Imperial College London

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Tracking the Liquid-Vapour interface at the Molecular Scale

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19th April 2022

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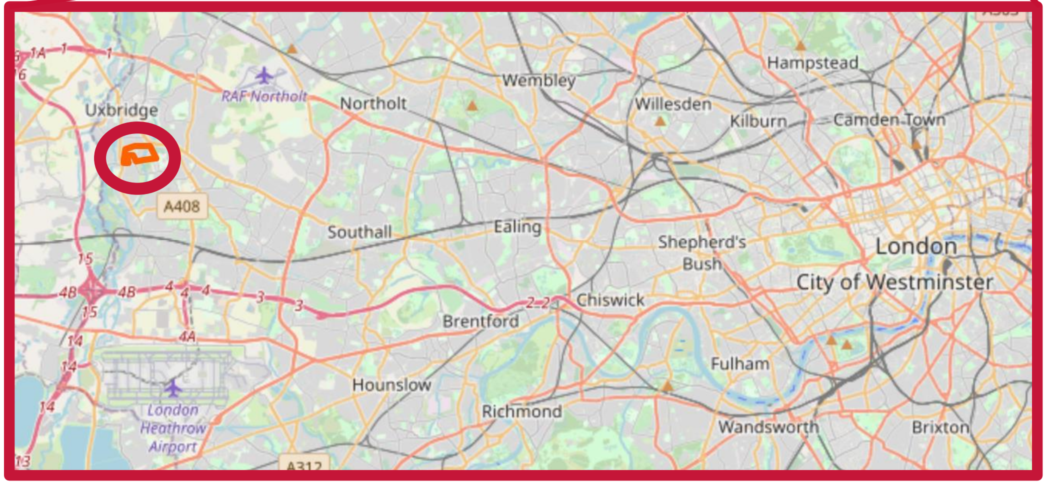
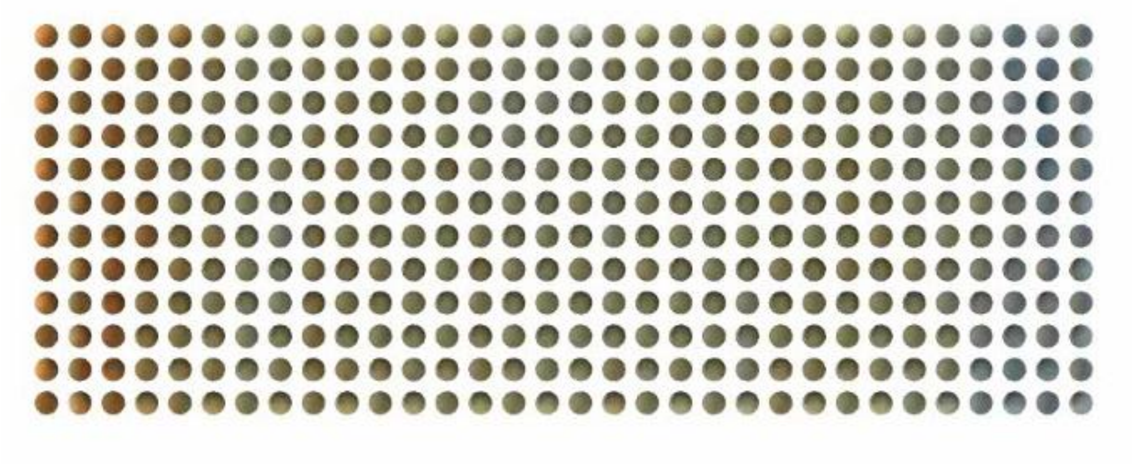
A Research-Focused Engineering University



Overview

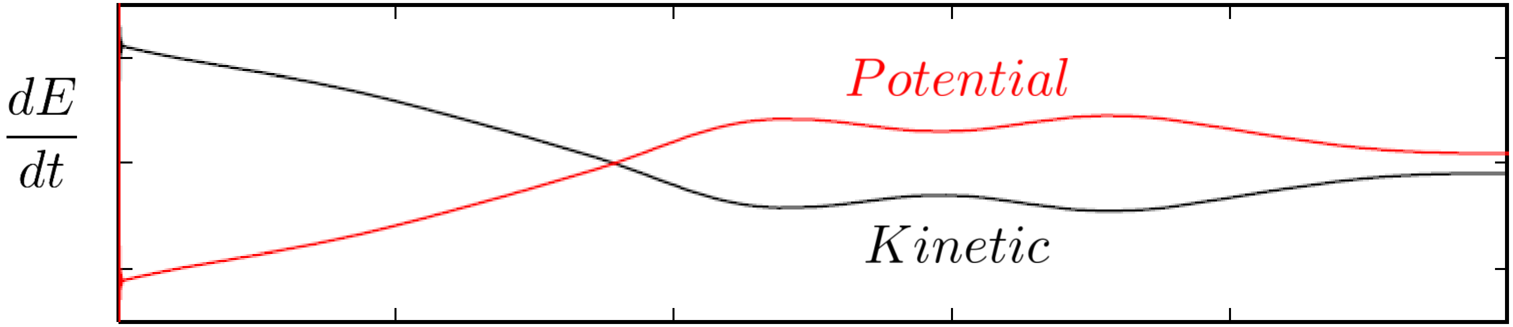
- An introduction to Molecular Dynamics (MD)
- The moving contact line
- The liquid-vapour interface - a Lagrangian reference frame
- Some applications

Molecular Dynamics



Molecular Dynamics

- Solving just Newton's law
  - Energy is automatically conserved → total = kinetic + potential



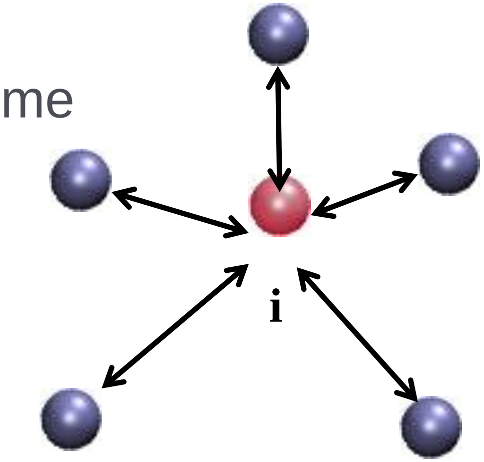
  - Pressure, viscosity, heat flux and surface tension do not need to be specified and, are in fact, all outputs of the simulation
  - Phase change (evaporation, condensation) occur with no additional models needed
  - Solid constructed with molecular roughness
  - Can model complex molecules, water, polymers, biomolecules

Molecular Dynamics

Discrete molecules in continuous space

- Molecular position evolves continuously in time
- Acceleration→Velocity→Position

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



Acceleration obtained from forces

- Governed by Newton's law for an N-body system
- Pairwise electrostatics interactions from quantum mechanics

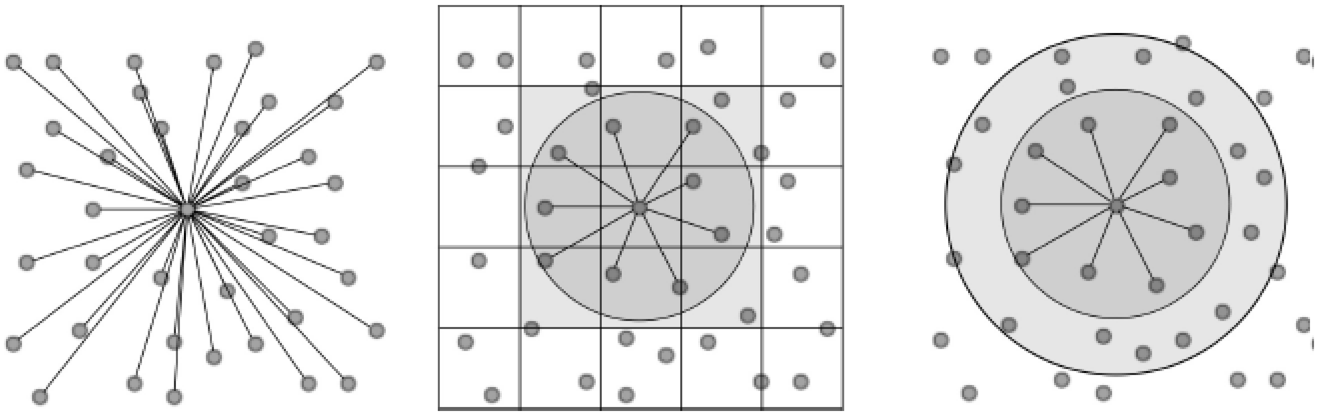
$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i \neq j}^{N} \boldsymbol{f}_{ij}$$

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

MD Computing

- Force Calculation
  - All pairs simulation uses local cell and neighbour lists to reduce the N^2 calculation to order N

$$F_i = \sum_{j \neq i}^{N} f_{ij}$$



- Move particles (leapfrog in time)

$$m_i \frac{dv_i}{dt} \approx m_i \frac{v_i(t + \Delta t/2) - v_i(t - \Delta t/2)}{\Delta t} = F_i$$

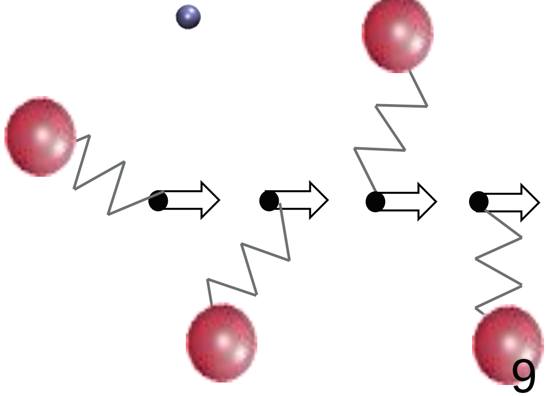
$$\frac{dr_i}{dt} \approx \frac{r_i(t + \Delta t) - r_i(t)}{\Delta t}$$

Non-Equilibrium Molecular Dynamics

- Non-Equilibrium Molecular Dynamics (NEMD) is the study of cases beyond thermodynamic equilibrium, with:
  - Temperature gradients
  - Flow of fluid (e.g. Couette or Poiseuille flow)
- Essentially fluid dynamics - temperature gradients and flows
  - Thermostats (e.g. Nosé Hoover) remove heat from system
  - Solids of molecules with (an)harmonic springs linking them to tether site
  - Sliding walls by moving molecules
  - Many techniques for inducing flows…

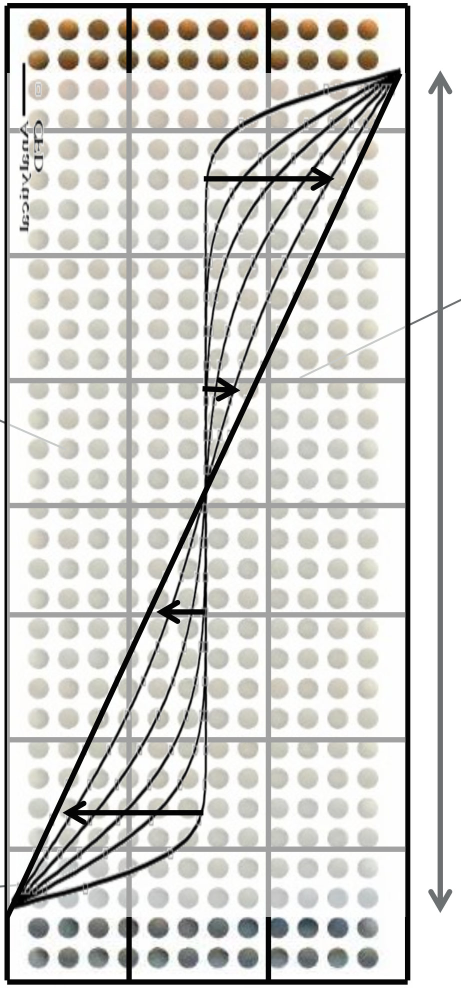
$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{teth} - \psi m_i \boldsymbol{c}_i$$

$$\dot{\psi} = \frac{1}{Q} \left[T - 3T_{target} \right]$$



Wall Bounded Flow

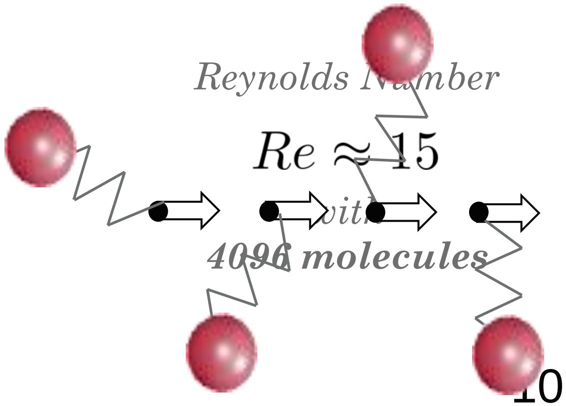
Liquid structure causes viscosity



Average behaviour reproduces hydrodynamics (coloured by velocity)

$H \approx 9nm$

Stick-slip near walls



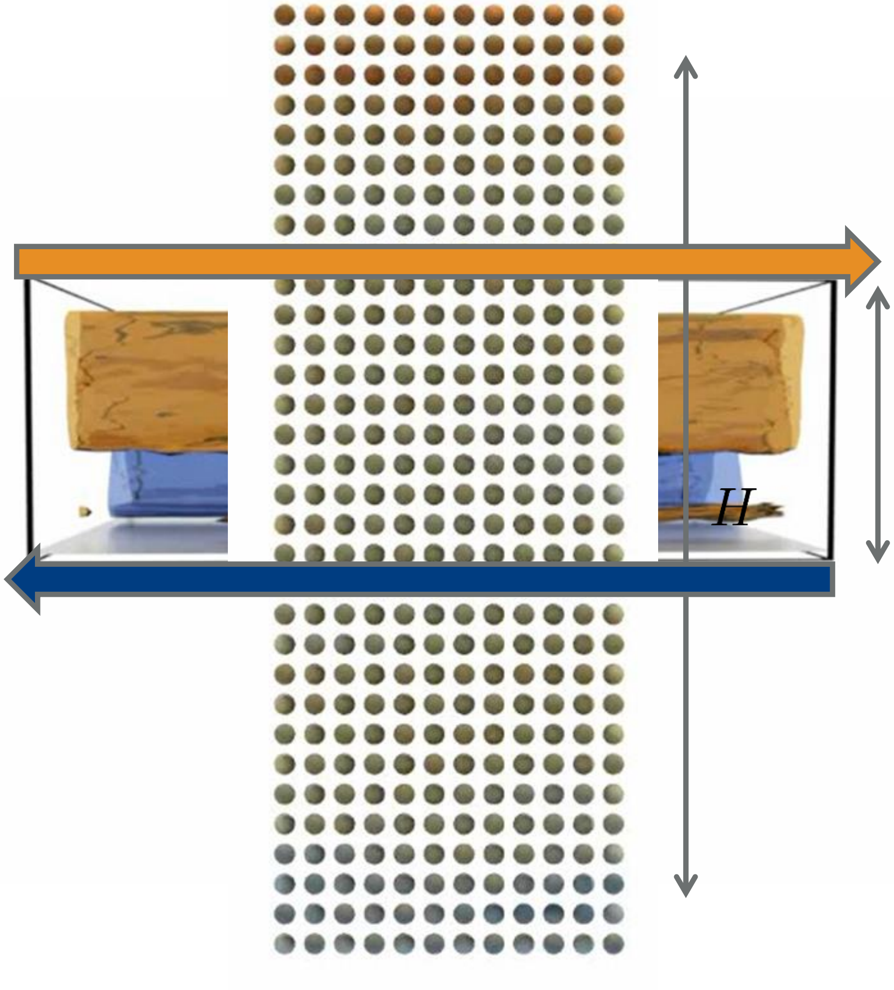
Reynolds Number

$Re \approx 15$

with

4096 molecules

Wall Bounded Flow



Reynolds Number

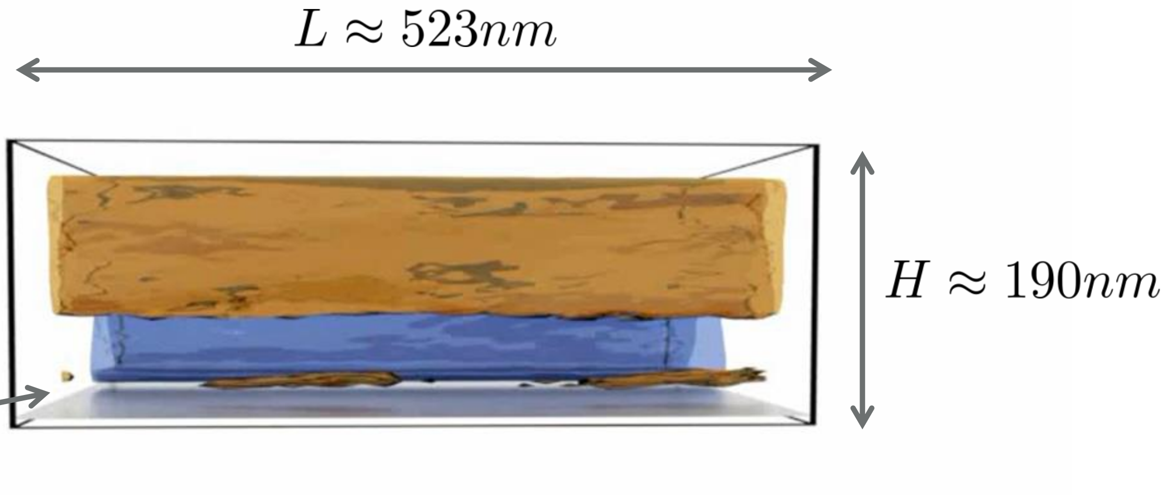
$$Re \approx 400$$

with

300 million
molecules

Wall Bounded Flow

Minimal channel Couette flow



$L \approx 523nm$

$H \approx 190nm$

$W \approx 359nm$

Reynolds Number

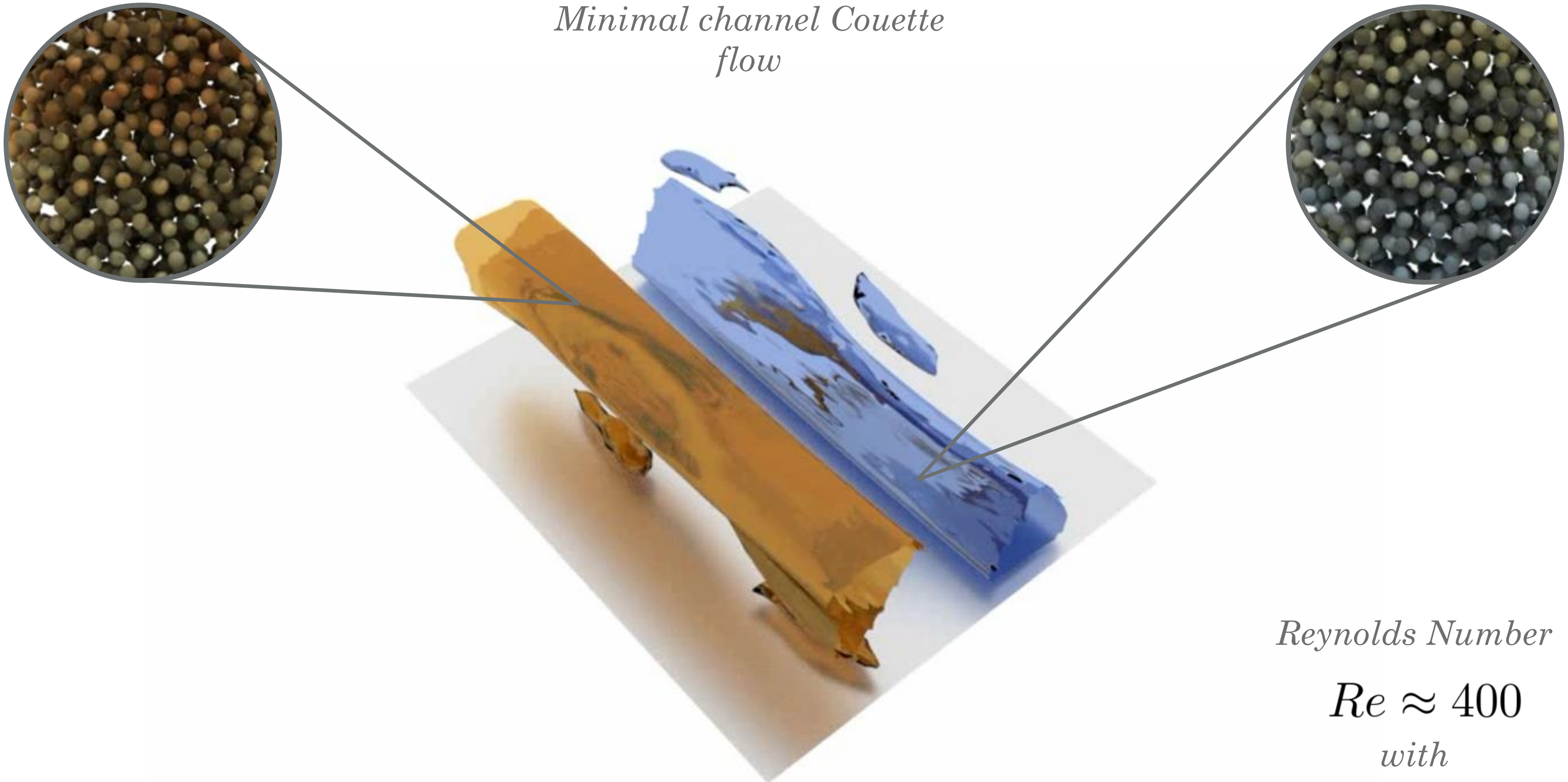
$Re \approx 400$

with

300 million molecules

Molecular Dynamics - Turbulence

Minimal channel Couette flow



Isosurfaces of turbulent kinetic energy coloured by velocity

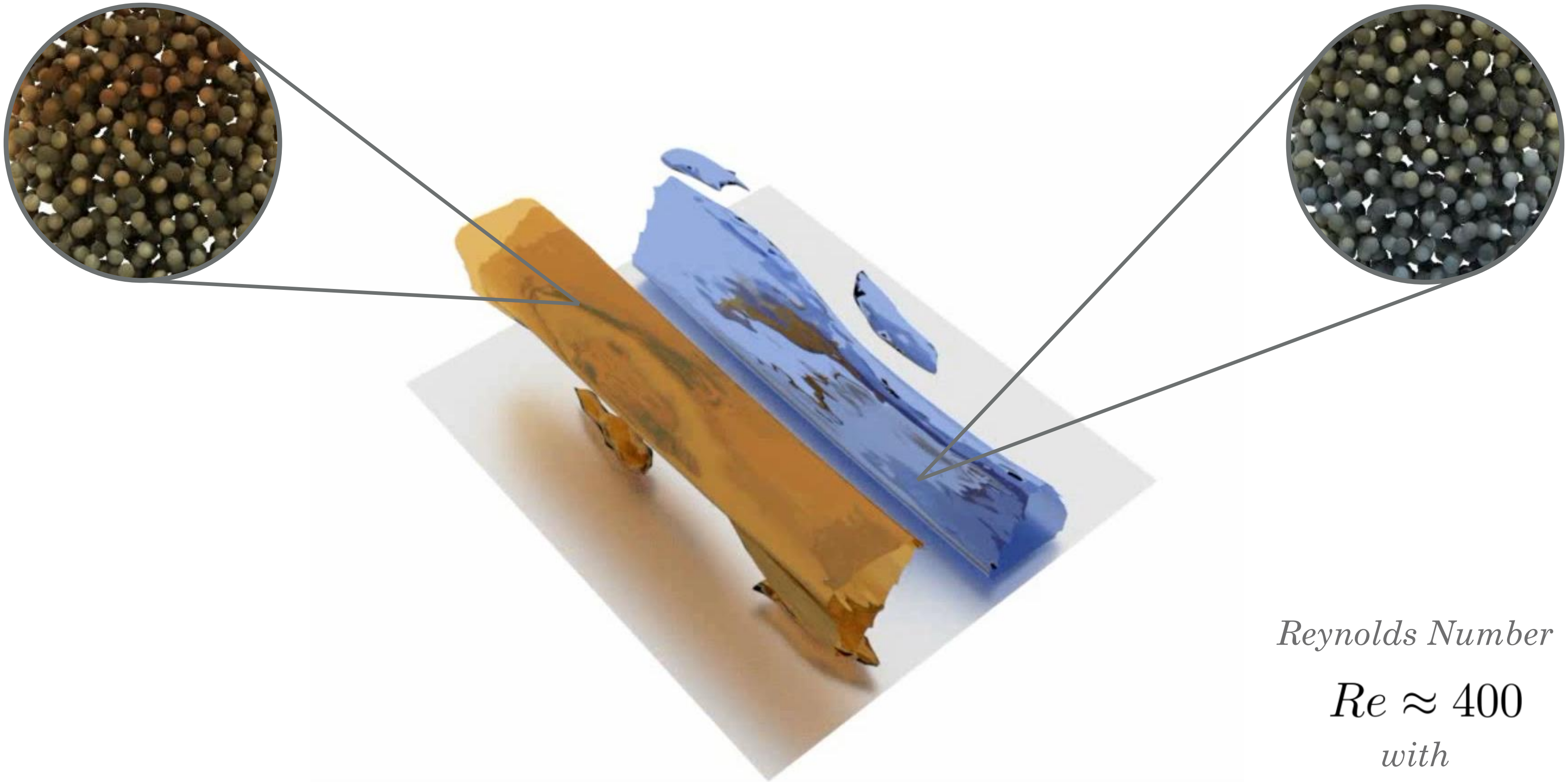
Reynolds Number

$$Re \approx 400$$

with

300 million molecules

Molecular Dynamics - Turbulence



Isosurfaces of turbulent kinetic energy coloured by velocity

Reynolds Number

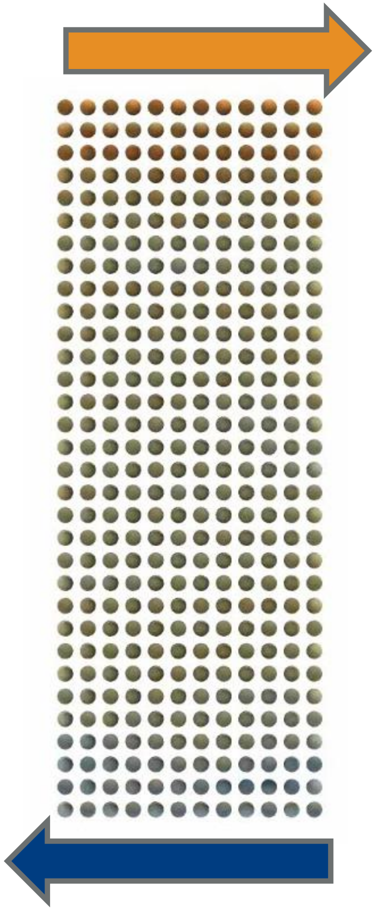
$Re \approx 400$

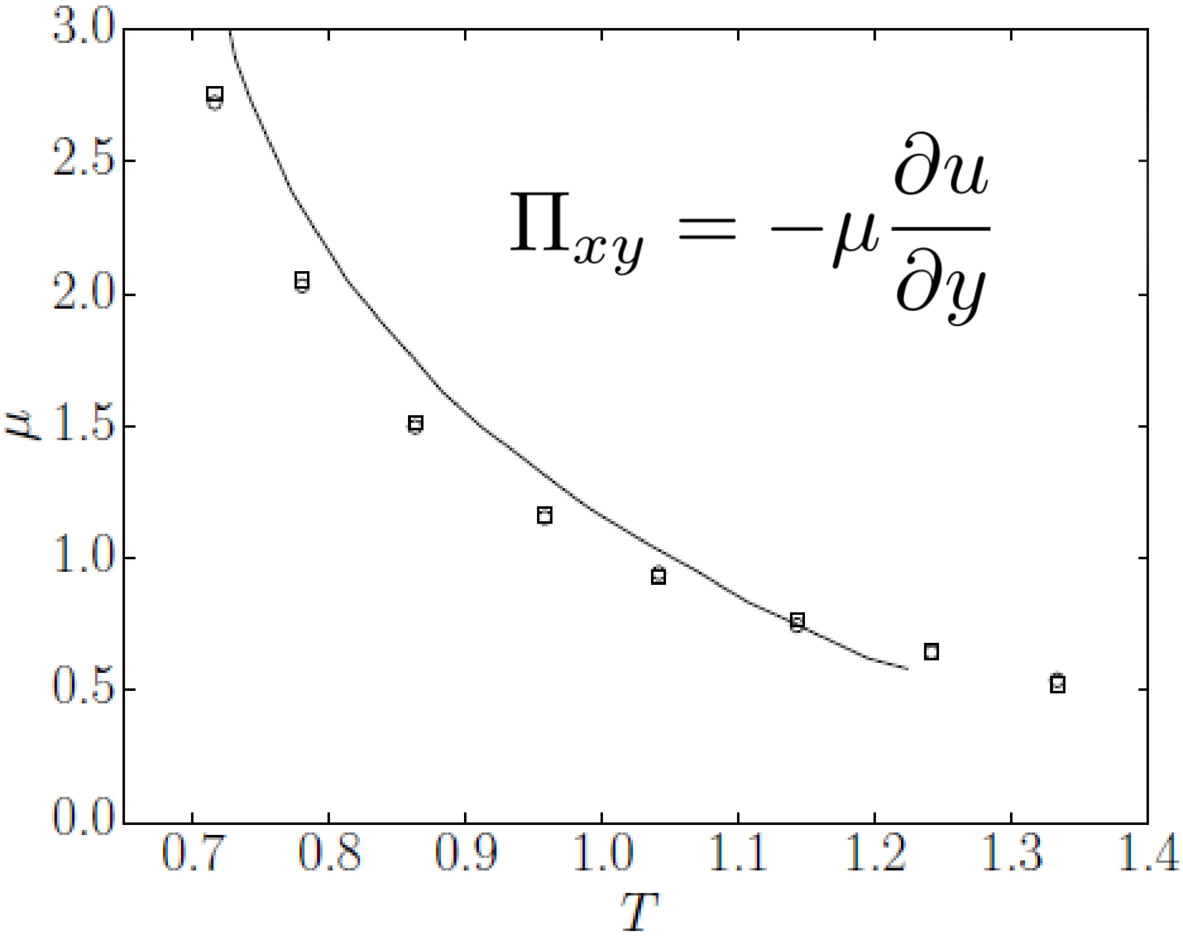
with

300 million molecules

Viscosity

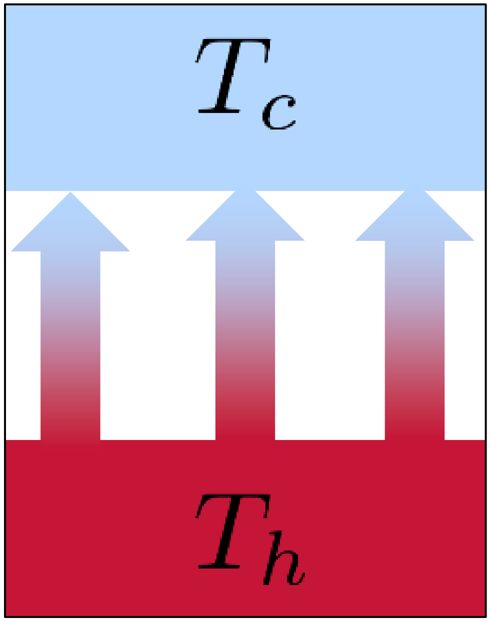
- Good agreement with experiments

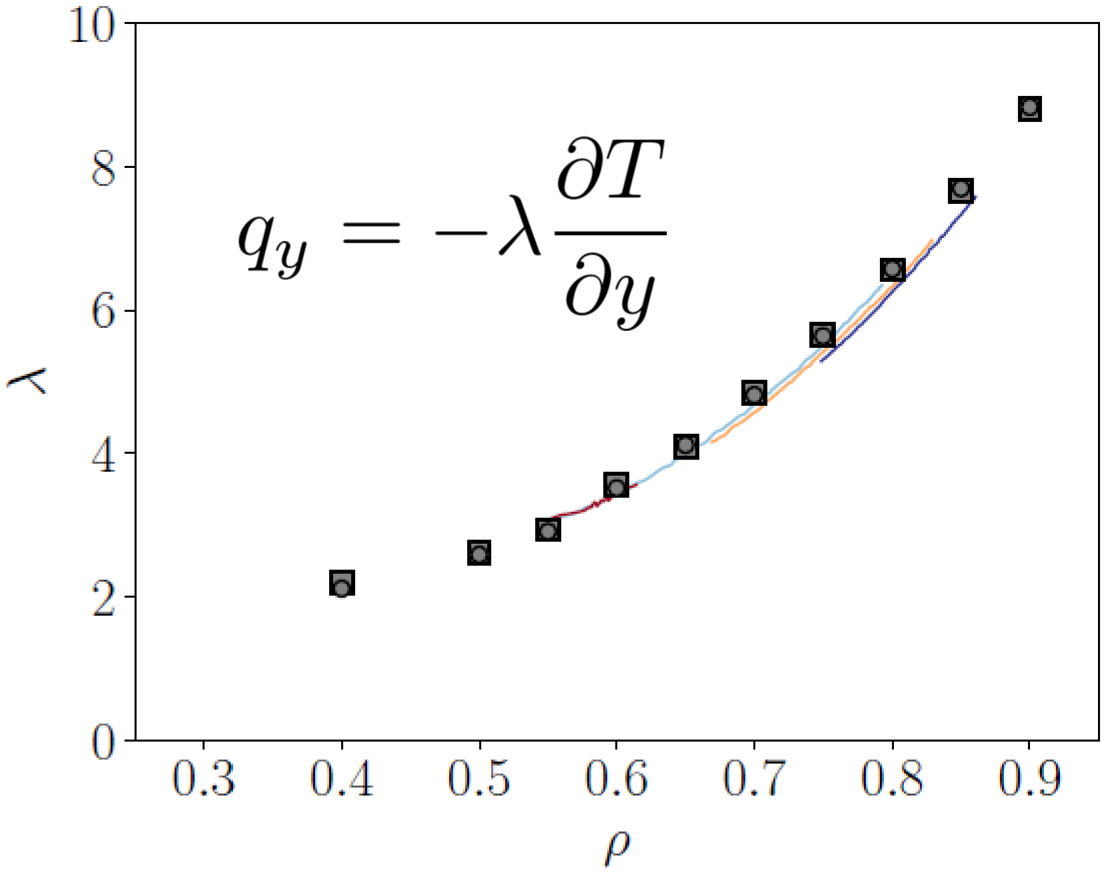




Heat Conduction

- Good agreement with experiments

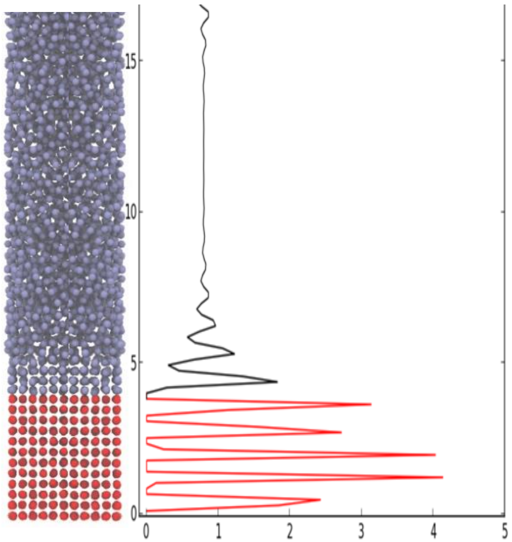




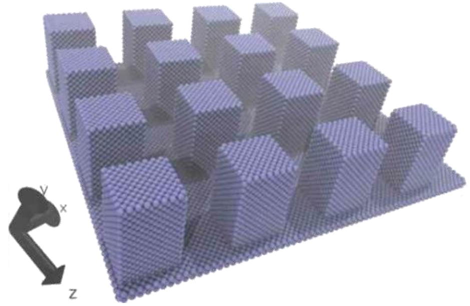
Molecular Dynamics – Complex Walls and Fluids

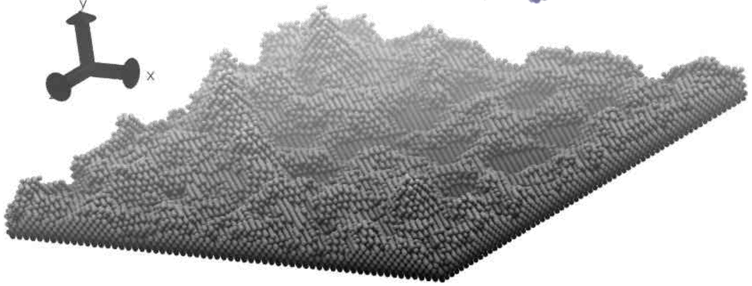
Liquid structure causes viscosity

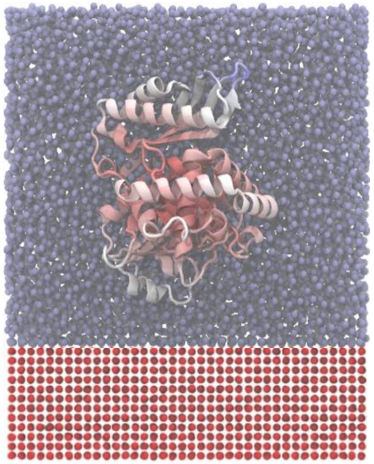
Stick-slip near walls



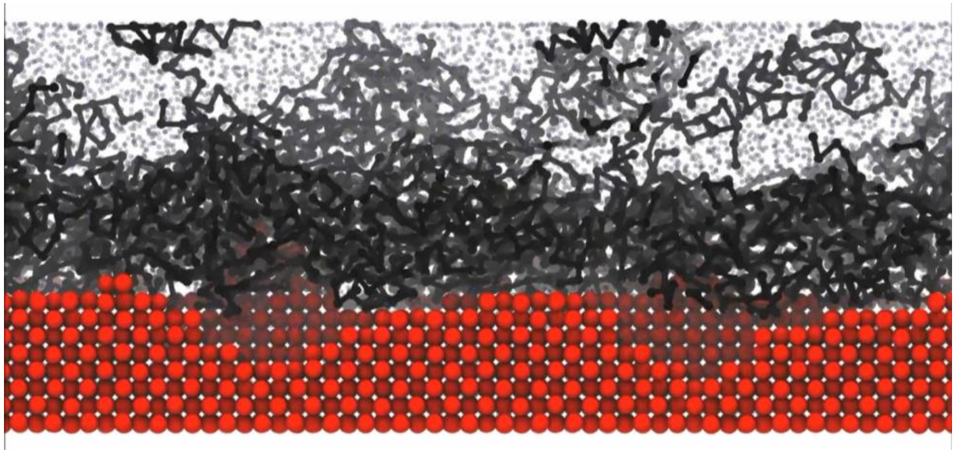
Wall Texture







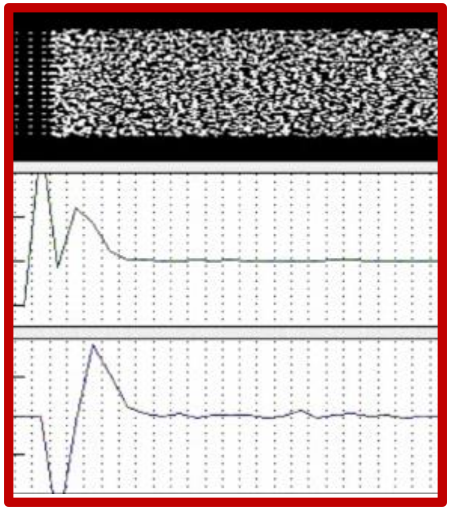
Molecules of arbitrary complexity



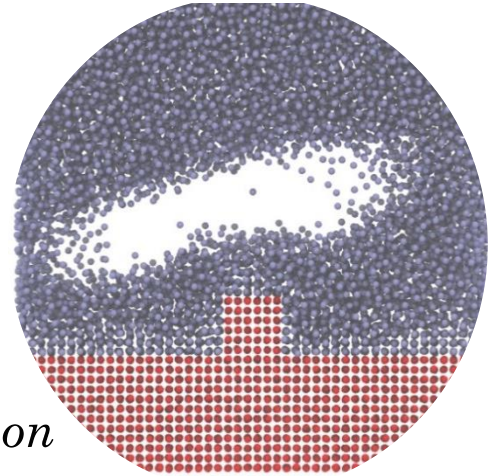
Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

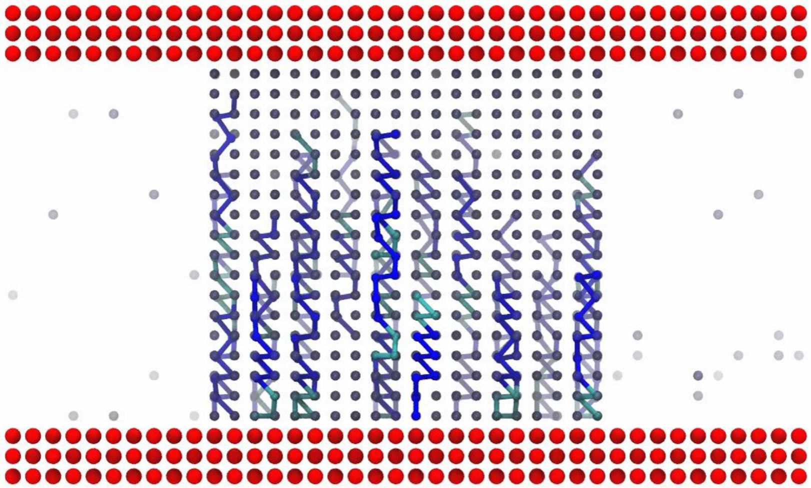
Shockwave



Droplet Formation

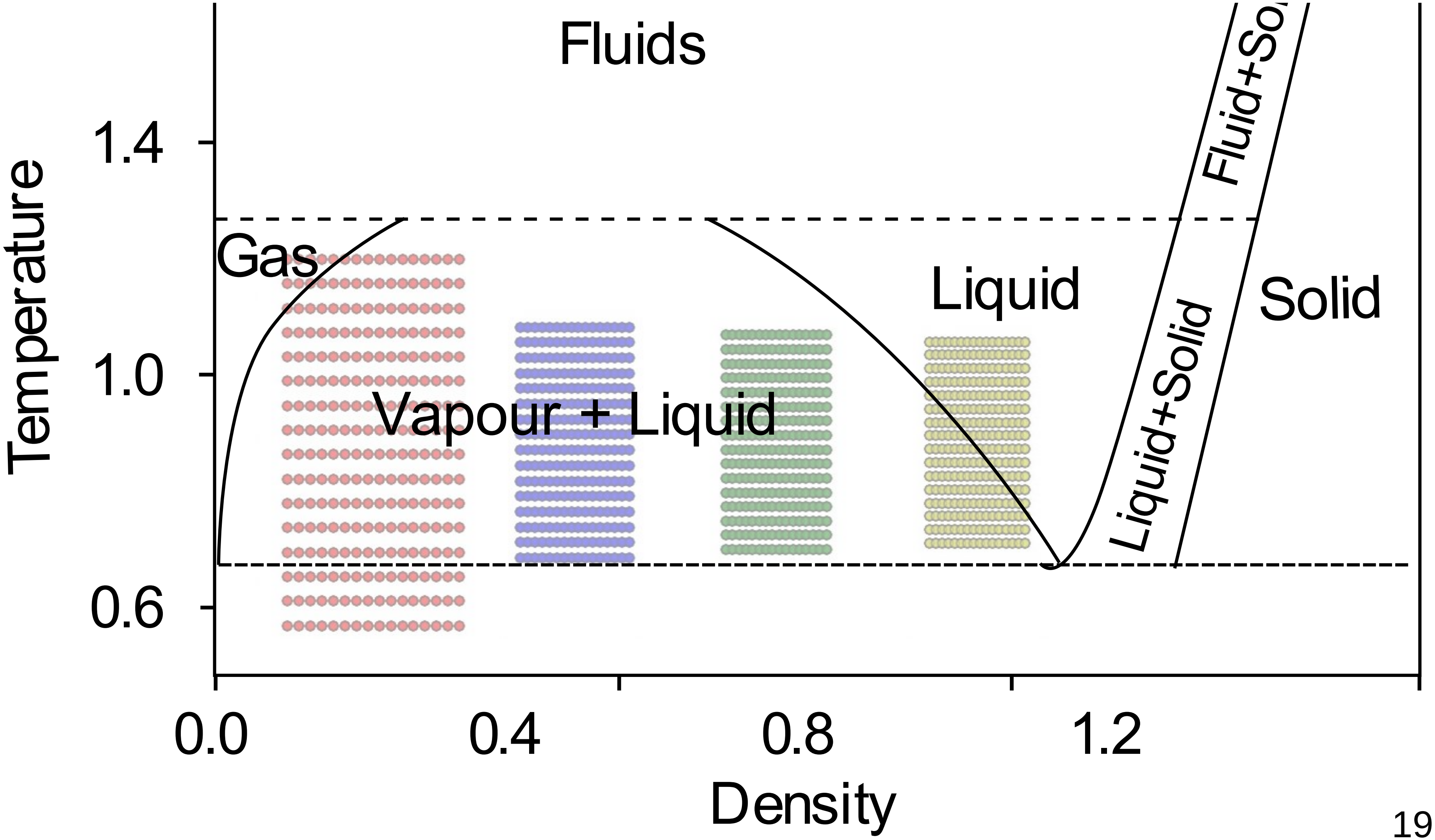


Nucleation



Contact line

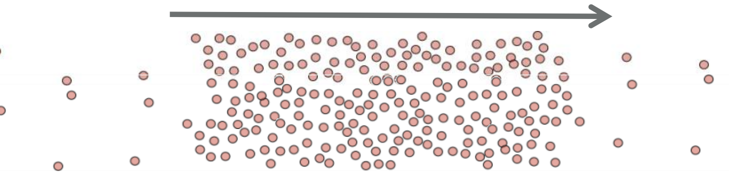
Phase Change



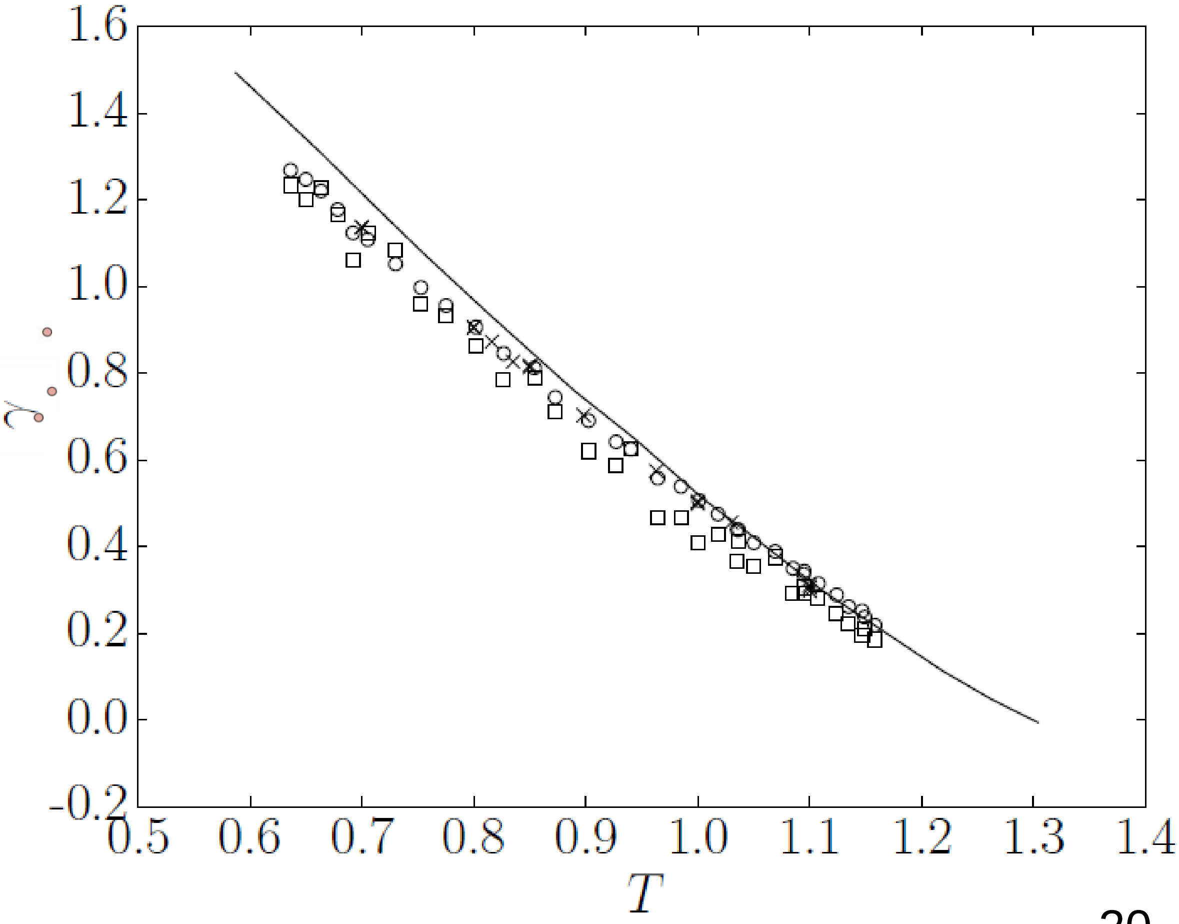
Results for Surface Tension

- Good agreement with experiments

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



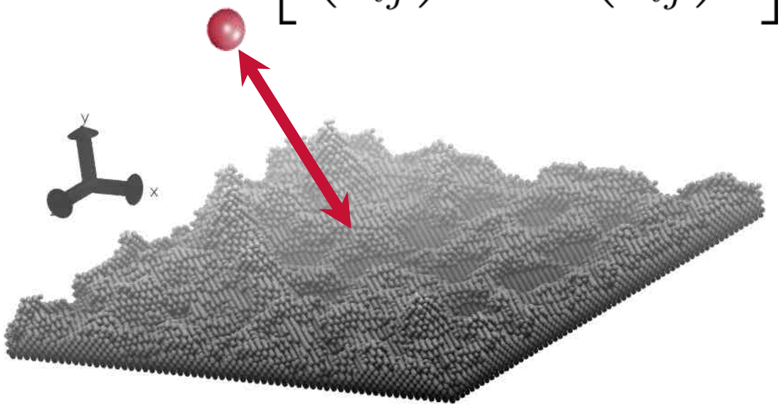
Integrate over Liquid Vapour interface(s)

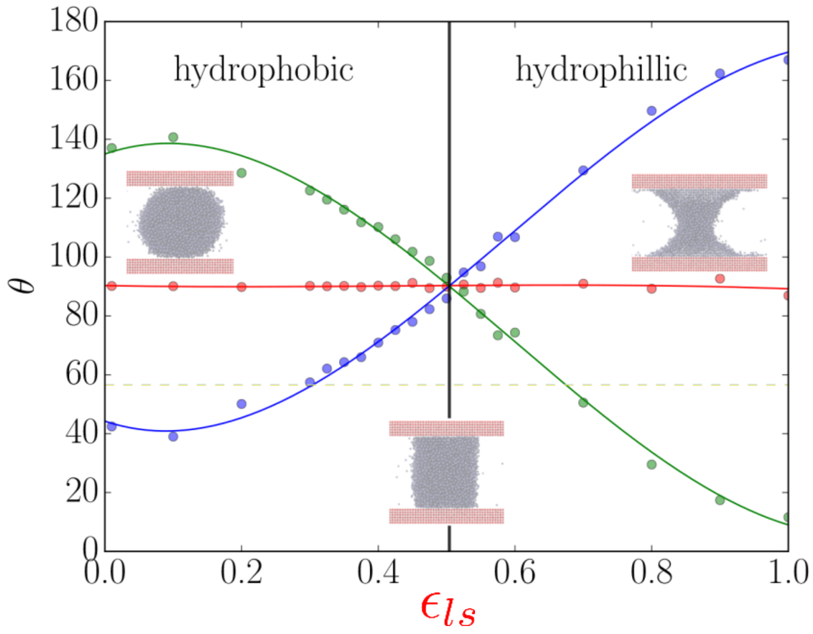


Surface Wettability

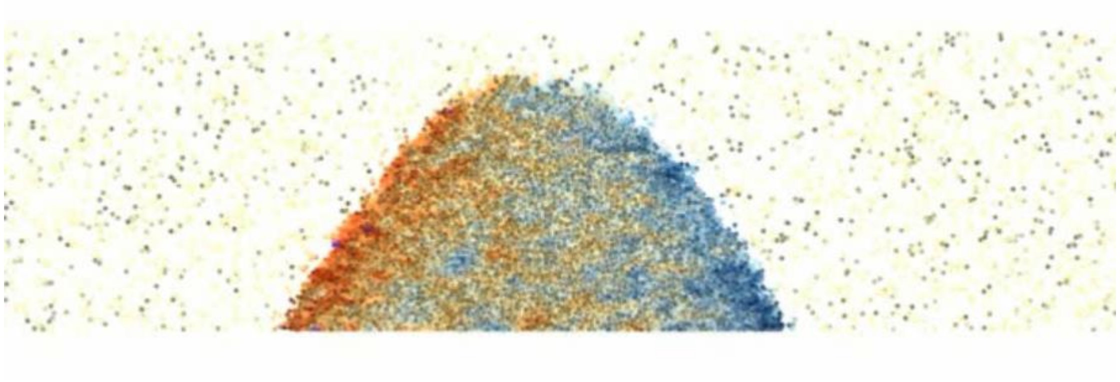
- Depends entirely on the “wetting” interaction between surface and fluid, tuned using:
  - Mixing rules, e.g. Lorentz-Berthelot $\epsilon_{ls} = \sqrt{\epsilon_l \epsilon_s}$
  - Bottom up simulation e.g. quantum mechanics
  - Top down e.g. to get desired contact angle

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



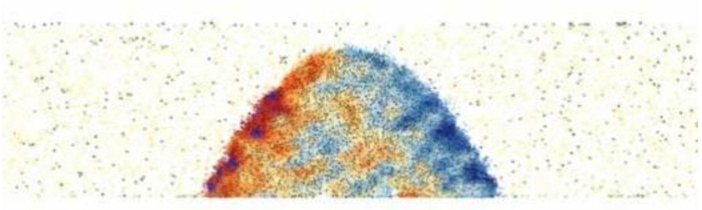


The Moving Contact Line

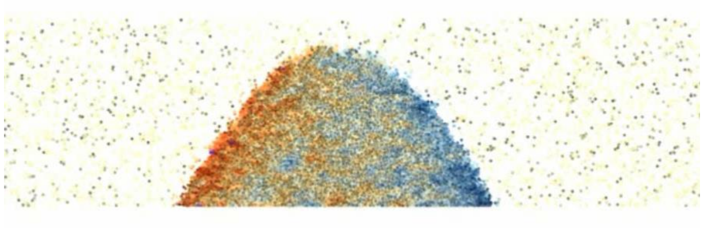


MD Simulation of Droplets

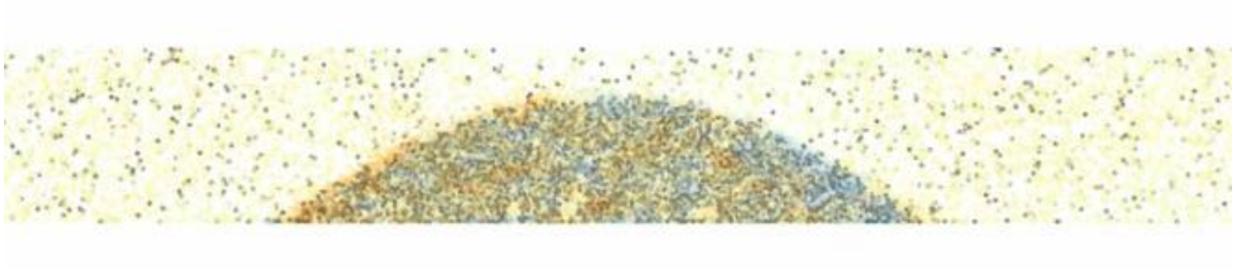
- Low Wettability



- Intermediate Wettability

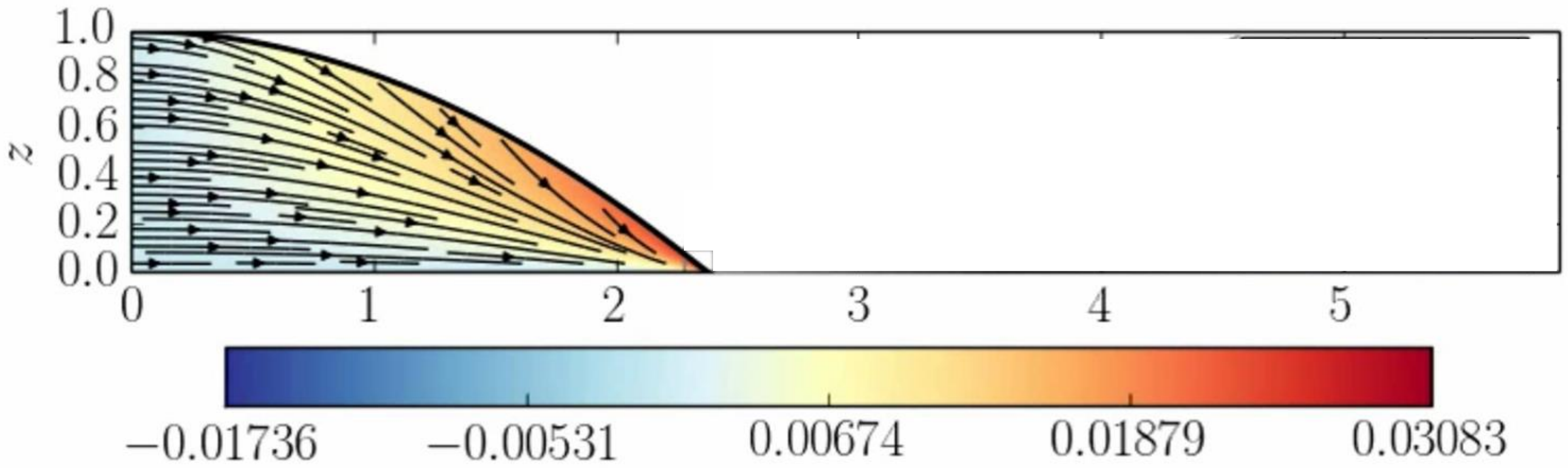


- High Wettability



Work with Omar Matar, Erich Muller and Richard Craster

Dynamic Contact Line



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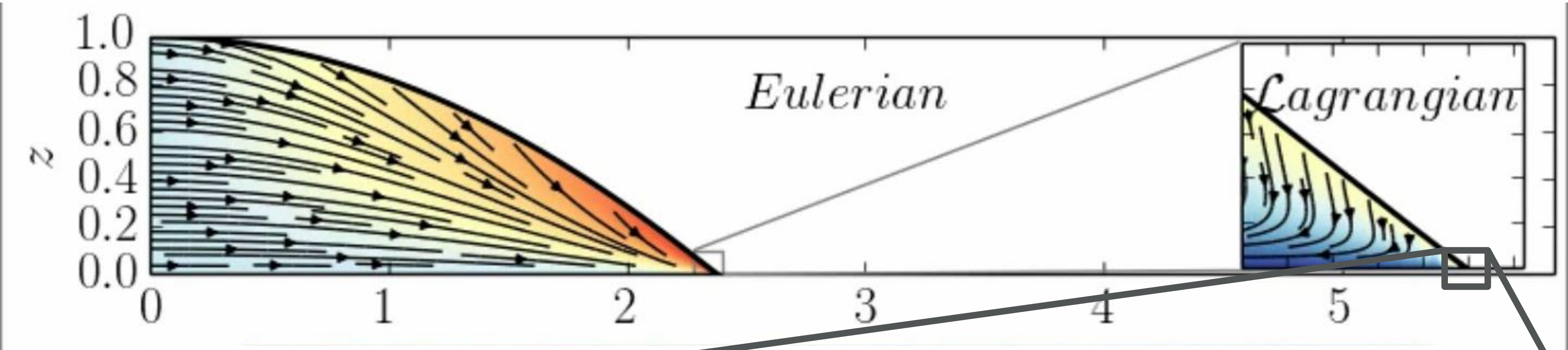
Dynamic Contact Line



- Model the moving contact line with MD

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

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

Work with Omar Matar, Erich Muller and Richard Craster

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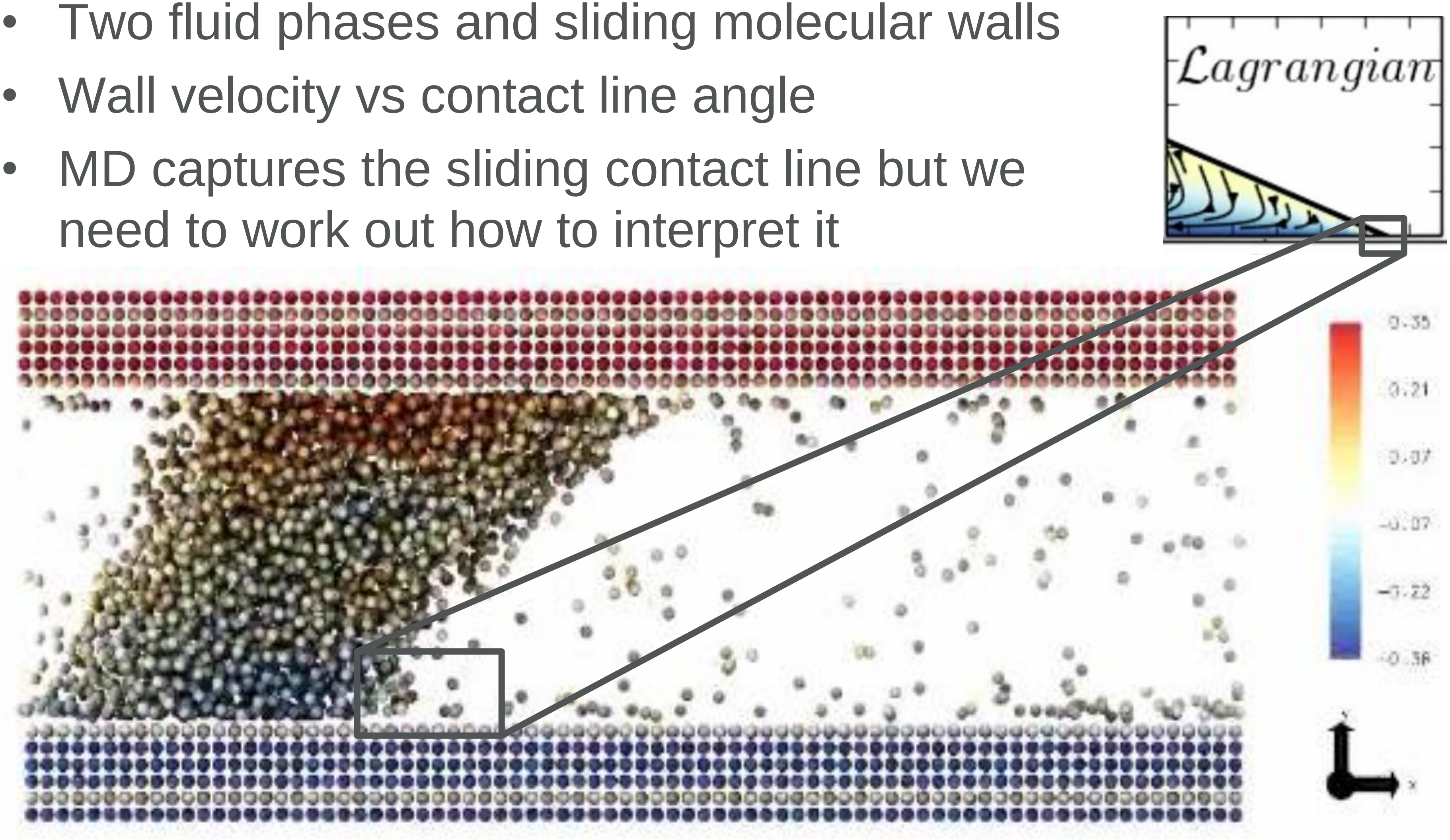
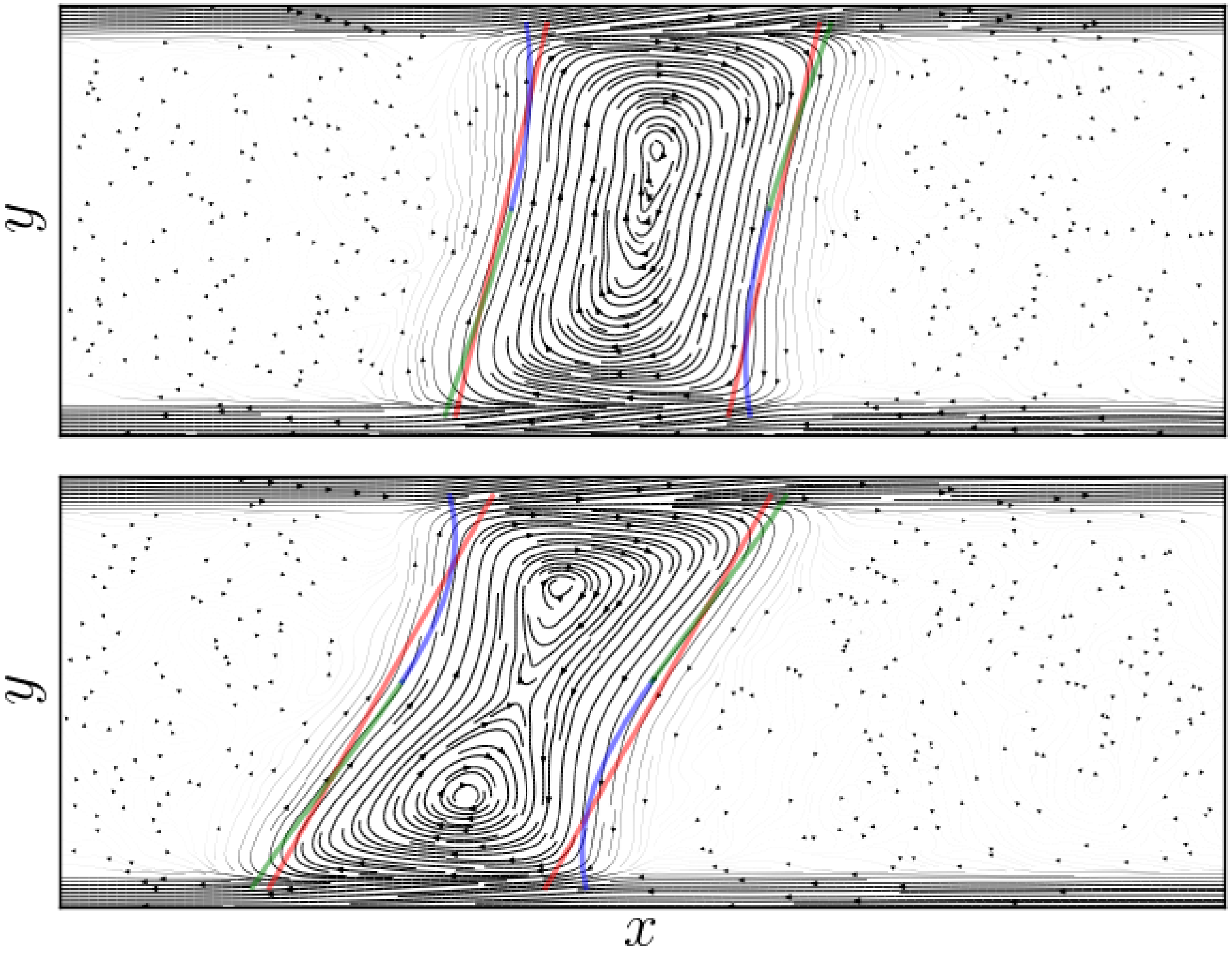
Dynamic Contact Line

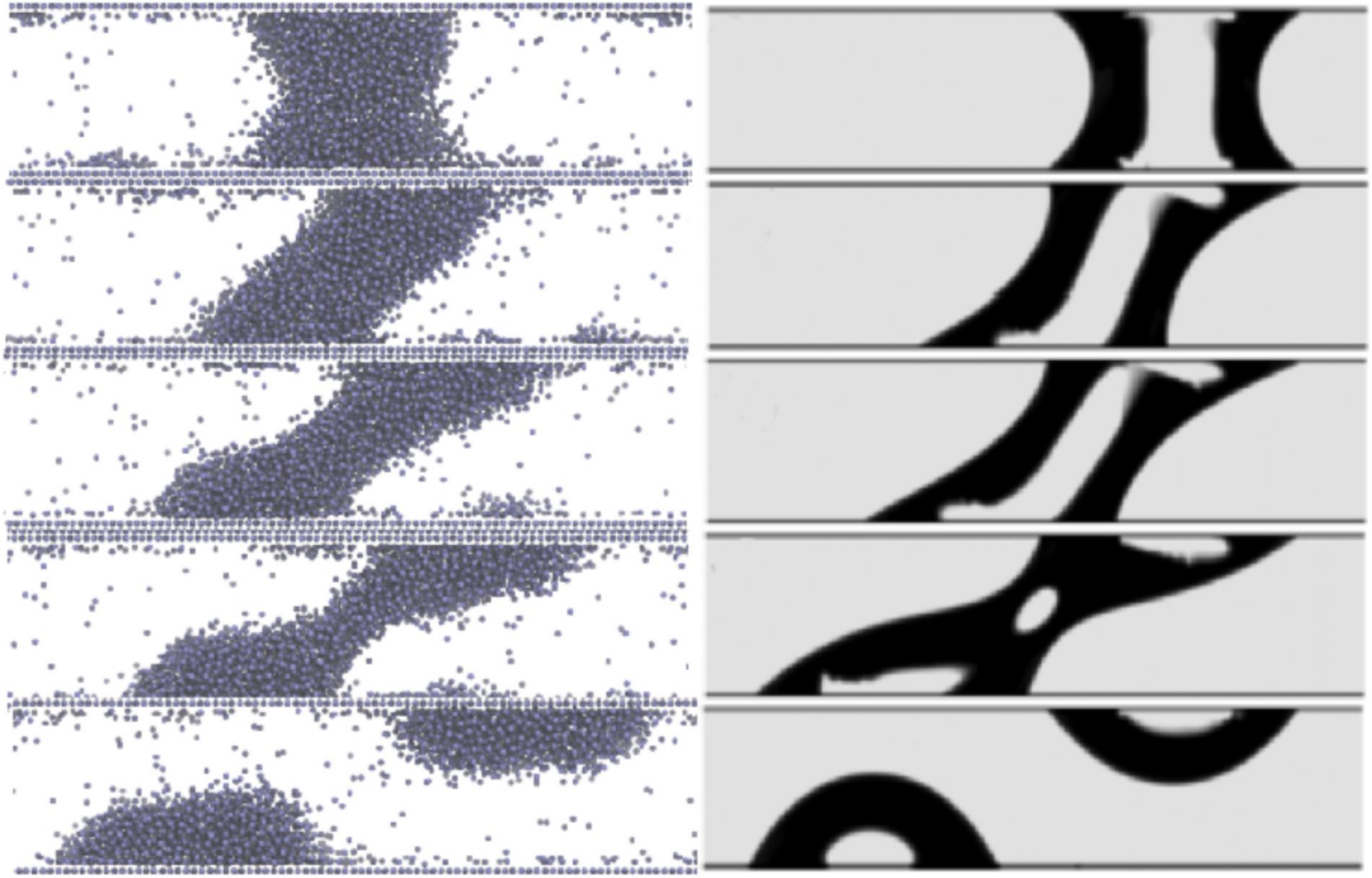
- Two fluid phases and sliding molecular walls
- Wall velocity vs contact line angle
- MD captures the sliding contact line but we need to work out how to interpret it



Flowfields



Link to Experiments

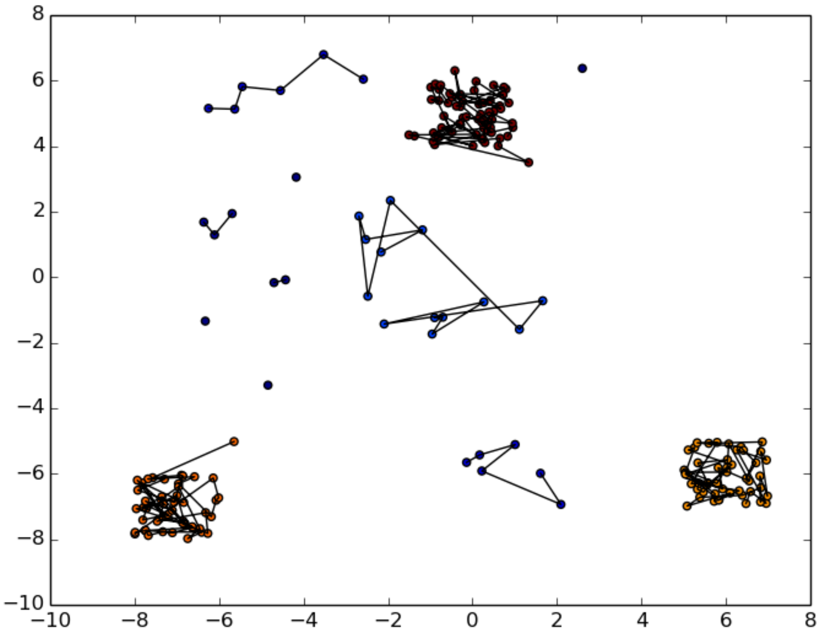


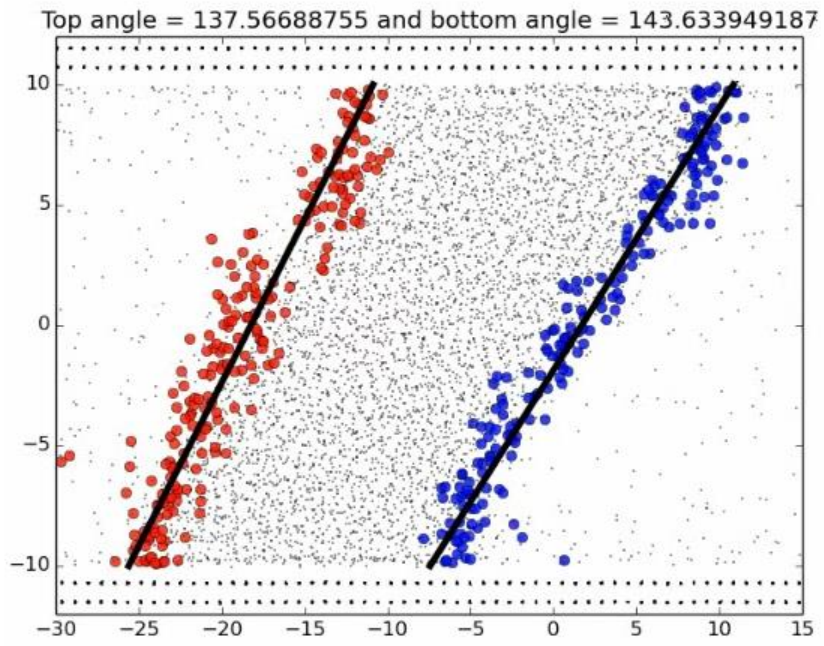
L. Wang and T. J. McCarthy, Langmuir, 2013, 29, 7776

Identifying the Liquid and Surface Fitting

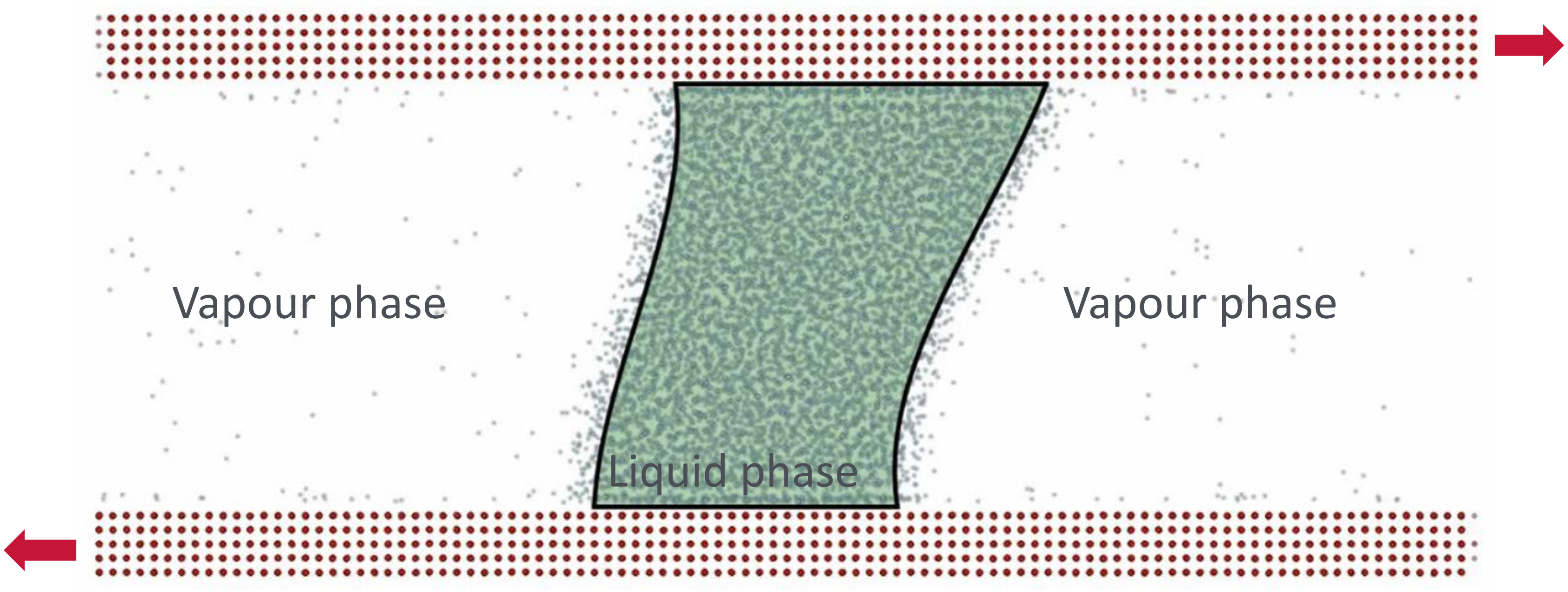
Cluster Analysis to identify the liquid droplets

Least Square fitting to outer molecules, linear example here



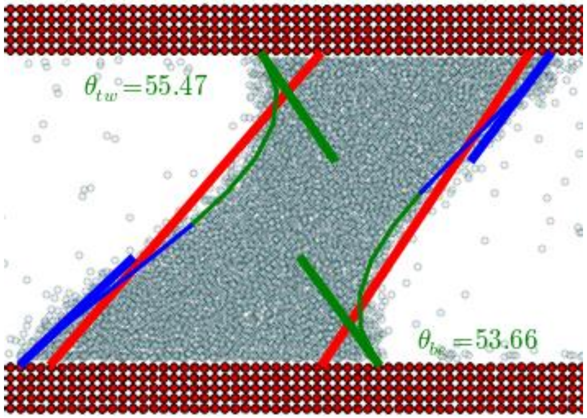


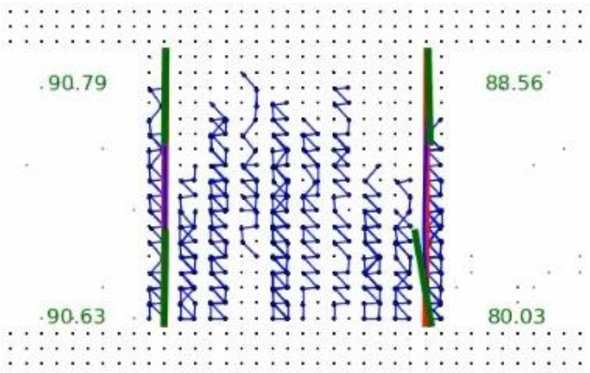
A Cubic Fit to the Interface

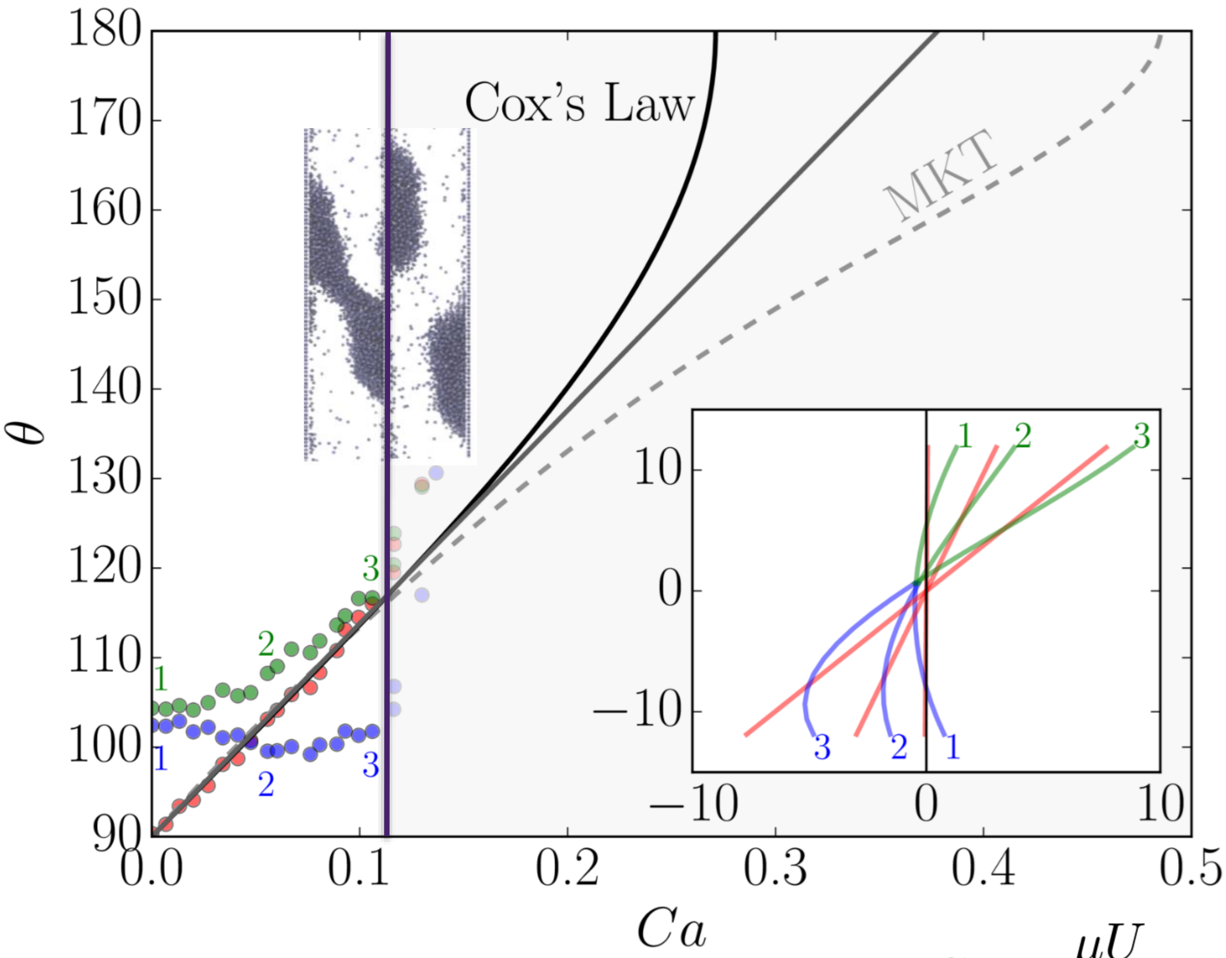


Sliding Solid walls (tethered)

Angle vs. Velocity



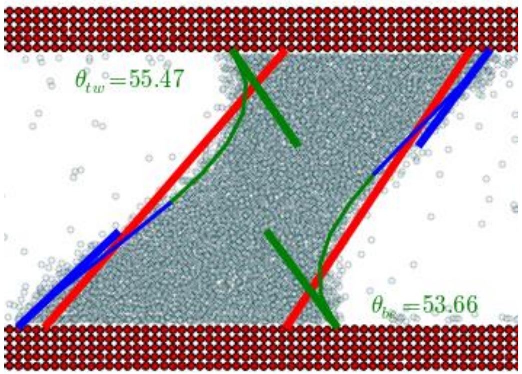


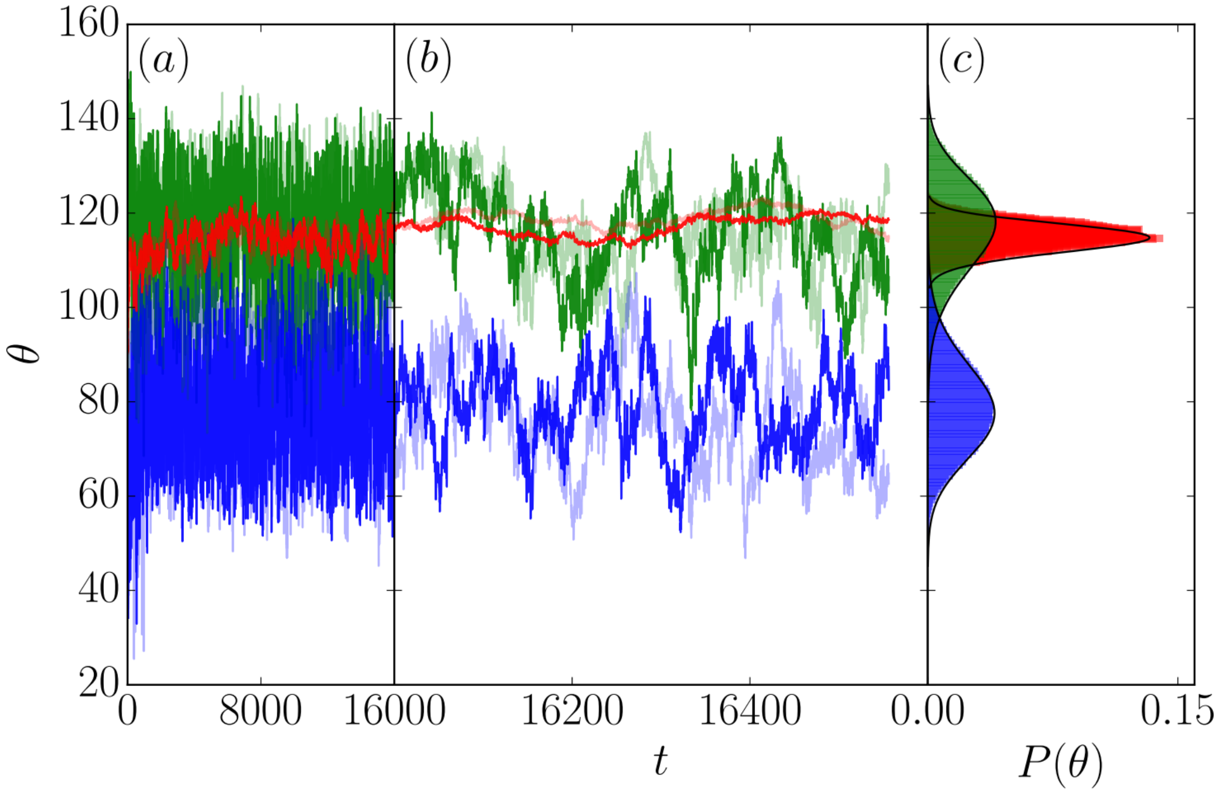


$$Ca = \frac{\mu U}{\gamma}$$

Time Evolution of Contact Angle

- Linear and Cubic Fitting angles fluctuates over time





- Steady state so we can take the probability density function of angle

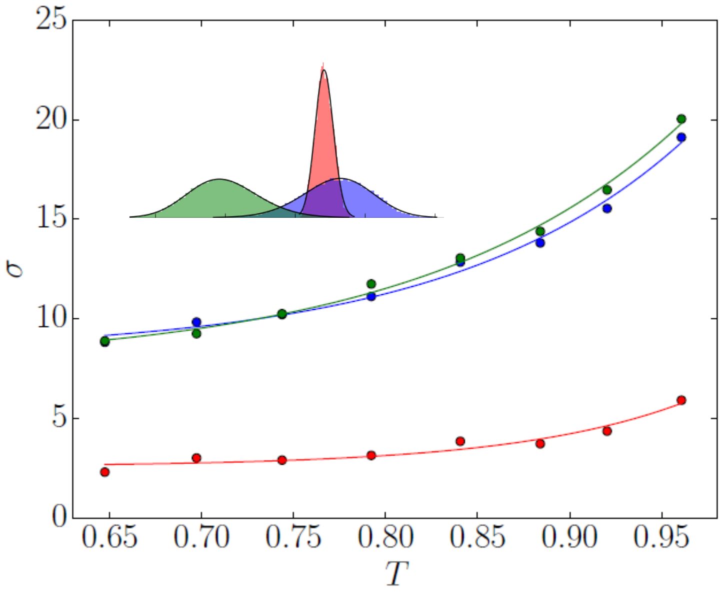
- *Linear*, *Advancing* and *Receding angles*

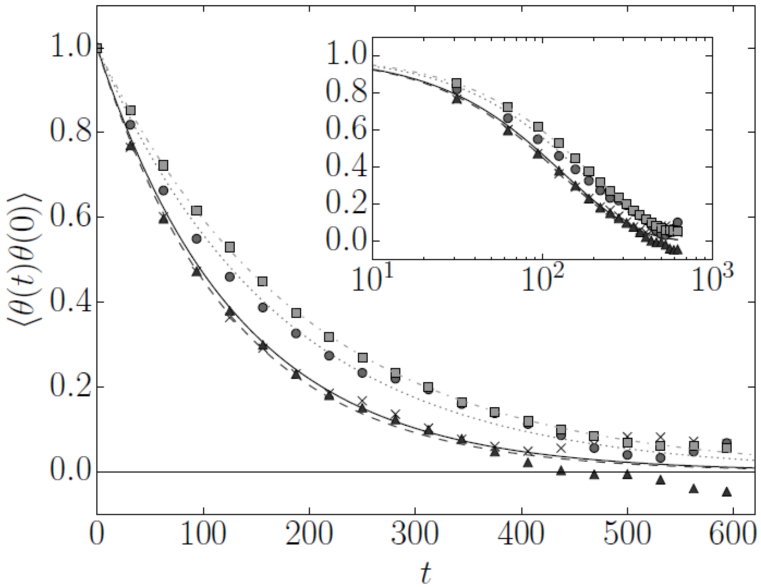
Building this into the Continuum Model

- A Langevin Equation uses random noise to model this

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

- Coefficients parameterised using
  - Standard deviation – range of fluctuations
  - Autocorrelation – how quickly they decay.





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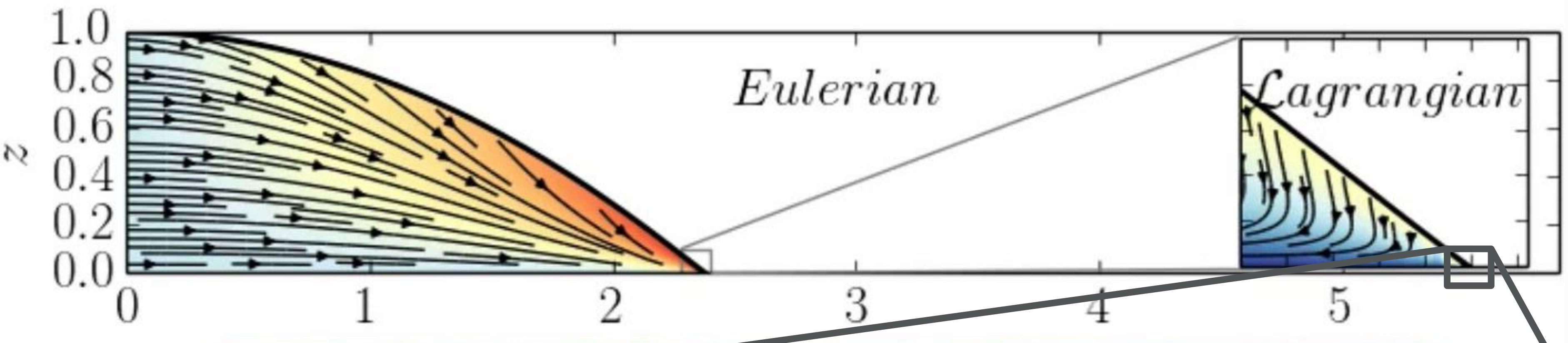
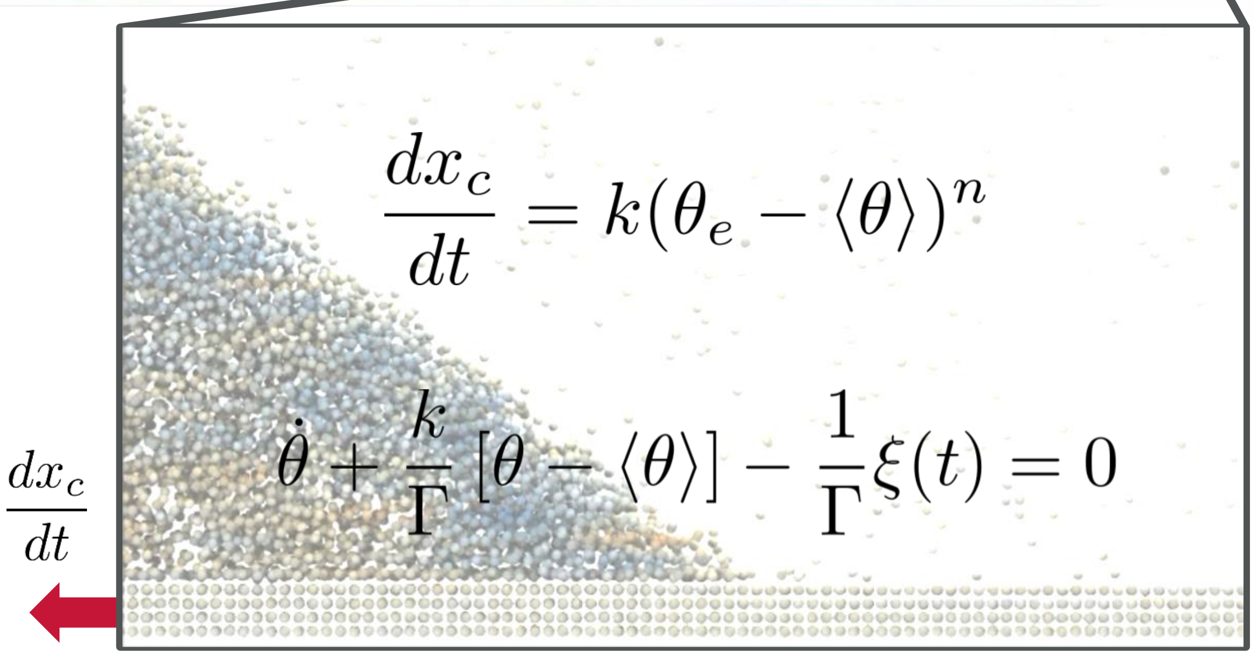
Building this into the Continuum Model



- Bulk dynamics from a law like Tanners or Cox

- Add in fluctuations from the MD using the Langevin model

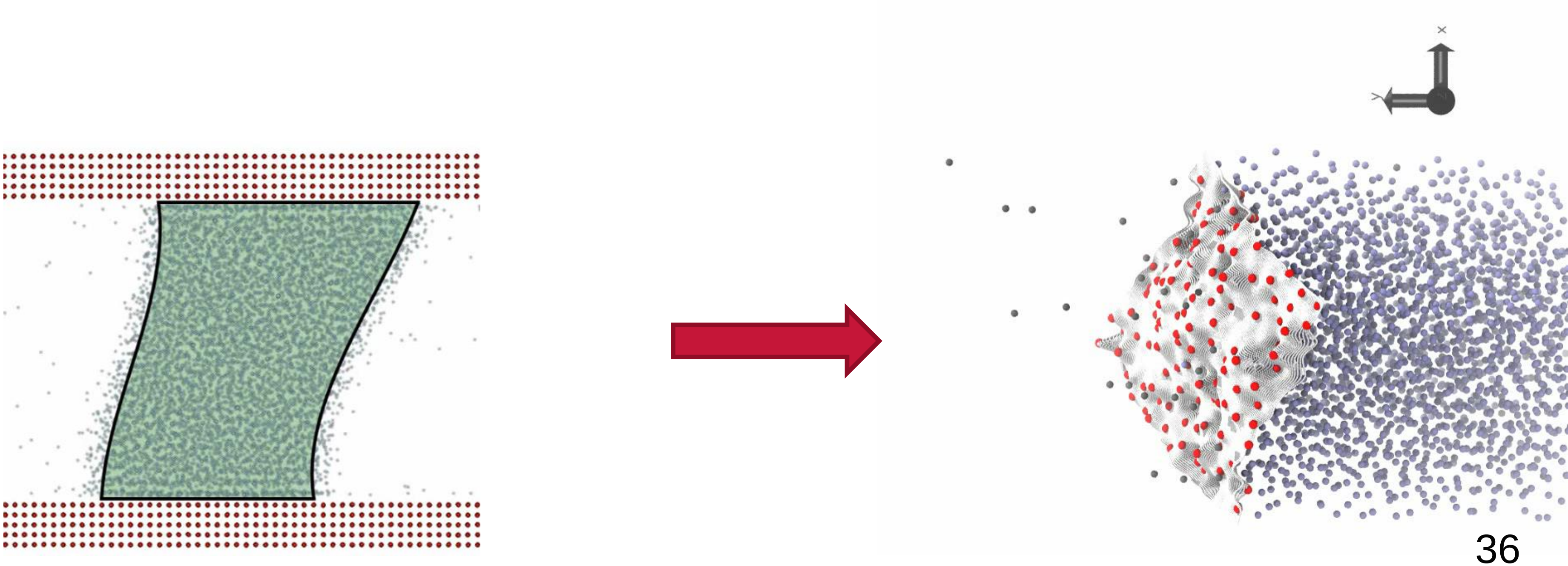


$$\frac{dx_c}{dt} = k(\theta_e - \langle\theta\rangle)^n$$

$$\dot{\theta} + \frac{k}{\Gamma}[\theta - \langle\theta\rangle] - \frac{1}{\Gamma}\xi(t) = 0$$

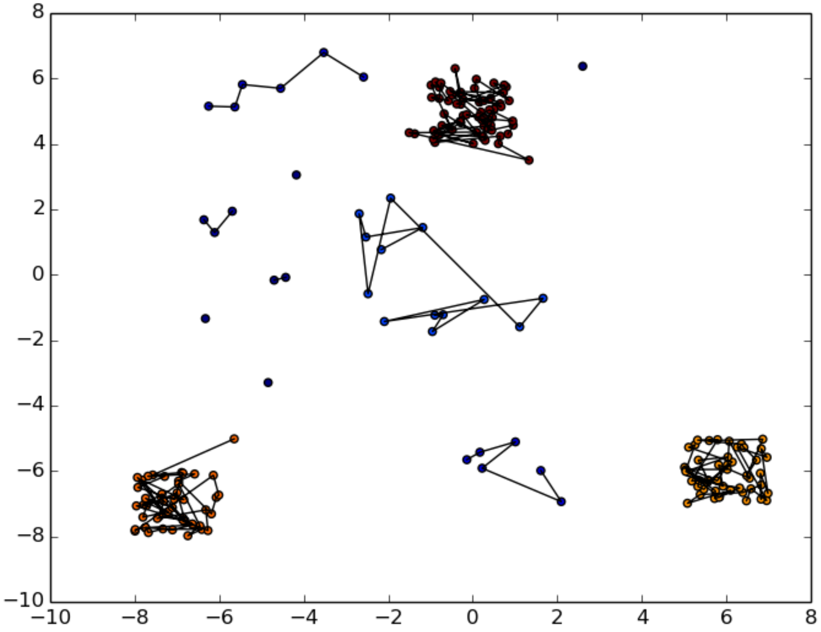
$$\frac{dx_c}{dt}$$

The Intrinsic Interface

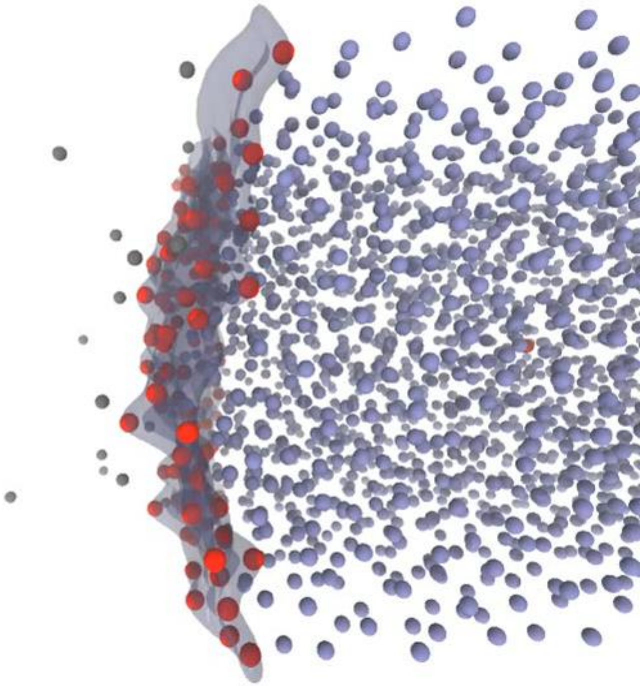


Identifying the Liquid

Cluster Analysis to identify the liquid droplets

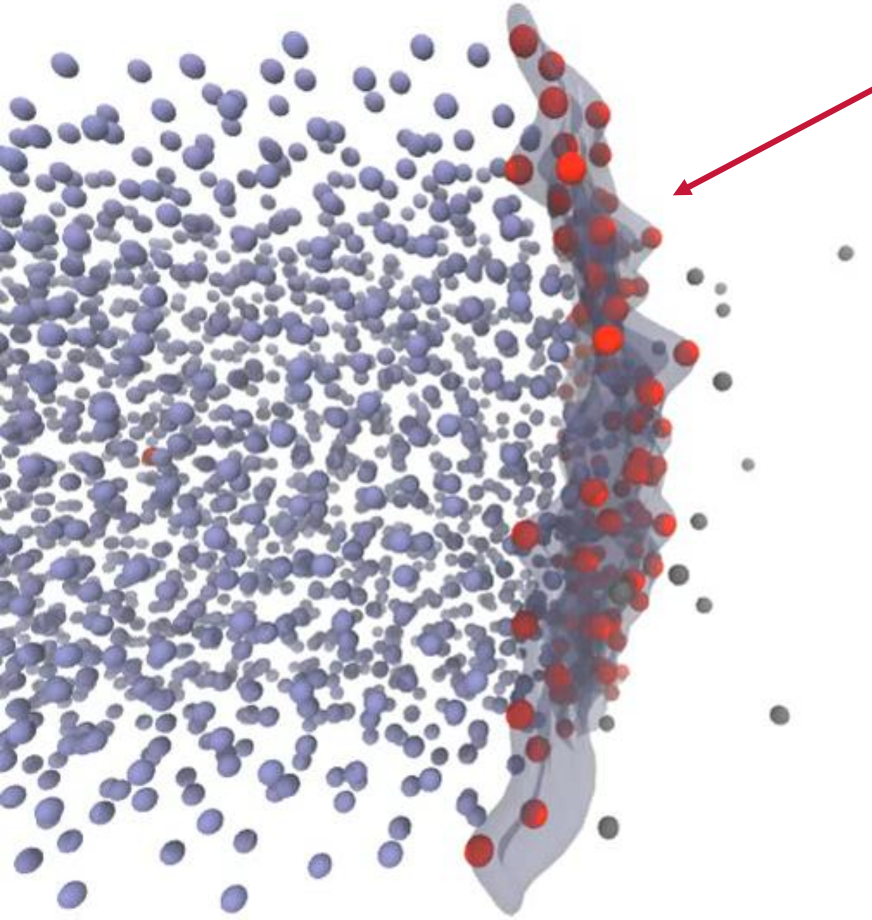


Least Square fitting to outer molecules



The Intrinsic Interface

- The Intrinsic Interface method

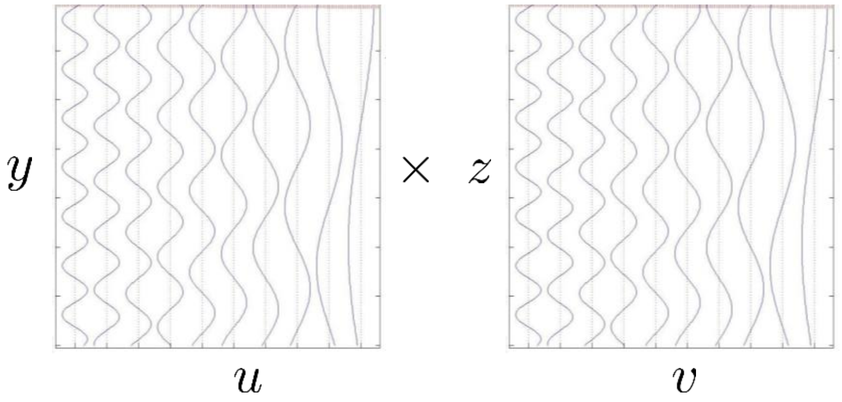


  - Surface fitted by least squares

$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}} \approx \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t)\xi_u(y)\xi_v(z),$$

  - Sum of sines and cosines down to intermolecular spacing

$$\xi_a(b) = \begin{cases} cos\left(2\pi ab\right) & \text{if } \ a>0 \\ sin\left(2\pi|a|b\right) & \text{otherwise,}\end{cases}$$

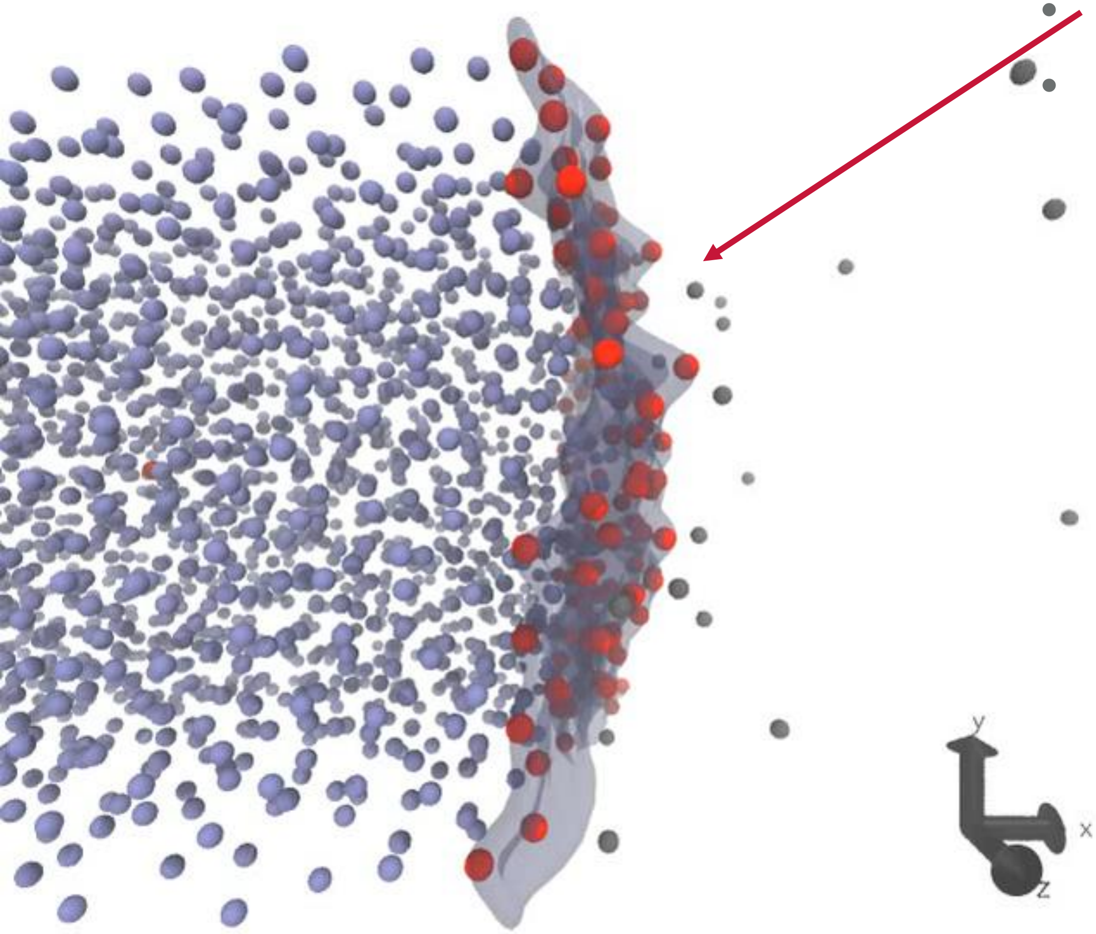


Chacon & Tarazona (2003) PRL 91, 166103

Work with Carlos Braga and Serafim Kalliadasis

The Intrinsic Interface

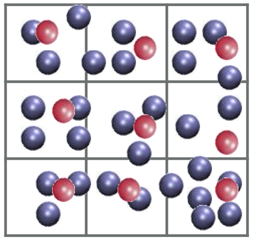
- The Intrinsic Interface method



- Surface fitted by least squares
- Sum of sines and cosines down to intermolecular spacing

Fitting occurs in stages

> Fit to an outer set using a grid (e.g. 3 by 3)



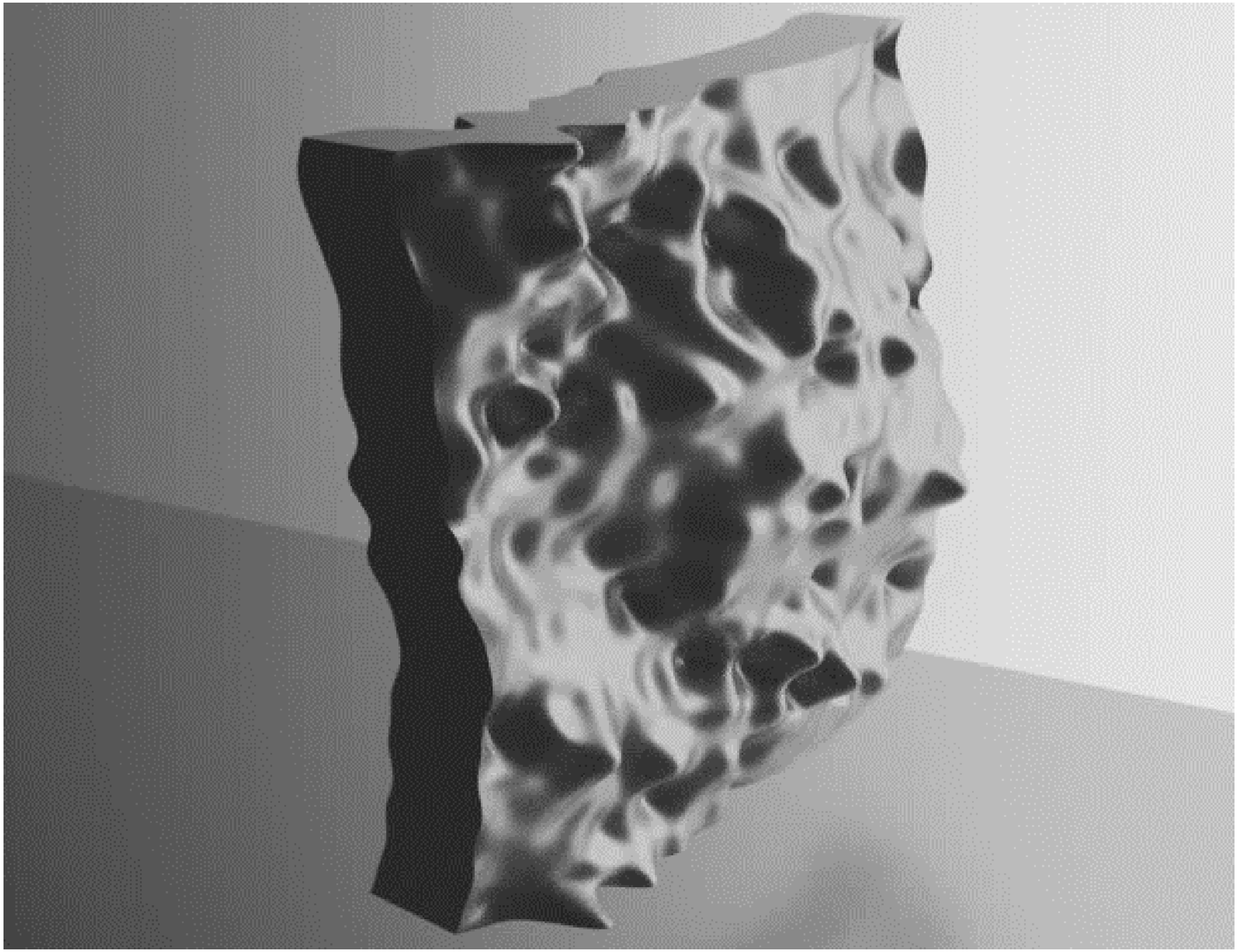
> Order molecules based on distance from surface

> Add nearest

> Repeat until surface density reaches target value (~0.7)

Chacon & Tarazona (2003) PRL 91, 166103

The Intrinsic Interface



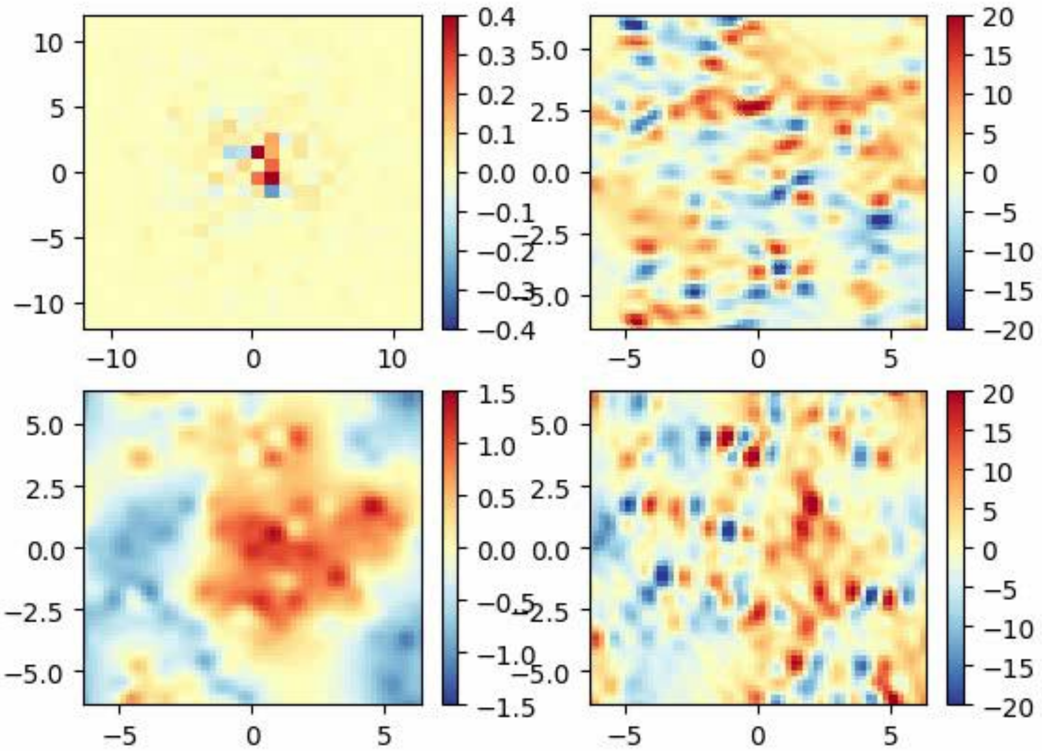
Getting Curvature

- Tensor product surface $\xi \approx \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t)\xi_u(y)\xi_v(z),$

$$\xi_a(b) = \begin{cases} cos\,(2\pi ab) & \text{if } \; a > 0 \\ sin\,(2\pi |a| b) & \text{otherwise,} \end{cases}$$

$\hat{\xi}_{\boldsymbol{k}}(t)$

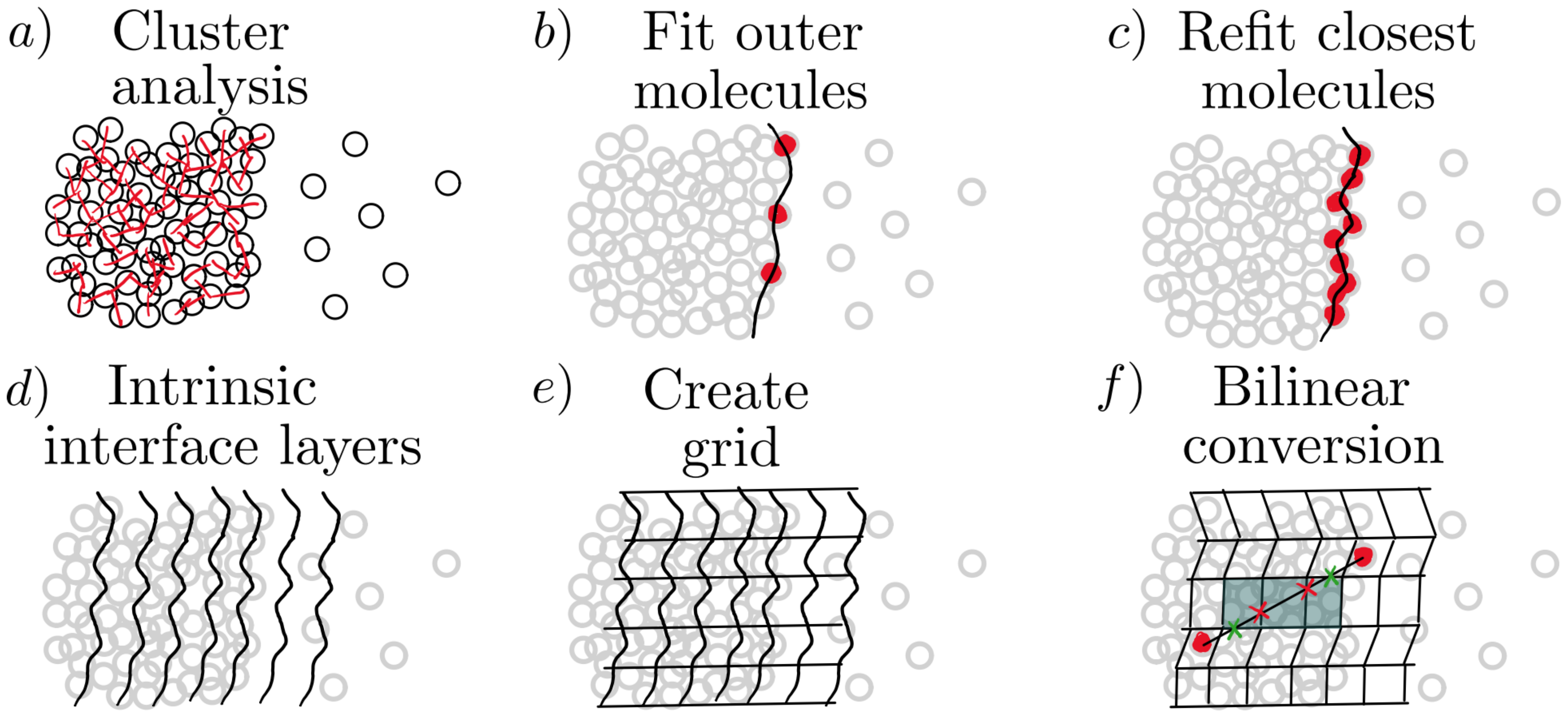
ξ



$\frac{\partial \xi}{\partial y}$

$\frac{\partial \xi}{\partial z}$

Moving Reference Frame - Overview



a) Cluster analysis

b) Fit outer molecules

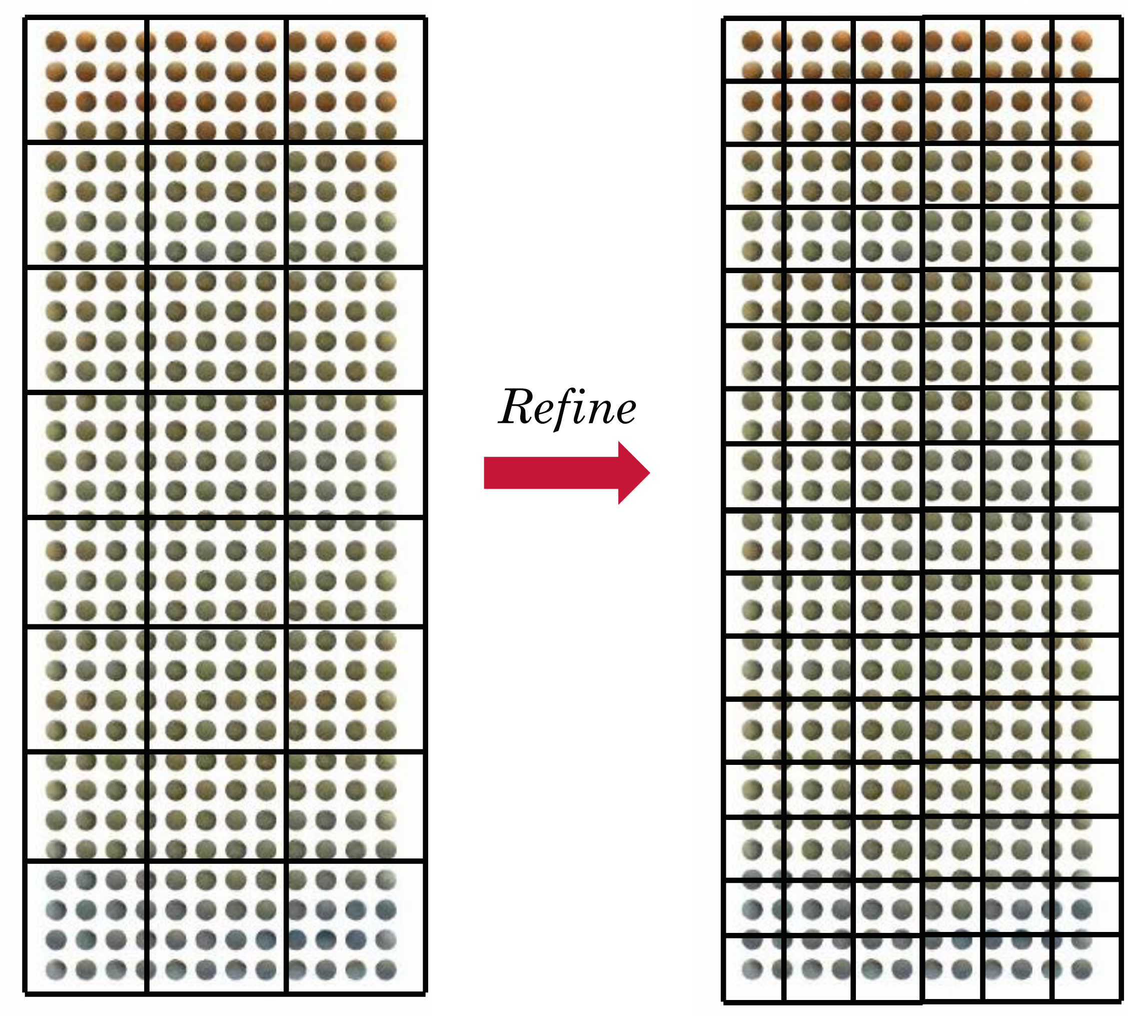
c) Refit closest molecules

d) Intrinsic interface layers

e) Create grid

f) Bilinear conversion

Molecular Dynamics - Averaging



- Density in a cell

$$\rho = \frac{1}{V}\sum_{i=1}^{N}\langle m_i \rangle$$

- Momentum in a cell

$$\rho \boldsymbol{u} = \frac{1}{V}\sum_{i=1}^{N}\langle m_i \boldsymbol{v}_i \rangle$$

- Temperature in a cell

$$T = \frac{1}{3N}\sum_{i=1}^{N}\langle \boldsymbol{v}_i^2 \rangle$$

Irving and Kirkwood (1950)

777.9 cm^{-1}. The band at 809.7 cm^{-1} has been interpreted as 2×394, the rather large difference between calculated and observed frequency being ascribed to the proximity to the A_g fundamental. However, this band could be an upper-stage band corresponding to 819 cm^{-1}.

The interpretation of the faint sharp band at 769.4 cm^{-1} as an upper-stage band, $778+\nu_i-\nu_j$ seems more plausible than its interpretation as the B_{1g} combination, $210+558$ cm^{-1}. The faint sharp Raman band at 828.7 cm^{-1} has been interpreted as an upper-stage band, $2\times 407+\nu_a-\nu_b$, rather than as the B_{3g} difference band $1340-510$ cm^{-1}, because the corresponding sum band has not been observed. If the preferred interpretations are correct, the group of Raman bands, 769, 778, 819, and 829 cm^{-1}, are related to each other in much the same manner as similar groups in the spectra of CO_2 and CS_2.

ACKNOWLEDGMENTS

The writers wish to express their indebtedness to Dr. C. F. Hammer and E. I. du Pont de Nemours and Company for the samples; to Doctors Isabella and Jerome Karle for electron diffraction data; and to Dr. E. K. Plyler and the National Bureau of Standards for data in the long wave-length region.

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The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics*

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(Received November 21, 1949)

The equations of hydrodynamics—continuity equation, equation of motion, and equation of energy transport—are derived by means of the classical statistical mechanics. Thereby, expressions are obtained for the stress tensor and heat current density in terms of molecular variables. In addition to the familiar terms occurring in the kinetic theory of gases, there are terms depending upon intermolecular force. The contributions of intermolecular force to the stress tensor and heat current density are expressed, respectively, as quadratures of the density and current density in the configuration space of a pair of molecules.

INTRODUCTION

THIS paper will be concerned with a derivation of the equations of hydrodynamics from the principles of the classical statistical mechanics. In particular, the equation of continuity, the equation of motion, and the equation of energy transport will be derived. By so doing, the stress tensor and heat current density can be expressed in terms of molecular variables. The stress tensor consists of a kinetic part (which occurs in the kinetic theory of gases) and another term (dominant for a liquid) which will be expressed as a quadrature involving the potential of intermolecular force and the density of pairs of molecules. The heat current density is the sum of the familiar kinetic part and a quadrature involving the potential of intermolecular force and the density and current density in the configuration space of a pair of molecules. The results were previously stated in the first article of this series,[1] when this derivation was promised.

To obtain explicit expressions for the pair probability density and probability current density one would in principle need to solve the Liouville equation [Eq. (2.2)] for the probability distribution in Gibbs phase space and then perform repeated integrations. Since this program is untenable for a liquid, various attempts have been made to obtain a closed equation satisfied approximately by the probability distribution function in the phase space of a pair of molecules. One such equation has been derived by Born and Green[2] using a generalized "superposition" assumption. Another, a generalization of the well-known Fokker-Planck equation of stochastic theory, has been derived by Kirkwood[1] by introducing the concepts of time smoothing and a friction constant. This latter equation has been applied to obtain an expression for the stress tensor linear in gradients of fluid velocity and, thereby, expressions (in terms of molecular variables) for coefficients of shear and volume viscosity.[3] The same equation generalized to non-uniform temperatures, after linearizing in the temperature gradient, leads to an explicit expression for the heat current and thereby to an expression for the coefficient of thermal conductivity.[4] We shall assume, for purposes of mathematical simplicity, a single component, single phase fluid system consisting of molecules which interact under central forces only. It is not difficult to generalize the treatment to a multiple component or multiple

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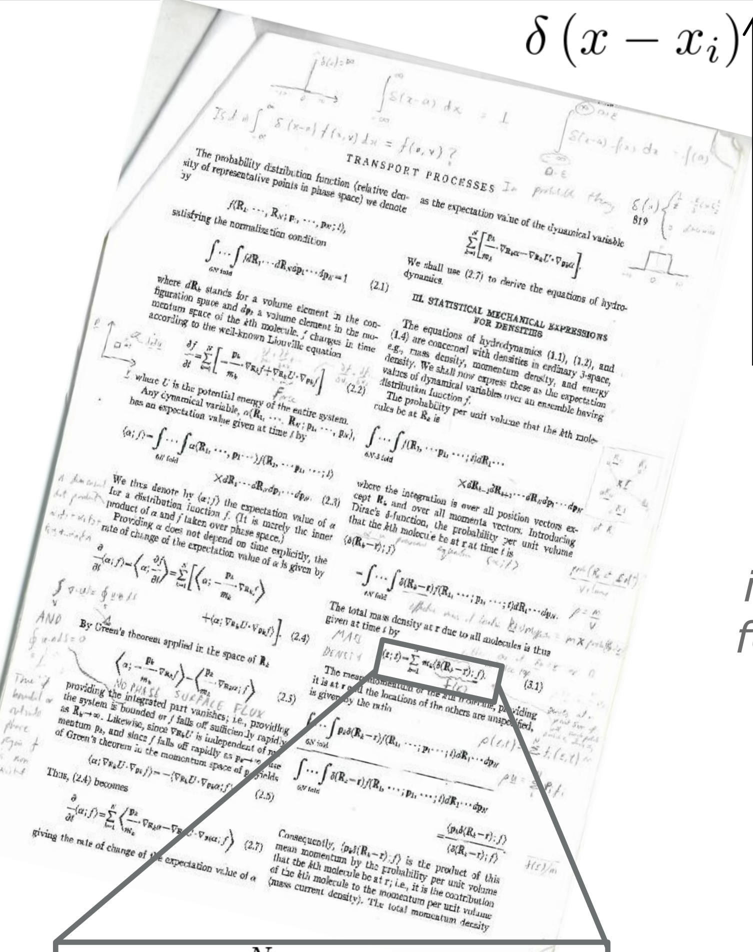
[*] This work was supported by the U. S. ONR under Contract N6onr-244 with the California Institute of Technology.

[1] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).

[2] M. Born and H. S. Green, Proc. Roy. Soc. A188, 10 (1946).

[3] Kirkwood, Buff, and Green, J. Chem. Phys. 17, 988 (1949).

[4] Kirkwood, Standart, and Irving (in preparation). The numerical evaluation awaits a more precise computation of the theoretical radial distribution function.



$\int_{-\infty}^{\infty} \delta(x-a)\,dx = 1$

Is it $\int_{-\infty}^{\infty} \delta(x-a)\, f(x,v)\,dx = f(a,v)$?

$\int_{-\infty}^{\infty} \delta(x-a)\, f(x)\,dx = f(a)$

In practice they $\delta(x)\begin{cases} \frac{1}{\varepsilon} \\ 0 \end{cases}$

The probability distribution function (relative density of representative points in phase space) we denote by

$$f(\mathbf{R}_1,\cdots,\mathbf{R}_N;\mathbf{p}_1,\cdots,\mathbf{p}_N;t),$$

satisfying the normalization condition

$$\underset{6N\text{ fold}}{\int\cdots\int} f\,d\mathbf{R}_1\cdots d\mathbf{R}_N d\mathbf{p}_1\cdots d\mathbf{p}_N=1 \qquad (2.1)$$

where $d\mathbf{R}_k$ stands for a volume element in the configuration space and $d\mathbf{p}_k$ a volume element in the momentum space of the kth molecule. f changes in time according to the well-known Liouville equation

$$\frac{\partial f}{\partial t}=\sum_{k=1}^{N}\Big[-\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}f+\underbrace{\nabla_{\mathbf{R}_k}U}_{\text{Force}}\cdot\nabla_{\mathbf{p}_k}f\Big] \qquad (2.2)$$

where U is the potential energy of the entire system.

Any dynamical variable, $\alpha(\mathbf{R}_1,\cdots,\mathbf{R}_N;\mathbf{p}_1,\cdots,\mathbf{p}_N)$, has an expectation value given at time t by

$$\langle\alpha;f\rangle=\underset{6N\text{ fold}}{\int\cdots\int}\alpha(\mathbf{R}_1,\cdots,\mathbf{p}_1\cdots)f(\mathbf{R}_1,\cdots\mathbf{p}_1,\cdots;t)\times d\mathbf{R}_1\cdots d\mathbf{R}_N d\mathbf{p}_1\cdots d\mathbf{p}_N. \qquad (2.3)$$

We thus denote by $\langle\alpha;f\rangle$ the expectation value of α for a distribution function f. (It is merely the inner product of α and f taken over phase space.)

Providing α does not depend on time explicitly, the rate of change of the expectation value of α is given by

$$\frac{\partial}{\partial t}\langle\alpha;f\rangle=\left\langle\alpha;\frac{\partial f}{\partial t}\right\rangle=\sum_{k=1}^{N}\left[\left\langle\alpha;-\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}f\right\rangle+\langle\alpha;\nabla_{\mathbf{R}_k}U\cdot\nabla_{\mathbf{p}_k}f\rangle\right]. \qquad (2.4)$$

$\int_V \nabla\cdot u\,dV = \oint_S u\cdot n\,dS$

AND

$\oint u\cdot n\,dS = 0$

By Green's theorem applied in the space of $\mathbf{R}_k$

$$\left\langle\alpha;-\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}f\right\rangle=\left\langle\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}\alpha;f\right\rangle \qquad (2.5)$$

NO PHASE SURFACE FLUX

providing the integrated part vanishes; i.e., providing the system is bounded or f falls off sufficiently rapidly as $\mathbf{R}_k\to\infty$. Likewise, since $\nabla_{\mathbf{R}_k}U$ is independent of momentum $\mathbf{p}_k$, and since f falls off rapidly as $\mathbf{p}_k\to\infty$, use of Green's theorem in the momentum space of $\mathbf{p}_k$ yields

$$\langle\alpha;\nabla_{\mathbf{R}_k}U\cdot\nabla_{\mathbf{p}_k}f\rangle=-\langle\nabla_{\mathbf{R}_k}U\cdot\nabla_{\mathbf{p}_k}\alpha;f\rangle \qquad (2.6)$$

Thus, (2.4) becomes

$$\frac{\partial}{\partial t}\langle\alpha;f\rangle=\sum_{k=1}^{N}\left\langle\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}\alpha-\nabla_{\mathbf{R}_k}U\cdot\nabla_{\mathbf{p}_k}\alpha;f\right\rangle \qquad (2.7)$$

giving the rate of change of the expectation value of α as the expectation value of the dynamical variable

$$\sum_{k=1}^{N}\left[\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}\alpha-\nabla_{\mathbf{R}_k}U\cdot\nabla_{\mathbf{p}_k}\alpha\right].$$

We shall use (2.7) to derive the equations of hydrodynamics.

III. STATISTICAL MECHANICAL EXPRESSIONS FOR DENSITIES

The equations of hydrodynamics (1.1), (1.2), and (1.4) are concerned with densities in ordinary 3-space, e.g., mass density, momentum density, and energy density. We shall now express these as the expectation values of dynamical variables over an ensemble having distribution function f.

The probability per unit volume that the kth molecules be at $\mathbf{R}_k$ is

$$\underset{6N-3\text{ fold}}{\int\cdots\int} f(\mathbf{R}_1,\cdots\mathbf{p}_1,\cdots;t)\,d\mathbf{R}_1\cdots\times d\mathbf{R}_{k-1}d\mathbf{R}_{k+1}\cdots d\mathbf{R}_N d\mathbf{p}_1\cdots d\mathbf{p}_N$$

where the integration is over all position vectors except $\mathbf{R}_k$ and over all momenta vectors. Introducing Dirac's δ-function, the probability per unit volume that the kth molecule be at $\mathbf{r}$ at time t is

$$\langle\delta(\mathbf{R}_k-\mathbf{r});f\rangle=\underset{6N\text{ fold}}{\int\cdots\int}\delta(\mathbf{R}_k-\mathbf{r})f(\mathbf{R}_1,\cdots;\mathbf{p}_1,\cdots;t)\,d\mathbf{R}_1\cdots d\mathbf{p}_N.$$

$\rho = \frac{m}{V}$

The total mass density at $\mathbf{r}$ due to all molecules is thus given at time t by

MASS DENSITY

$$\rho(\mathbf{r};t)=\sum_{k=1}^{N}m_k\langle\underbrace{\delta(\mathbf{R}_k-\mathbf{r});f}_{f(r)}\rangle. \qquad (3.1)$$

The mean momentum of the kth molecule, providing it is at $\mathbf{r}$ and the locations of the others are unspecified, is given by the ratio

$$\frac{\underset{6N\text{ fold}}{\int\cdots\int}\mathbf{p}_k\delta(\mathbf{R}_k-\mathbf{r})f(\mathbf{R}_1,\cdots;\mathbf{p}_1\cdots;t)\,d\mathbf{R}_1\cdots d\mathbf{p}_N}{\underset{6N\text{ fold}}{\int\cdots\int}\delta(\mathbf{R}_k-\mathbf{r})f(\mathbf{R}_1,\cdots;\mathbf{p}_1,\cdots;t)\,d\mathbf{R}_1\cdots d\mathbf{p}_N}=\frac{\langle\mathbf{p}_k\delta(\mathbf{R}_k-\mathbf{r});f\rangle}{\langle\delta(\mathbf{R}_k-\mathbf{r});f\rangle}.$$

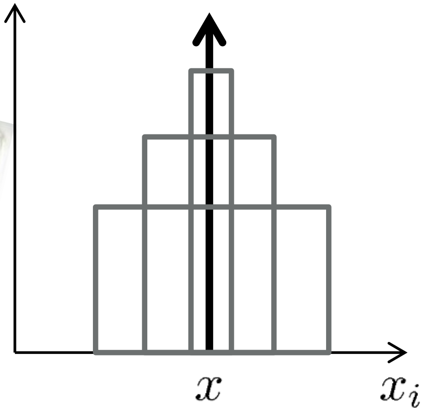
$\rho(r,t)=\sum_{i}^{N} f_i(r,t)\,m$

$\rho u = \sum_i p_i f_i$

Consequently, $\langle\mathbf{p}_k\delta(\mathbf{R}_k-\mathbf{r});f\rangle$ is the product of this mean momentum by the probability per unit volume that the kth molecule be at $\mathbf{r}$; i.e., it is the contribution of the kth molecule to the momentum per unit volume (mass current density). The total momentum density

$f(r)/m$

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



The Dirac delta infinitely high, infinitely thin peak formally equivalent to the continuum differential formulation

The Control Volume Functional

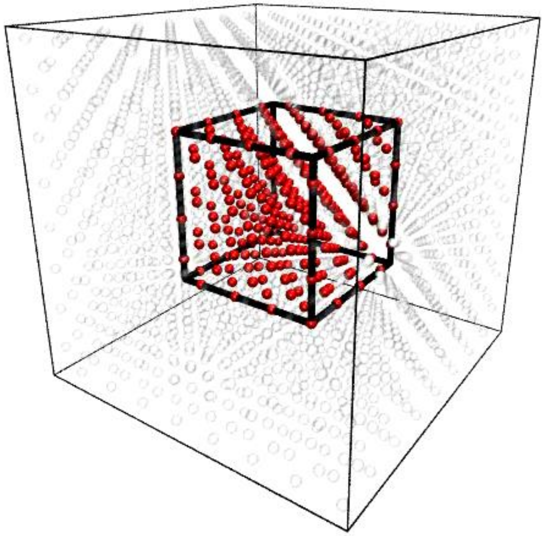
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

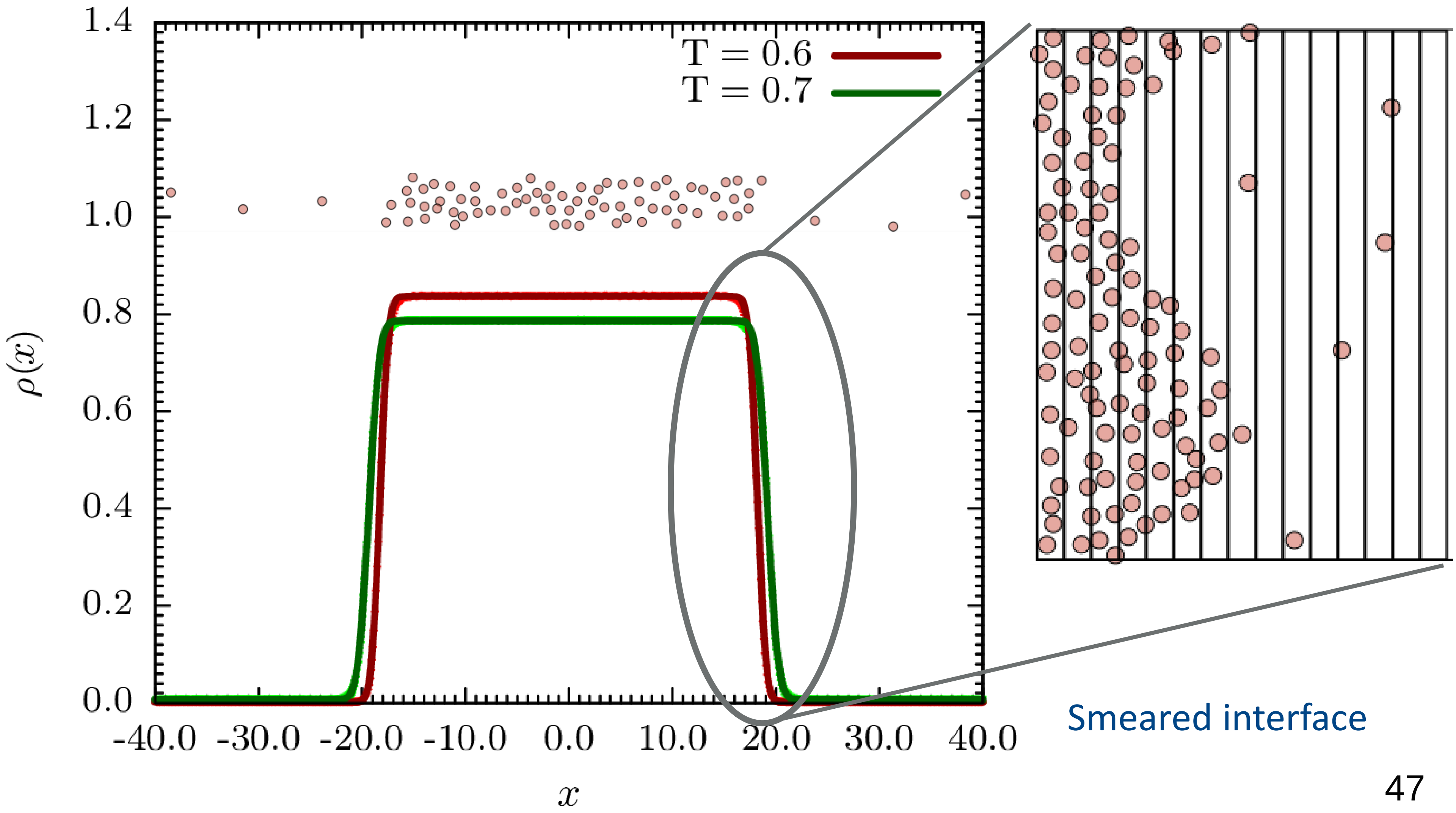
$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$



- In words

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

Density



Smeared interface

A more general Control Volume Functional

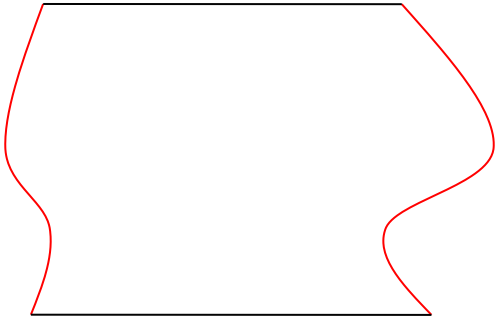
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

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

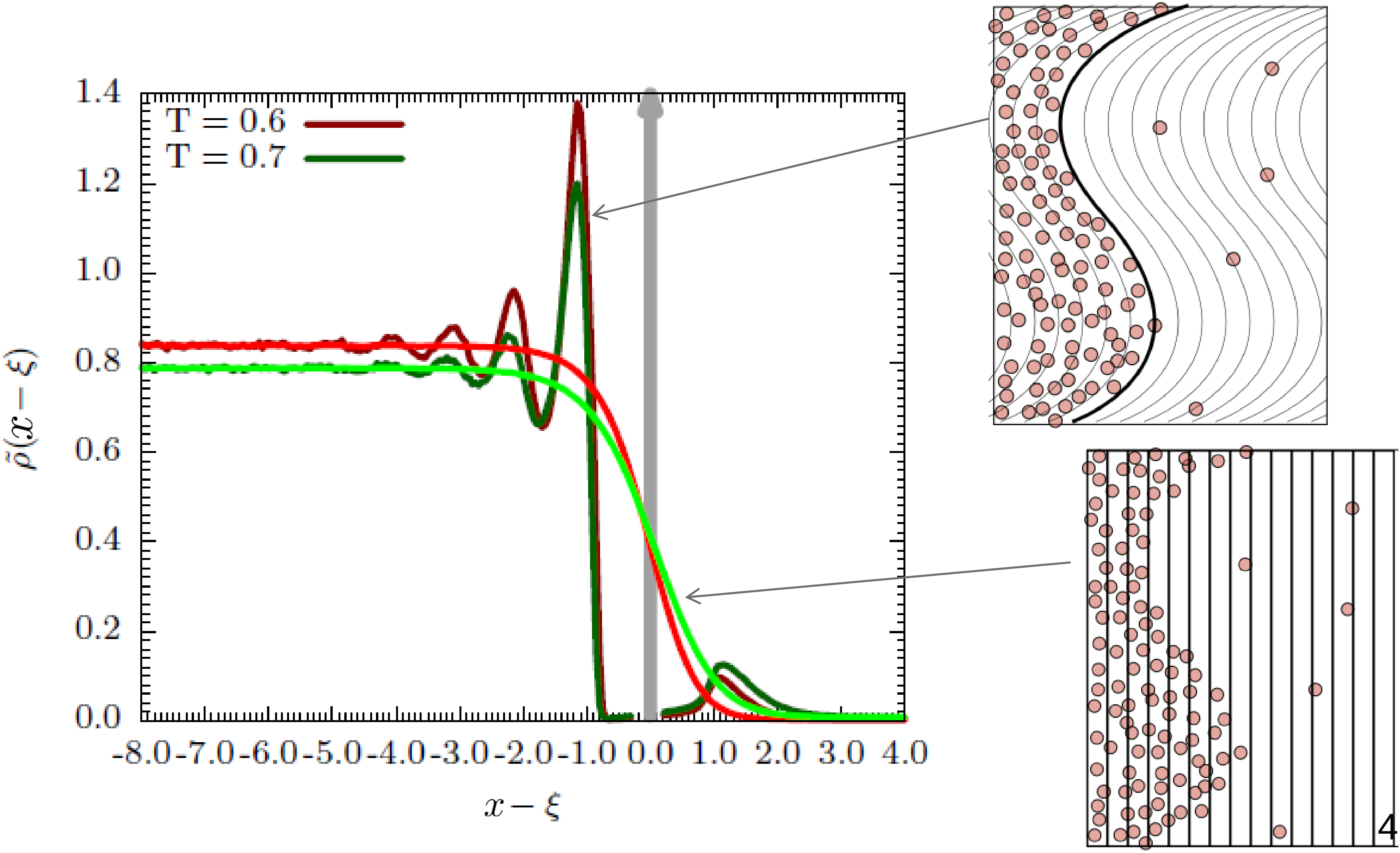


- In words

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

Work with Carlos Braga and Serafim Kalliadasis

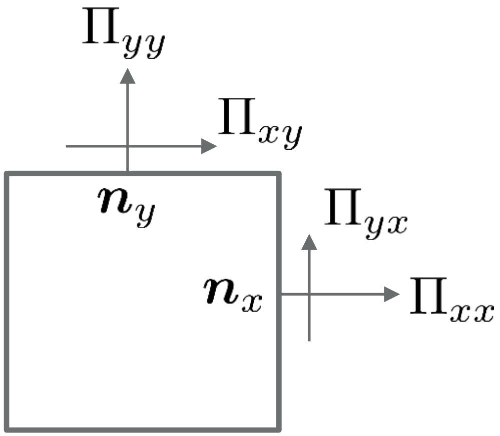
The Intrinsic Interface



Pressure (Stress)

- We need pressure to understand the surface
  - Using Cauchy's original definition
  - In two dimensions the tensor is then,

$$\boldsymbol{\Pi} = \left[\begin{array}{cc} \Pi_{xx} & \Pi_{xy} \\ \Pi_{yx} & \Pi_{yy} \end{array} \right]$$



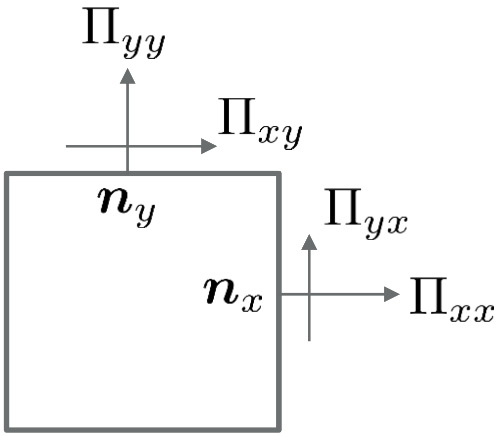
- Where pressure in molecular systems include kinetic and configurational

$$\oint_S \Pi_{xx} \cdot dS_x = \underbrace{\sum_{i=1}^{N} \left\langle m_i v_{xi} v_{xi} dS_{xi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left\langle f_{xij} dS_{xij} \right\rangle}_{\text{Configurational}}$$

Pressure (Stress)

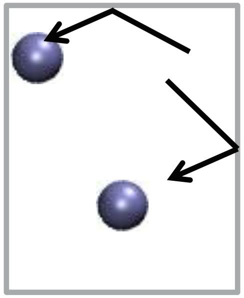
- We need pressure to understand the surface
  - Using Cauchy’s original definition
  - In two dimensions the tensor is then,

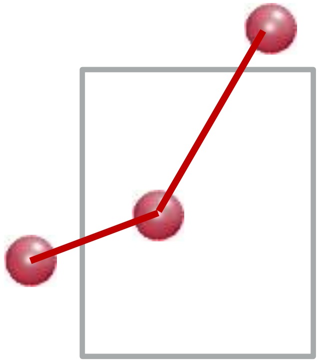
$$\mathbf{\Pi} = \begin{bmatrix} \Pi_{xx} & \Pi_{xy} \\ \Pi_{yx} & \Pi_{yy} \end{bmatrix}$$



Kinetic theory part

Momentum due to average of molecules crossing a plane and returning





Configurational part

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

Derivative for Fluxes and Stresses

- Taking the Derivative of the CV function

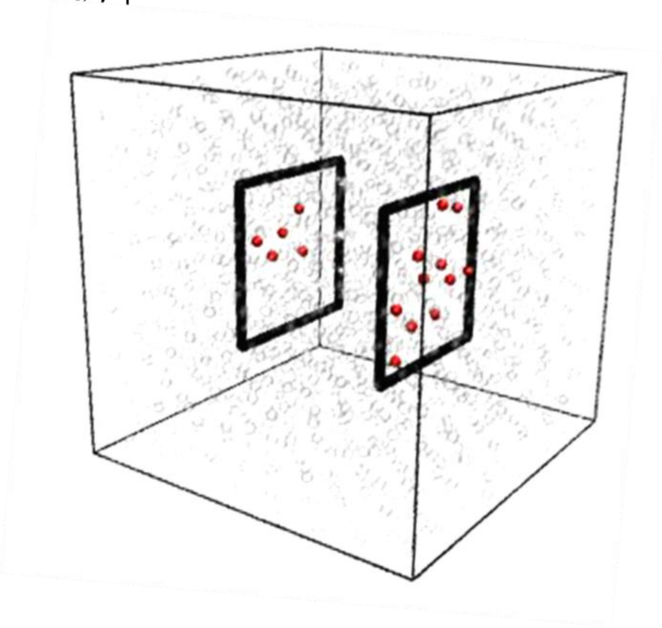
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right]$$
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$
$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

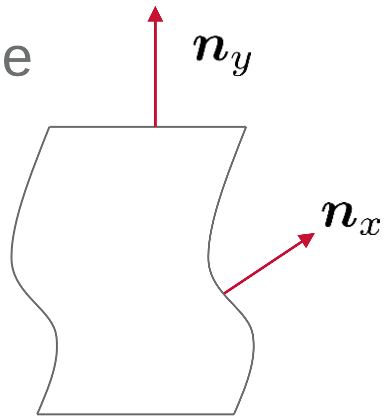
- Or in words

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



Pressure Components (normal form)

- Working through the mathematics, a form in terms of the unit vectors



$$\boldsymbol{\Pi}_\alpha^{\text{kinetic}} = \boxed{\frac{1}{\Delta S_\alpha}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \boldsymbol{r}_{12} \cdot \frac{\boldsymbol{n}_\alpha}{|\boldsymbol{r}_{12}\cdot\boldsymbol{n}_\alpha|} dS_\alpha}$$

$$\boldsymbol{\Pi}_\alpha^{\text{Moving surf}} = \boxed{\frac{1}{\Delta S_\alpha}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_t}$$

$$\boldsymbol{\Pi}_\alpha^{\text{config}} = \boxed{\frac{1}{2\Delta S_\alpha}\sum_{i,j}^{N} \boldsymbol{f}_{ij} \boldsymbol{r}_{ij} \cdot \frac{\boldsymbol{n}_\alpha}{|\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_\alpha|} dS_\alpha}$$

$$\boldsymbol{n}_\alpha = \frac{\boldsymbol{\nabla}_\alpha(\xi - z_\alpha)}{||\boldsymbol{\nabla}_\alpha(\xi - z_\alpha)||}$$

- Calculating pressure on a surface:
  - Obtain a crossing on a surface (a moving molecule or a force)
  - Dot this with the unit vector to the surface

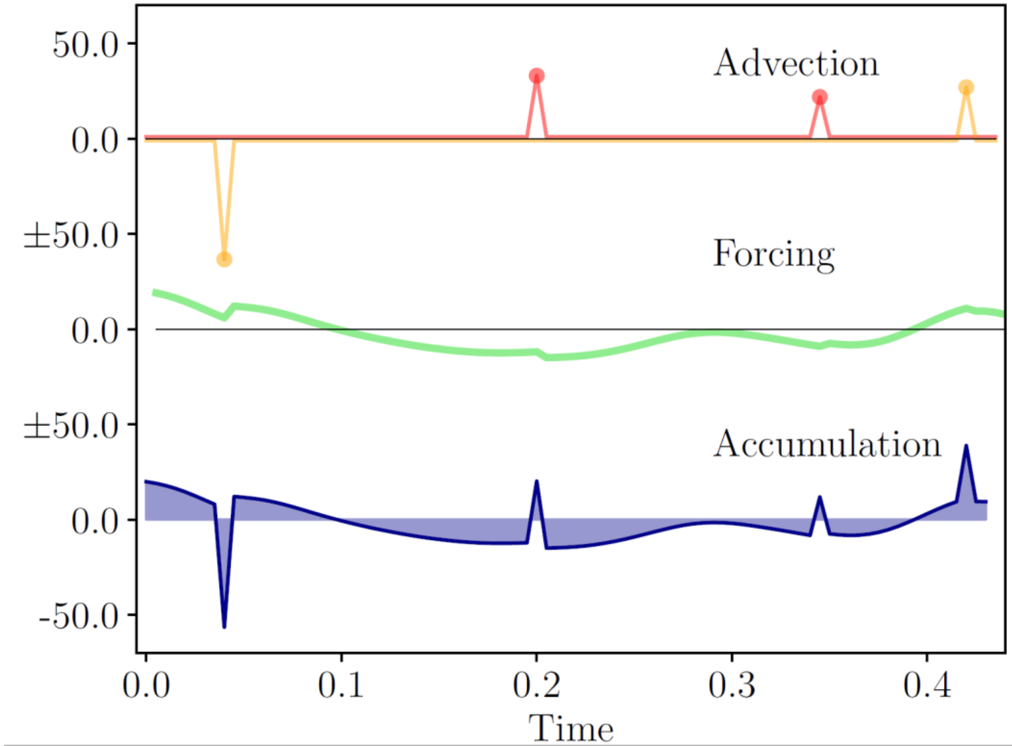
CV Balance Per Bilinear Cube

$$\text{Advection} = \boxed{\frac{1}{\Delta S_z}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \frac{\boldsymbol{r}_{12}\cdot\boldsymbol{n}_z}{|\boldsymbol{r}_{12}\cdot\boldsymbol{n}_z|} dS^+} + \boxed{\frac{1}{\Delta S_z}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_t}$$

$$\text{Forcing} = \boxed{\frac{1}{2\Delta S_z}\sum_{i,j}^{N} \boldsymbol{f}_{ij} \frac{\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z}{|\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z|} dS^+}$$

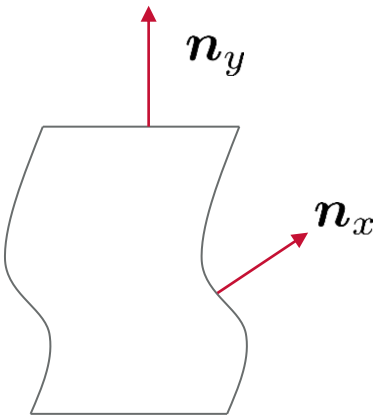
$$\text{Accumulation} = \boxed{\frac{d}{dt}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_i}$$

$$\begin{aligned}\text{Accumulation} = {} & \text{Advection} \\ & + \text{Forcing}\end{aligned}$$



Pressure (Stress)

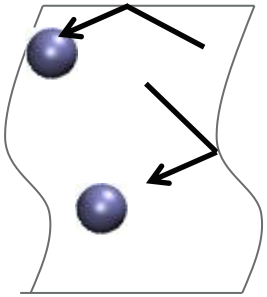
- We need pressure to understand the surface
  - Using Cauchy’s original definition
  - In two dimensions the tensor is,

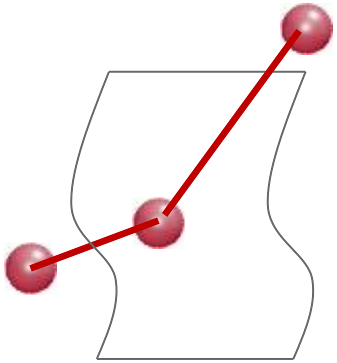


$$\mathbf{\Pi} = \begin{bmatrix} \Pi_{xx} & \Pi_{xy} \\ \Pi_{yx} & \Pi_{yy} \end{bmatrix} = \begin{bmatrix} \Pi_N & 0 \\ 0 & \Pi_T \end{bmatrix}$$

Kinetic theory part

Momentum due to average of molecules crossing a plane and returning

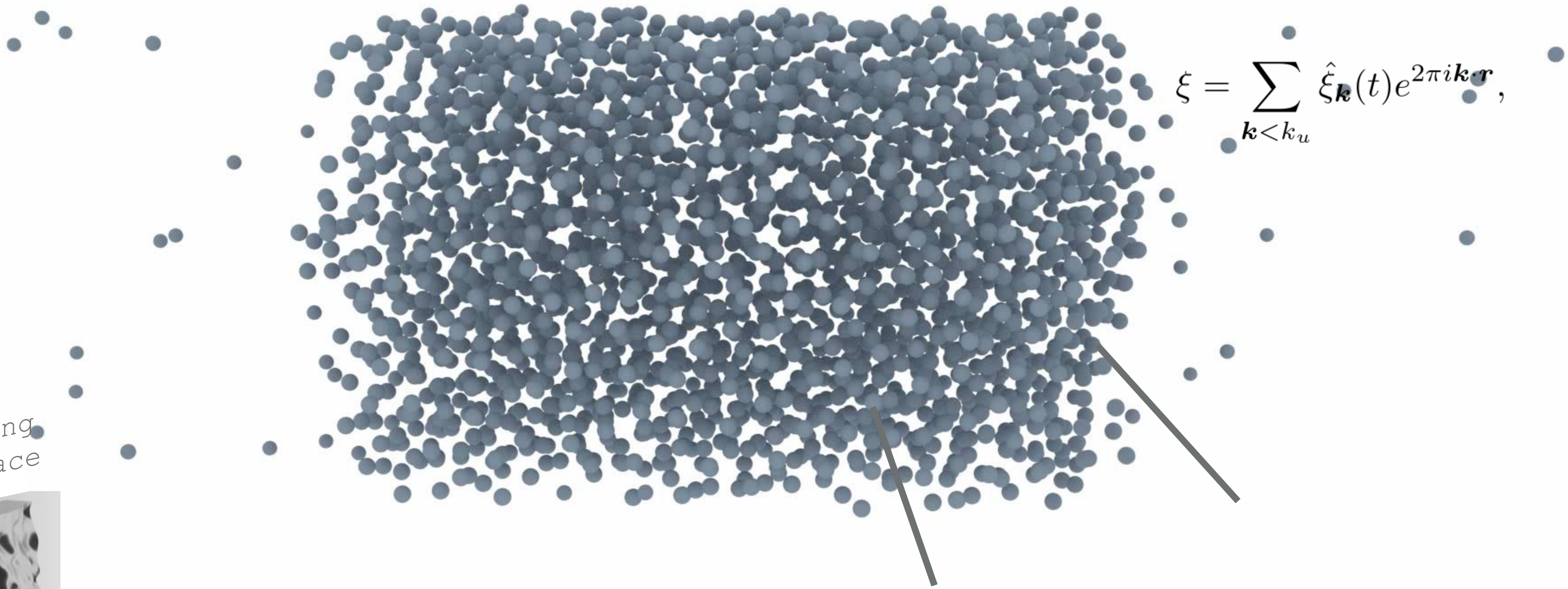




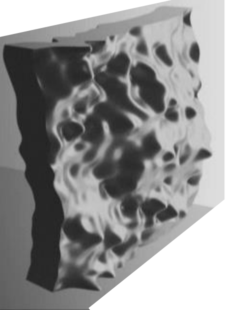
Configurational part

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

Liquid-Vapour interface

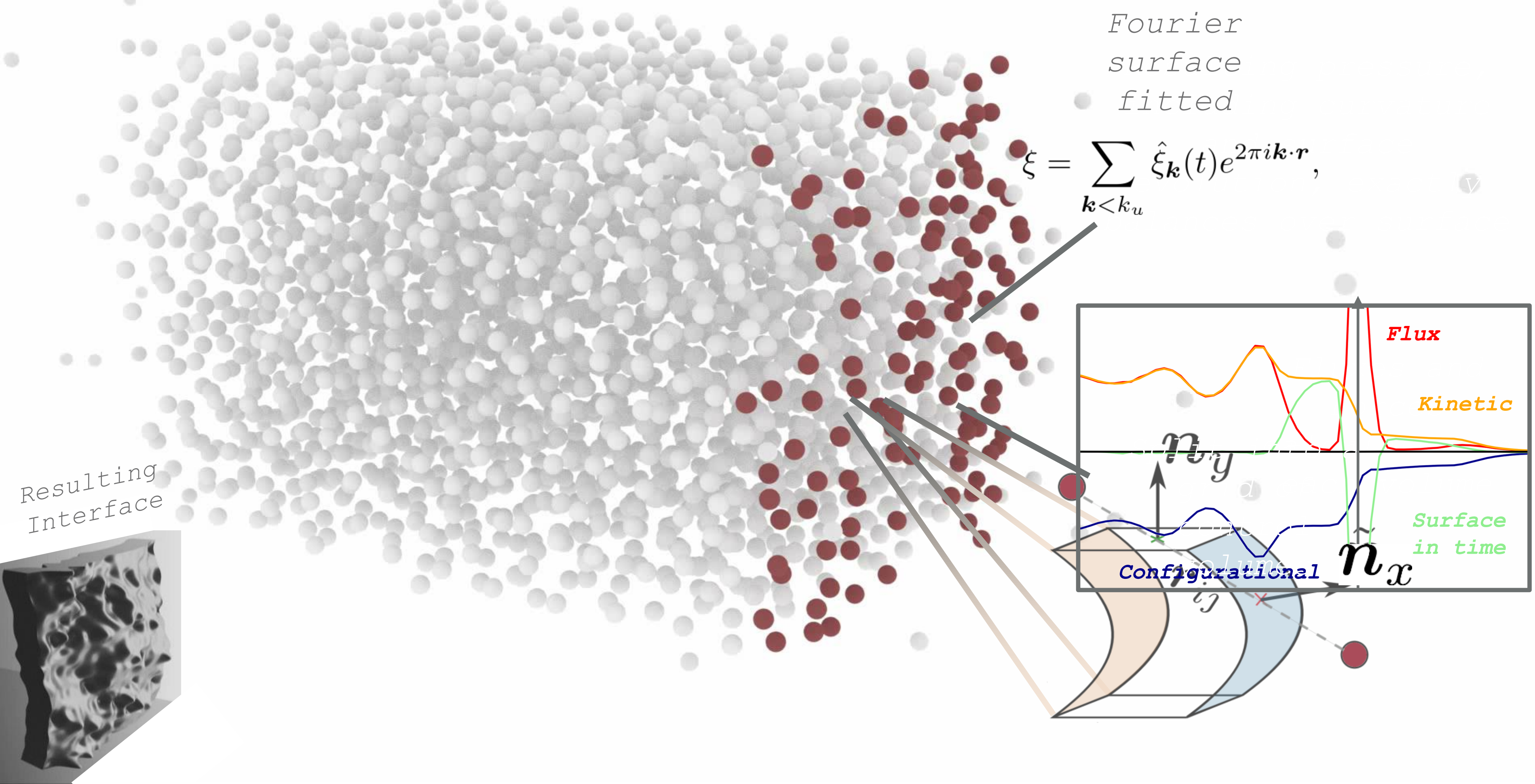


$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}},$$



Resulting Interface

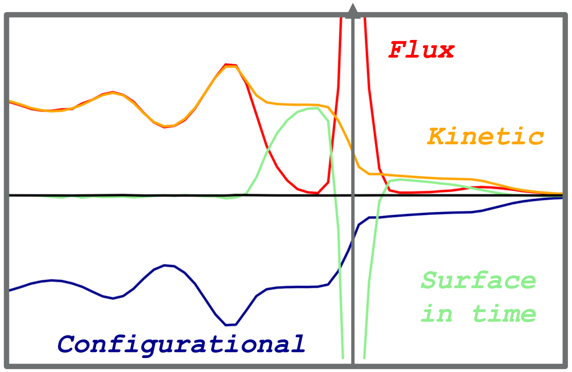
Liquid-Vapour interface



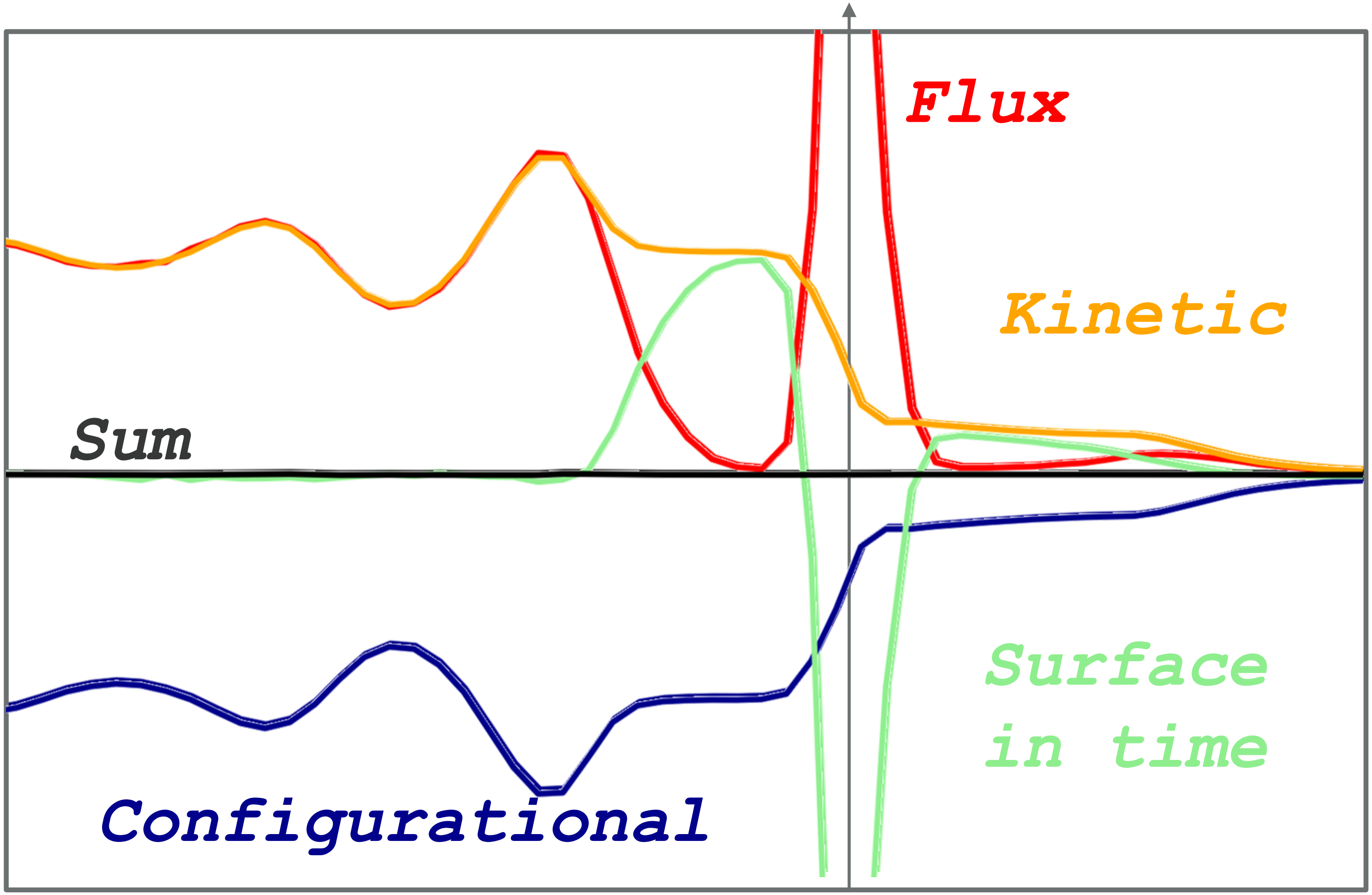
Time evolving Fourier surface fitted

$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}},$$

Normal Pressure

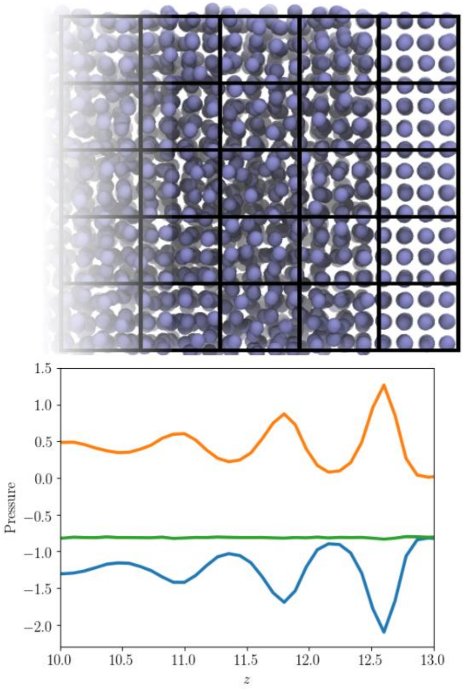


Normal Pressure

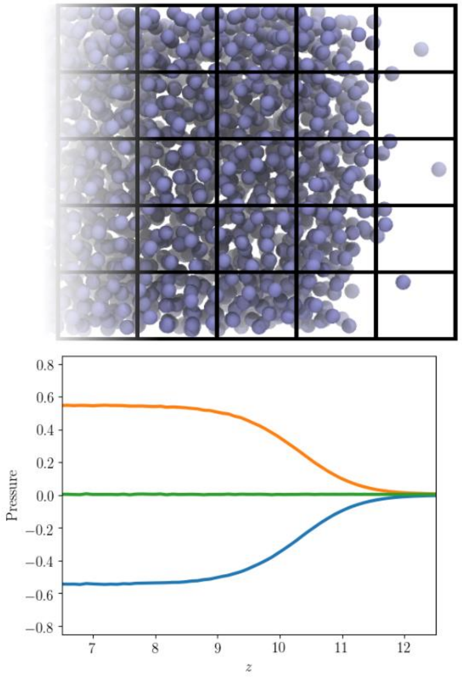


Normal Pressure is Flat (equilibrium)

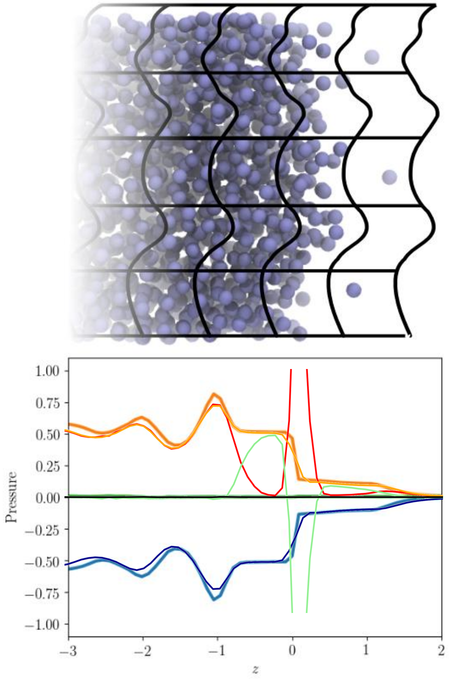
Solid-liquid
Eulerian
reference



Liquid-vapour
Eulerian
reference



Liquid-vapour
Lagrangian
reference



Other Pressure Definitions

- Only surface pressures satisfy this balance correctly

- Volume Average (VA) Pressure ●

$$\overset{VA}{\Pi} = \frac{1}{\Delta V}\left[\sum_{i=1}^{N} \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{m_i}\vartheta_i + \frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\boldsymbol{r}_{ij}\int_0^1 \vartheta_\lambda d\lambda\right]$$

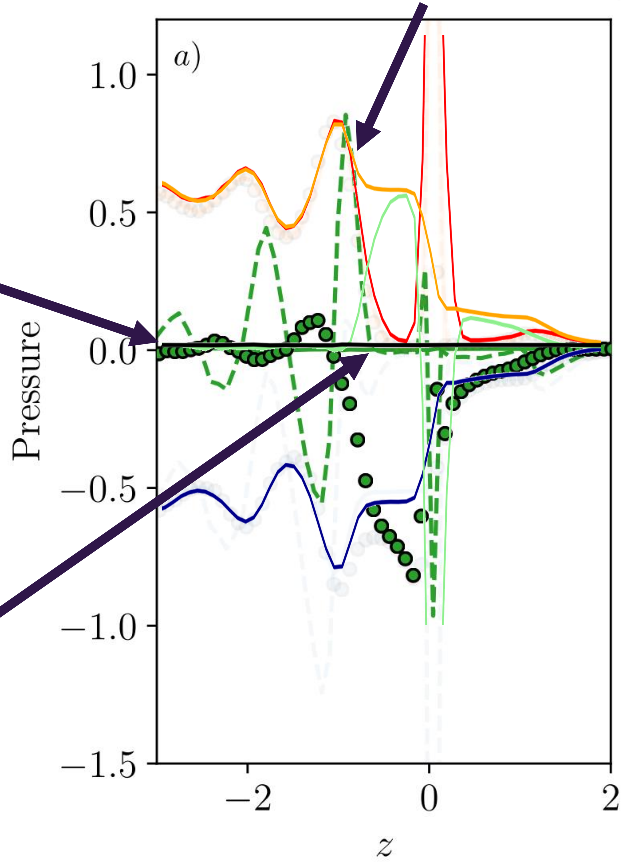
- Surface Pressure (Generalised Method of Planes) —

$$\int_{t_1}^{t_2} \rho \boldsymbol{u} u_z + \overset{SF}{\Pi}{}^k_z dt = \frac{1}{\Delta S_z}\sum_{i=1}^{N} m_i\dot{\boldsymbol{r}}_i \frac{\boldsymbol{r}_{12}\cdot\boldsymbol{n}_z}{|\boldsymbol{r}_{12}\cdot\boldsymbol{n}_z|} dS^+ + \frac{1}{\Delta S_z}\sum_{i=1}^{N} m_i\dot{\boldsymbol{r}}_i\vartheta_t$$

$$\overset{SF}{\Pi}{}^c_z = \frac{1}{2\Delta S_z}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\frac{\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z}{|\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z|} dS^+$$

- Irving Kirkwood 1 (IK1) or Virial Pressure - - -

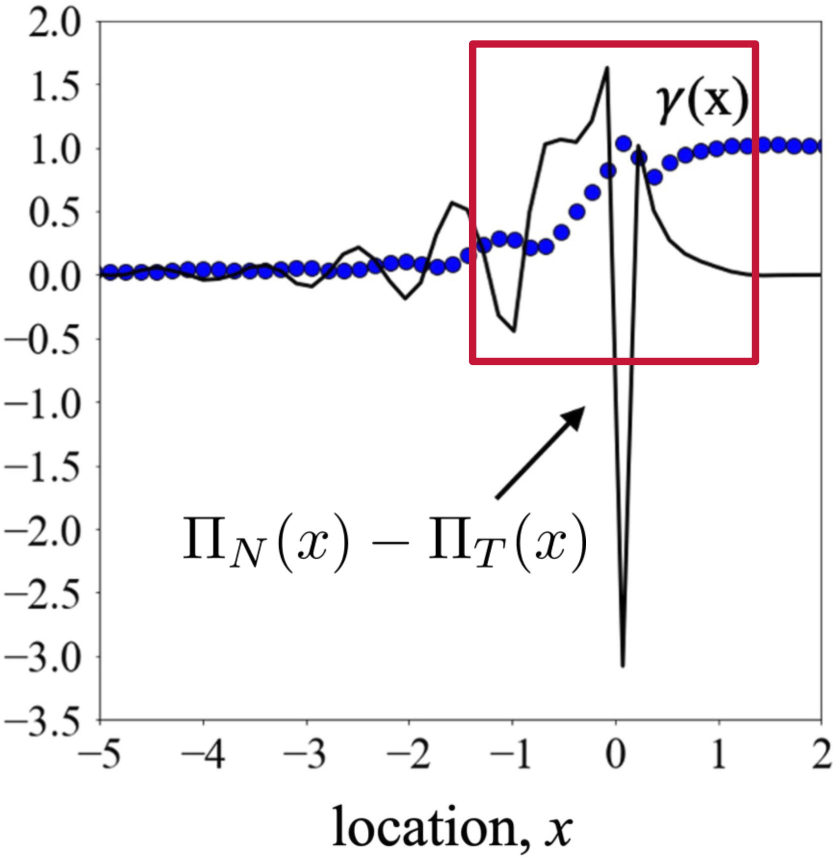
$$\overset{IK1}{\Pi}(\boldsymbol{r},t) = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{m_i}\delta(\boldsymbol{r}-\boldsymbol{r}_i) + \frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\boldsymbol{r}_{ij}\delta(\boldsymbol{r}-\boldsymbol{r}_i) .$$

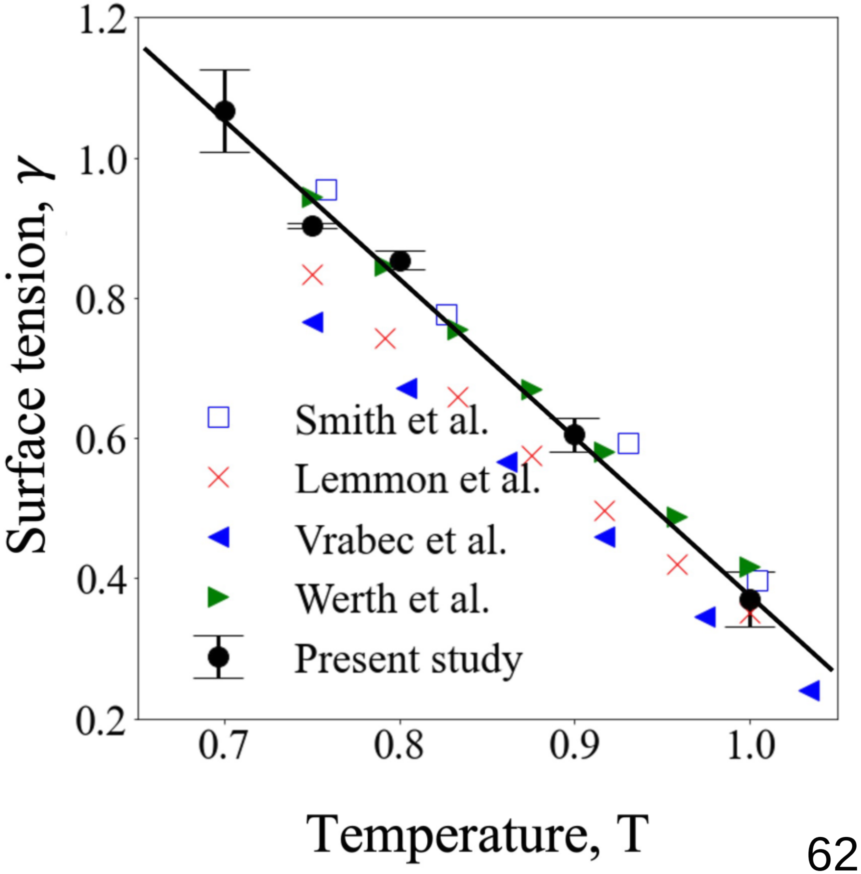


Tangential Pressure and Surface Tension

- Contribution to surface tension localised to very thin region at interface

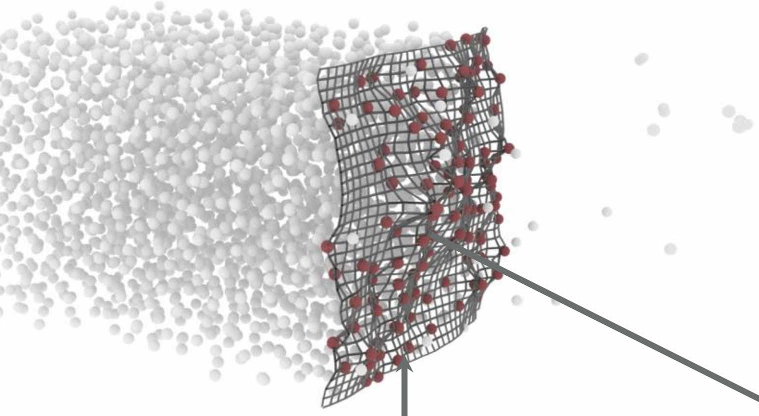
$$\gamma = \int_{-2^{\frac{1}{6}}}^{2^{\frac{1}{6}}} \left[\Pi_N - \Pi_T\right] dx$$



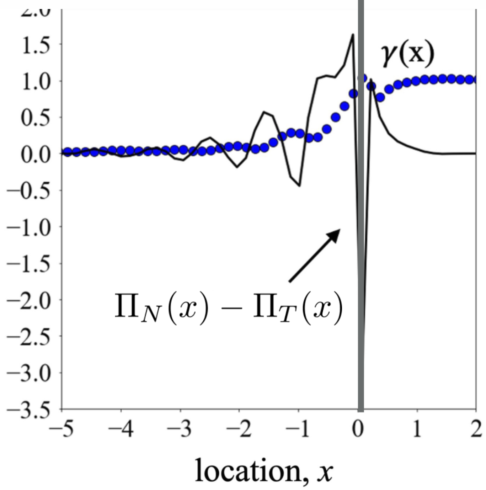


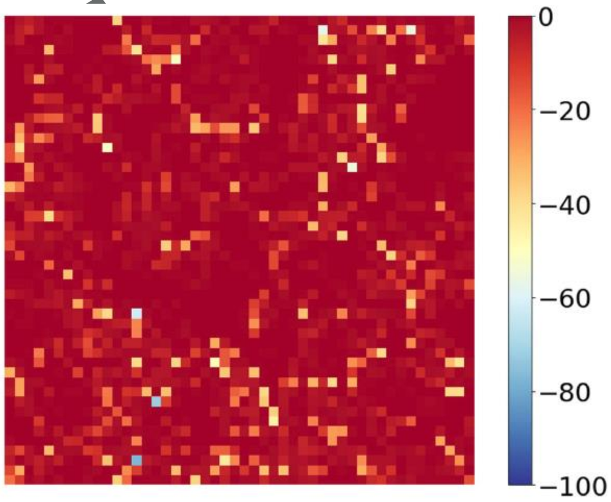
Stress Networks

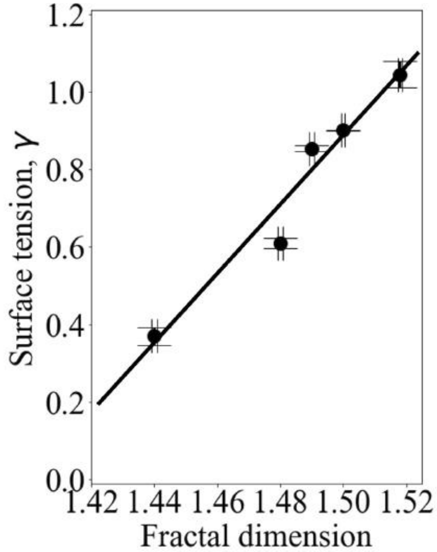
- Taking the instant Tangential Pressures on the intrinsic interface itself



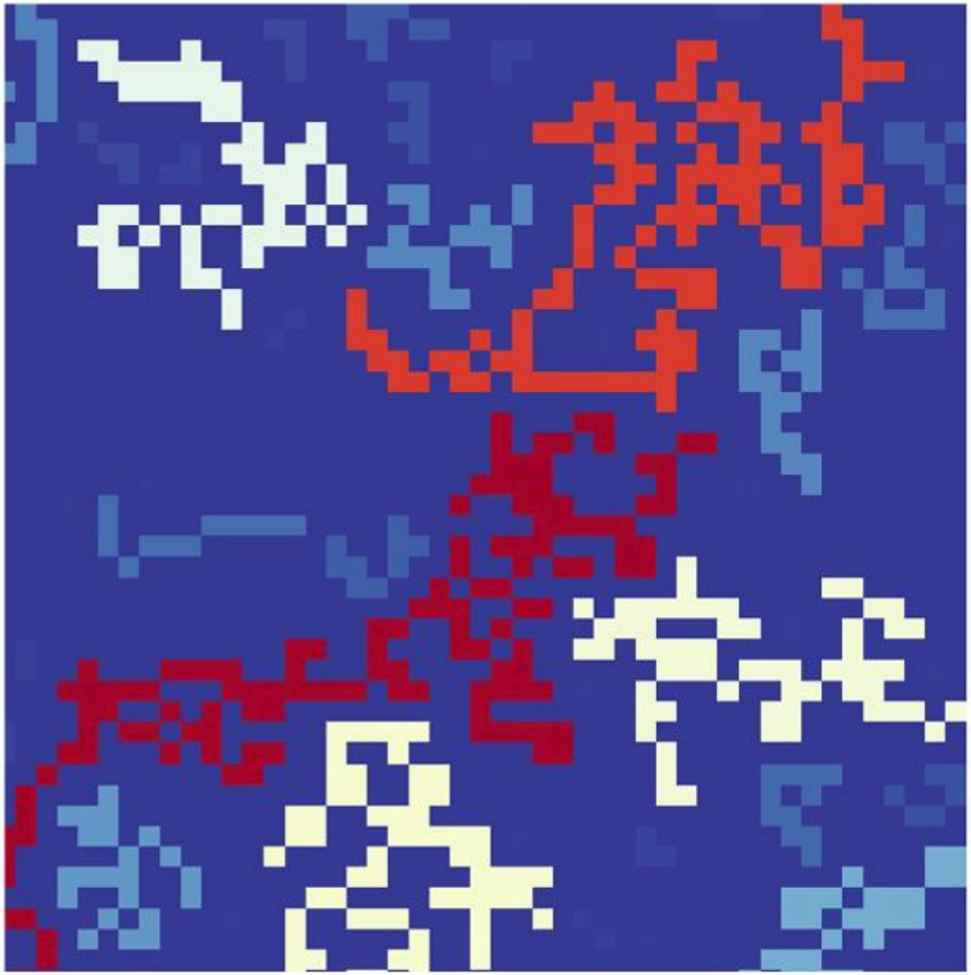
Work by
Muhammad Rizwanur Rahman
at
Imperial College







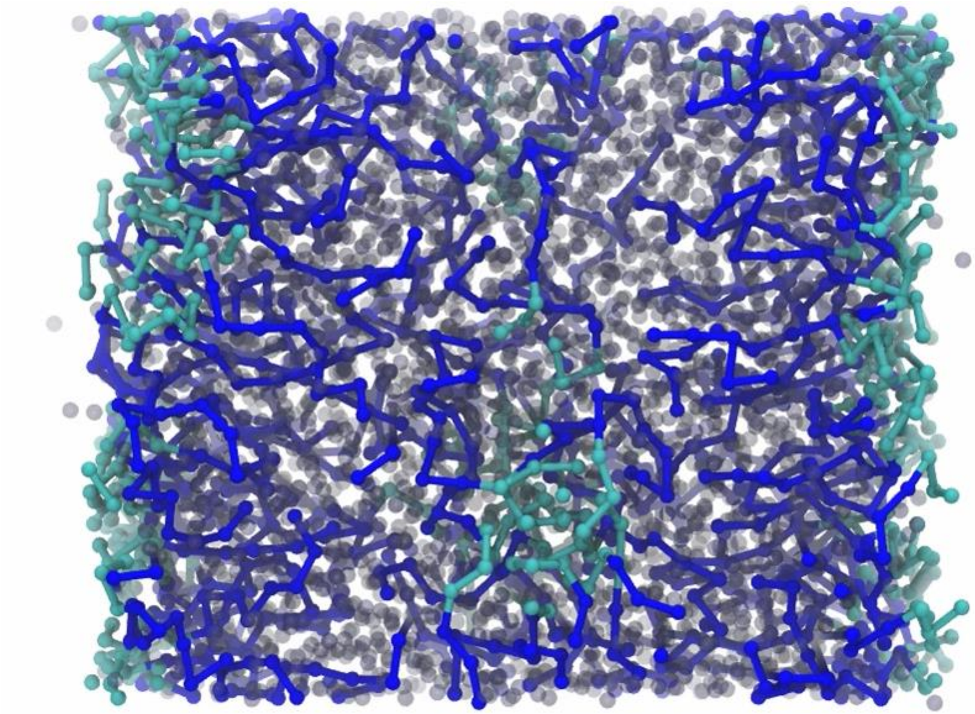
Percolating Cluster



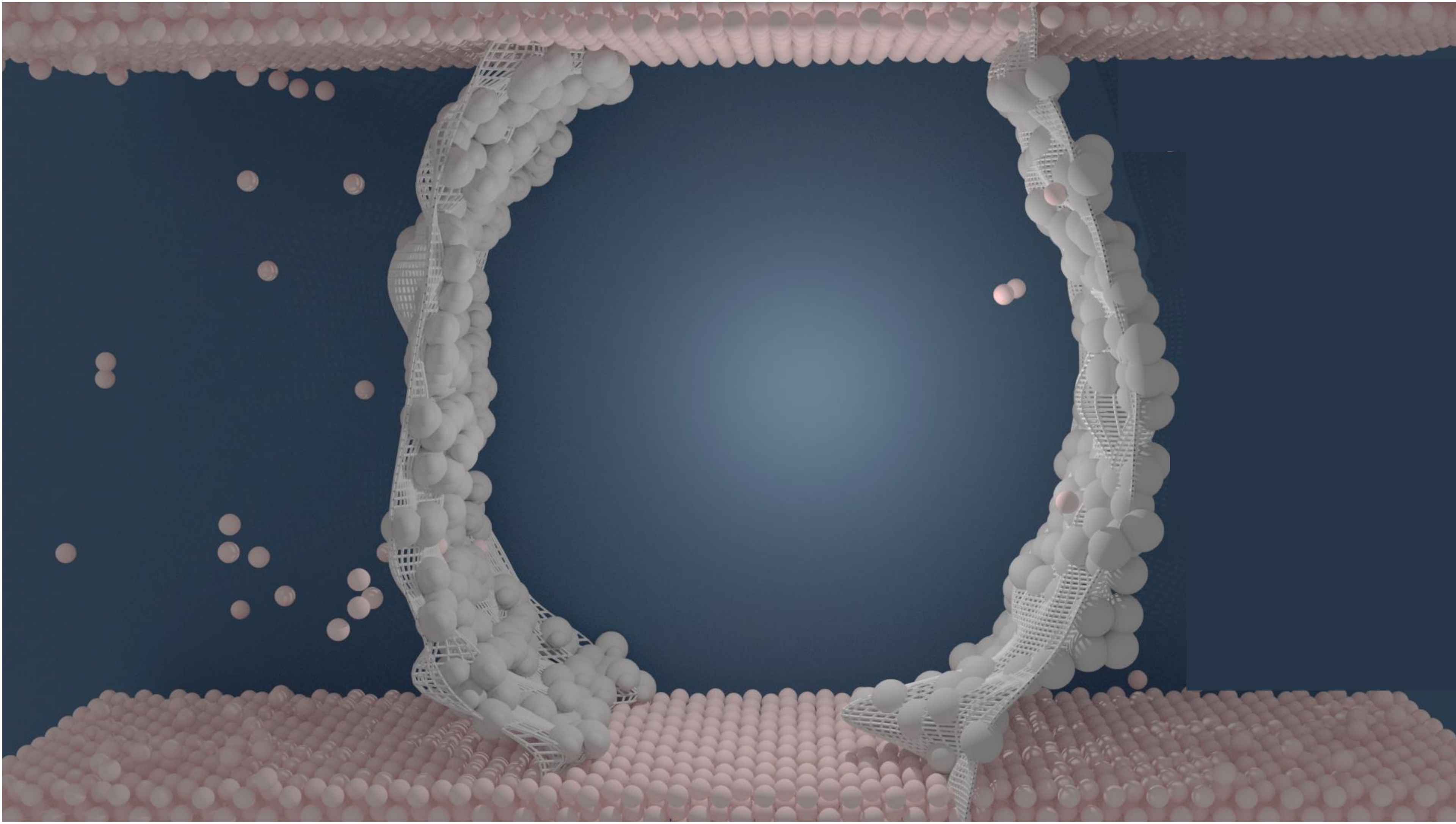
Applications

Marangoni flows

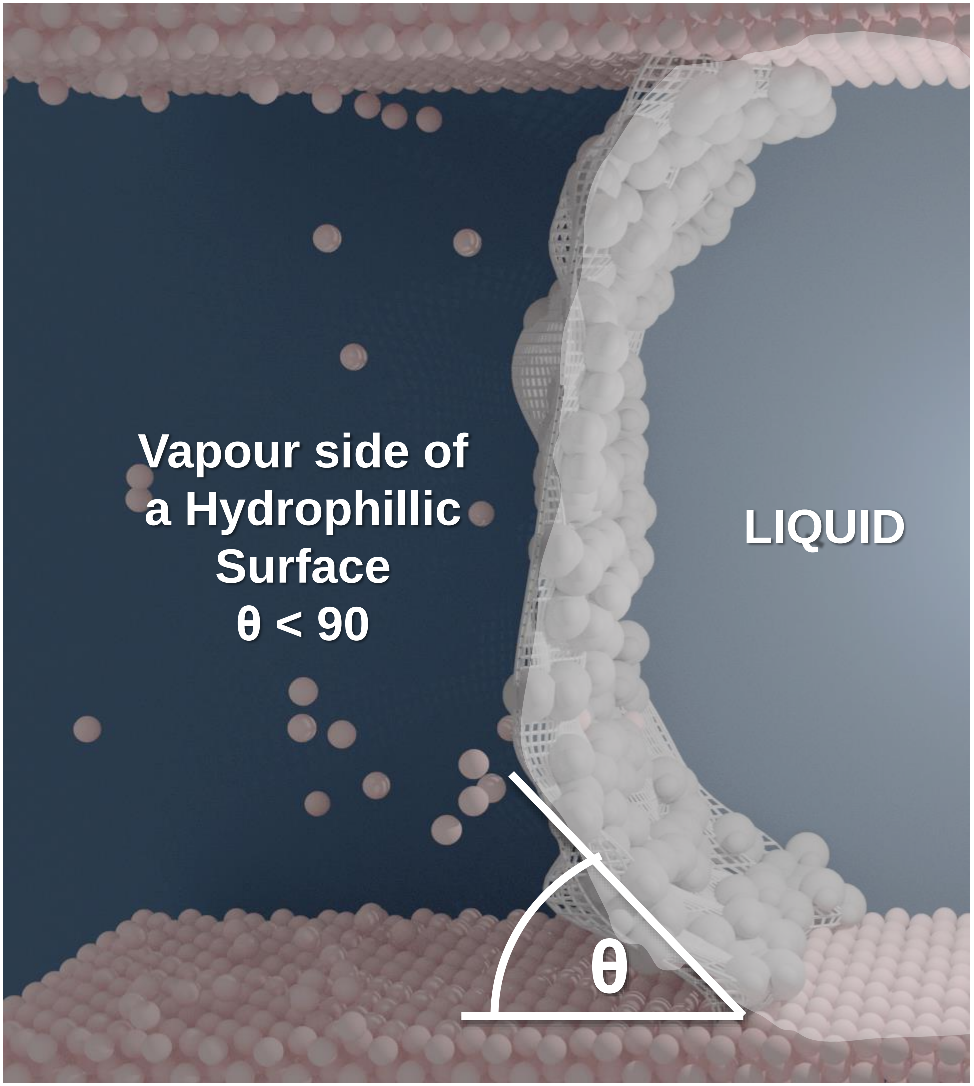
- Formation of concentrations gradients linked to surface



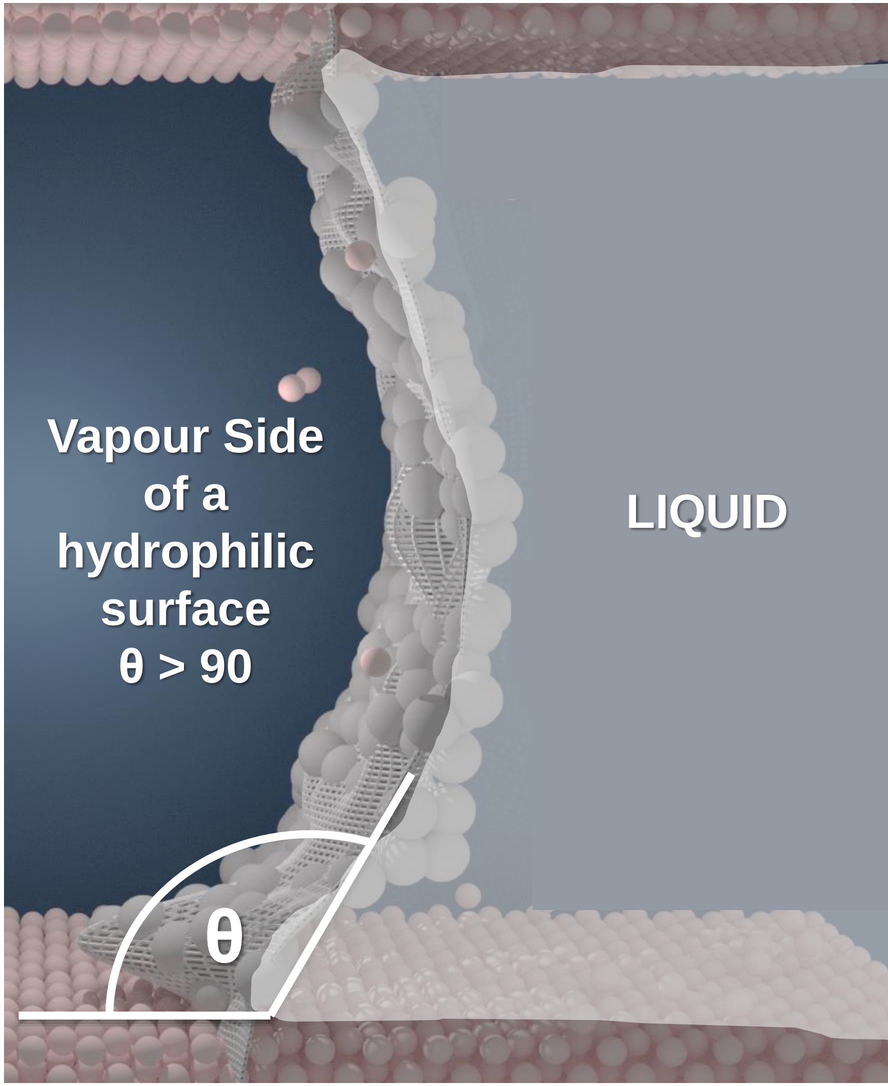
The Contact Line



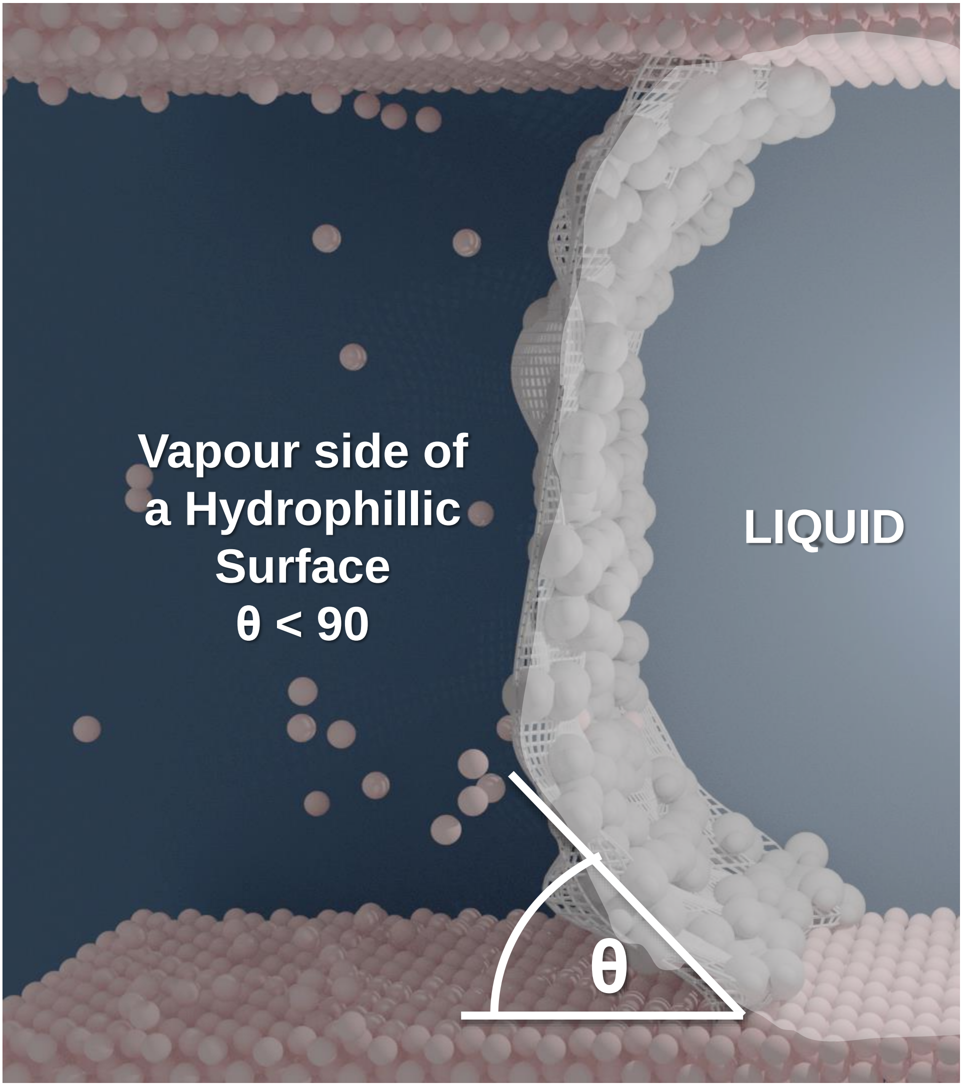
The Static Contact Line

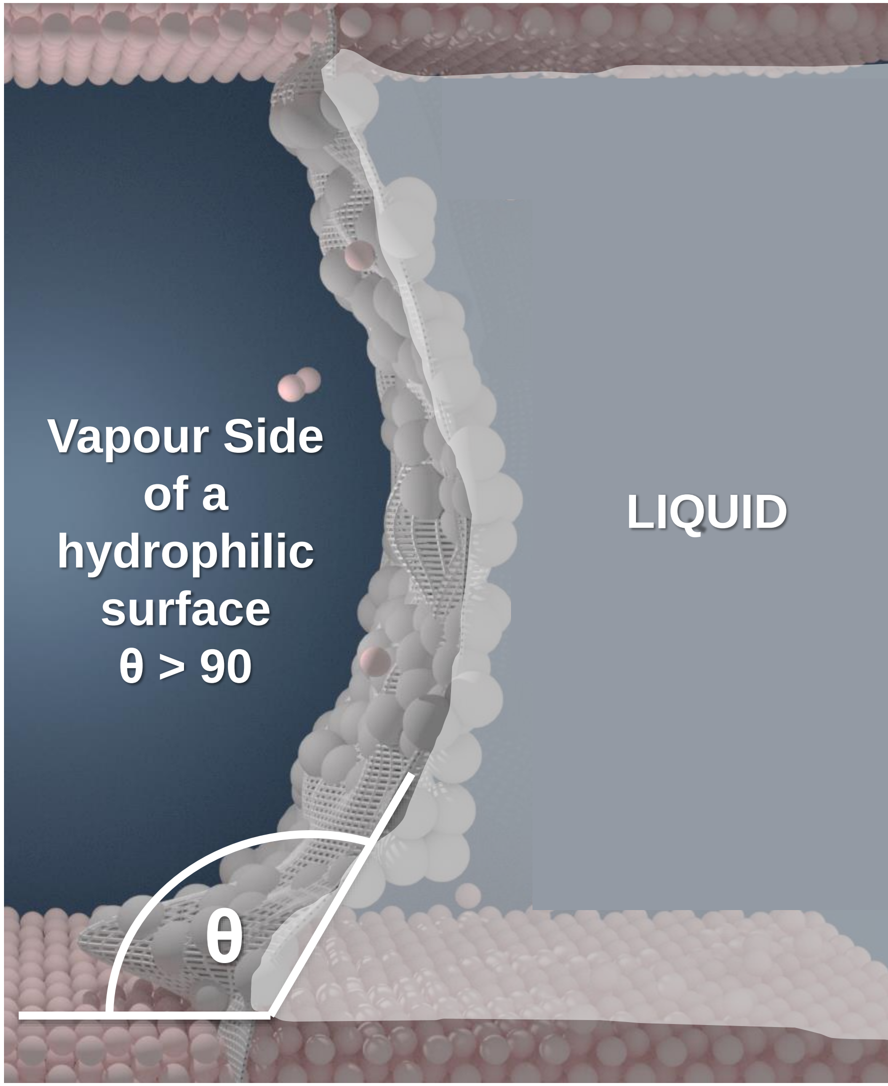


The Static Contact Line

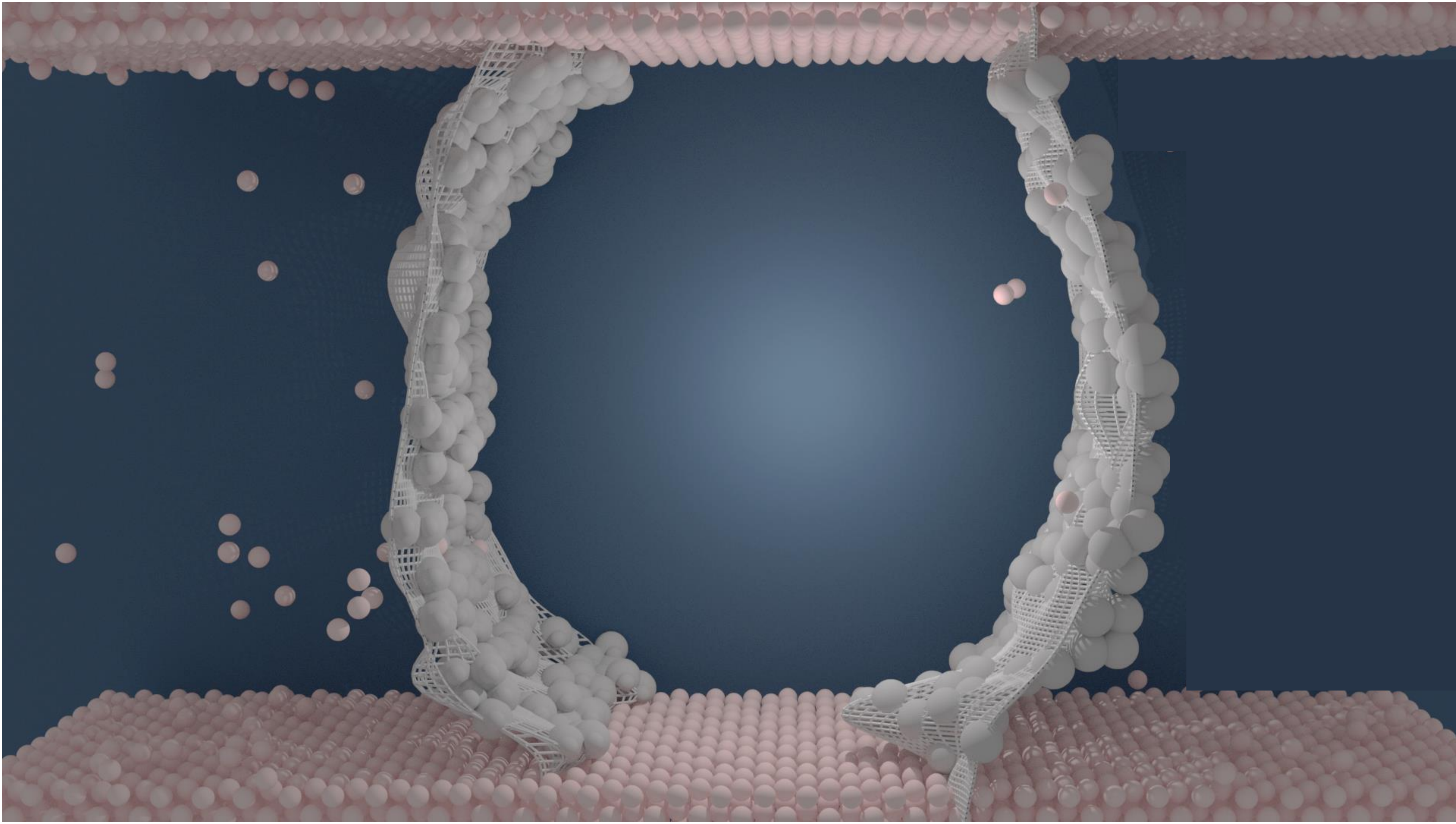


The Static Contact Line

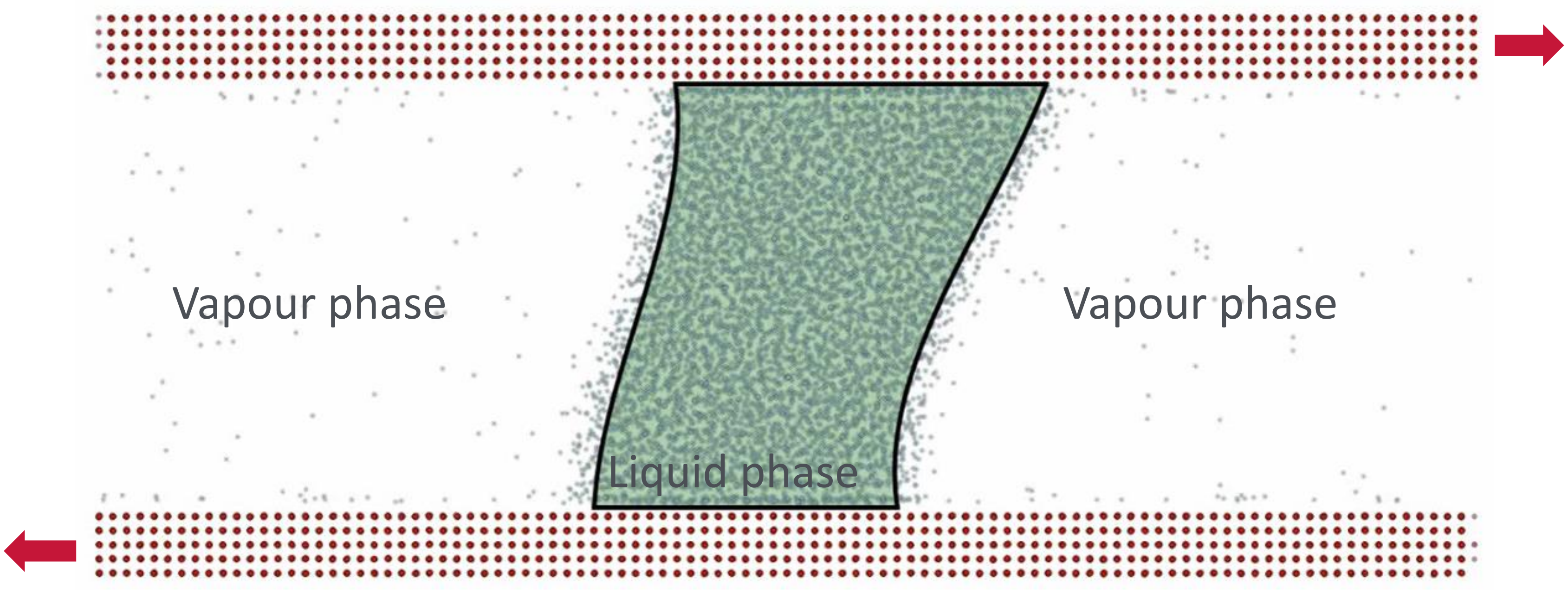




The Static Contact Line

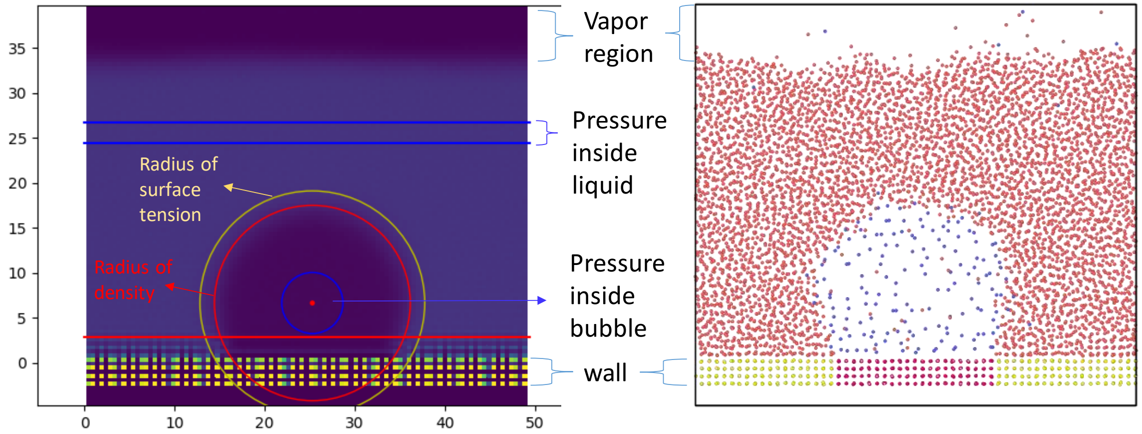


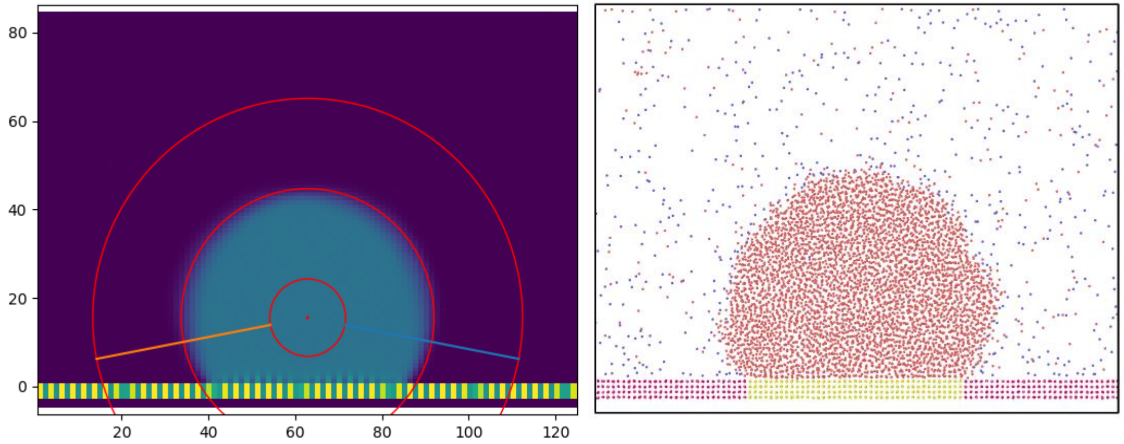
The Dynamic Contact Line



Sliding Solid walls (tethered)

Droplet vs. Bubbles





Work by

Wen Jun (Sonic)

at Imperial

Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

Molecular Dynamics - Nucleation

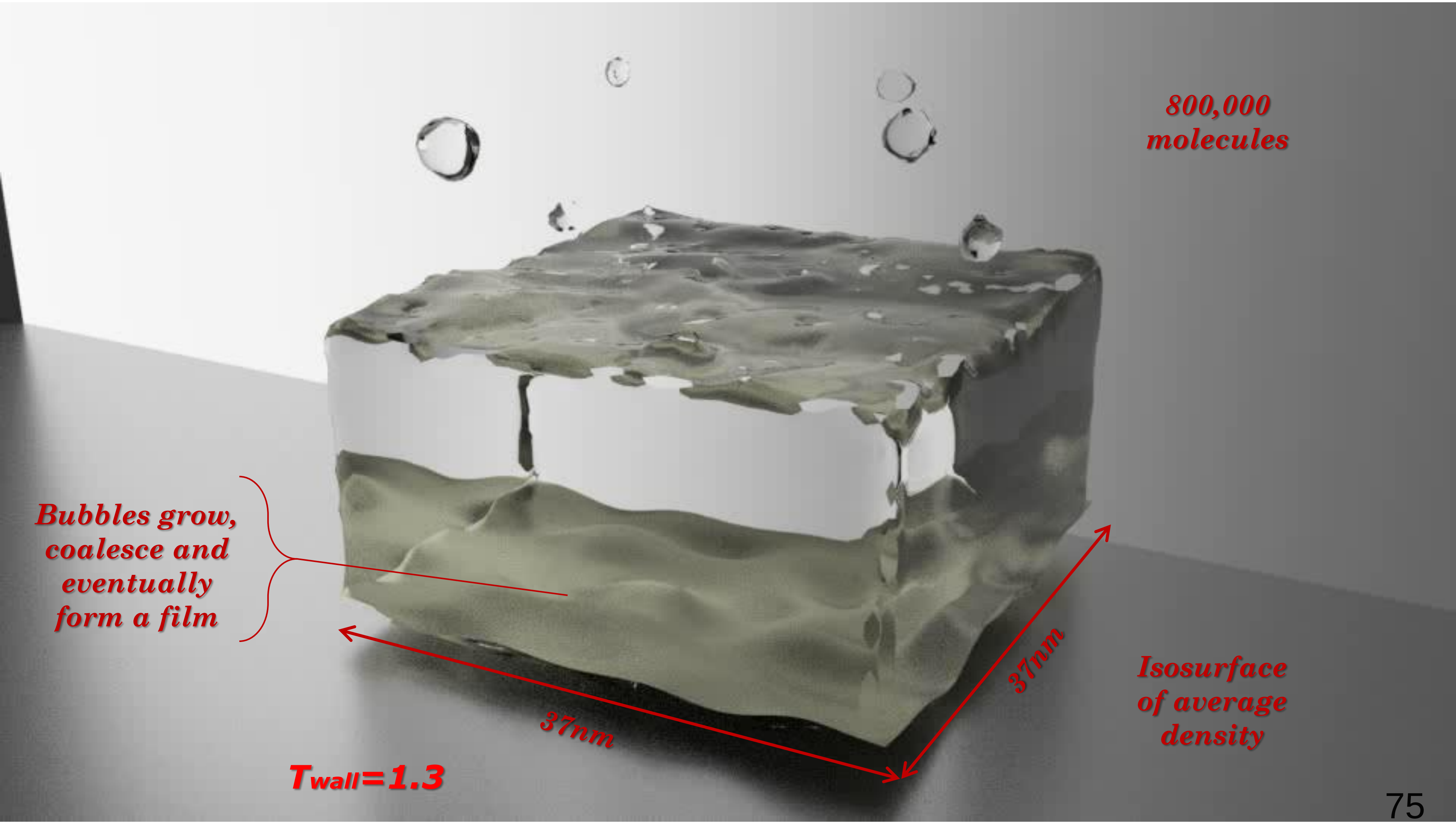
Wall w
mo
rou

800,000 molecules

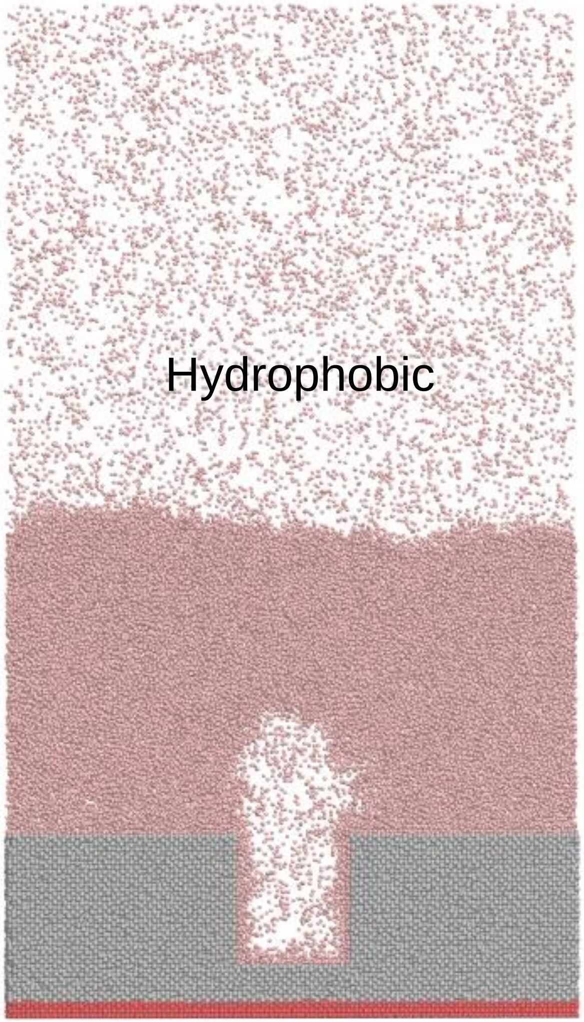
Isosurface of average density

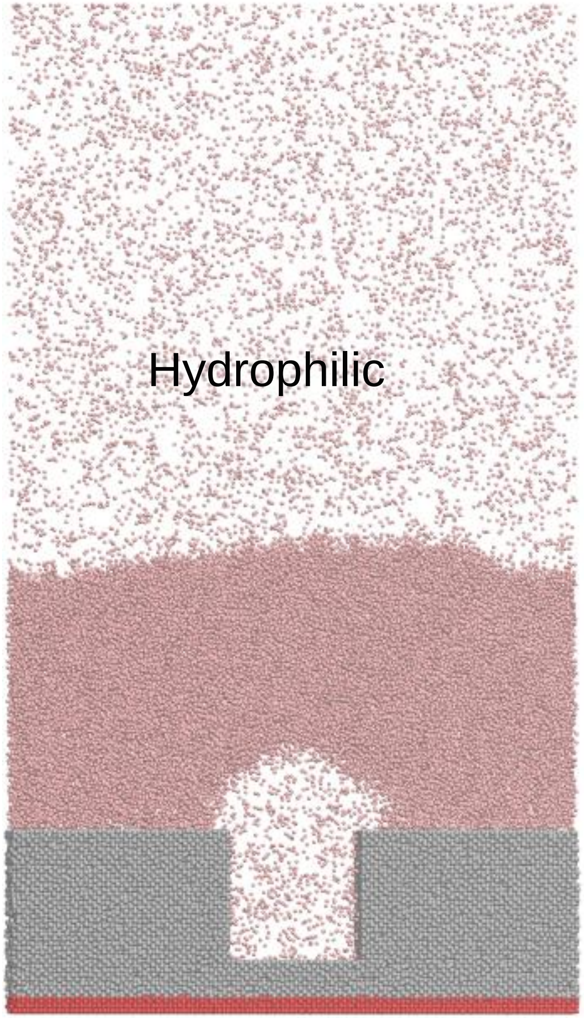
Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

Isosurface of Density



Wetting and Nucleation



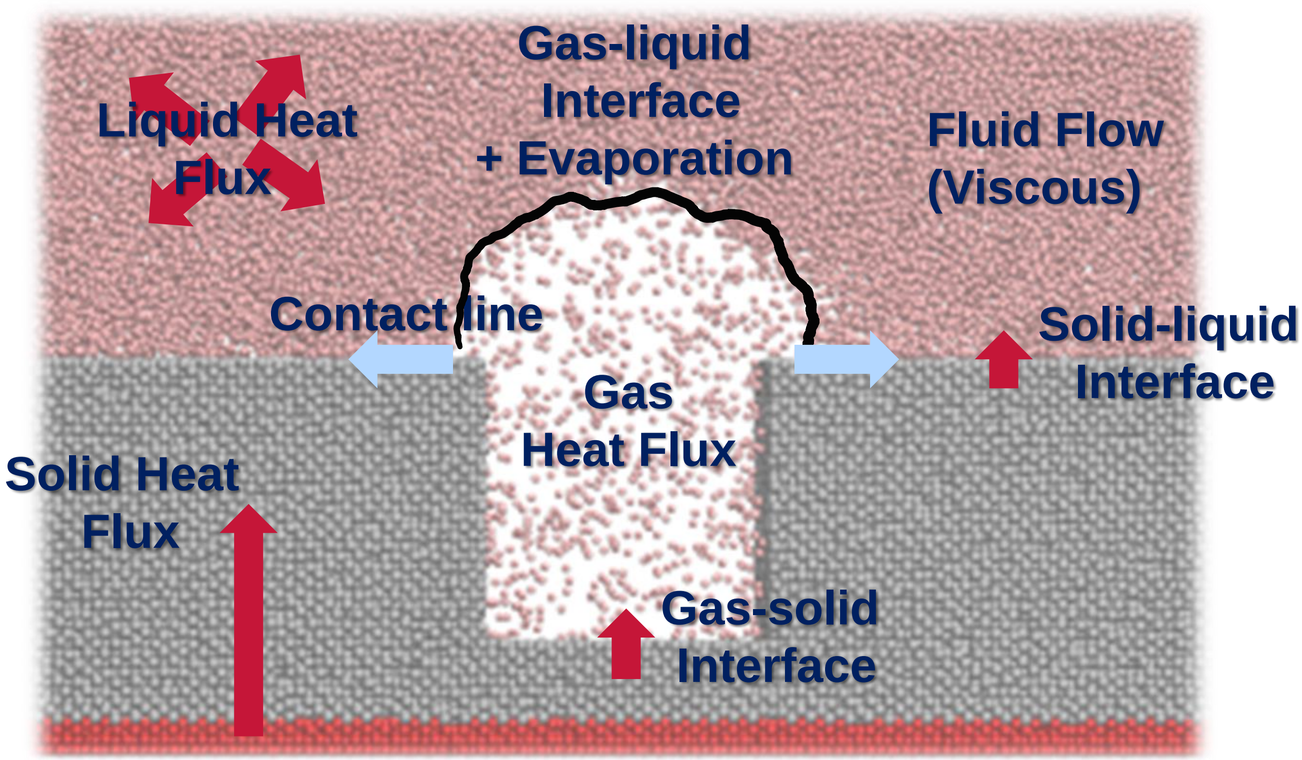


Work by

Alessio Lavino

at Imperial

Factors in Bubble Nucleation



Coupled Simulation of Boiling

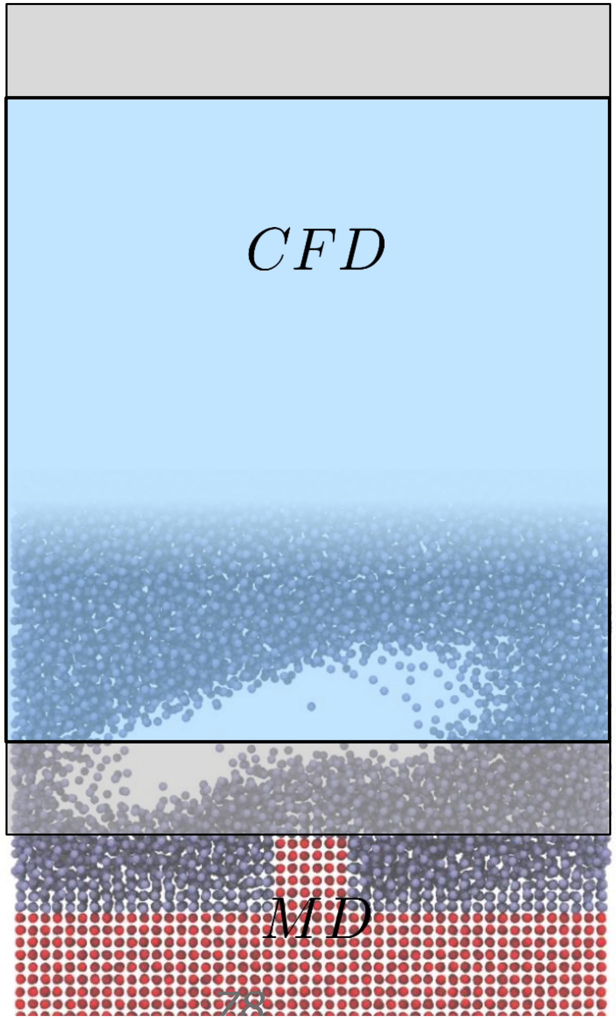
- Density at a point

$$\rho(\boldsymbol{r}, t)$$

Build MD detail into CFD

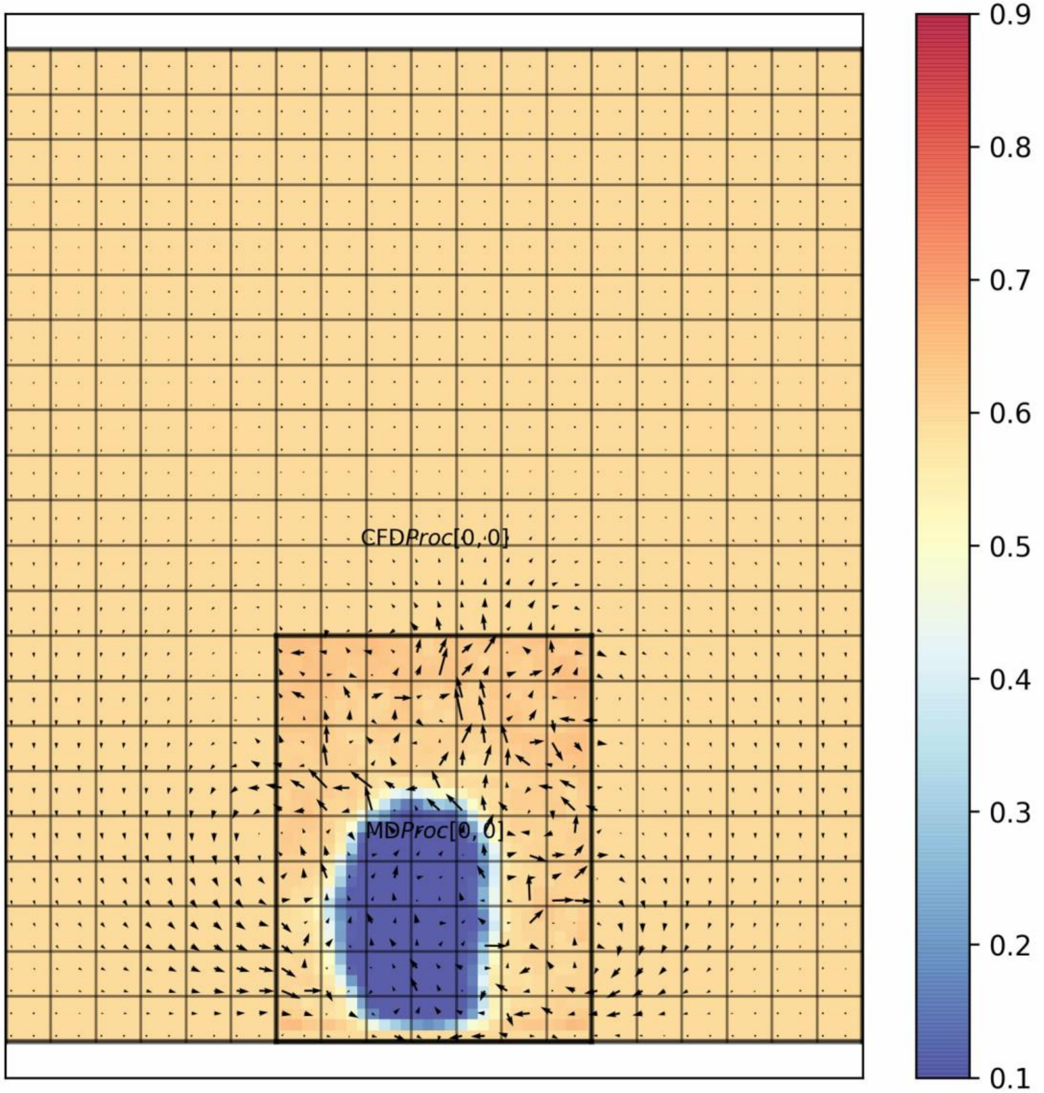
- Discrete molecules

$$m_i \text{ for all i in N}$$



Coupled Simulation of Boiling

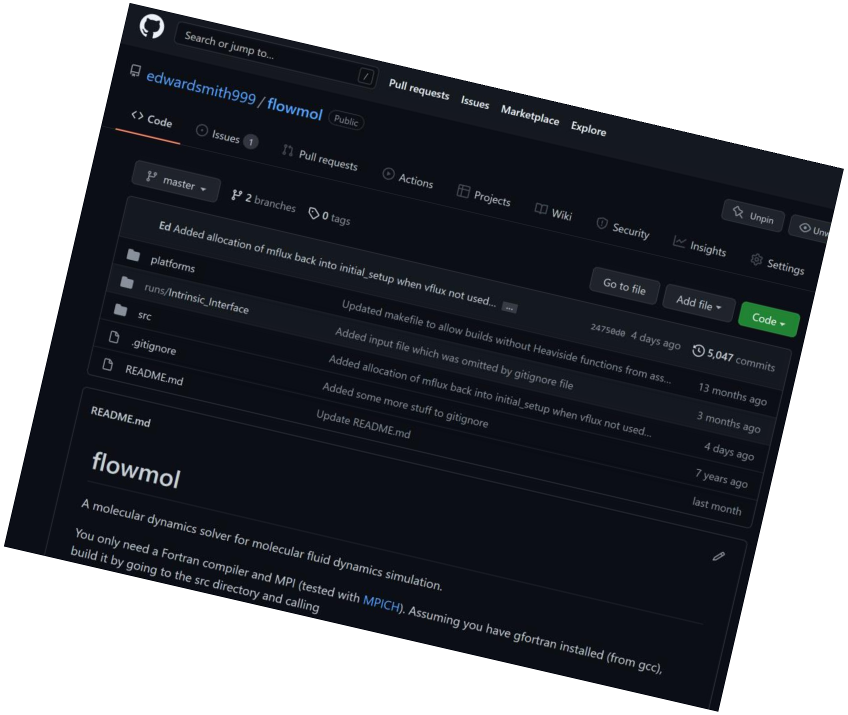
- Bubble nucleation occurs naturally in MD
- Density, velocity and temperature passed as boundary conditions



Application to Experimental Results

Open-source code

- ➢ Designed for particles
- ➢ Can be used for cells/pixels
- ➢ Surface fitting can be made as refined as necessary



Ed Added allocation of mflux back into initial_setup when vflux not used... 24750d0 4 days ago 5,047 commits

platforms	Updated makefile to allow builds without Heaviside functions from ass...	13 months ago
runs/Intrinsic_Interface	Added input file which was omitted by gitignore file	3 months ago
src	Added allocation of mflux back into initial_setup when vflux not used...	4 days ago
.gitignore	Added some more stuff to gitignore	7 years ago
README.md	Update README.md	last month

README.md

flowmol

A molecular dynamics solver for molecular fluid dynamics simulation.

You only need a Fortran compiler and MPI (tested with MPICH). Assuming you have gfortran installed (from gcc), build it by going to the src directory and calling

Overview

- An introduction to Molecular Dynamics (MD)
- The moving contact line
- The liquid-vapour interface - a Lagrangian reference frame
- Some applications

Further Talks and Collaboration

1- Talks from Brunel

- (a) **Thermofluids** (Fluid Mech/Heat Transfer/Thermodynamics/Energy)
- (b) Manufacturing (automation/sustainability/design/materials
- (c) Biosystems (LOC/Biomaterials)

2- Talks from York:

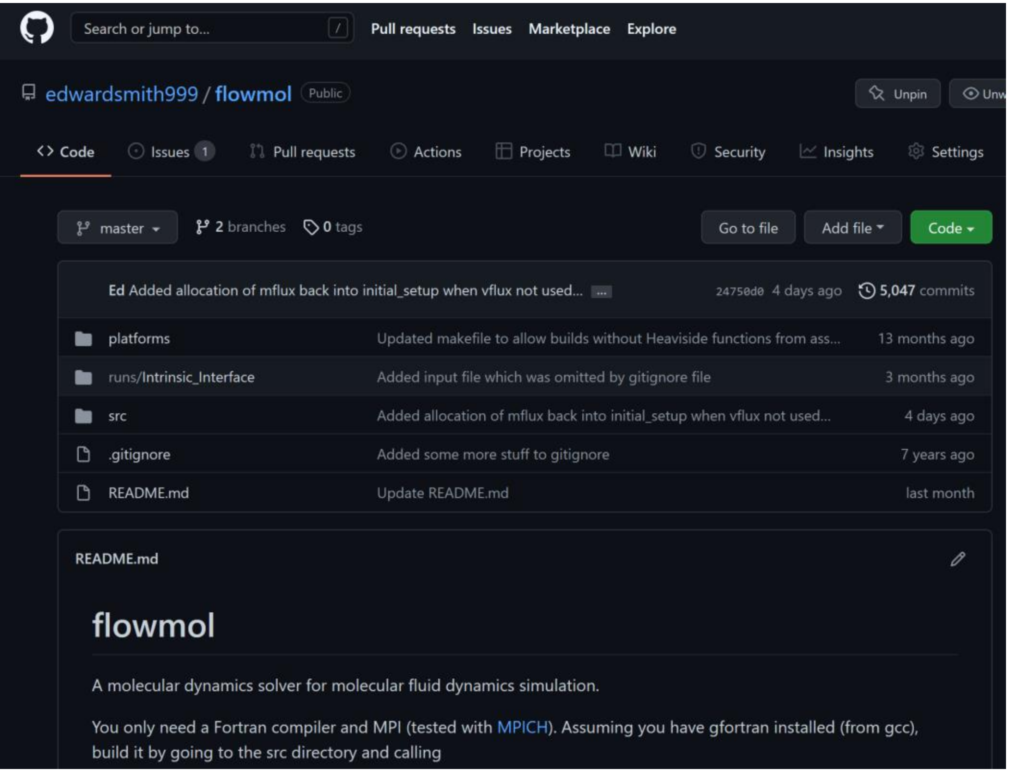
- (a) Microfluidics with or without a bio twist;
- (b) Automation with space applications;
- (c) Thermal systems with applications to vehicles; or for solar systems;
- (d) Materials (Bio, polymeric, or composites);
- (e) Droplet-surface interactions and applications in various industries.

3- UKRI (the UK funding Body) offers the UK-Canada Globallink doctoral exchange scheme, a 12 week research visit for PhD students (up to £15k)

Deadline 26th April 2022

Questions

Thank you, any questions?



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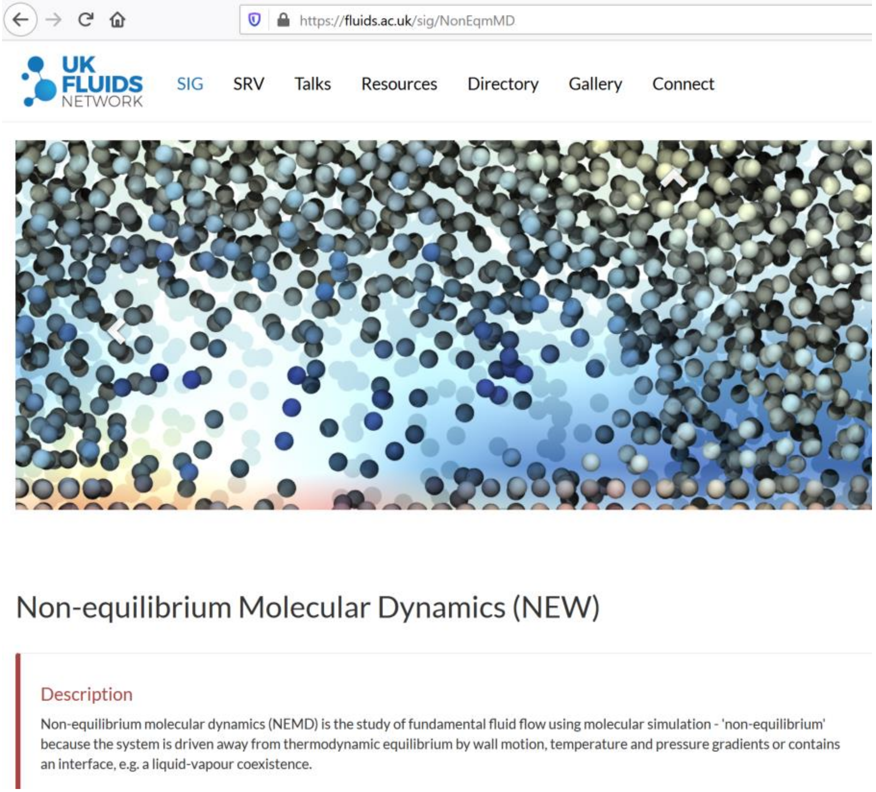


Non-equilibrium Molecular Dynamics (NEW)

Description

Non-equilibrium molecular dynamics (NEMD) is the study of fundamental fluid flow using molecular simulation - 'non-equilibrium' because the system is driven away from thermodynamic equilibrium by wall motion, temperature and pressure gradients or contains an interface, e.g. a liquid-vapour coexistence.

Please see https://edwardsmith.co.uk

Pressure (Stress)

- Working through the mathematics

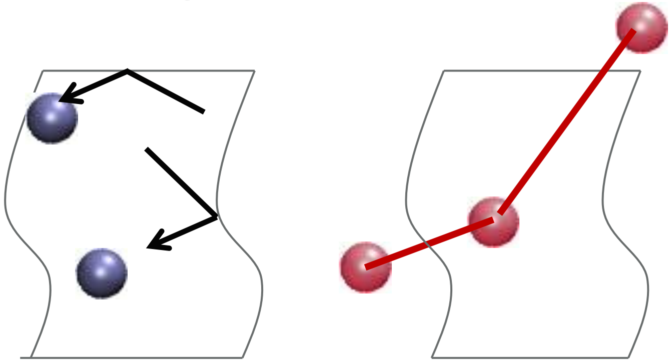
$$\boldsymbol{\Pi}_{\alpha}^{\text{kinetic}} = \frac{1}{\Delta S_{\alpha}} \sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \boldsymbol{r}_{12} \cdot \frac{\boldsymbol{n}_{\alpha}}{|\boldsymbol{r}_{12} \cdot \boldsymbol{n}_{\alpha}|} dS_{\alpha}$$

$$\boldsymbol{\Pi}_{\alpha}^{\text{Moving surf}} = \frac{1}{\Delta S_{\alpha}} \sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_t$$

$$\boldsymbol{\Pi}_{\alpha}^{\text{config}} = \frac{1}{2\Delta S_{\alpha}} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \boldsymbol{r}_{ij} \cdot \frac{\boldsymbol{n}_{\alpha}}{|\boldsymbol{r}_{ij} \cdot \boldsymbol{n}_{\alpha}|} dS_{\alpha}$$

Kinetic theory part

Momentum due to average of molecules crossing a plane and returning



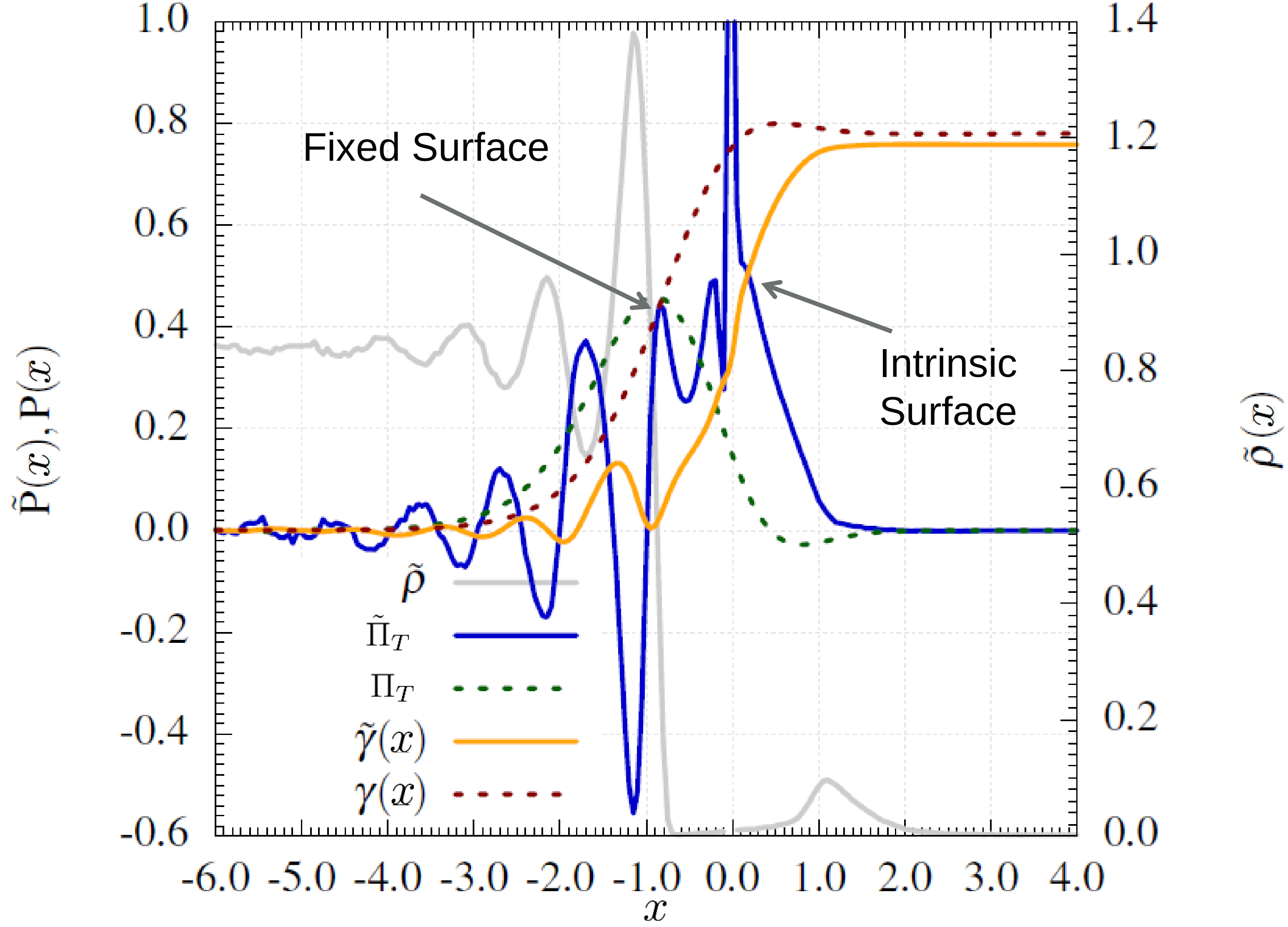
$$\dot{\boldsymbol{r}}_i = m_i \boldsymbol{v}_i + \boldsymbol{u}$$

Configurational part

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

Work with Carlos Braga and Serafim Kalliadasis

Tangential Pressure

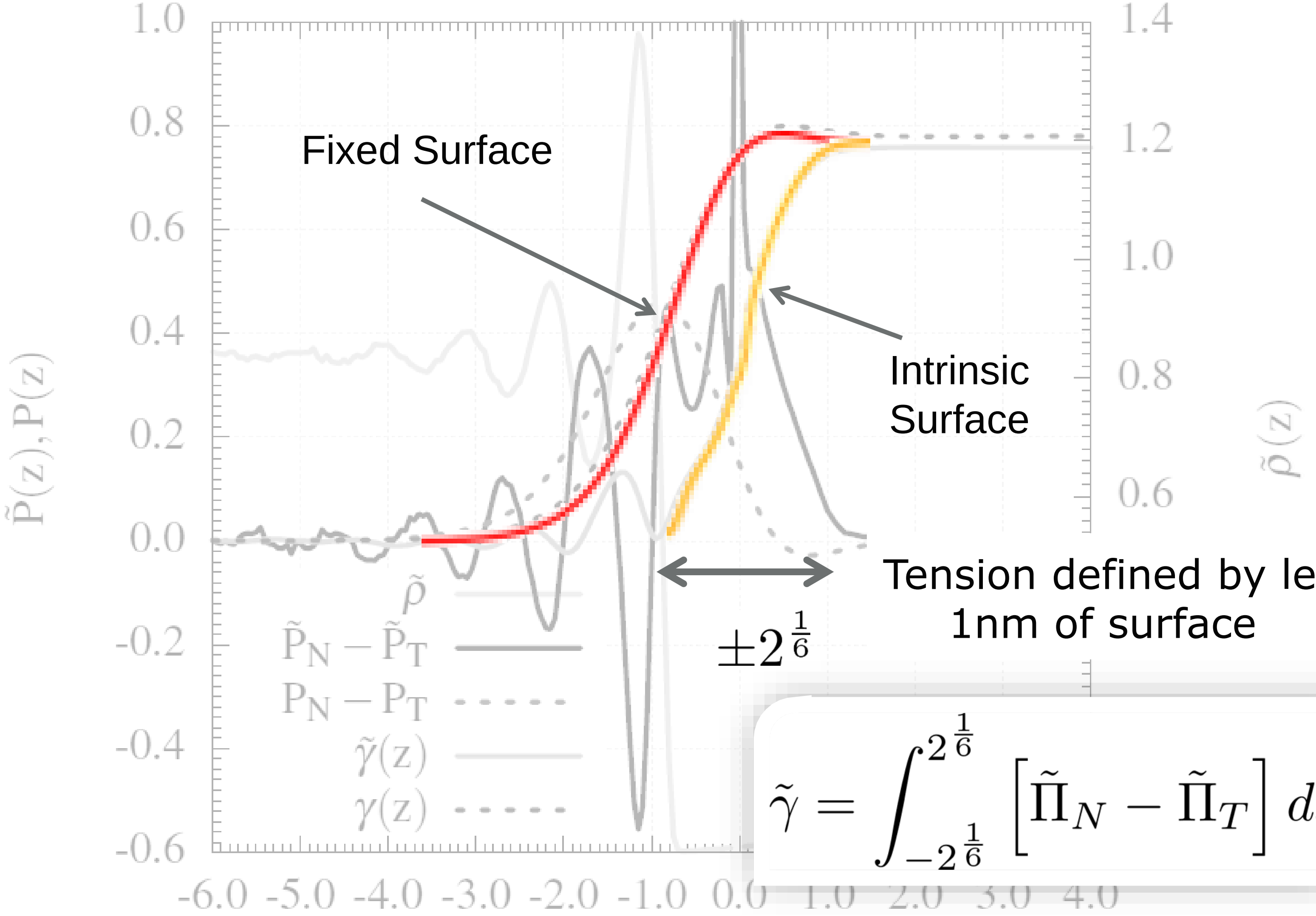


Fixed Surface

Intrinsic Surface

Work with Carlos Braga and Serafim Kalliadasis

Results for Surface Tension



Fixed Surface

Intrinsic Surface

Tension defined by less than 1nm of surface

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