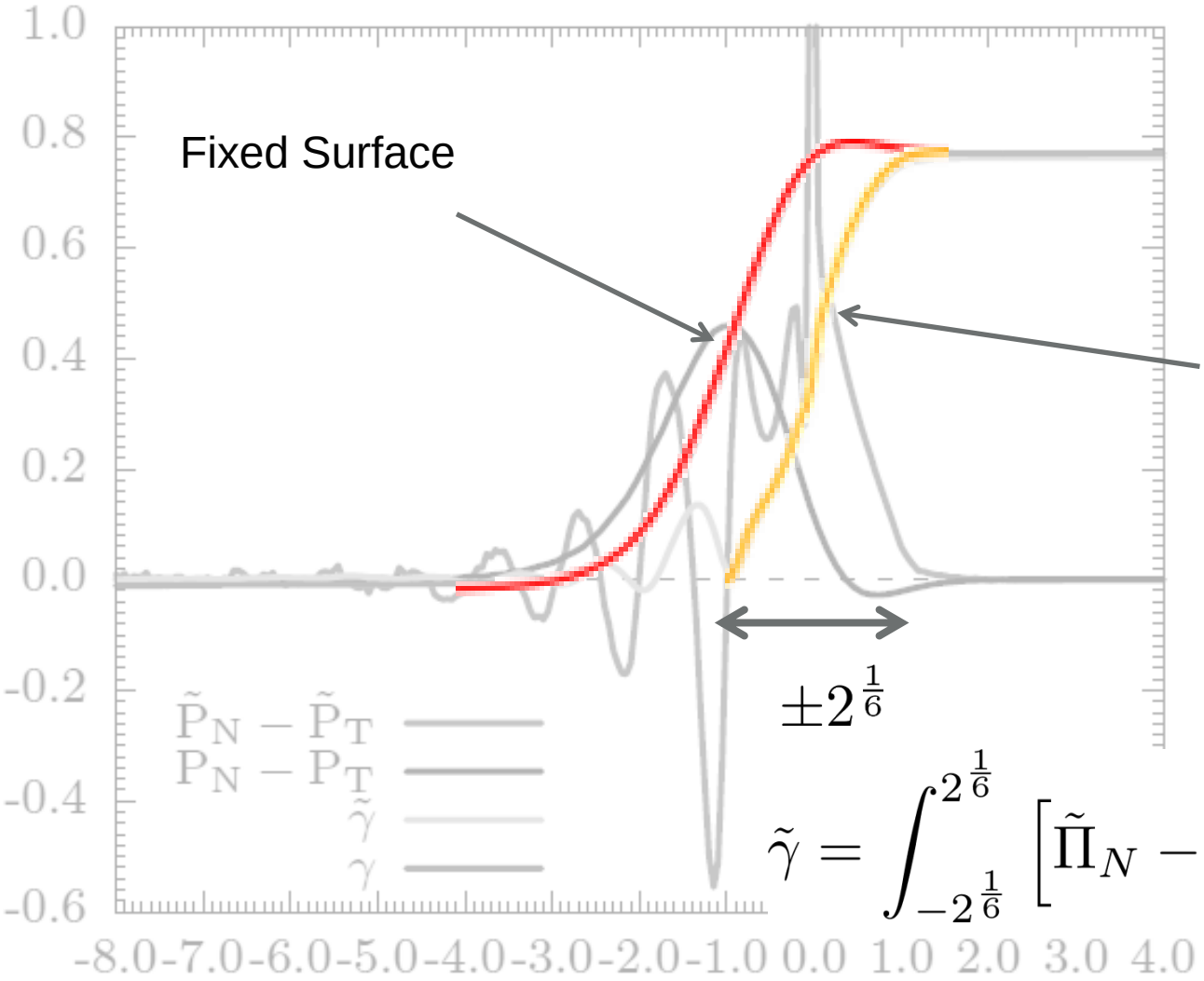


N.B. $\Pi \equiv P$

Results for Surface Tension



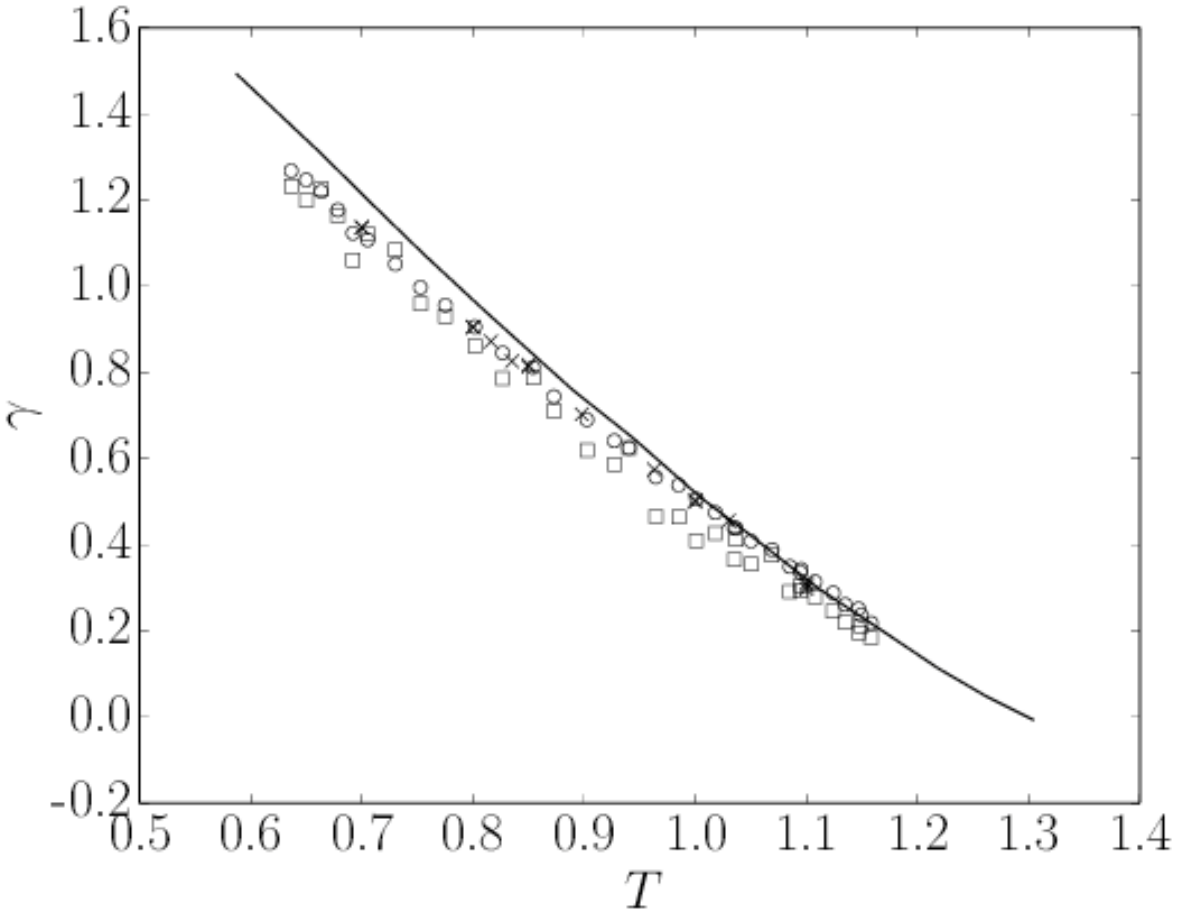
Intrinsic Surface

Tension defined by less than 1nm of surface

$$\tilde{\gamma} = \int_{-2^{\frac{1}{6}}}^{2^{\frac{1}{6}}} \left[\tilde{\Pi}_N - \tilde{\Pi}_T\right] dx$$

Validation Against Experiments

- Surface tension matched to results for liquid Argon using both intrinsic surface and flat surface



- Kirkwood Buff to get surface tension from normal and tangential stresses

$$\gamma = \int_{-\infty}^{x} [\Pi_N - \Pi_T]\, dx$$

Overview

Control volume for intrinsic surface

$$\vartheta = \int_{V(t)} \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

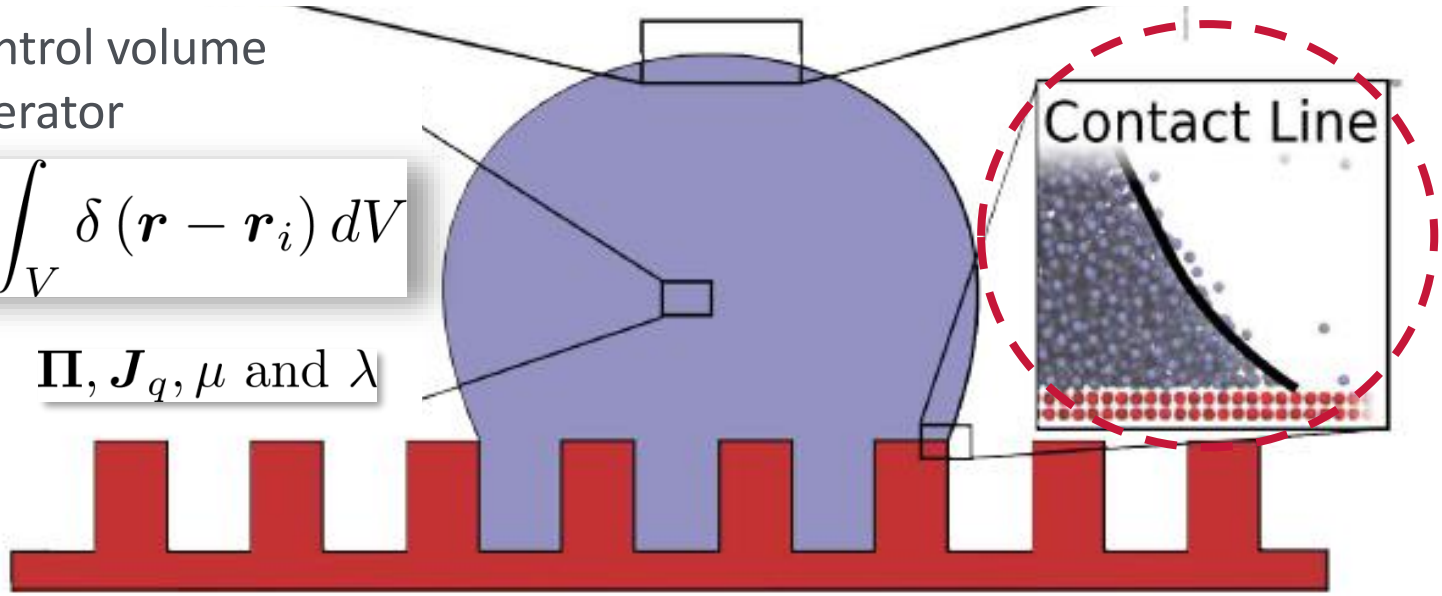
gets $\tilde{\boldsymbol{\Pi}}, \tilde{\boldsymbol{J}}_q$ and γ

Volume moving with fitted spectral surface to molecular spacing

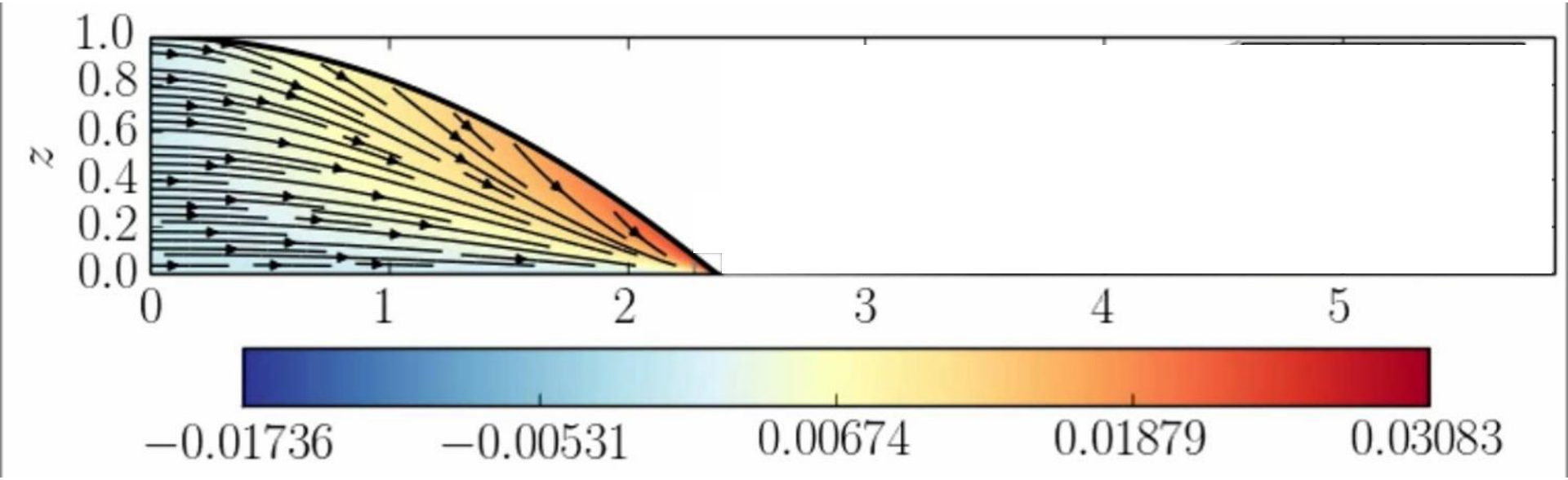
Control volume operator

$$\vartheta = \int_{V} \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

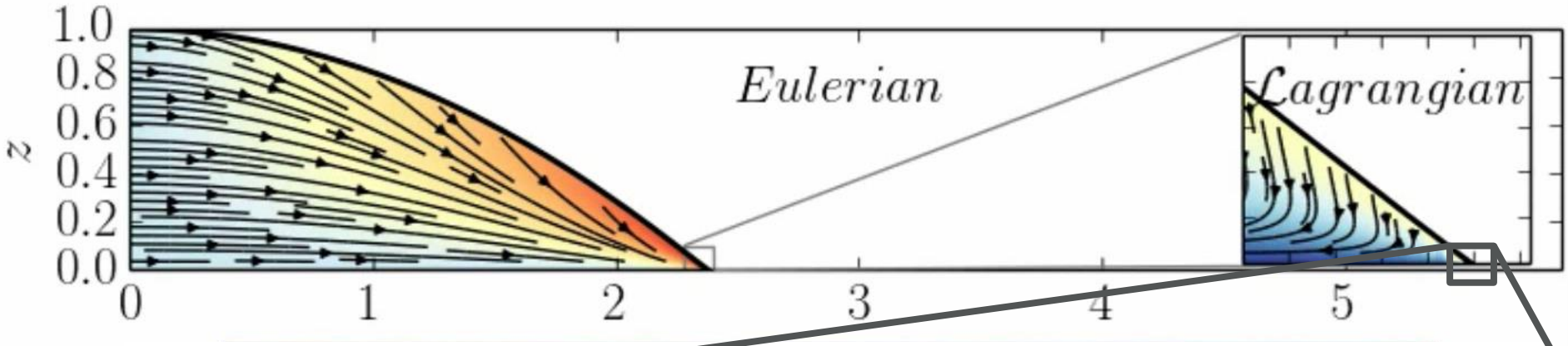
gets $\boldsymbol{\Pi}, \boldsymbol{J}_q, \mu$ and λ



Coupled Droplet Spreading and MD



Coupled Droplet Spreading and MD

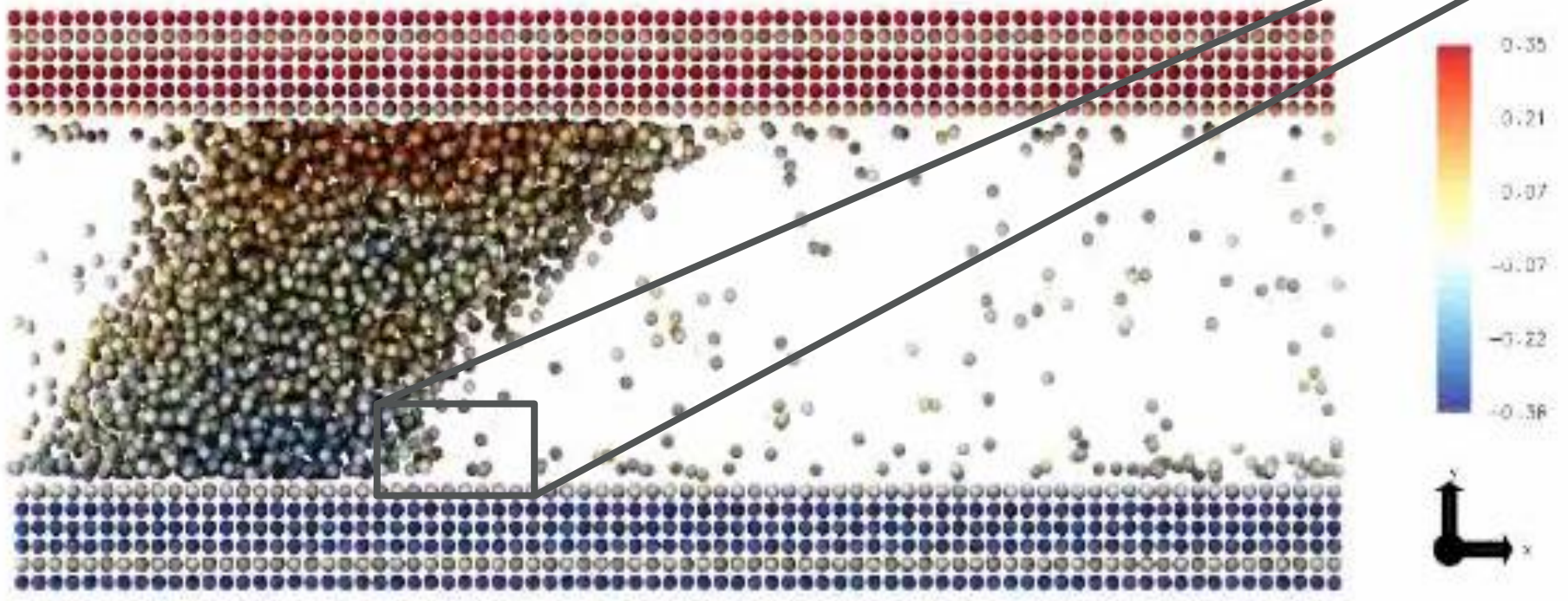


- Model the moving contact line with MD
- We want contact line speed as a function of continuum contact angle

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

Sheared Liquid Bridge

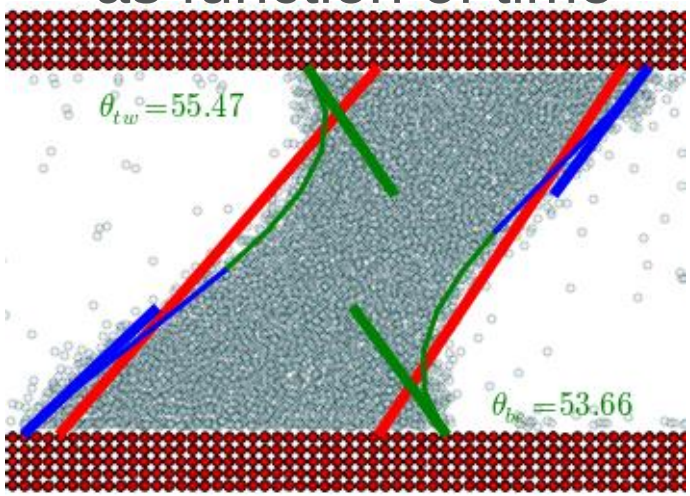
- Two fluid phases and sliding molecular walls
- Simple test case to explore wall velocity vs contact line angle
- Non-Equilibrium Steady State

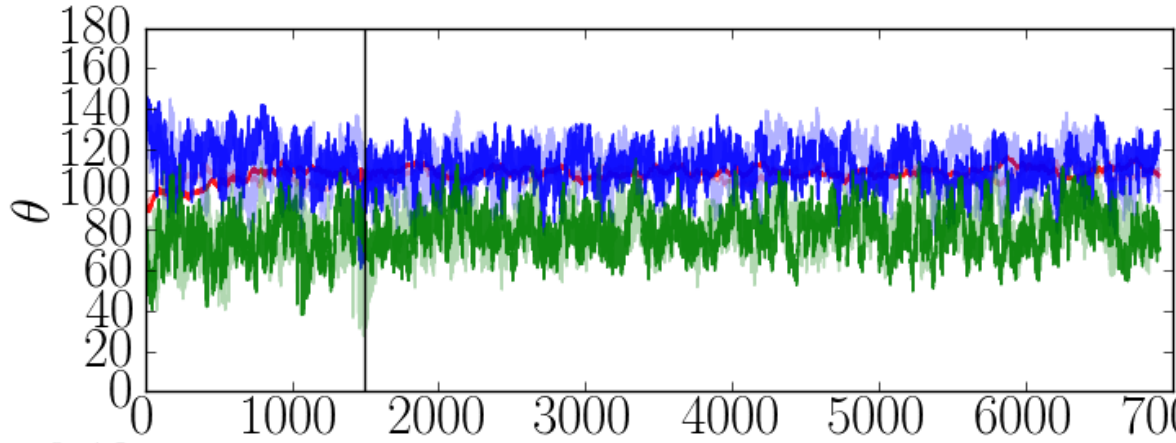


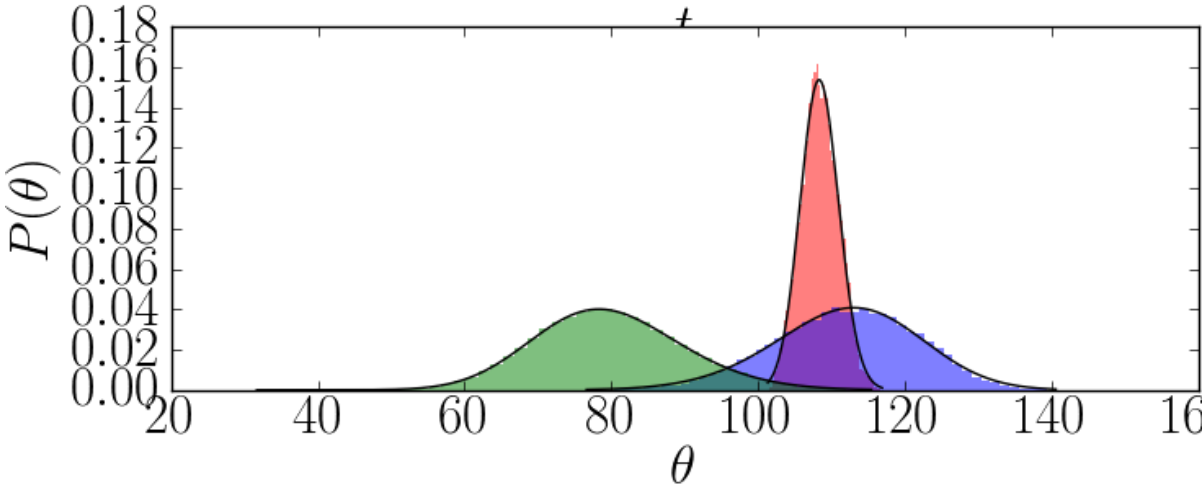
Smith et al **2016** Soft Matter, 12, 48

Time Evolution of Contact Angle

- Fit (simple) surface to cluster and get contact angle evolution as function of time





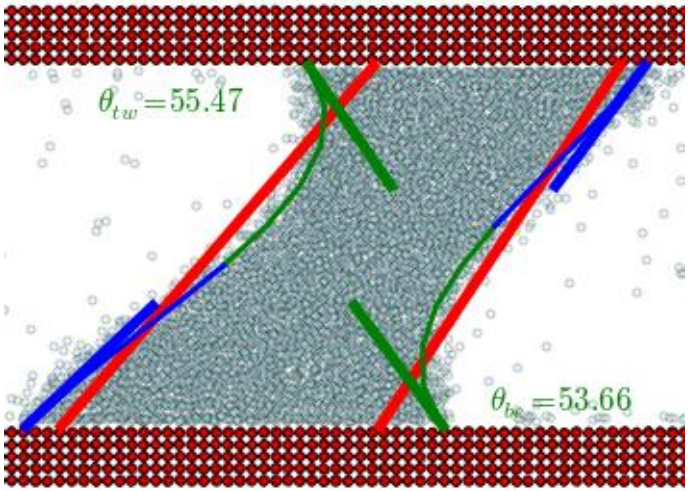


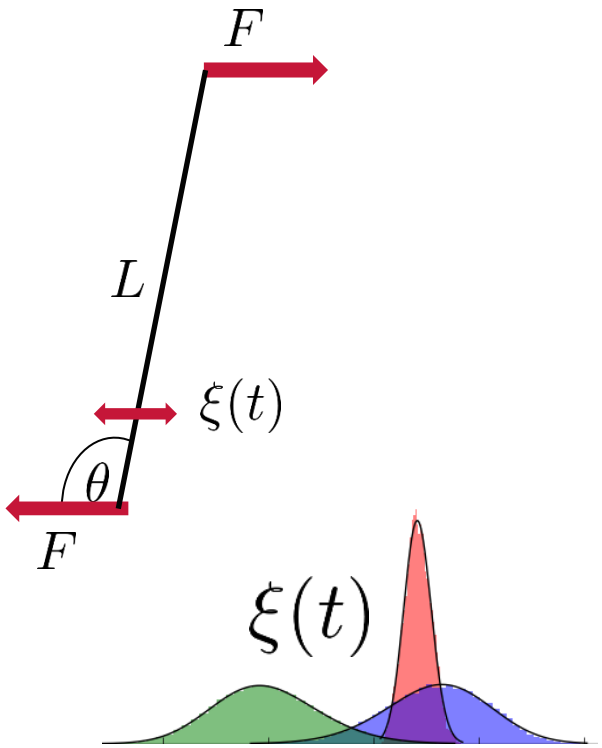
- Probability density function of angle shows range of micro-scale behaviour

- 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





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

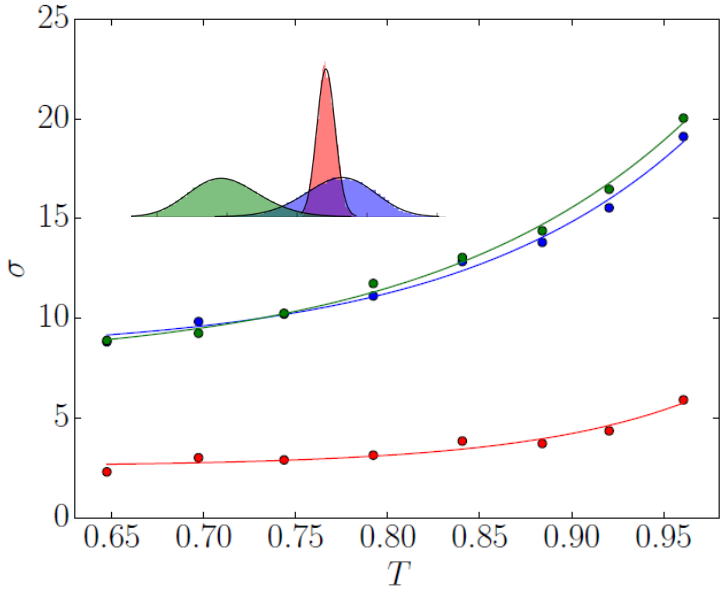
- Torque $\mathcal{T} = F \times L$ approximately equal to wall sliding

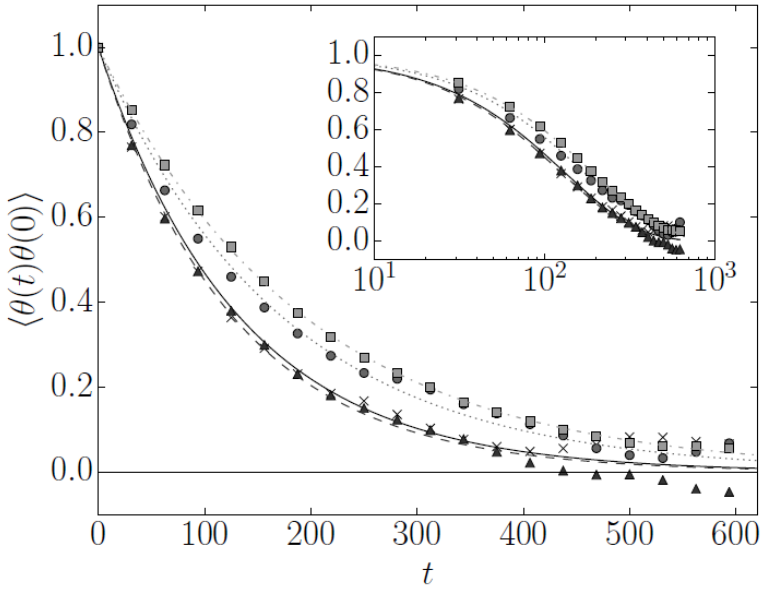
Building this into the Continuum Model

- 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 velocity independent
  - Autocorrelation - roughly velocity and temperature independent.





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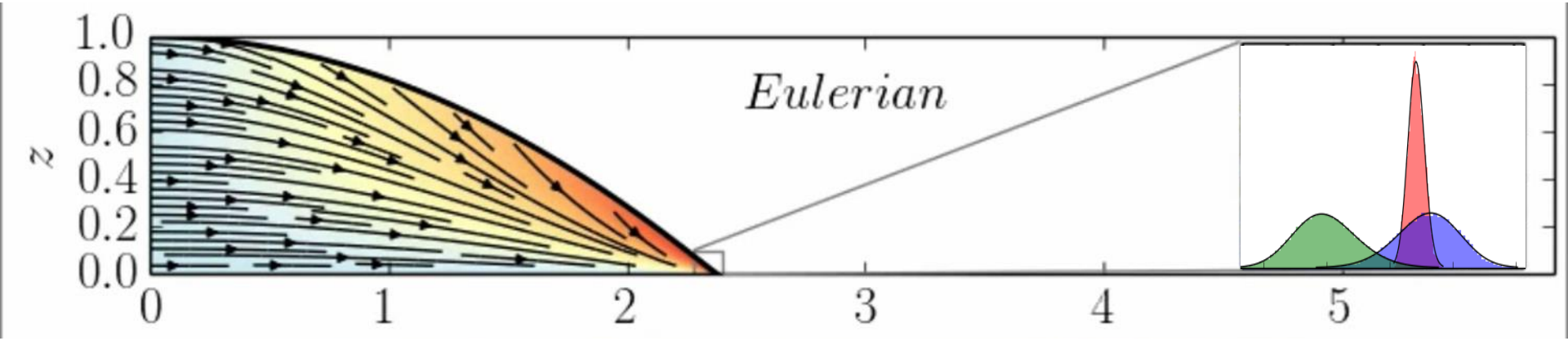
Building this into the Continuum Model



- Speed of contact line obtained from a Langevin model tuned by the molecular PDF

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

Evolution of the mean governed by macroscopic laws (Tanners, MKT, Cox)

Random term tuned to match MD contact line fluctuation and autocorrelation

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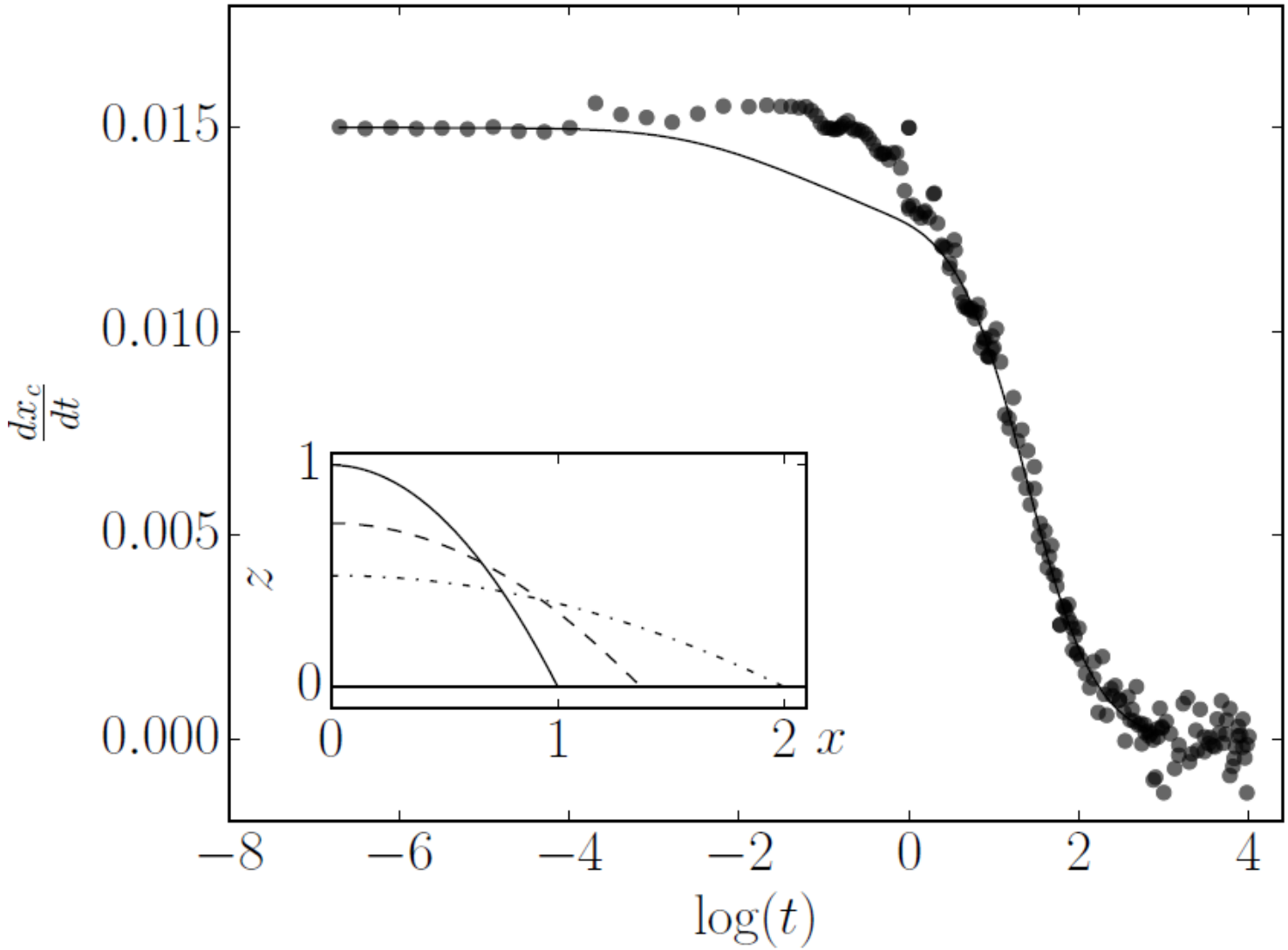
Brunel University London

Coupled with CFD model



Overview

Control volume for intrinsic surface

$$\vartheta = \int_{V(t)} \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

gets $\tilde{\boldsymbol{\Pi}}, \tilde{\boldsymbol{J}}_q$ and γ

Volume moving with fitted spectral surface to molecular spacing

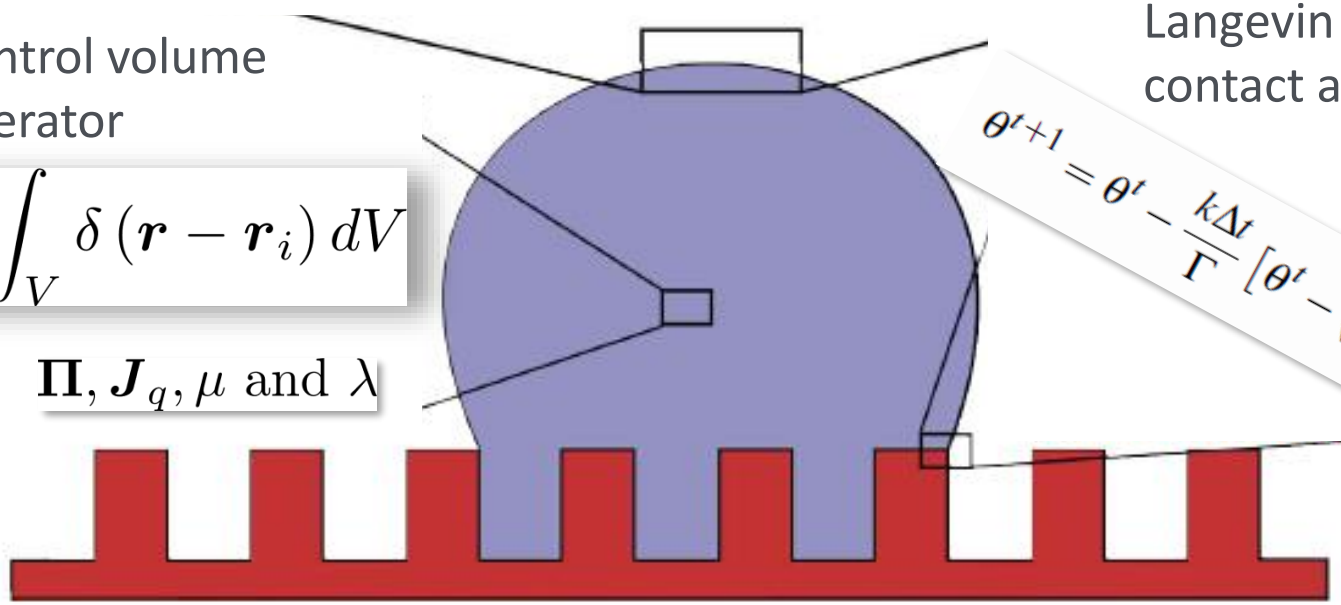
Control volume operator

$$\vartheta = \int_{V} \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

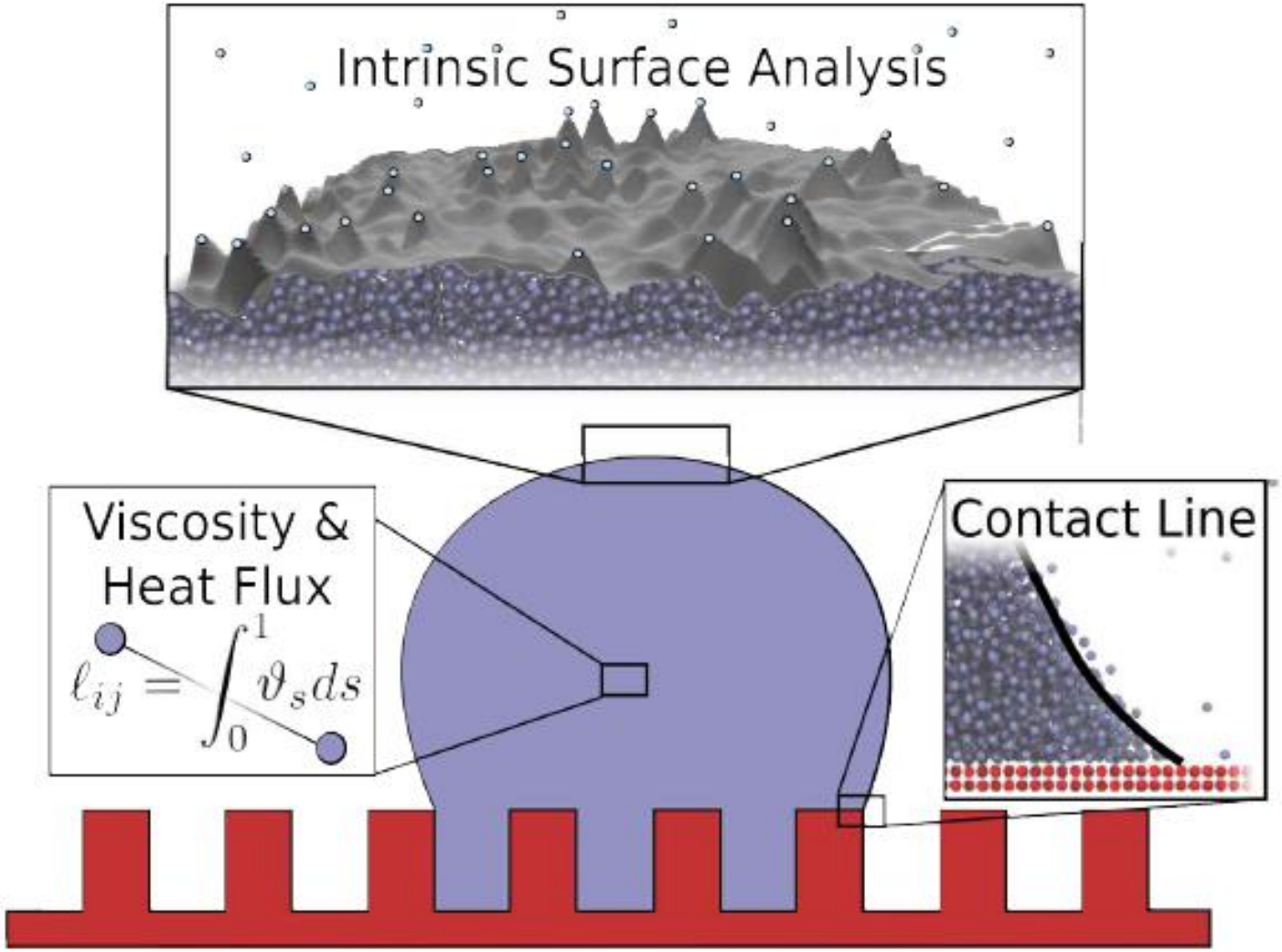
gets $\boldsymbol{\Pi}, \boldsymbol{J}_q, \mu$ and λ

Langevin equation for contact angle

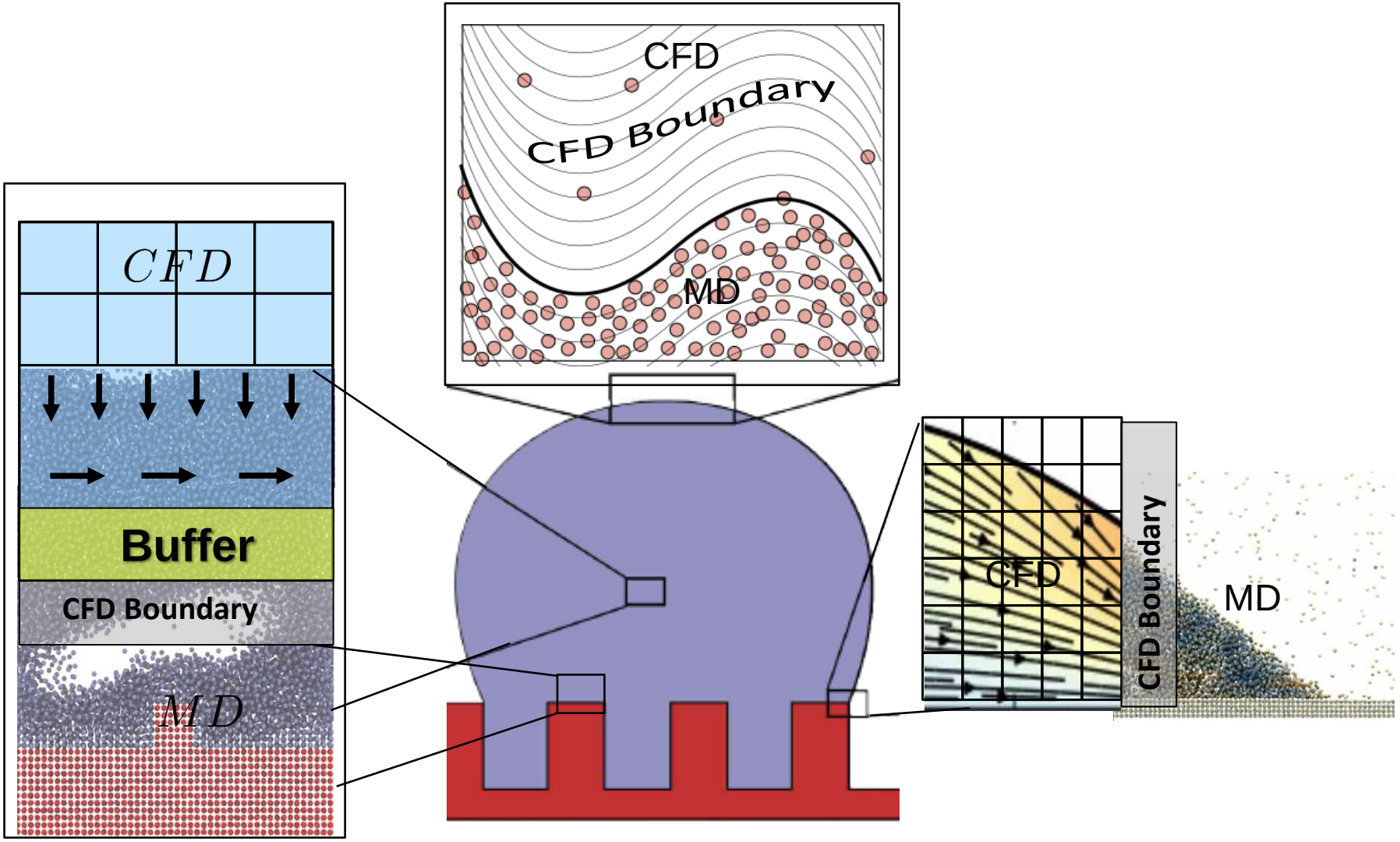
$$\theta^{t+1} = \theta^{t} - \frac{k\Delta t}{\Gamma}\left[\theta^{t} - \langle\theta\rangle\right] + \xi\frac{\sqrt{C\Delta t}}{\Gamma}$$



Overview


Intrinsic Surface Analysis
Viscosity &
Heat Flux
$\ell_{ij} = \int_0^1 \vartheta_s ds$
Contact Line

Longer Term Plans - Direct Coupling



Coupled CFD-MD Simulation

- Control Volume Solver

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

$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i + \mathbf{F}_i^C \quad i \in \text{cell}$$

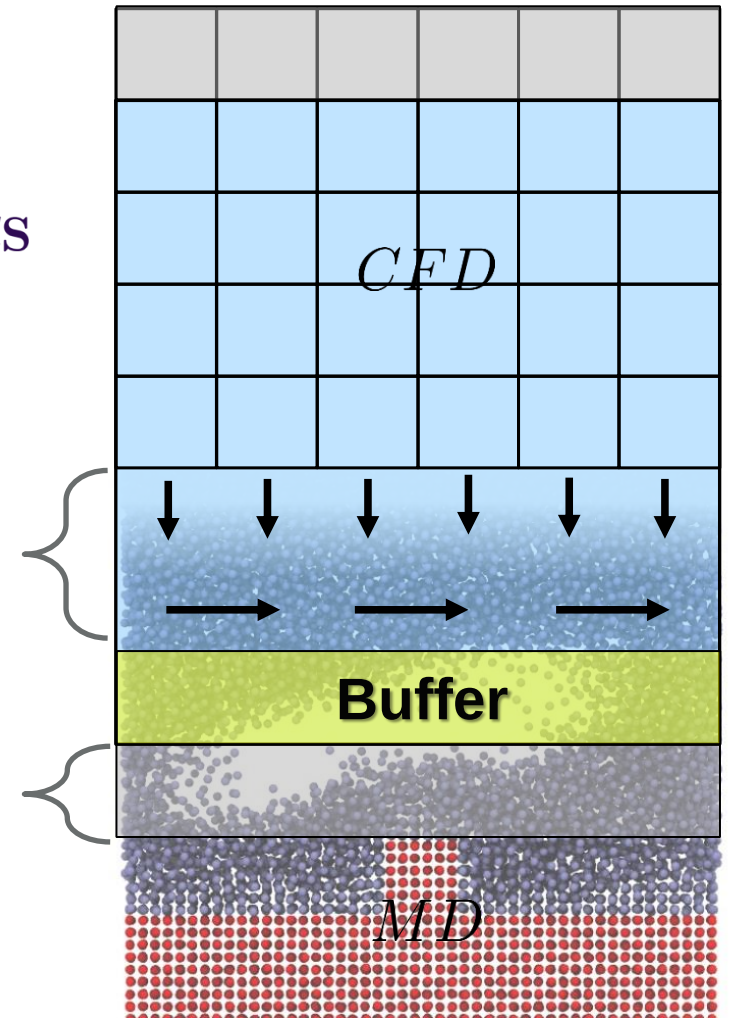
CFD→MD Boundary condition

$$\boldsymbol{u}^{BC} = \sum_{i\in\text{cell}} \boldsymbol{v}_i$$

MD→CFD Boundary condition

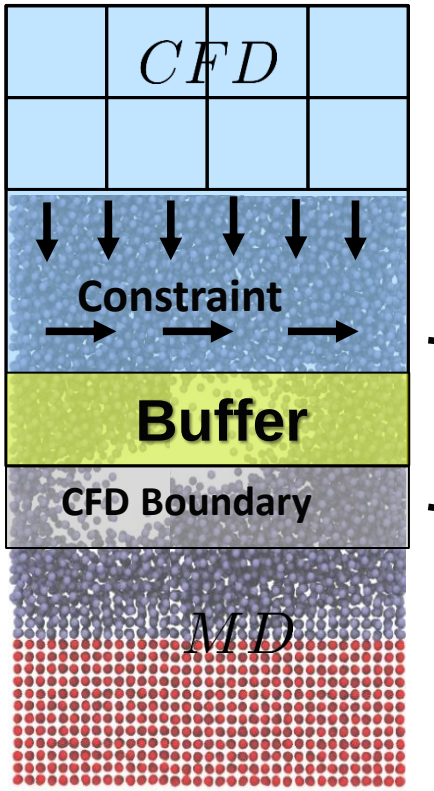
- Discrete molecules

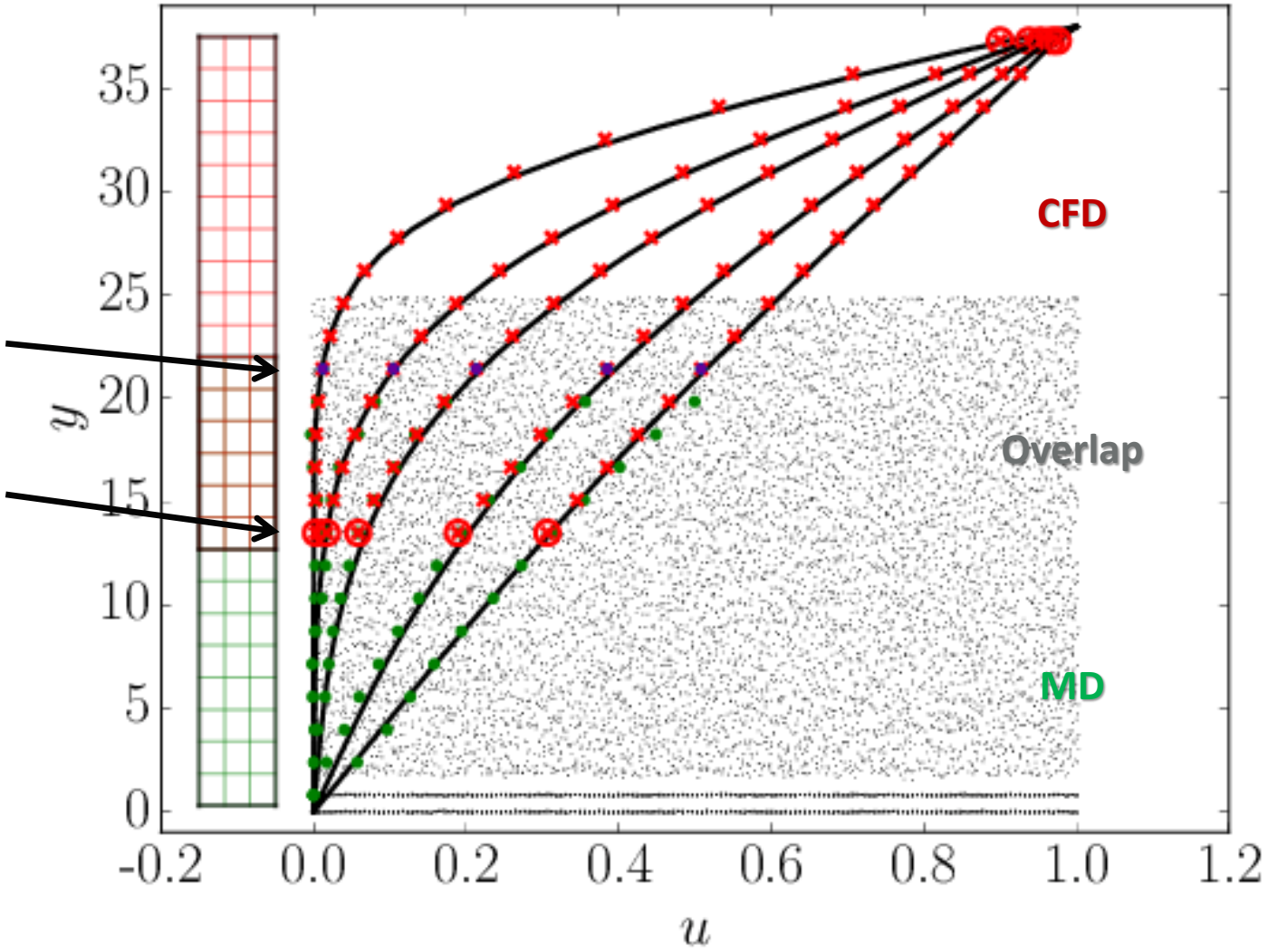
$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i \text{ for all i in N}$$



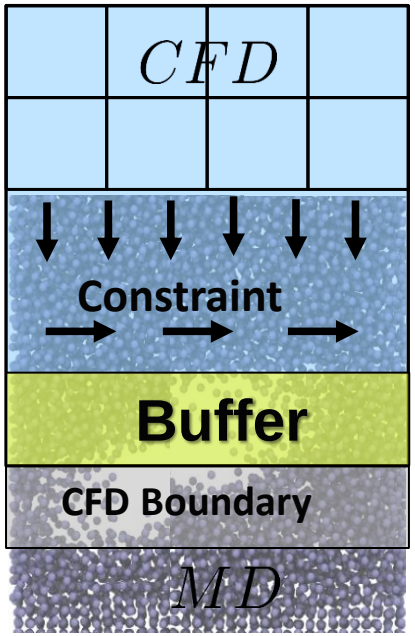
O'Connell Thompson (1995), Hadjiconstantinou (1998), Flekkoy (2000), Nie et al (2004).

Coupling Results – Couette Flow

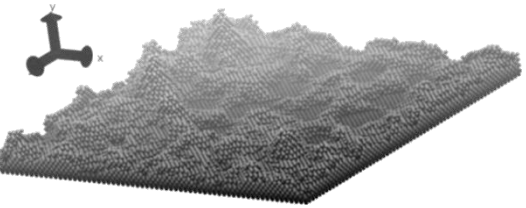


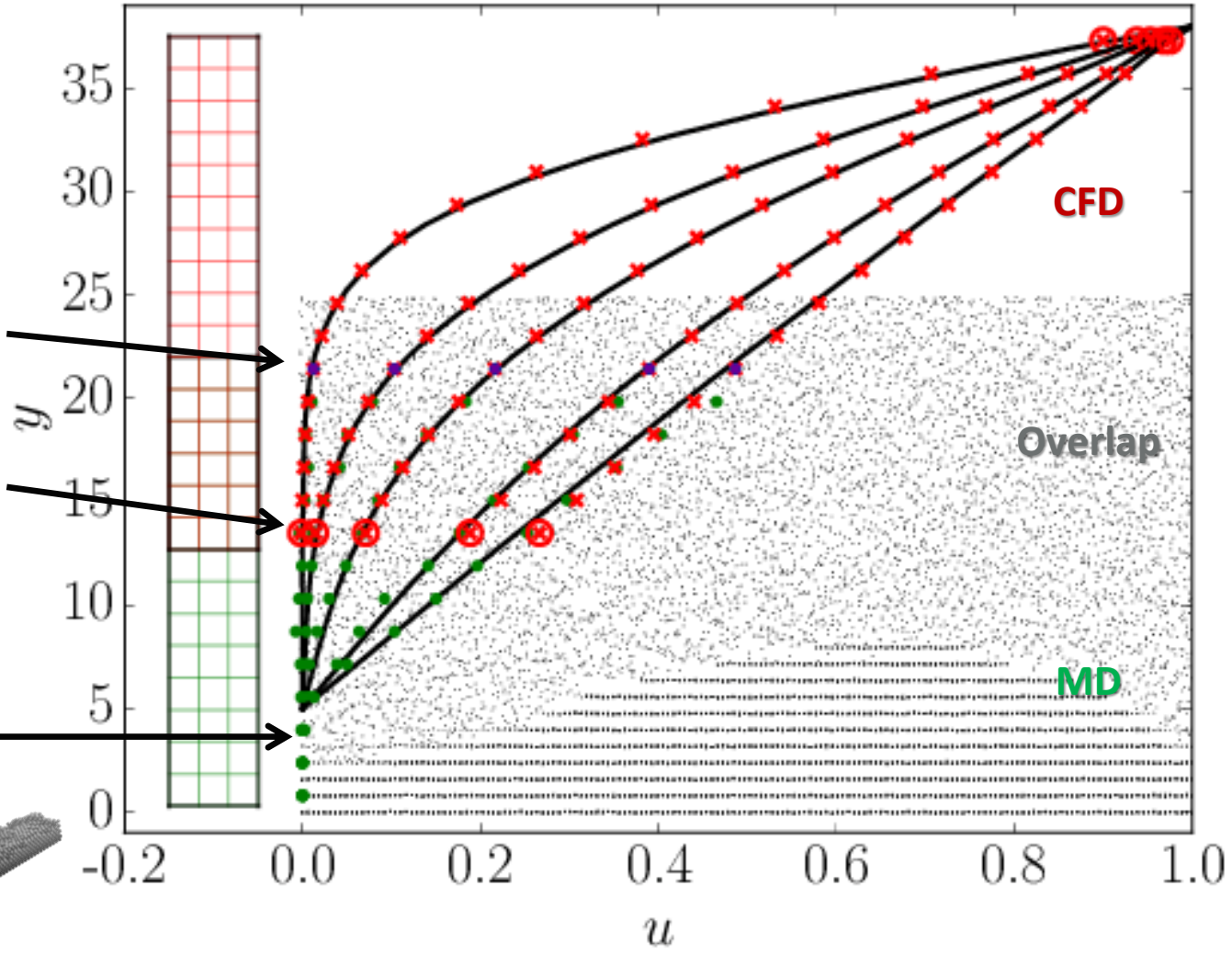


Coupling Results – Couette Flow



Rough wall shifts zero location





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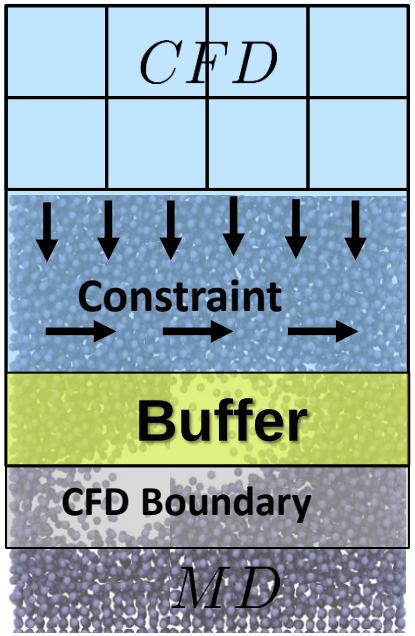
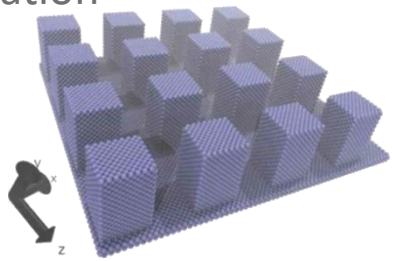
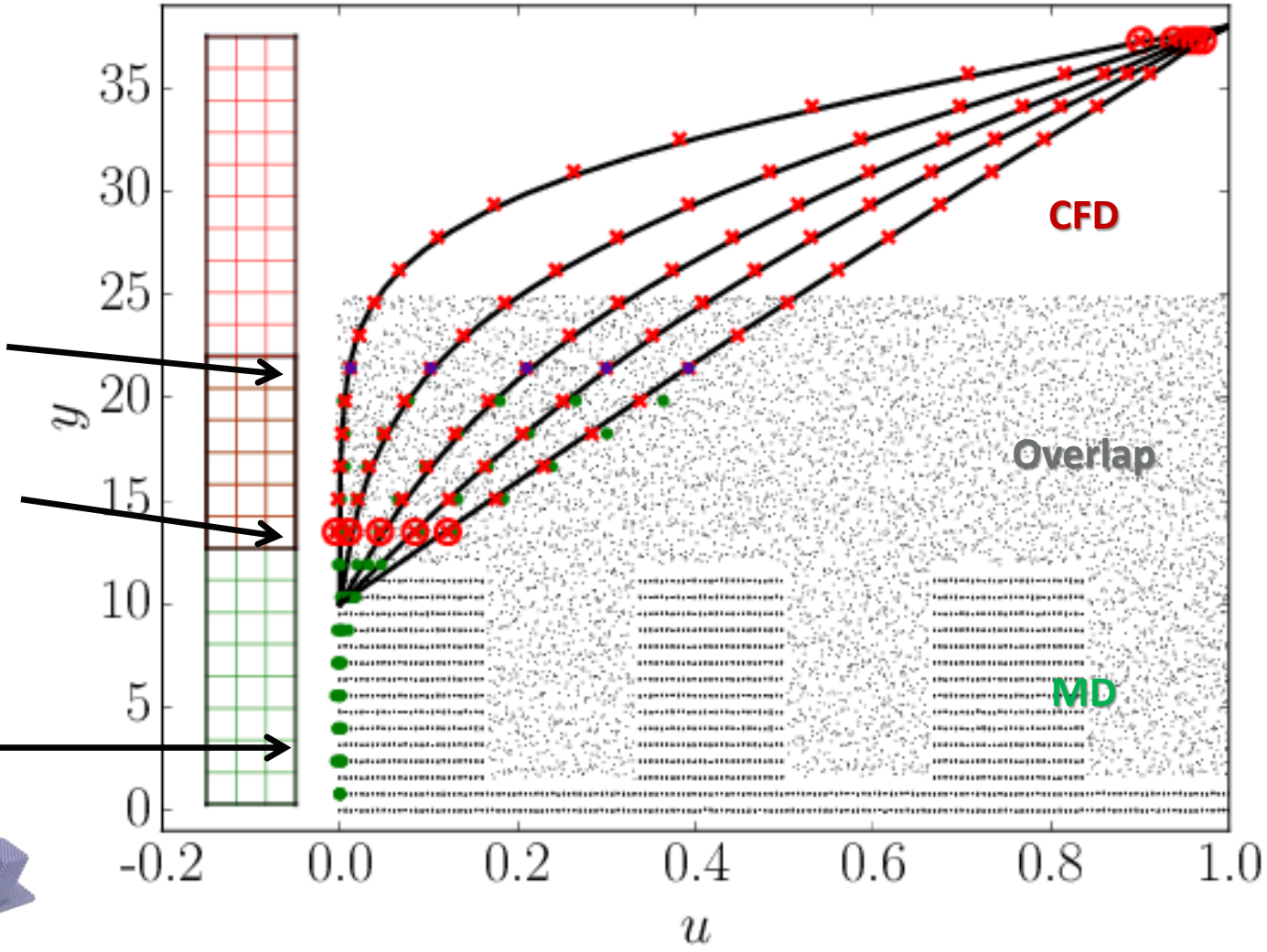


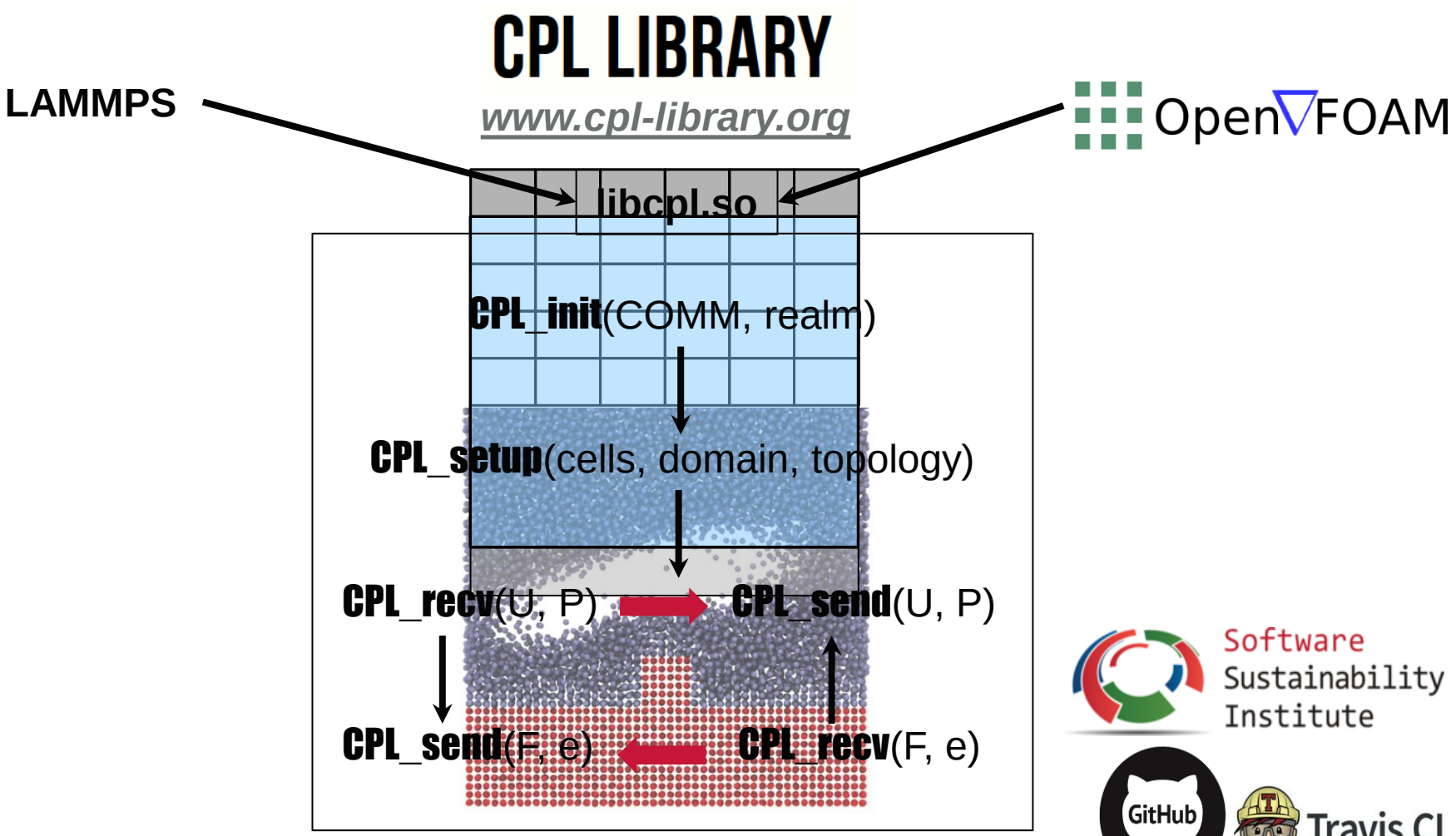
Posts shift zero location





Coupled Simulation Software

Brunel University London



Software Sustainability Institute

GitHub

Travis CI

Summary

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