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Exploring the Liquid-Vapour Interface with Molecular Fluid Dynamics

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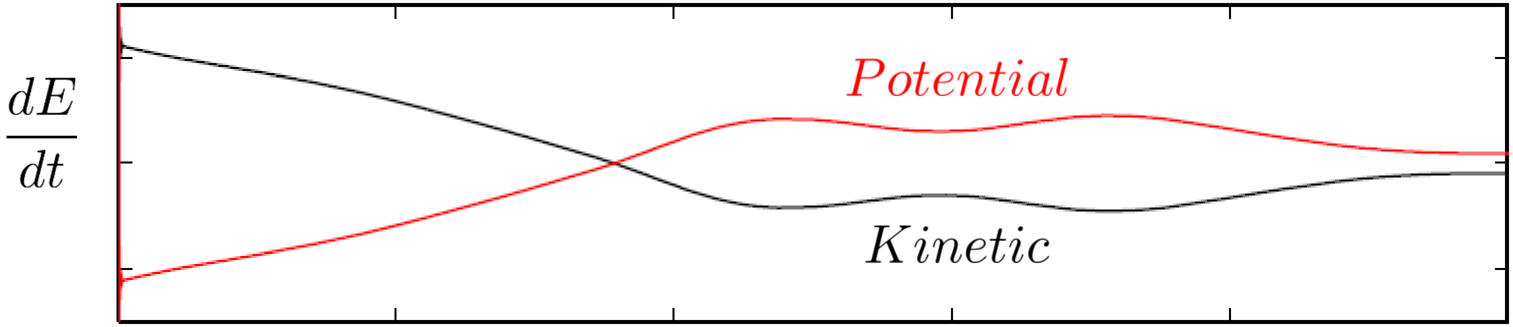
Overview

- An introduction to Molecular Dynamics (MD)
- Molecular Fluid Dynamics and getting quantities from a molecular system
- The liquid-vapour interface
- Defining a Lagrangian reference frame moving with the interface
- Some applications

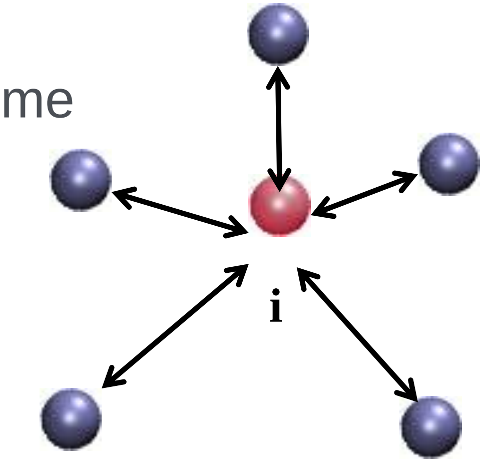
Molecular Dynamics

- 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

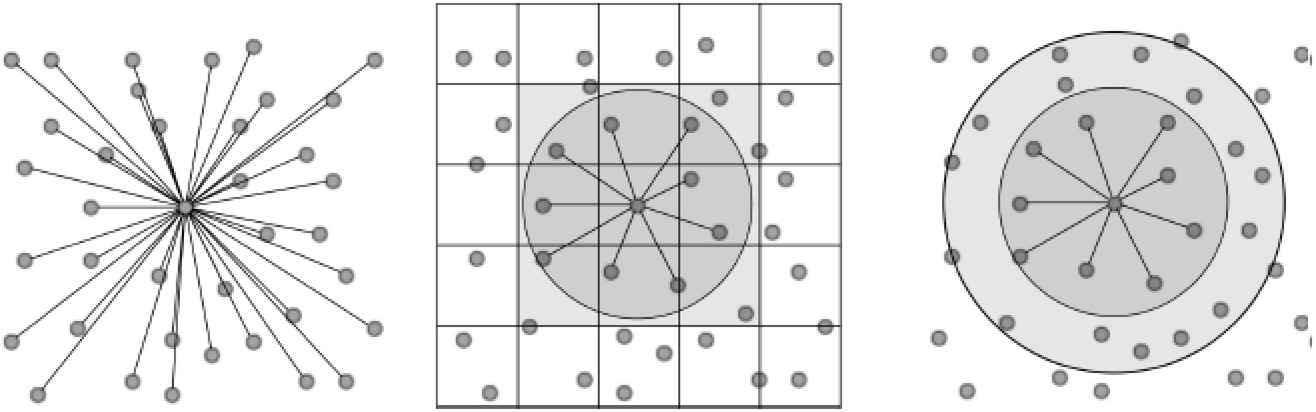
$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i \neq j}^{N} \boldsymbol{f}_{ij}$$

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

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)

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

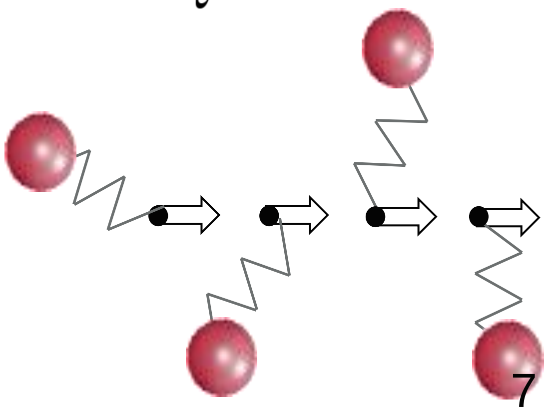
$$\frac{dr_i}{dt} \approx \frac{r_i(t + \Delta t) - r_i(t)}{\Delta t}$$

Non-Equilibrium Molecular Dynamics

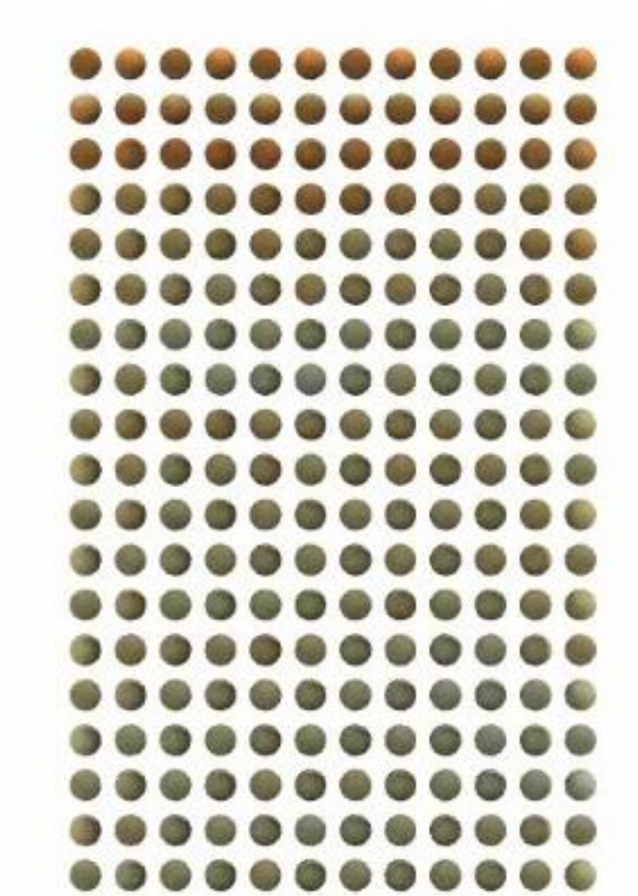
- Non-Equilibrium Molecular Dynamics (NEMD) is the study of cases beyond thermodynamic equilibrium, with:
  - Temperature gradients
  - Flow of fluid (e.g. Couette or Poiseuille flow)
- Essentially fluid dynamics - temperature gradients and flows
  - Thermostats (e.g. Nosé Hoover) remove heat from system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

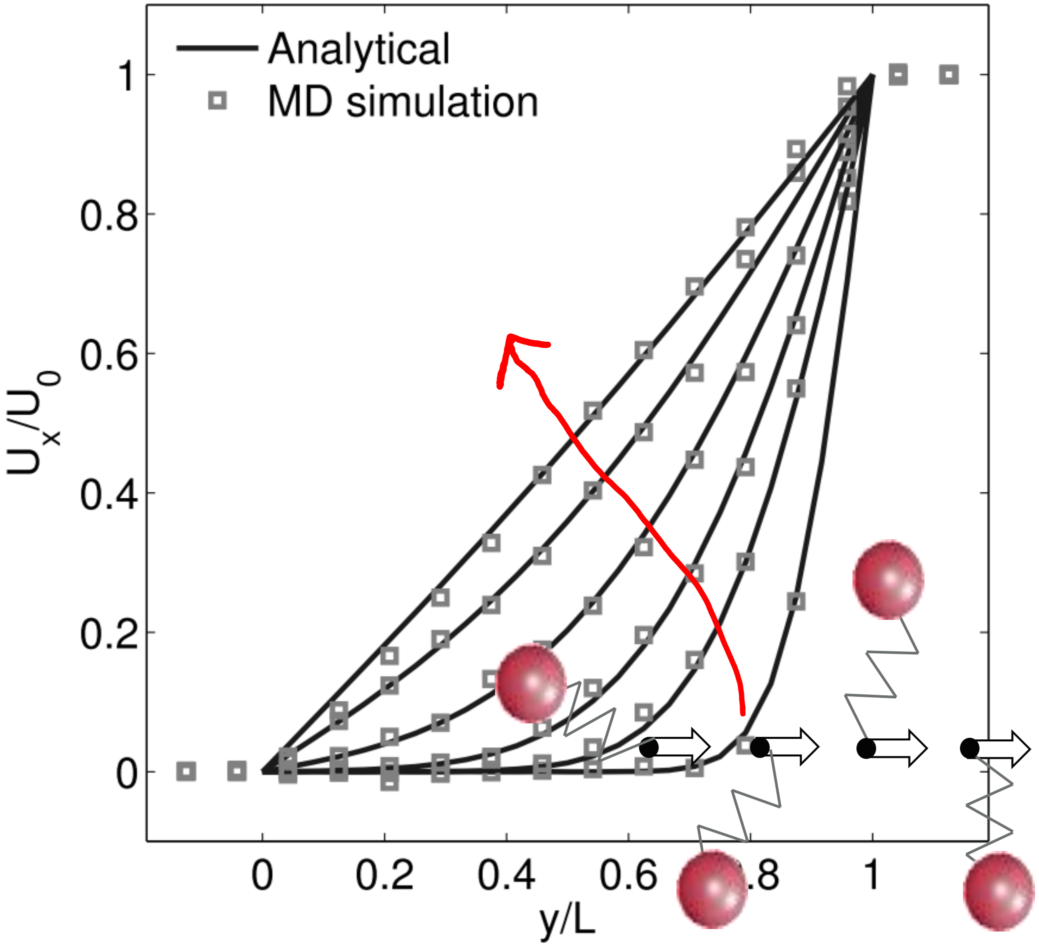
$$m_i\ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{teth} - \psi m_i \boldsymbol{c}_i$$

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

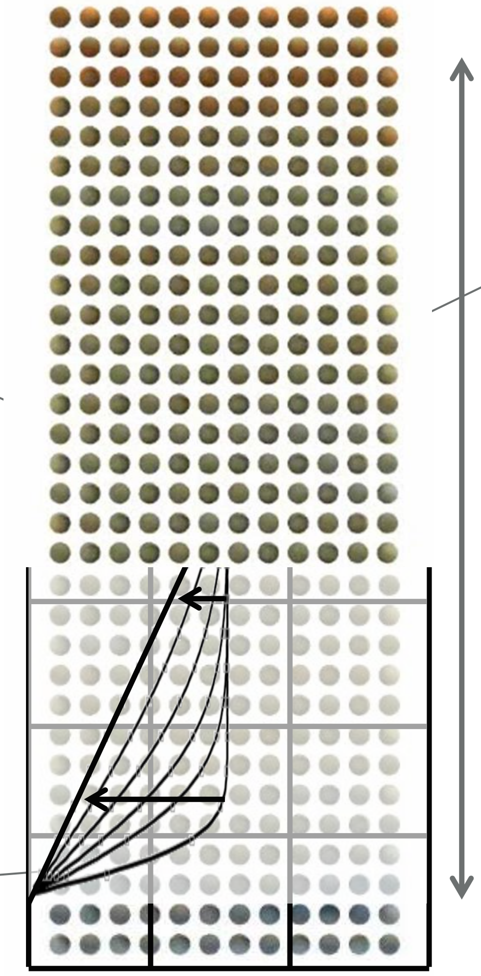


Wall Bounded Flow





Wall Bounded Flow



Liquid structure causes viscosity

Average behaviour reproduces hydrodynamics (coloured by velocity)

Stick-slip near walls

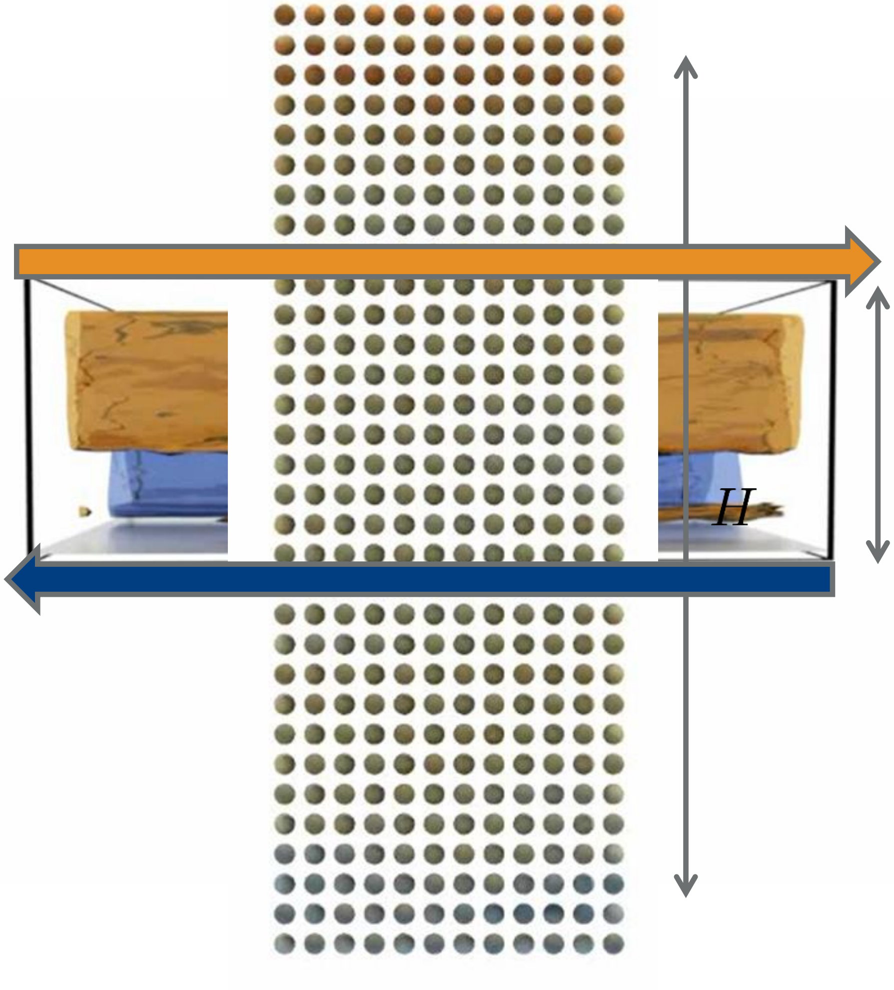
Reynolds Number

$Re \approx 15$

with

4096 molecules

Wall Bounded Flow



Reynolds Number

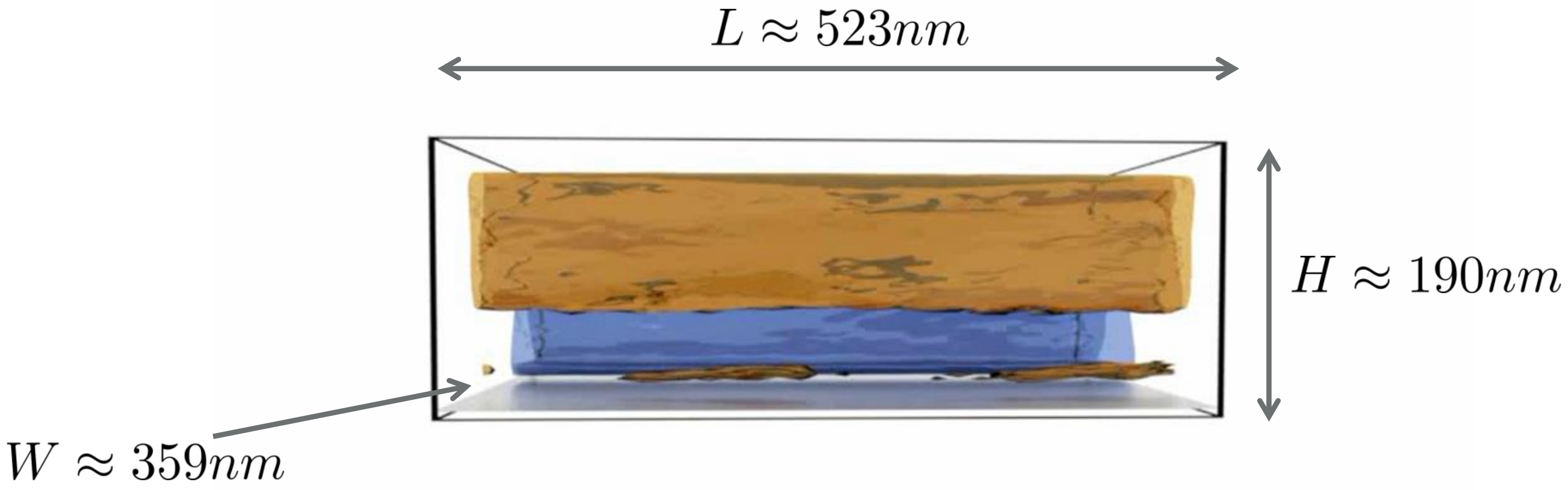
$$Re \approx 400$$

with

300 million molecules

Wall Bounded Flow

Minimal channel Couette flow



Reynolds Number

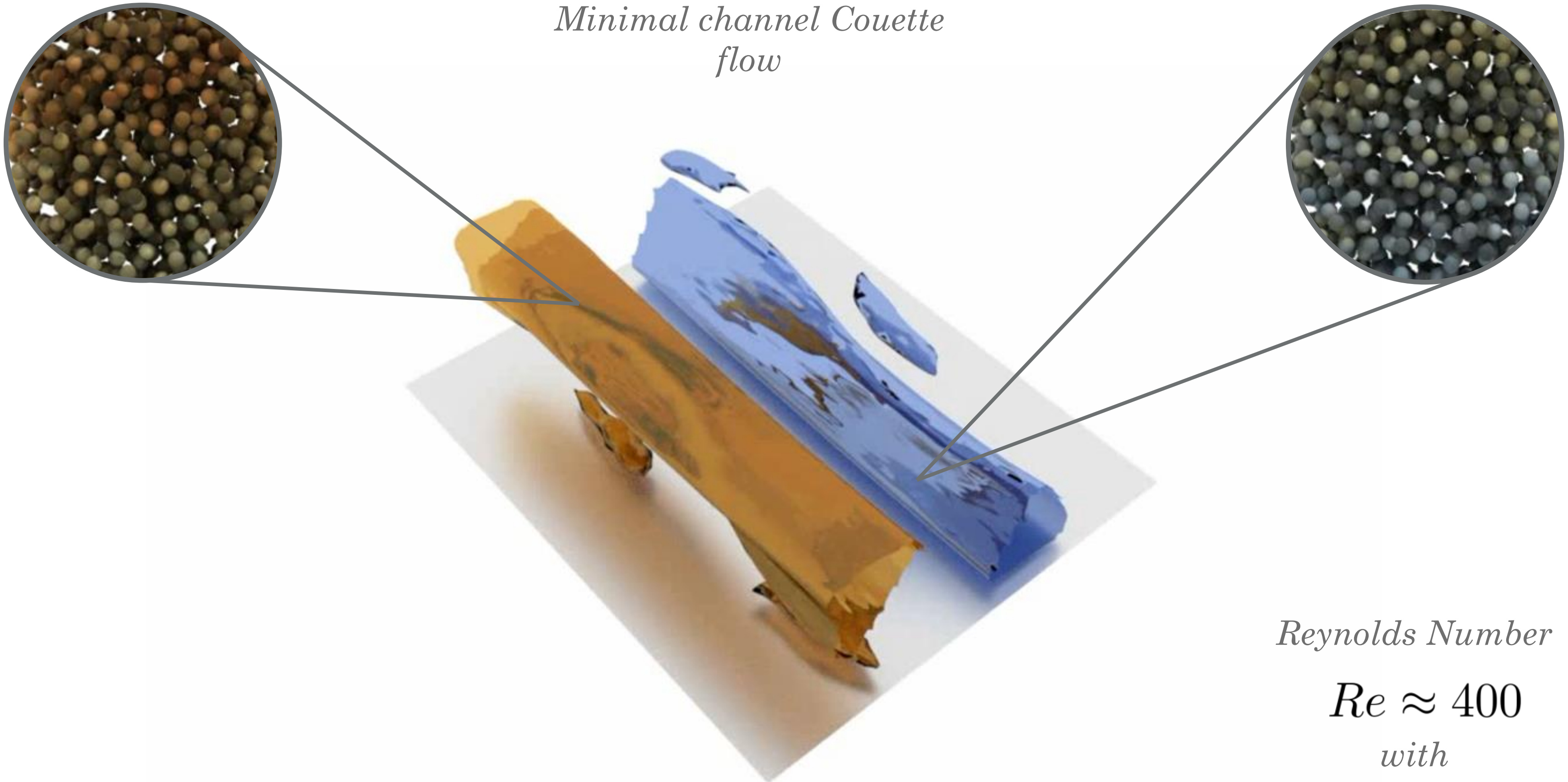
$$Re \approx 400$$

with

300 million molecules

Molecular Dynamics - Turbulence

Minimal channel Couette flow



Isosurfaces of turbulent kinetic energy coloured by velocity

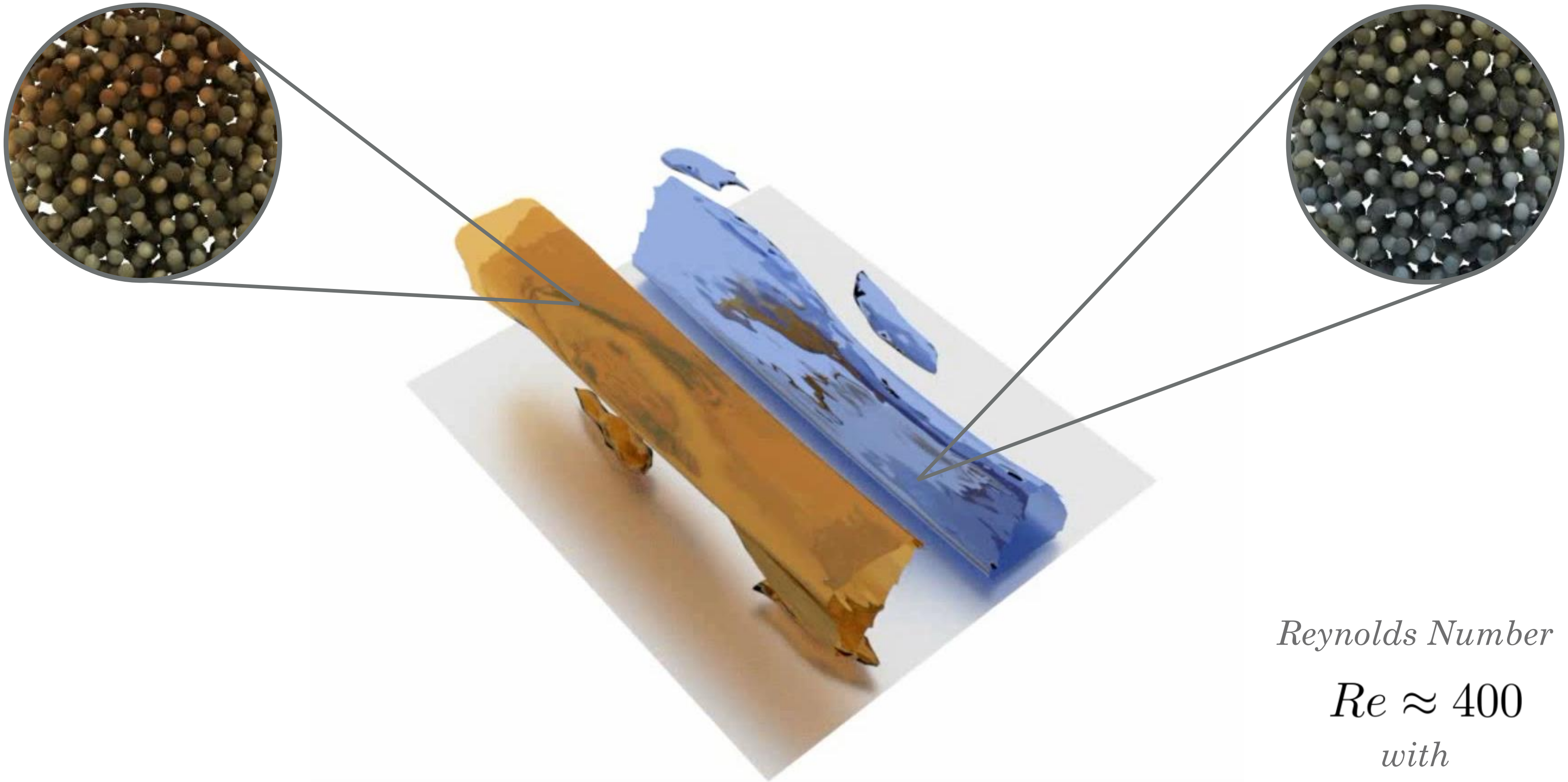
Reynolds Number

$$Re \approx 400$$

with

300 million molecules

Molecular Dynamics - Turbulence



Isosurfaces of turbulent kinetic energy coloured by velocity

Reynolds Number

$Re \approx 400$

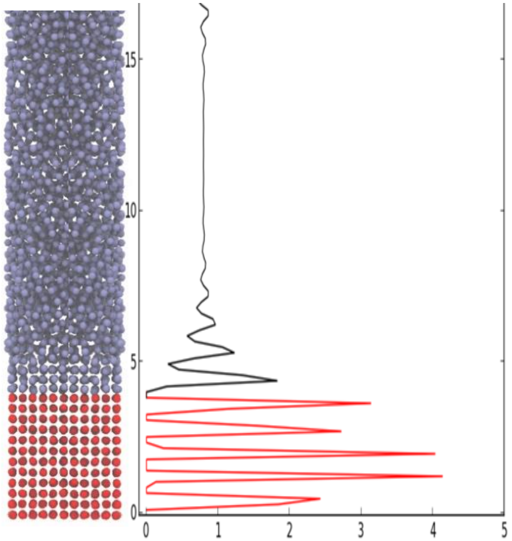
with

300 million molecules

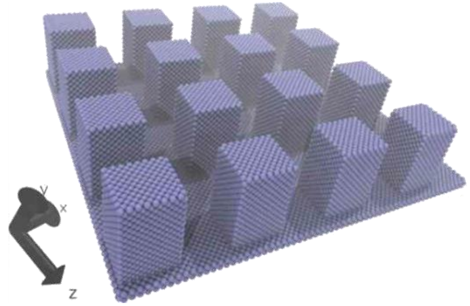
Molecular Dynamics – Complex Walls and Fluids

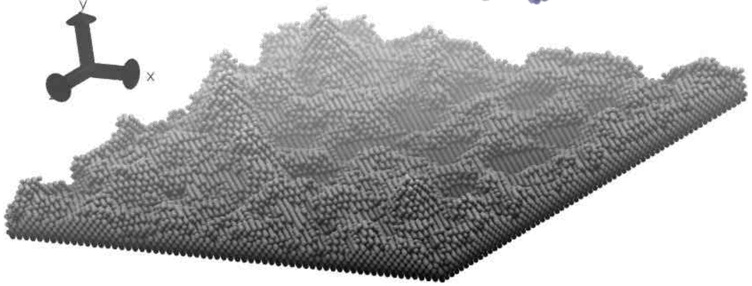
Liquid structure causes viscosity

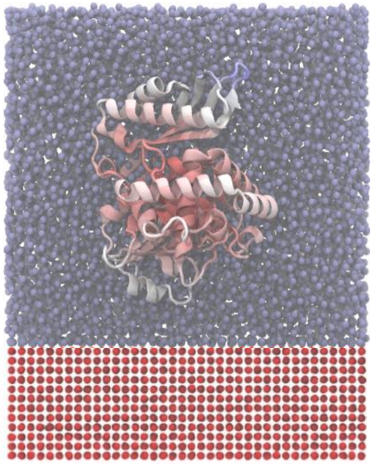
Stick-slip near walls



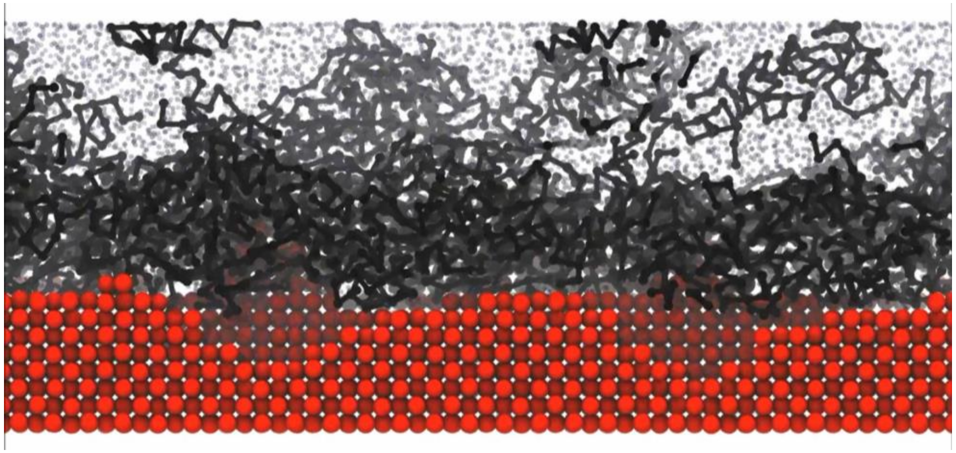
Wall Texture







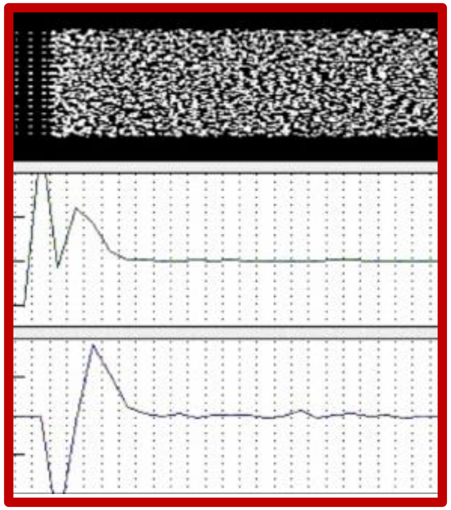
Molecules of arbitrary complexity



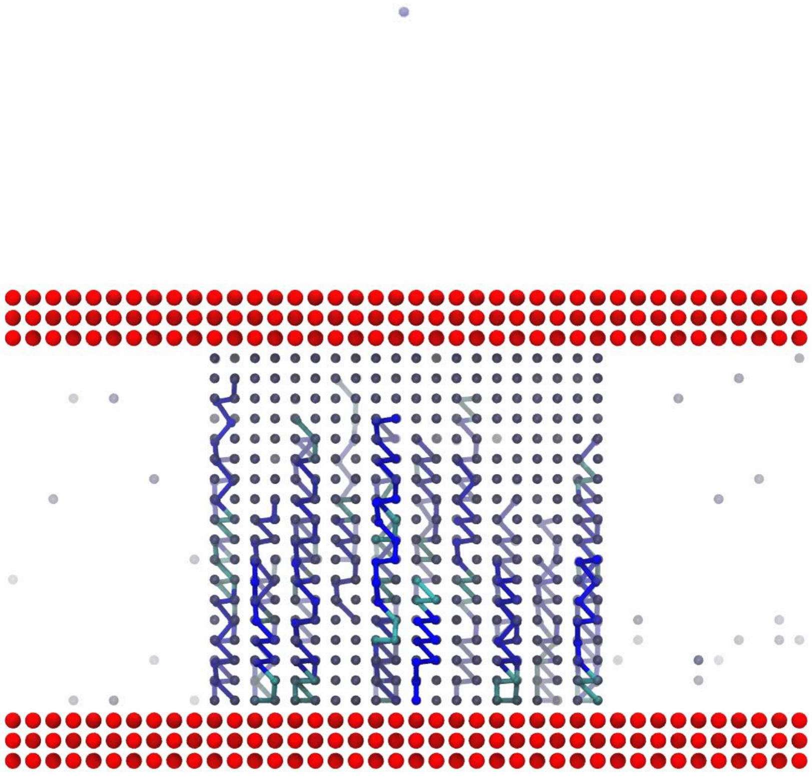
Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

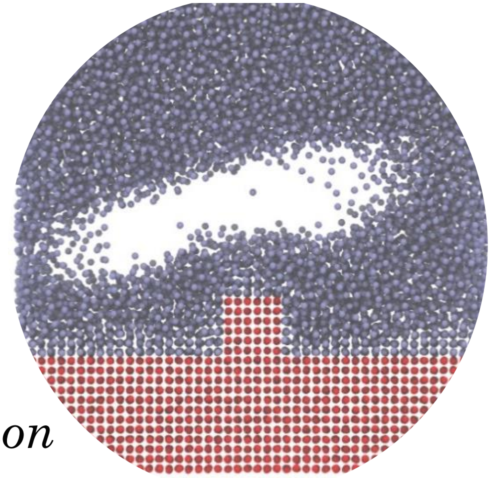
Shockwave



Droplet Formation

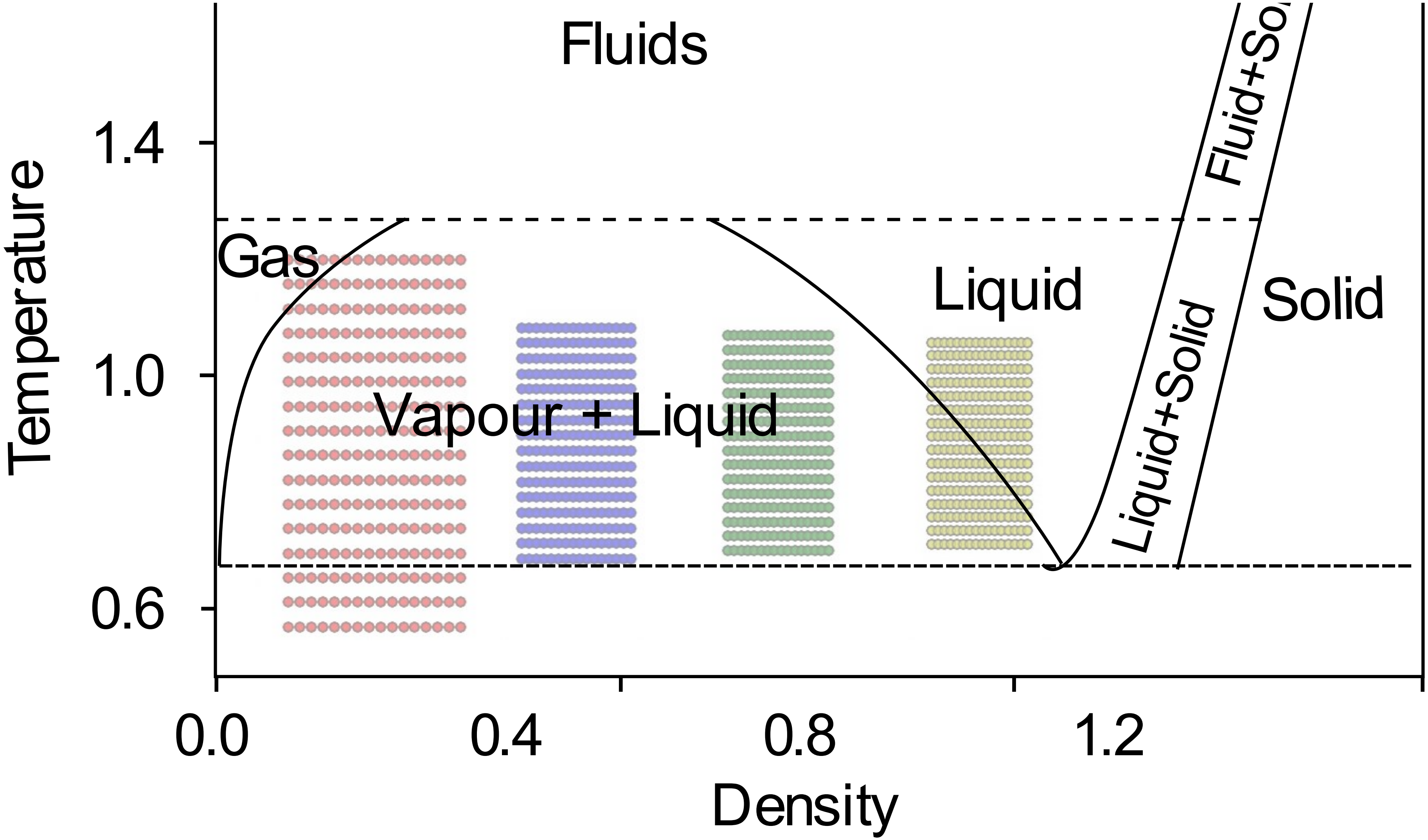


Contact line



Nucleation

Phase Change



Linking to Continuum Fluid Dynamics

Continuum Fluid Dynamics

- Assumed continuous at every point in space
  - Mass Conservation

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \rho \boldsymbol{u}$$

  - Momentum Balance (Newton's Law)

$$\frac{\partial}{\partial t} \rho \boldsymbol{u} + \boldsymbol{\nabla} \cdot \rho \boldsymbol{u} \boldsymbol{u} = \boldsymbol{\nabla} \cdot \boldsymbol{\Pi}$$

  - Energy Conservation

$$\frac{\partial}{\partial t} \rho \mathcal{E} dV = -\boldsymbol{\nabla} \cdot [\rho \mathcal{E} \boldsymbol{u} + \boldsymbol{\Pi} \cdot \boldsymbol{u} + \mathbf{q}]$$

Direct Numerical Simulation of Turbulent Couette Flow

Computational Fluid Dynamics

- The Navier-Stokes Equation

$$\frac{\partial}{\partial t}\rho\boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} \quad = \quad -\boldsymbol{\nabla}\cdot\Pi \qquad\qquad \boldsymbol{\Pi} = P\boldsymbol{I} - \mu\boldsymbol{\nabla}\boldsymbol{u}$$

- Solve for pressure assuming incompressibility

$$\frac{\partial}{\partial t}\rho\boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} = -\boldsymbol{\nabla}P + \mu\nabla^2\boldsymbol{u} \qquad\qquad \boldsymbol{\nabla}\cdot\boldsymbol{u} = 0$$

Viscosity Coefficient

- In two-phase flows we also need surface tension
  - This can appear as a boundary condition in the liquid/vapour parts of the model

$$\boldsymbol{n}\cdot\boldsymbol{\Pi}\cdot\boldsymbol{n} = \gamma\boldsymbol{\nabla}\cdot\boldsymbol{n}$$

  - Other models are possible using Dirac deltas, forcing terms, etc

Linking MD to the Continuum Representation

- Assumes a continuous field

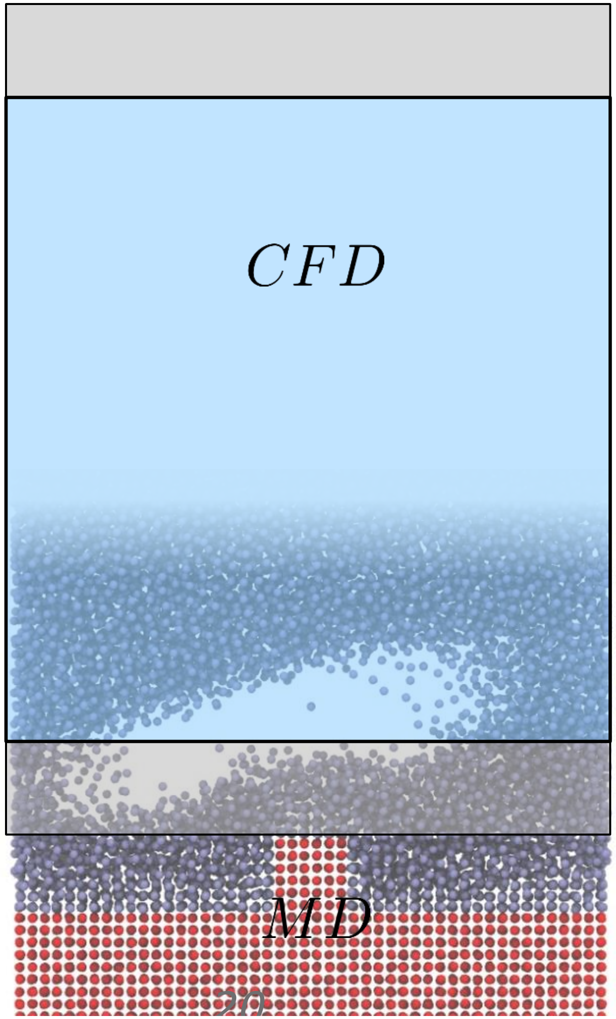
$$\frac{\partial}{\partial t}\rho \boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} = -\boldsymbol{\nabla}P + \mu\nabla^2\boldsymbol{u}$$

- Liquid-vapour interface

$$\boldsymbol{n}\cdot\boldsymbol{\Pi}\cdot\boldsymbol{n} = \gamma\boldsymbol{\nabla}\cdot\boldsymbol{n}$$

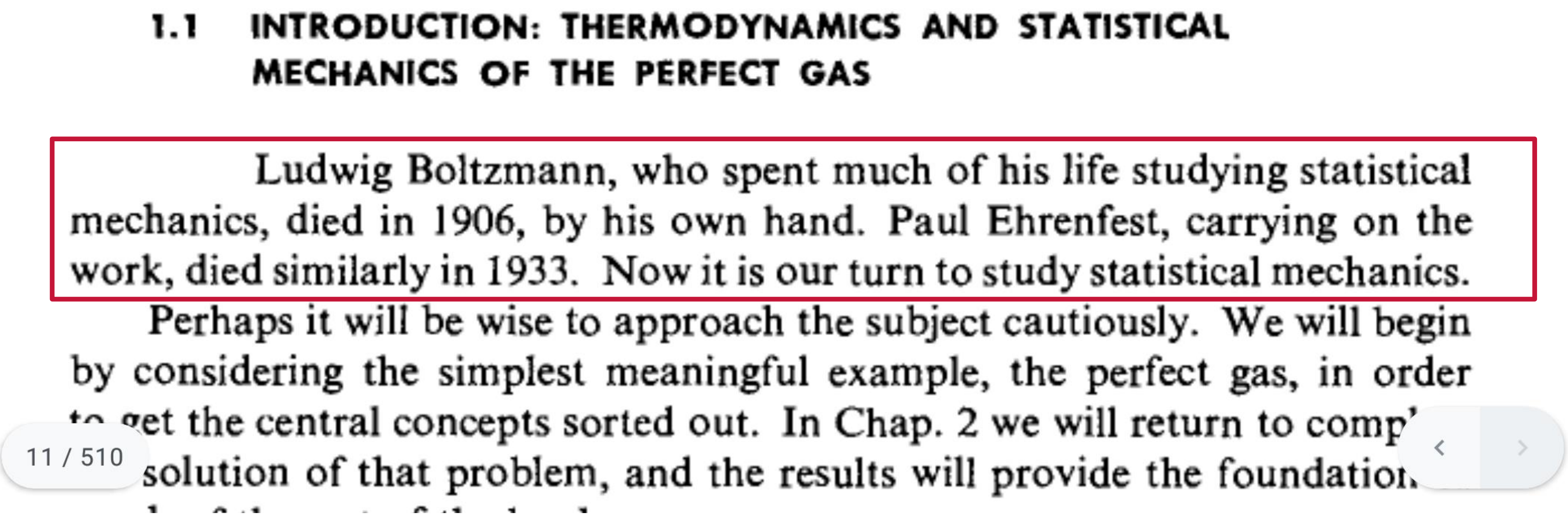
- Discrete molecules

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



Statistical Mechanics

- We need to use some statistical mechanics



1.1 INTRODUCTION: THERMODYNAMICS AND STATISTICAL MECHANICS OF THE PERFECT GAS

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously. We will begin by considering the simplest meaningful example, the perfect gas, in order to get the central concepts sorted out. In Chap. 2 we will return to comp solution of that problem, and the results will provide the foundation

From States of Matter by Goodstein

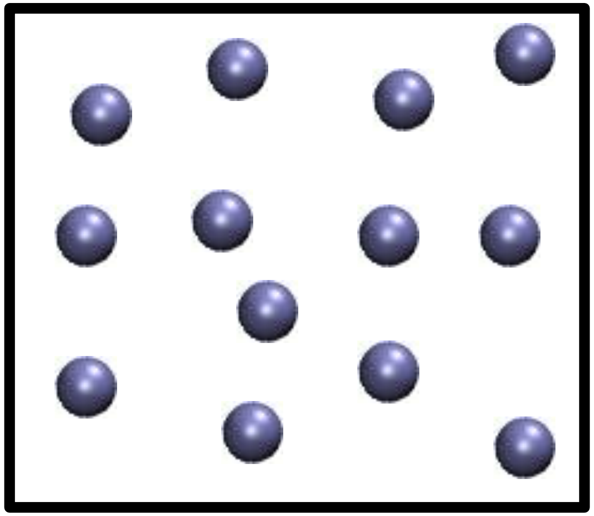
Getting Quantities from MD

- Density in a region of space

$$\rho(\boldsymbol{r},t) = \frac{1}{V}\sum_{i\in\mathrm{Box}}^{N_{\mathrm{Box}}} \langle m_i \rangle$$

Angular brackets denote time average

$$\rho(\boldsymbol{r},t) = \frac{1}{V}\sum \Bigg\langle$$



$$\Bigg\rangle$$

Getting Quantities from MD

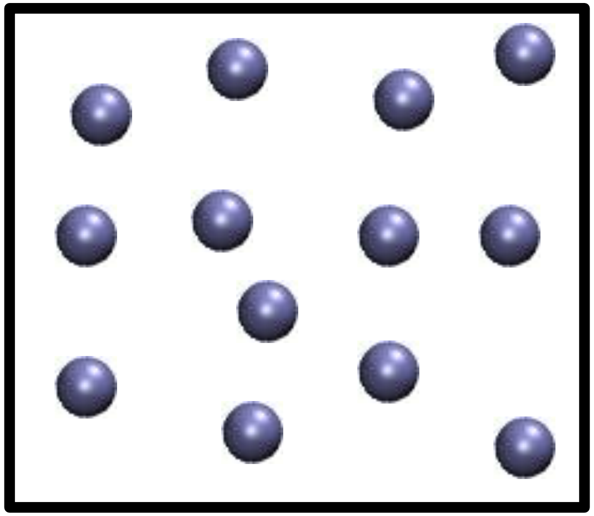
- Density in a region of space

$$\rho(\boldsymbol{r},t) = \frac{1}{V}\sum_{i\in\mathrm{Box}}^{N_{\mathrm{Box}}} \langle m_i\,; f\rangle$$

Angular brackets denote time average

or ensemble averaging

$$\rho(\boldsymbol{r},t) = \frac{1}{V}\sum \Bigg\langle$$



$$; f \Bigg\rangle$$

Irving and Kirkwood (1950)

TRANSPORT PROCESSES 817

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, $778+\nu_i-\nu_i$, 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, $2\times407+\nu_8-\nu_8$, 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.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 18, NUMBER 6 JUNE, 1950

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

J. H. Irving and John G. Kirkwood
Gates and Crellin Laboratories of Chemistry No. 1343, Pasadena, California
(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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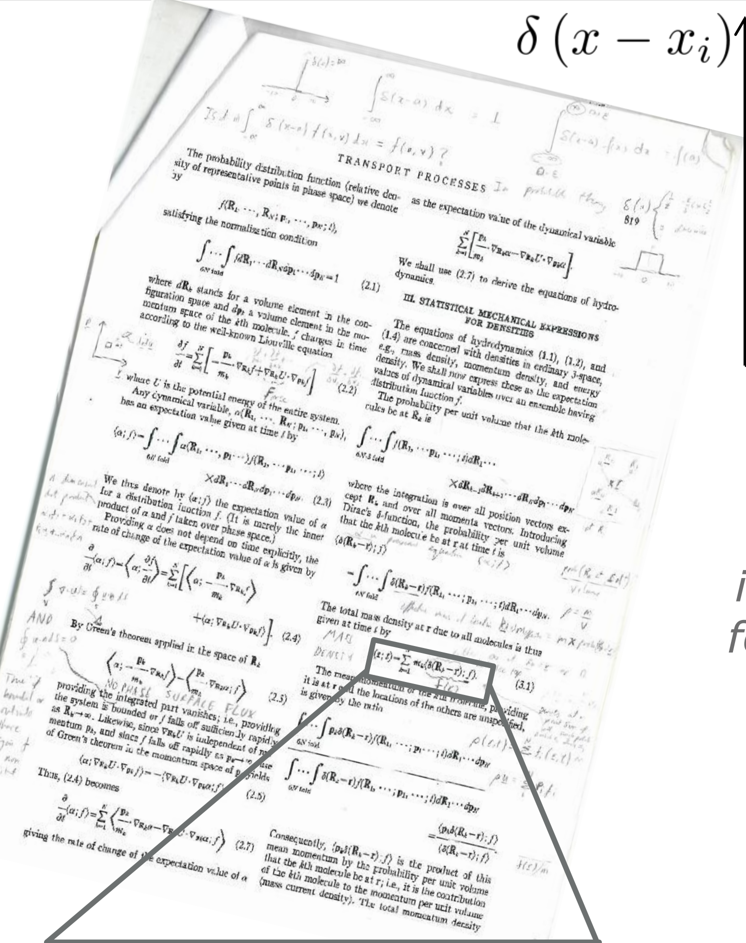
* This work was supported by the U. S. ONR under Contract N6onr-244 with the California Institute of Technology.

[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
merical evaluation awaits a more precise computation of the theoretical radial distribution function.



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

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

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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

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

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

$$\frac{\partial f}{\partial t}=\sum_{k=1}^{N}\left[-\frac{\mathbf{p}_k}{m_k}\cdot\nabla_{\mathbf{R}_k}f+\underset{\text{Force}}{\nabla_{\mathbf{R}_k}U}\cdot\nabla_{\mathbf{p}_k}f\right] \tag{2.2}$$

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

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

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

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

AND

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

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

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

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

Thus, (2.4) becomes

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

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

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

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

MASS DENSITY

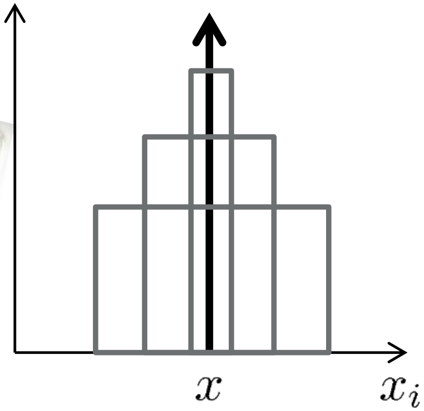
$$\rho(\mathbf{r};t)=\sum_{k=1}^{N}m_k\langle\delta(\mathbf{R}_k-\mathbf{r});f\rangle. \tag{3.1}$$

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

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

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

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

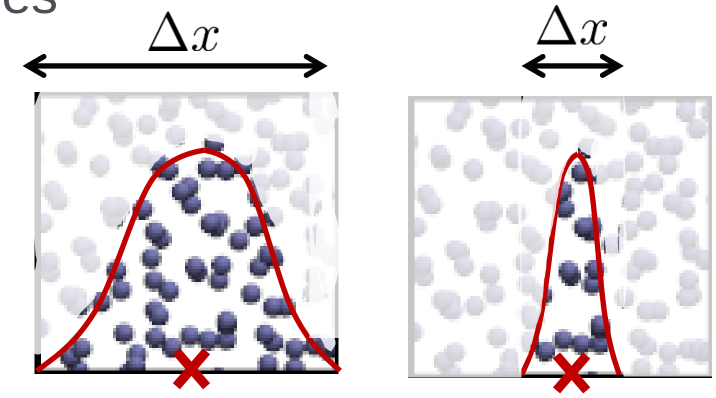


The Dirac delta infinitely high, infinitely thin peak formally equivalent to the continuum differential formulation

The Dirac Delta Function

- Irving and Kirkwood (1950) express field based quantities using the Dirac delta functional and ensemble averages

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



$$\delta(x) = \lim_{\Delta x \to 0} \frac{1}{\Delta x} e^{x^2/\Delta x^2}$$

- Formally equivalent to the continuum
  - » Demands ensemble or time average
  - » Dirac delta formally correct but no molecule ever at point r in limit
  - » Any approximation to the Dirac delta is no longer formally correct
- In conclusion - a discrete system can only be approximately represented using a continuous field

The Control Volume (Weak) Form

- The “weak formulation” expressed the equations in integrated form (and we can take without ensemble average)

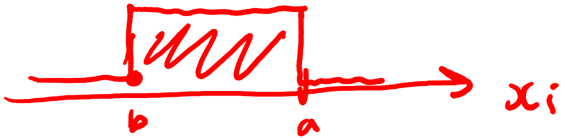
$$\int_V \rho(\boldsymbol{r},t)dV = \sum_{i=1}^{N} m_i \int_V \delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)dV$$

$$\xrightarrow{\quad} \int \int \quad dx \, dy$$

- Integrating the Dirac delta function exactly provides a combination of Heaviside functions

$$\delta(\underline{r}-\underline{r}_i) = \delta(x-x_i)\,\delta(y-y_i)$$

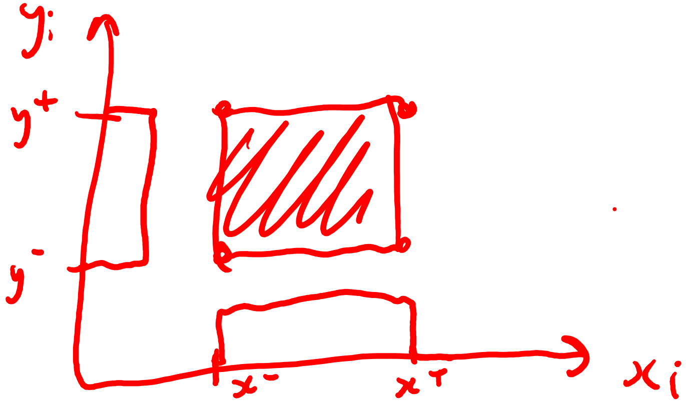
$$\Lambda_x = \int_a^b \delta(x-x_i) = \left[H(x-x_i)\right]_a^b = H(b-x_i) - H(a-x_i)$$



The Control Volume (Weak) Form

$$\alpha_i = \int_{y^-}^{y^+}\int_{x^-}^{x^+} \delta(x-x_i)\,\delta(y-y_i)\,dx\,dy$$

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



$$\alpha_i \begin{cases} 1 & x^- < x_i < x^+ \text{ and } \\ & y^- < y_i < y^+ \\ 0 & \text{othe} \end{cases}$$

The Control Volume Functional

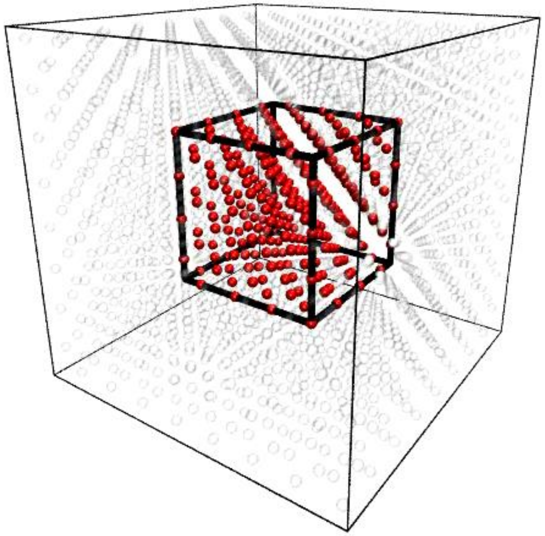
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

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



- In words

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

The Control Volume (Weak) Form

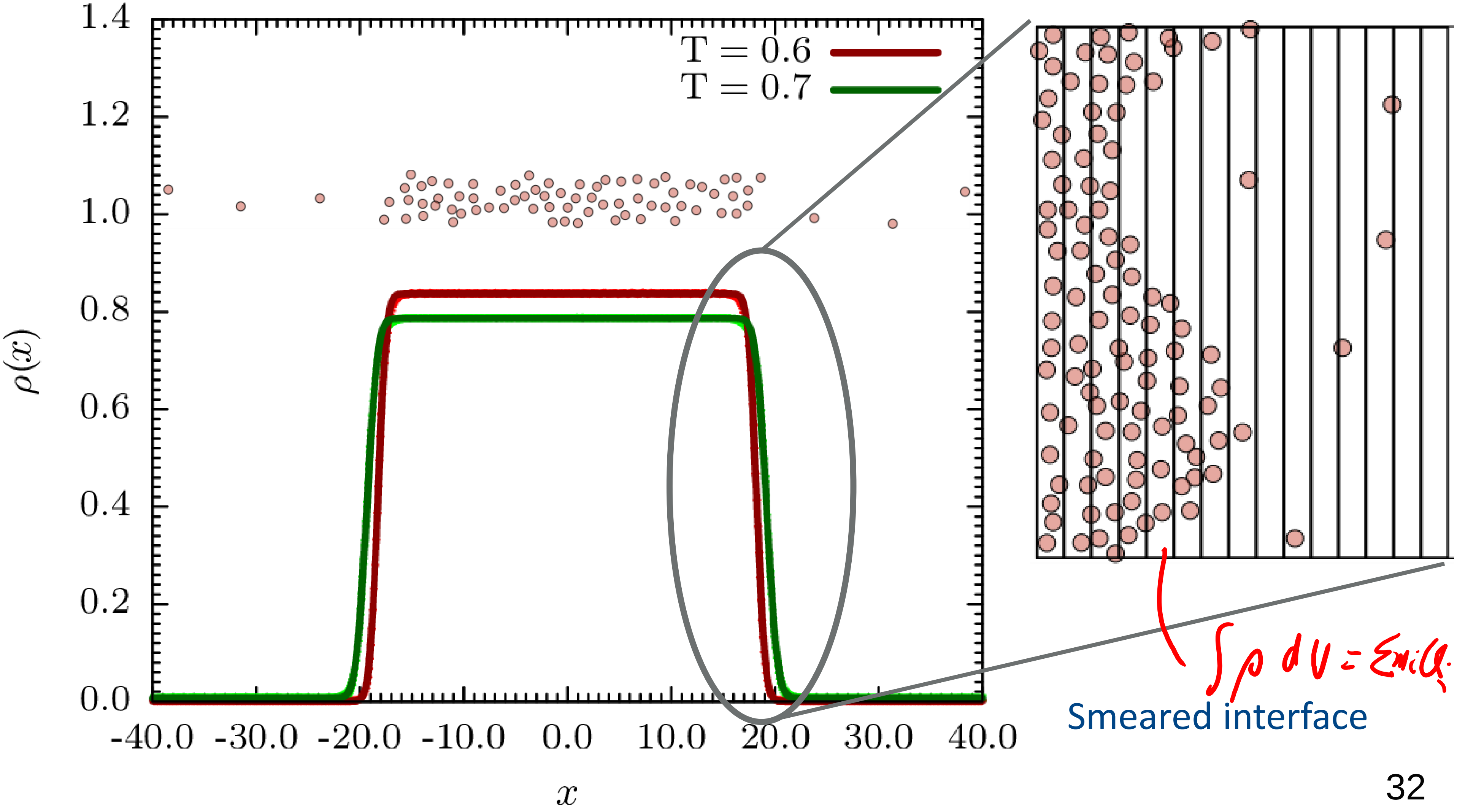
- The “weak formulation” expressed the equations in integrated form (and we can take without ensemble average)

$$\int_V \rho(\boldsymbol{r}, t) dV = \sum_{i=1}^{N} m_i \vartheta_i$$

- Integrating the Dirac delta function exactly provides a combination of Heaviside functions

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

Density



$\int \rho \, dV = \sum m_i a$

Smeared interface

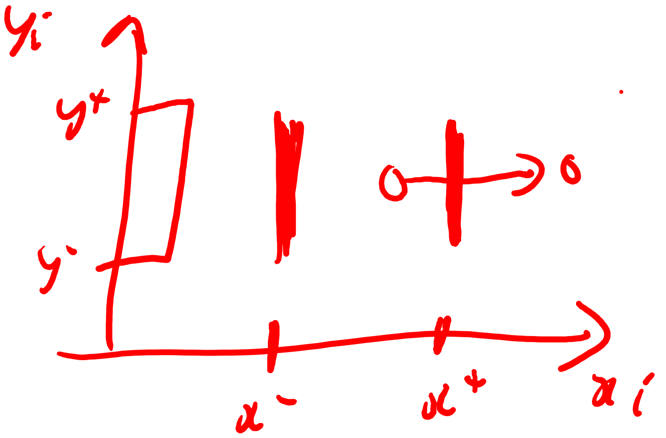
Derivative of the Control Volume

$$\Omega_i = \Delta_x \Delta_y$$

$$\Delta_x = H(x^+ - x_i) - H(x^- - x_i)$$

$$\frac{\partial \Omega_i}{\partial x} = \Delta_y \frac{\partial \Delta_x}{\partial x}$$

$$\frac{\partial \Delta_x}{\partial x} = \delta(\underline{x^+ - x_i}) - \delta(x^- - x_i)$$



Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

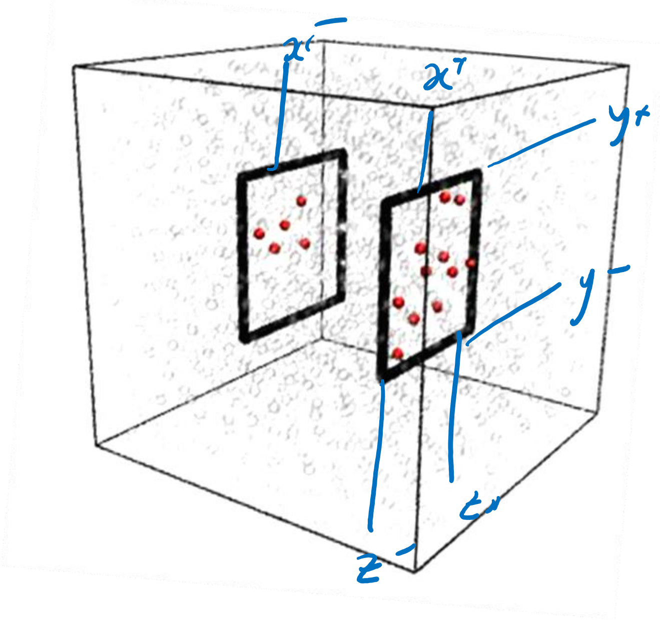
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right]$$
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$
$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

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



Coupled Simulation

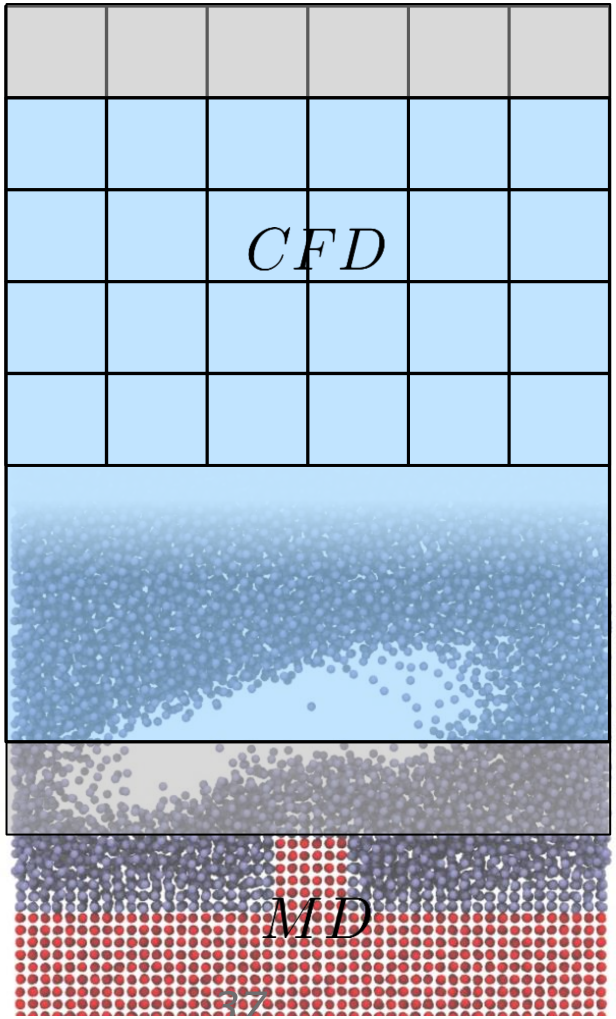
- Control (Finite) Volume form

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

Share the same **time** and **length** scales

- Discrete molecules

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



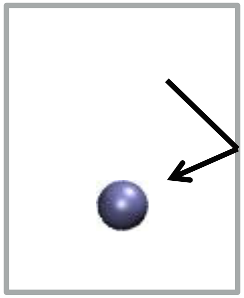
Pressure (stress) in an MD Simulation

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

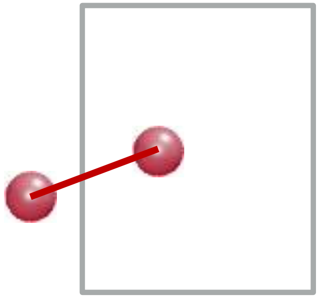
$$\oint_S \Pi_{xx} \cdot dS_x = \underbrace{\sum_{i=1}^{N} \left\langle m_i v_{xi} v_{xi} dS_{xi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left\langle f_{xij} dS_{xij} \right\rangle}_{\text{Configurational}}$$

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

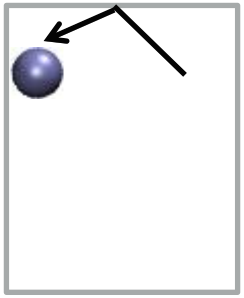
Pressure (stress) in an MD Simulation

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

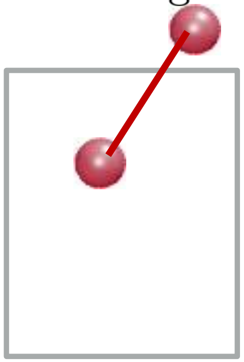
$$\oint_S \Pi_{yy} \cdot dS_y = \underbrace{\sum_{i=1}^{N} \left\langle m_i v_{yi} v_{yi} dS_{yi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left\langle f_{yij} dS_{yij} \right\rangle}_{\text{Configurational}}$$

Kinetic theory part

Momentum due to average of molecules crossing a plane and returning



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



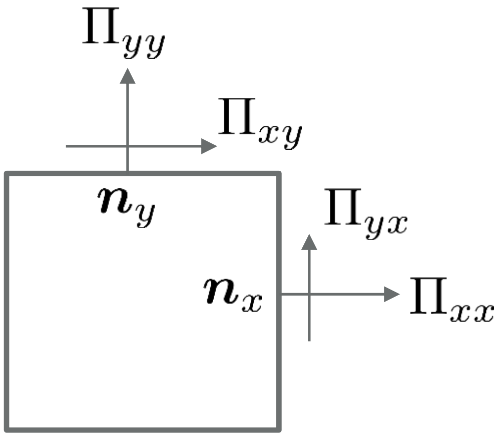
Configurational part

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

Pressure (stress) in an MD Simulation

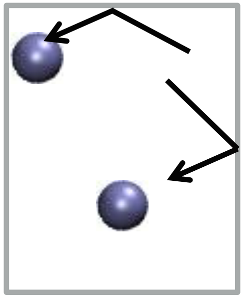
- Components of stress tensor from components and surface
  - Cauchy's original definition
  - Symmetry is not guaranteed
  - The two dimensions tensor is then,

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

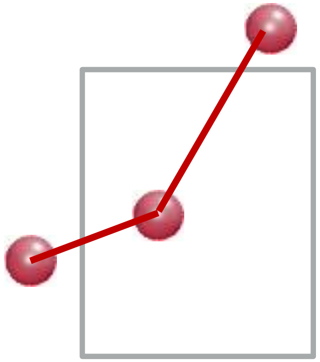


Kinetic theory part

Momentum due to average of molecules crossing a plane and returning



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



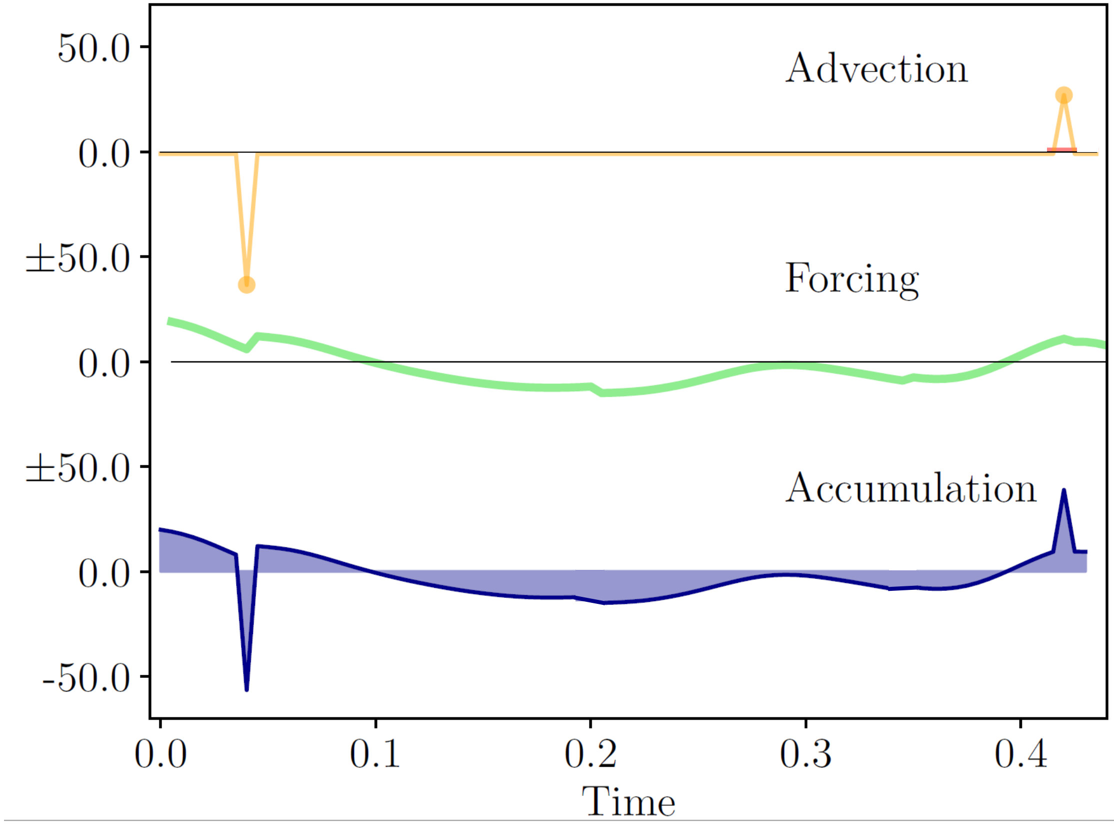
Configurational part

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

Control Volume Balance

- The balance can be shown to be exact for any control volume

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

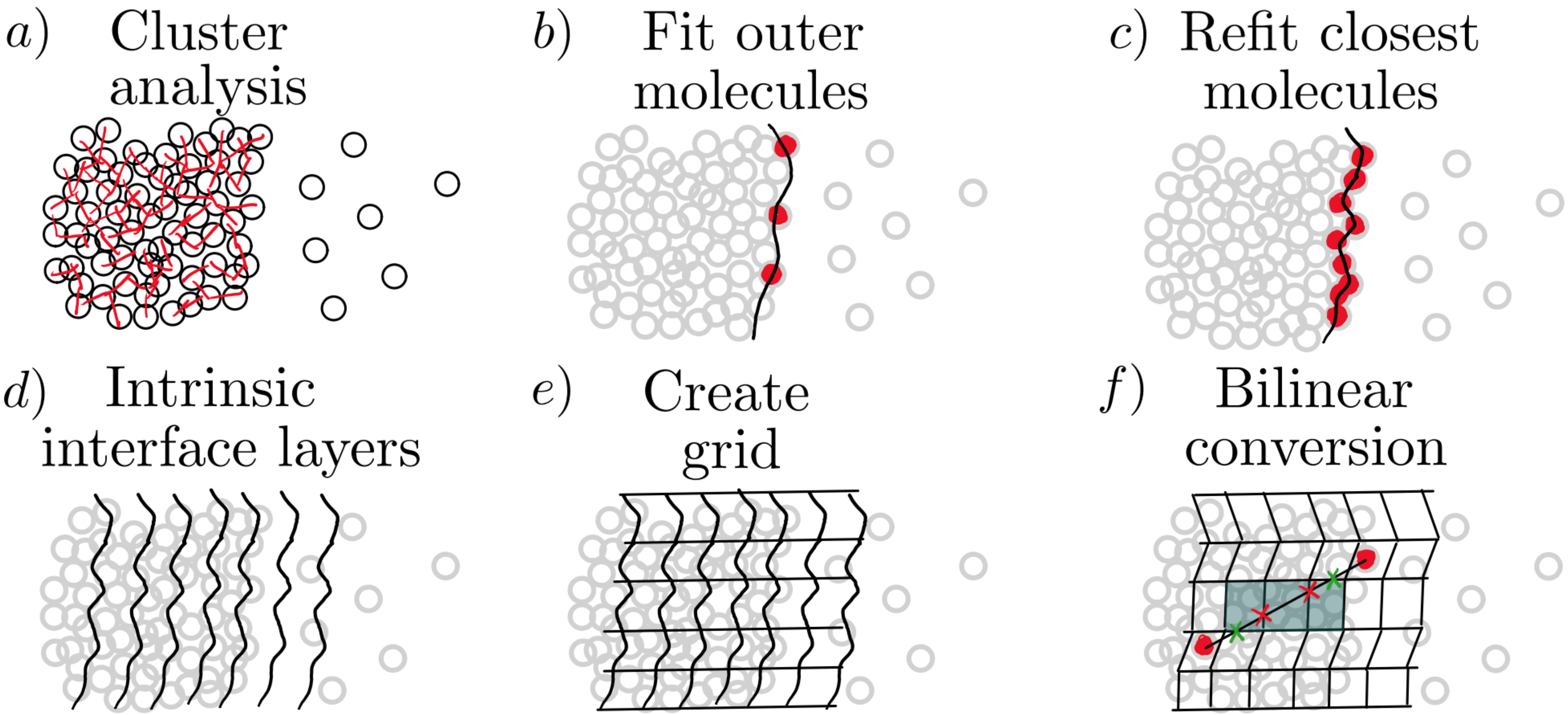


6 Surface of cube

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

The Moving Interface

Overview of the Process



A more general Control Volume Functional

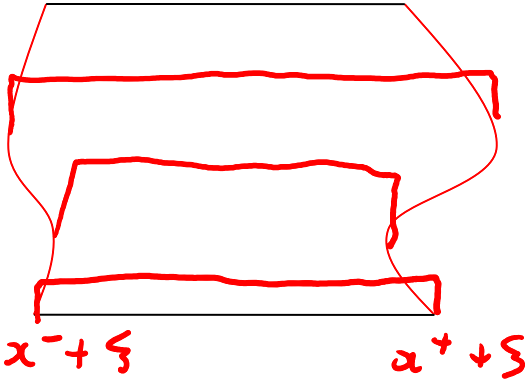
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

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

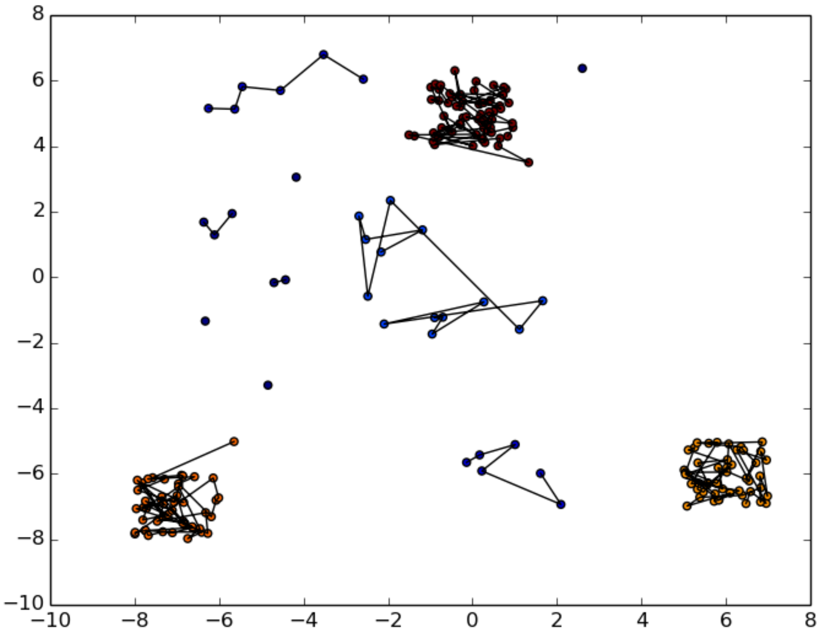


- In words

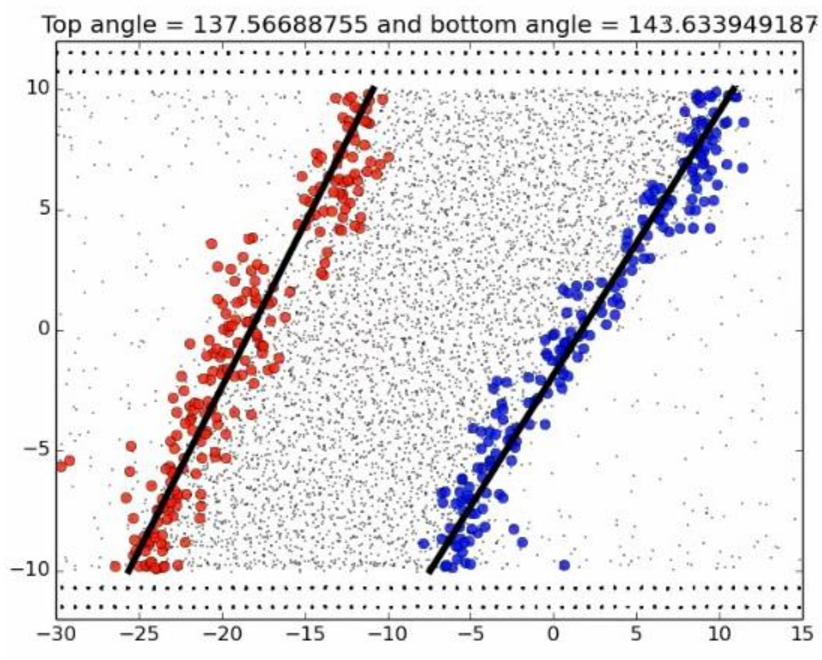
$$\vartheta \equiv \begin{cases} 1 & \text{if molecule is inside the moving volume} \\ 0 & \text{if molecule is outside the moving volume} \end{cases}$$

Identifying the Liquid

Cluster Analysis to identify the liquid droplets

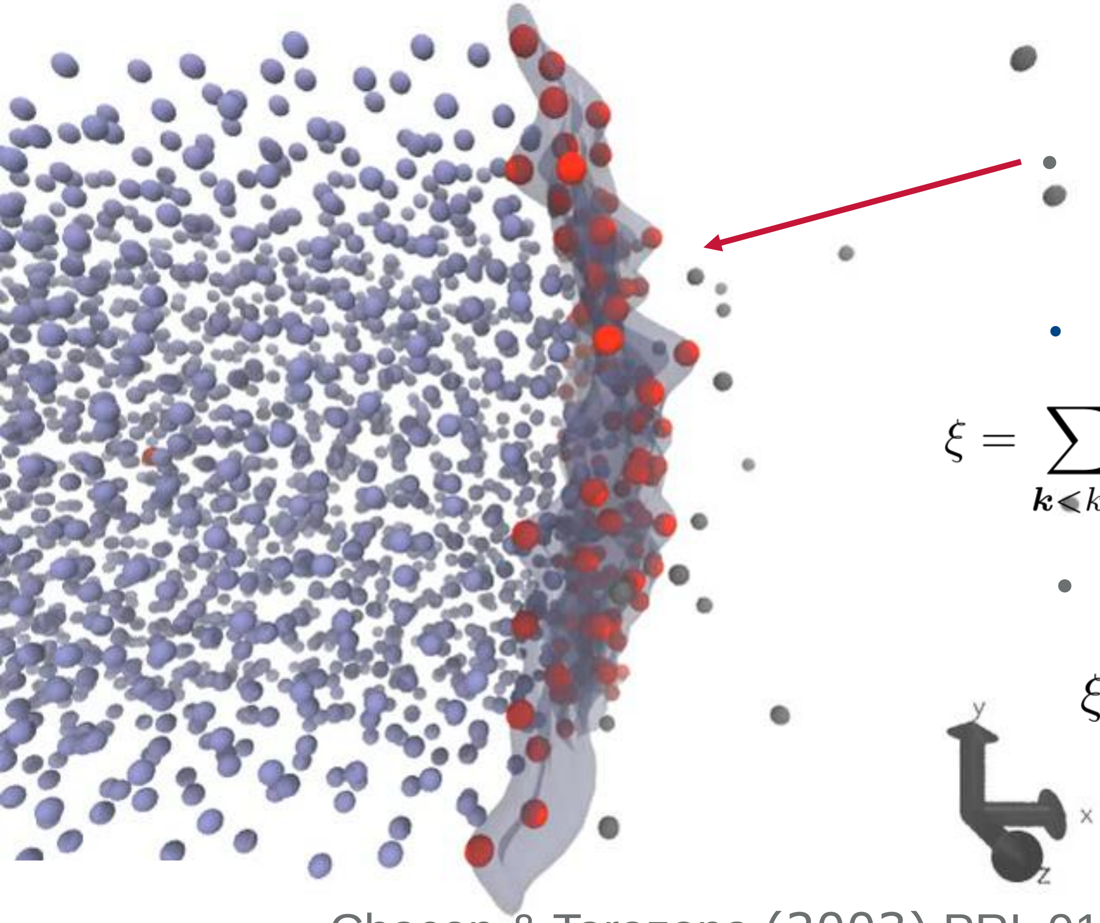


Least Square fitting to outer molecules, linear example here



Liquid-Vapour interface

- The Intrinsic Interface method



- Surface fitted by least squares
- Tensor product surface

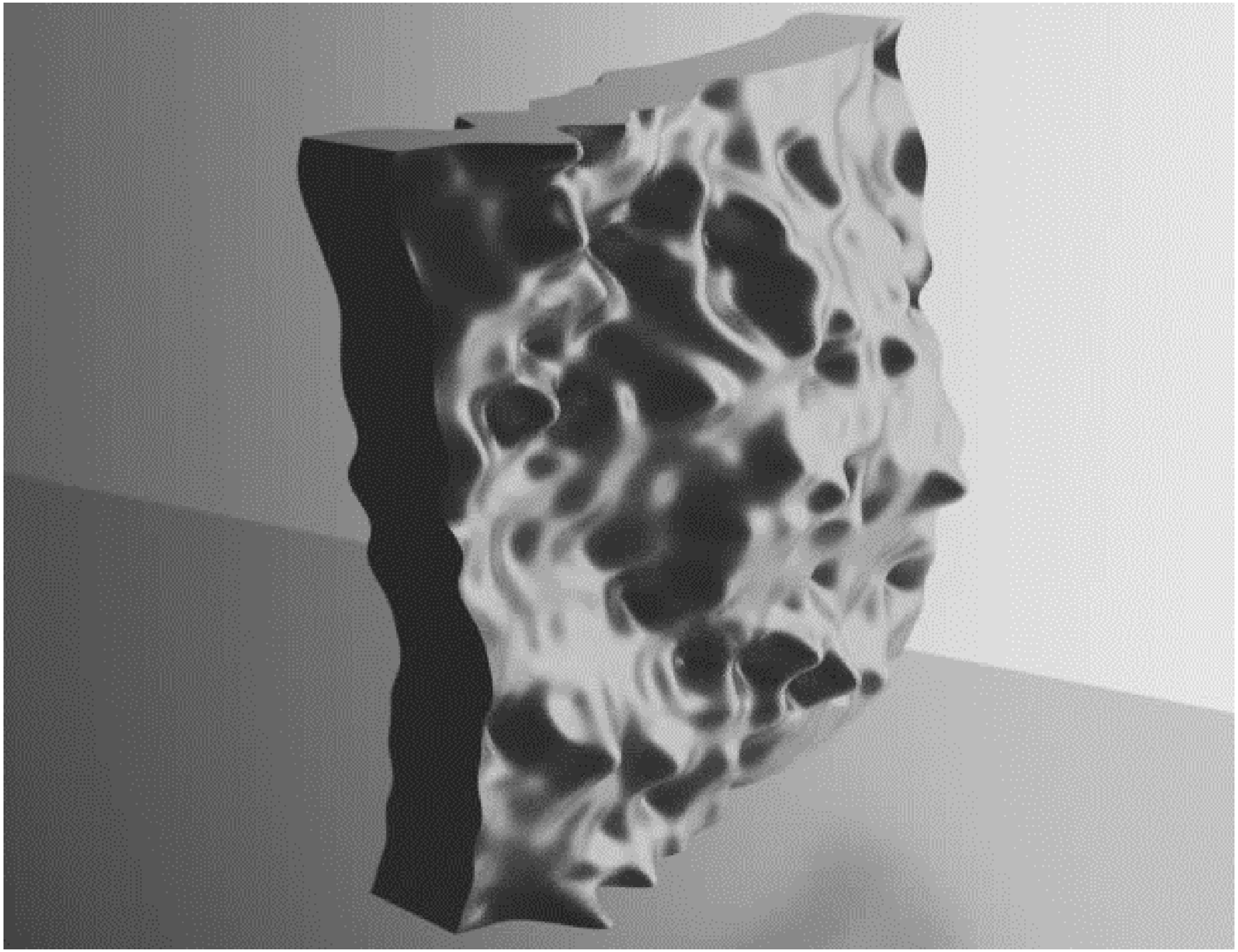
$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}} \approx \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t)\xi_u(y)\xi_v(z),$$

- Function of sines and cosines

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

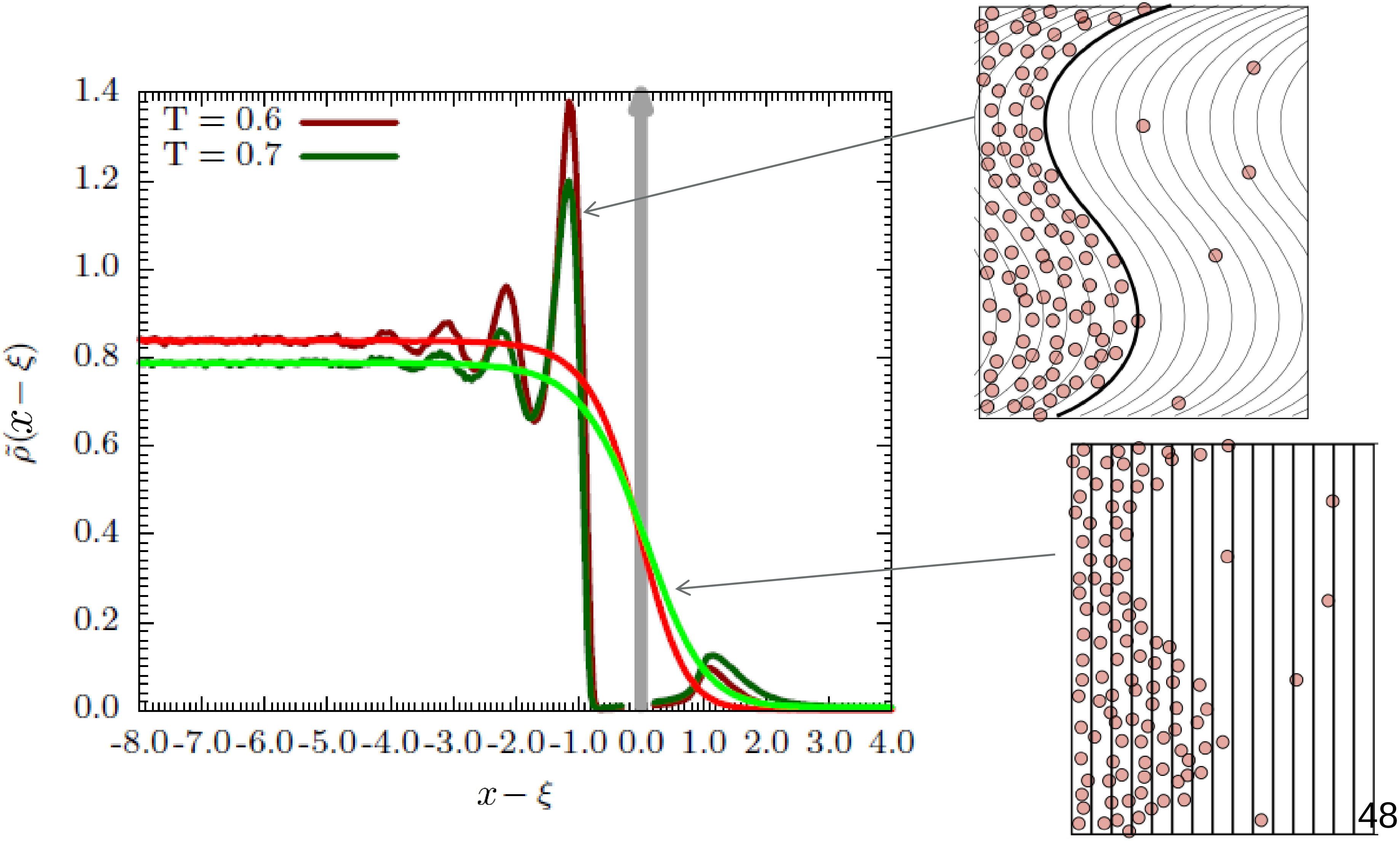
Chacon & Tarazona (2003) PRL 91, 166103

The Intrinsic Interface



Work with Carlos Braga and Serafim Kalliadasis

Liquid-Vapour interface



Derivative of the Moving Control Volume

$$\xi = \xi(y, z, t)$$

$$\frac{\partial \alpha_i}{\partial y} = \Delta_y \frac{\partial \Delta_x}{\partial y} + \Delta_x \frac{\partial \Delta_y}{\partial y}$$

$$\downarrow$$

$$\frac{\partial \xi}{\partial y}\, \delta(x^+ + \xi - x_i)$$

$$\frac{\partial \alpha_i}{\partial t} \qquad \frac{\partial \xi}{\partial t}\, \delta(x^+ + \xi - x_i)$$

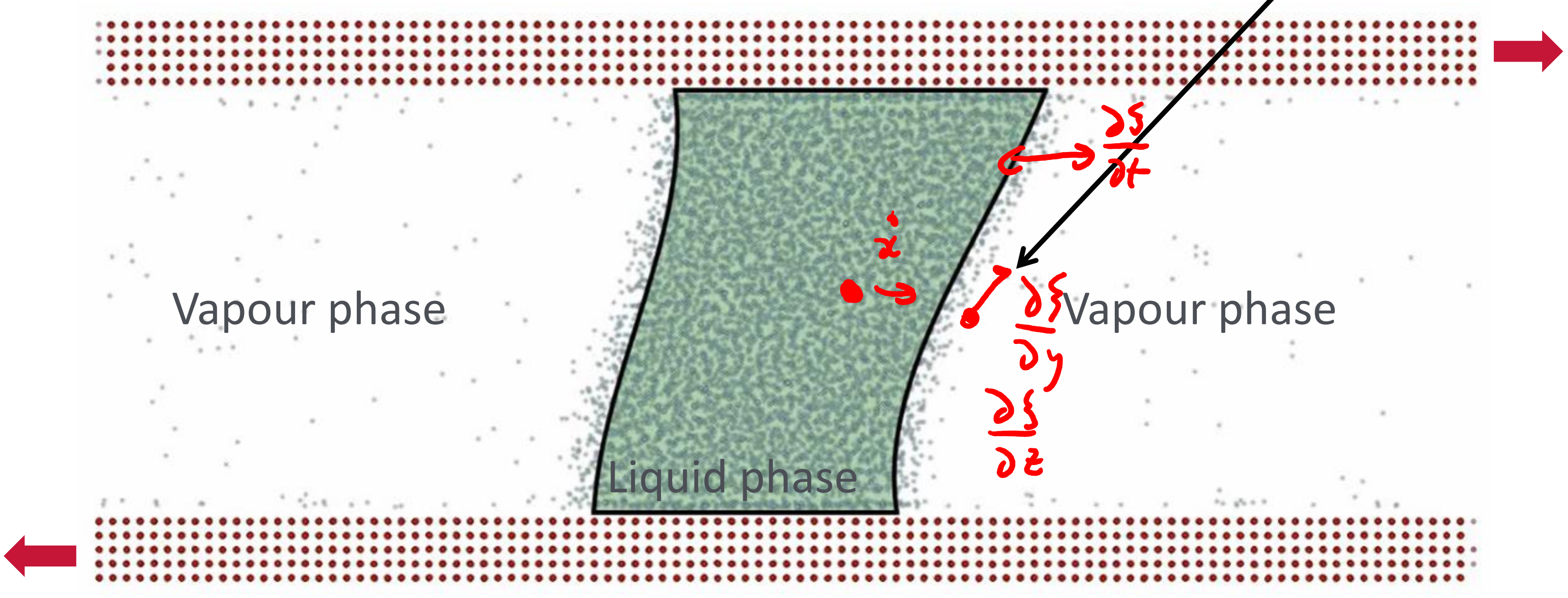
Moving liquid-vapour interfaces

- Derivative now includes terms for moving surface, curvature, etc

$$dS^{+}_{xi} = \left[\dot{x} - \underline{\dot{x}_i} + \dot{y}_i \frac{\partial \xi^{+}}{\partial y_i} + \dot{z}_i \frac{\partial \xi^{+}}{\partial z_i} + \frac{\partial \xi^{+}}{\partial t}\right] \delta\left(x^{+} + \xi^{+} - x_i\right)$$

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

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



Sliding Solid walls (tethered)

Pressure (stress) in an MD Simulation

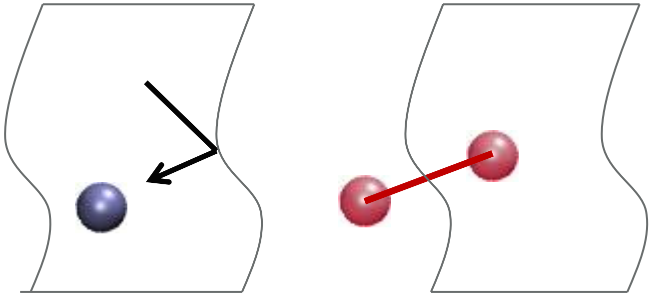
- Pressure definition in a dense molecular system
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

$$\oint_S \Pi_{xx} \cdot dS_x = \sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \left[\dot{x}_i + \overbrace{\dot{y}_i \frac{\partial \xi_i^+}{\partial y_i} + \dot{z}_i \frac{\partial \xi_i^+}{\partial z_i}}^{Kinetic\ Curvature} + \overbrace{\frac{\partial \xi_i^+}{\partial t}}^{Surface\ Evolution} \right] dS_{xi}^+$$

$$+ \frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \int_0^1 \left[x_{ij} + \underbrace{y_{ij} \frac{\partial \xi_\lambda^+}{\partial y_\lambda} + z_{ij} \frac{\partial \xi_\lambda^+}{\partial z_\lambda}}_{Configurational\ Curvature} \right] dS_{x\lambda}^+ d\lambda,$$

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

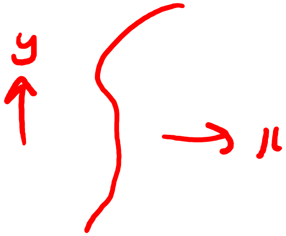
Inter-molecular bonds act like the stress in a stretched spring

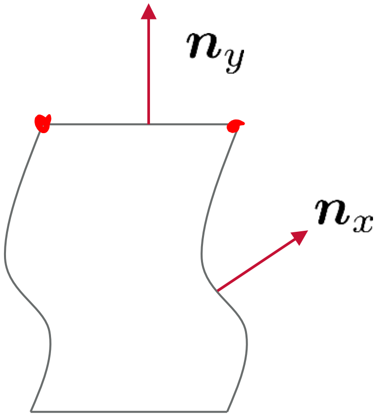
Pressure Components

- Tangential pressure given by sum of all crossings over flat surface tangential to interface

$$\Pi_T = \frac{1}{\Delta S_y} \sum_{i=1}^{N} m_i \dot{y}_i \dot{y}_i dS^{+}_{yi} + \frac{1}{2\Delta S_y} \sum_{i,j}^{N} f_{yij} \int_0^1 y_{ij} dS^{+}_{y\lambda} d\lambda,$$

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





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

- Normal pressure given by sum of all crossings over the interface

$$\Pi_N = \frac{1}{\Delta S_x} \sum_{i=1}^{N} m_i \dot{x}_i \left[\dot{x}_i + \overbrace{\dot{y}_i \frac{\partial \xi_i{}^{+}}{\partial y_i} + \dot{z}_i \frac{\partial \xi_i{}^{+}}{\partial z_i}}^{Kinetic\ Curvature} + \overbrace{\frac{\partial \xi_i{}^{+}}{\partial t}}^{Surface\ Evolution} \right] dS^{+}_{xi}$$

$$+ \frac{1}{2\Delta S_x} \sum_{i,j}^{N} f_{xij} \int_0^1 \left[x_{ij} + \underbrace{y_{ij} \frac{\partial \xi_\lambda^{+}}{\partial y_\lambda} + z_{ij} \frac{\partial \xi_\lambda^{+}}{\partial z_\lambda}}_{Configurational\ Curvature} \right] dS^{+}_{x\lambda} d\lambda,$$

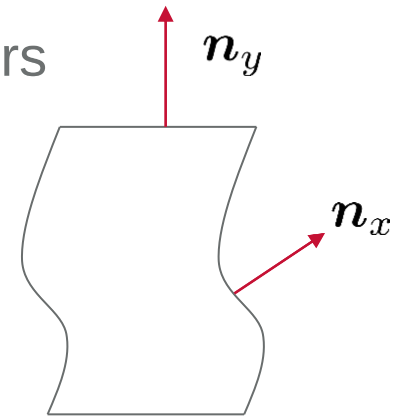
Pressure Components (normal form)

- A general form can be written in terms of the unit vectors

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

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

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



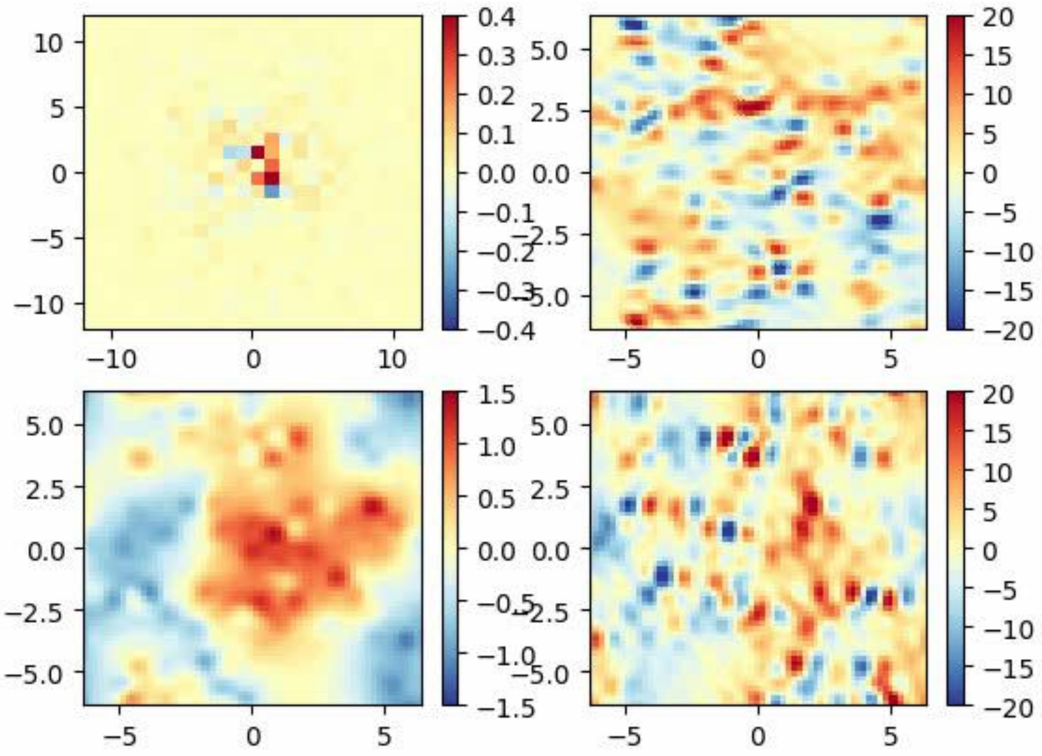
$$\boldsymbol{n}_\alpha = \frac{\boldsymbol{\nabla}_\alpha(\xi - z_\alpha)}{||\boldsymbol{\nabla}_\alpha(\xi - z_\alpha)||}$$

- 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

Getting Curvature

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

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



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

$\dfrac{\partial \xi}{\partial y}$

ξ

$\dfrac{\partial \xi}{\partial z}$

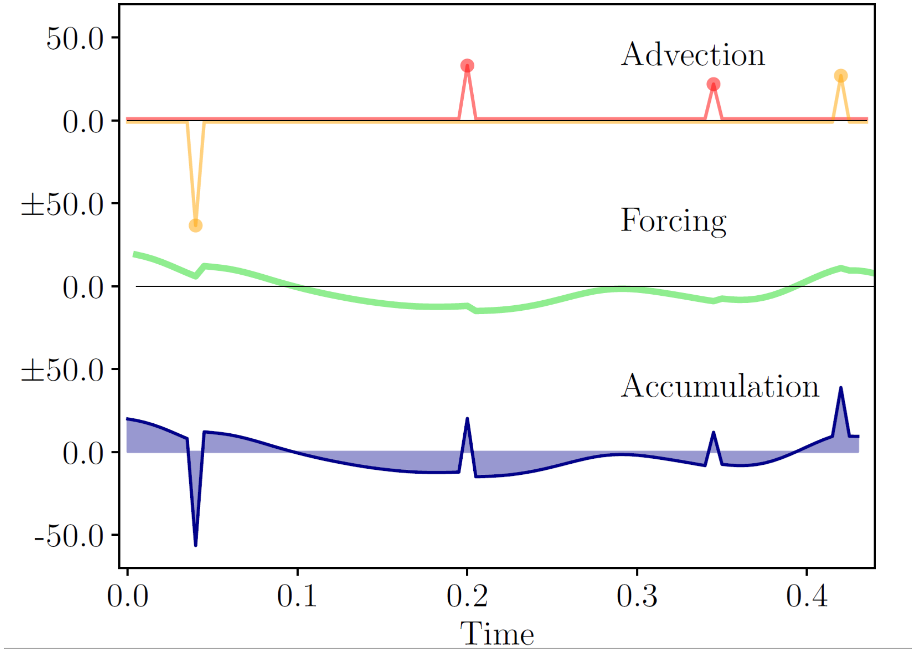
Checking CV Balance

$$\text{Advection} = \boxed{\frac{1}{\Delta S_x}\sum_{i=1}^{N} m_i \dot{x}_i \left[\dot{x}_i + \overbrace{\dot{y}_i \frac{\partial \xi_i^{+}}{\partial y_i} + \dot{z}_i \frac{\partial \xi_i^{+}}{\partial z_i}}^{Kinetic\ Curvature}\right.} \boxed{\overbrace{\frac{\partial \xi_i^{+}}{\partial t}}^{Surface\ Evolution}} \left.\vphantom{\frac{\partial}{\partial}}\right] dS_{xi}^{+}$$

$$\text{Forcing} = \boxed{\frac{1}{2\Delta S_x}\sum_{i,j}^{N} f_{xij} \int_0^1 \left[x_{ij} + \underbrace{y_{ij}\frac{\partial \xi_\lambda^{+}}{\partial y_\lambda} + z_{ij}\frac{\partial \xi_\lambda^{+}}{\partial z_\lambda}}_{Configurational\ Curvature}\right.} \left.\vphantom{\frac{\partial}{\partial}}\right] dS_{x\lambda}^{+} d\lambda,$$

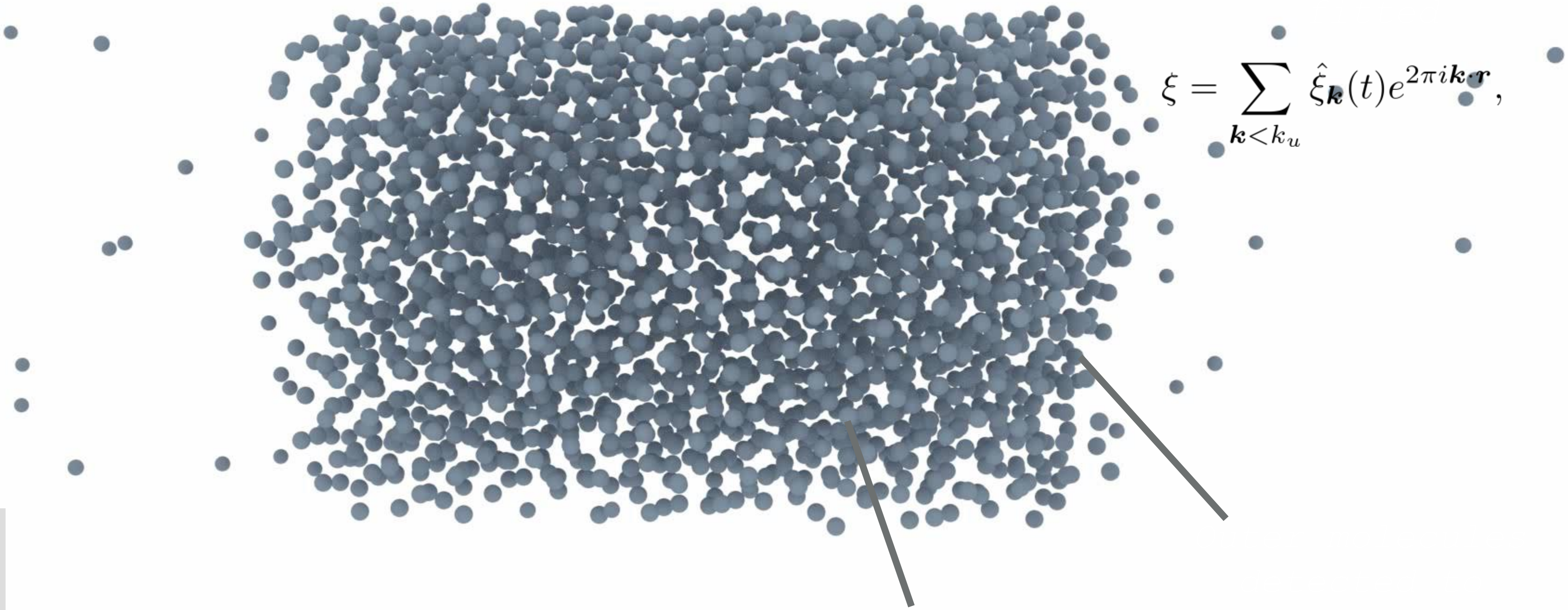
$$\text{Accumulation} = \boxed{\frac{d}{dt}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_i}$$

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



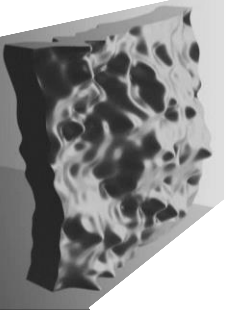
- We add components over all volume surfaces: normal and tangential

Liquid-Vapour interface

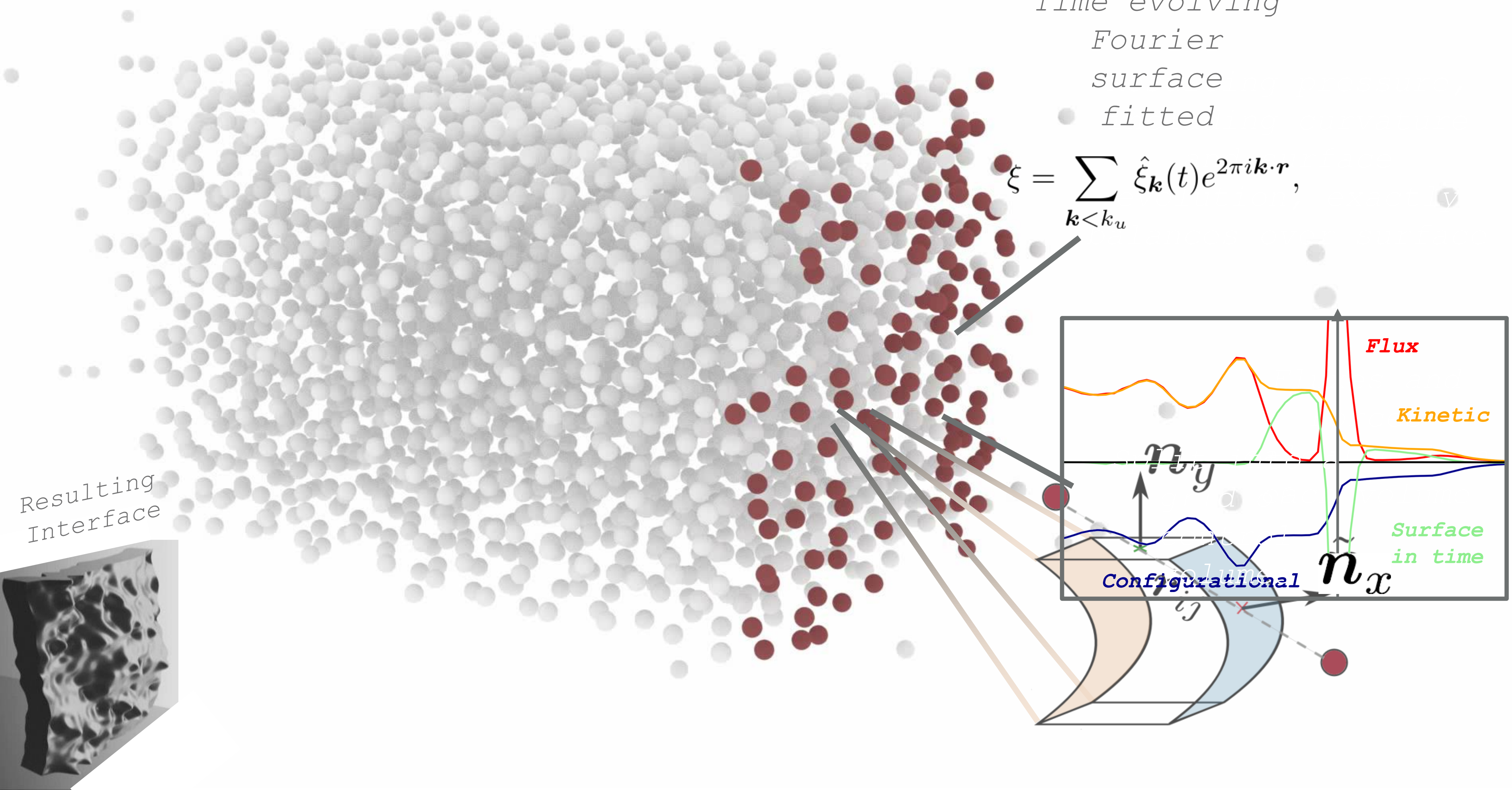


$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}},$$

Resulting Interface



Liquid-Vapour interface

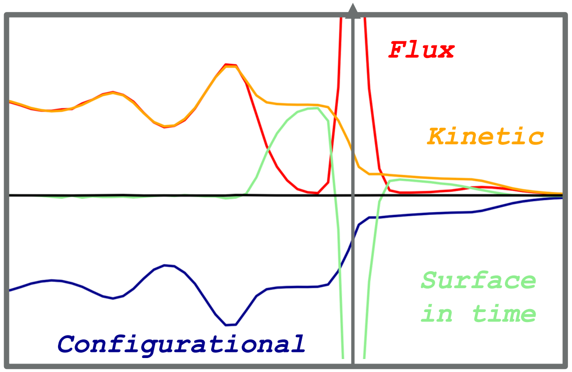


Time evolving Fourier surface fitted

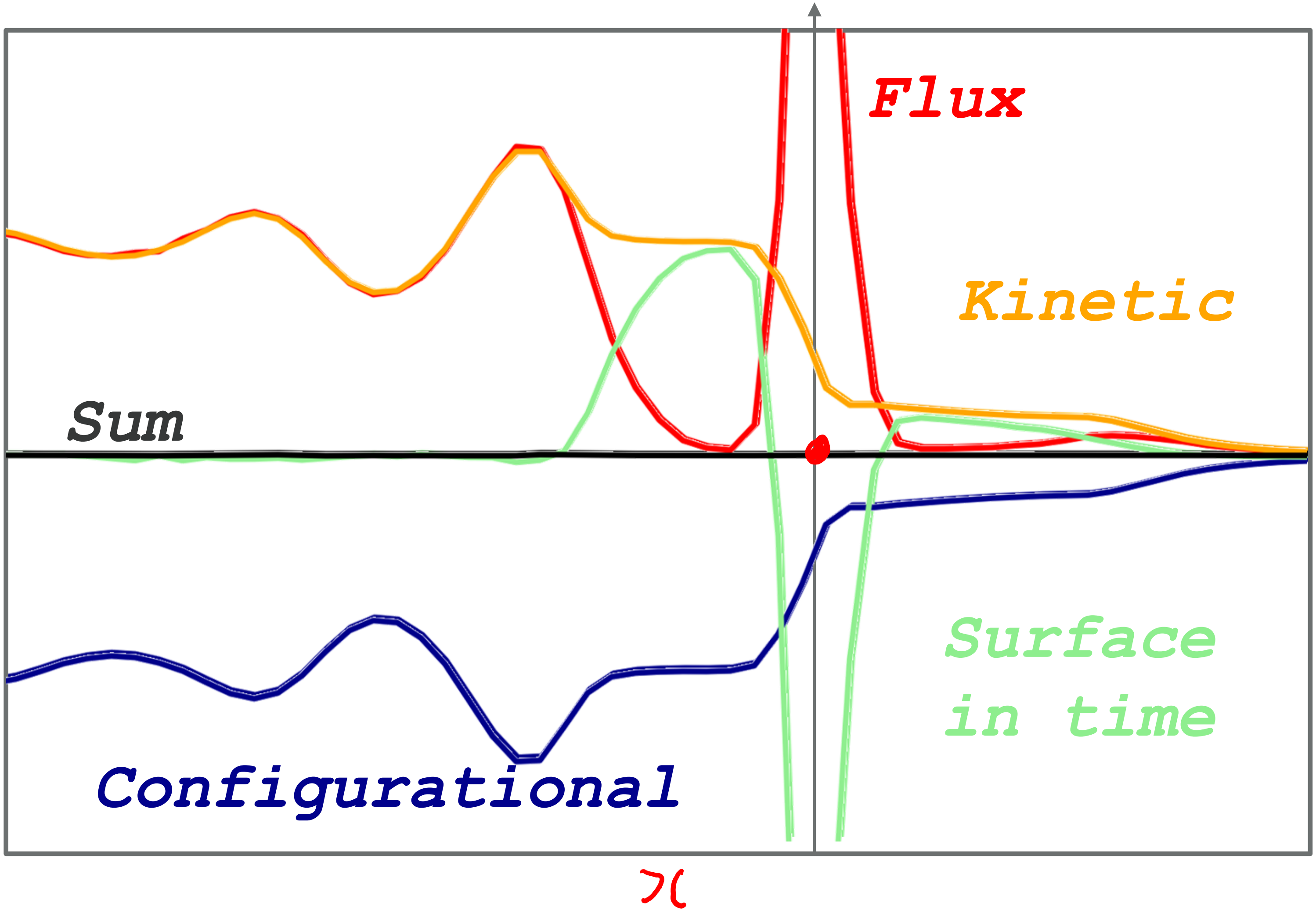
$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}},$$

Resulting Interface

Normal Pressure

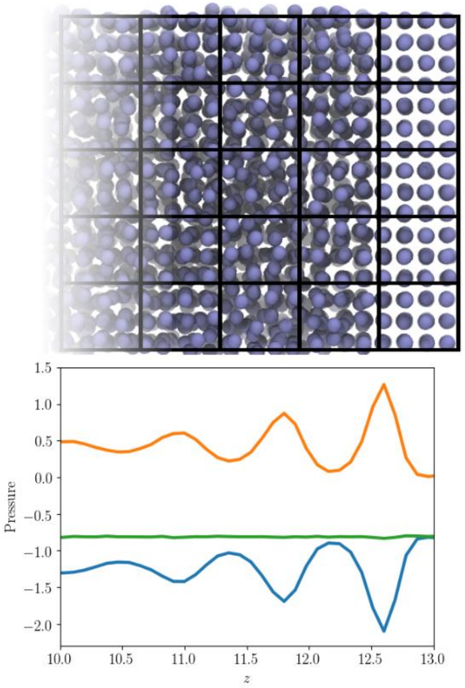


Normal Pressure

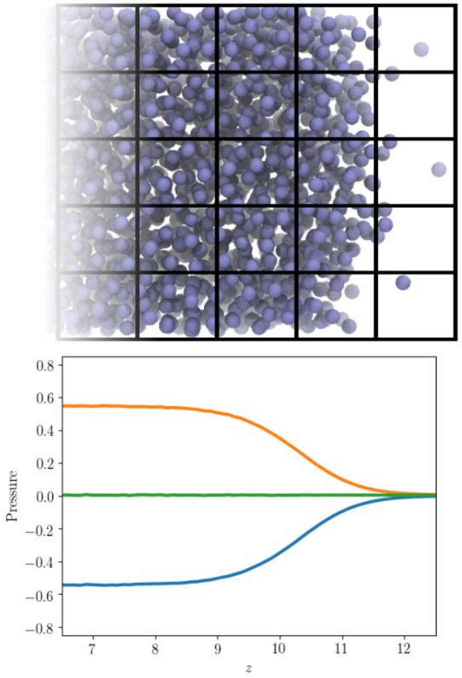


Normal Pressure is Flat (equilibrium)

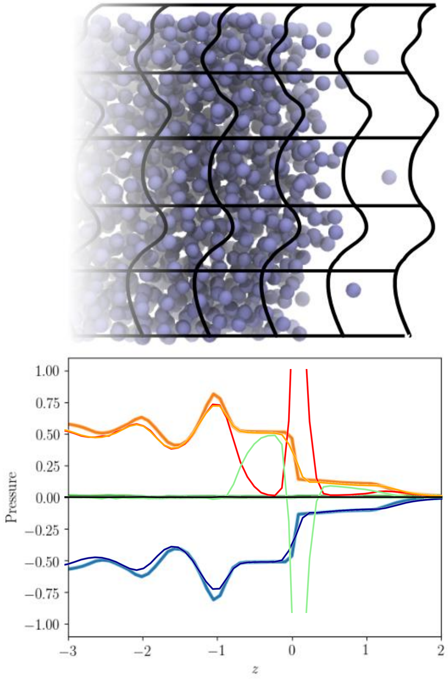
Solid-liquid
Eulerian
reference



Liquid-vapour
Eulerian
reference



Liquid-vapour
Lagrangian
reference



Missing from Other Pressure Definitions

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

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

- Only surface pressures satisfy this balance correctly

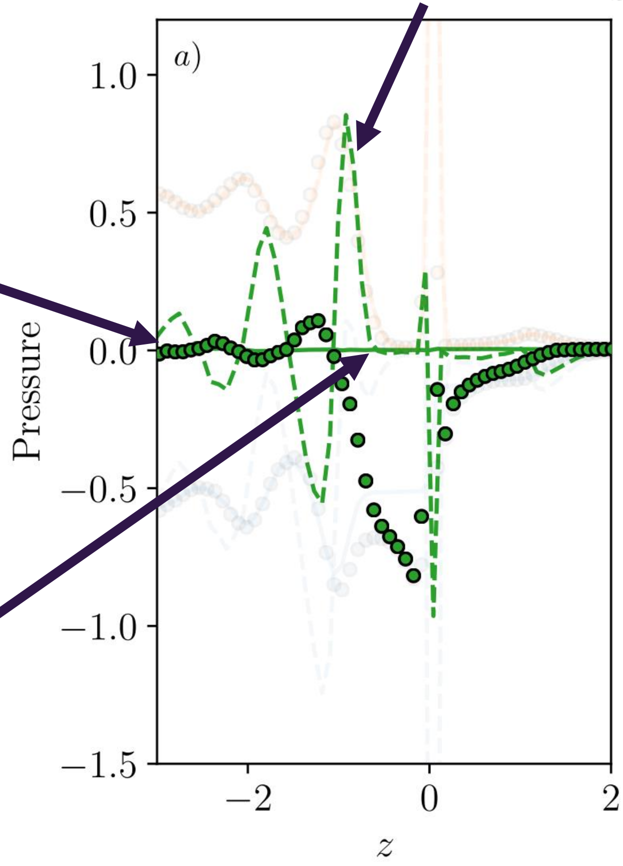
- Volume Average (VA) Pressure ●

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

- Surface Pressure (Generalised Method of Planes) ▬

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

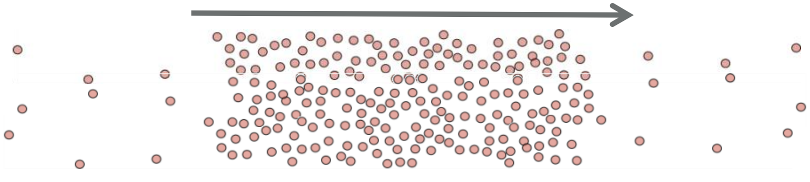
$$\overset{SF}{\mathrm{P}}{}^{c}_{z} = \frac{1}{2\Delta S_z}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\frac{\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z}{|\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z|}dS^{+}$$



Surface Tension

- Kirkwood Buff Method to get surface tension

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

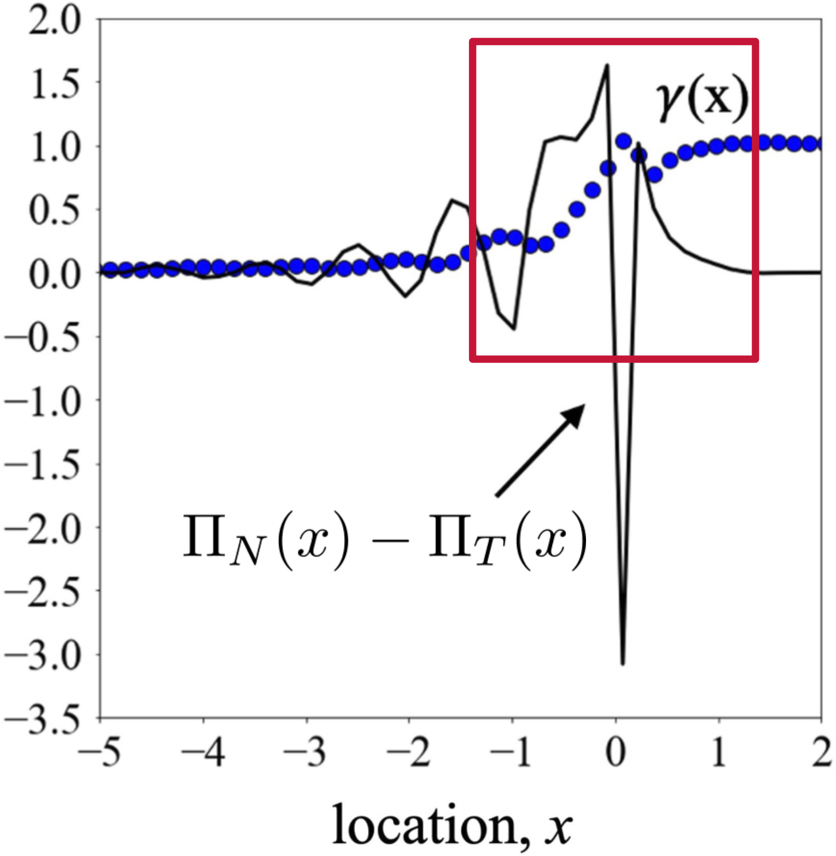


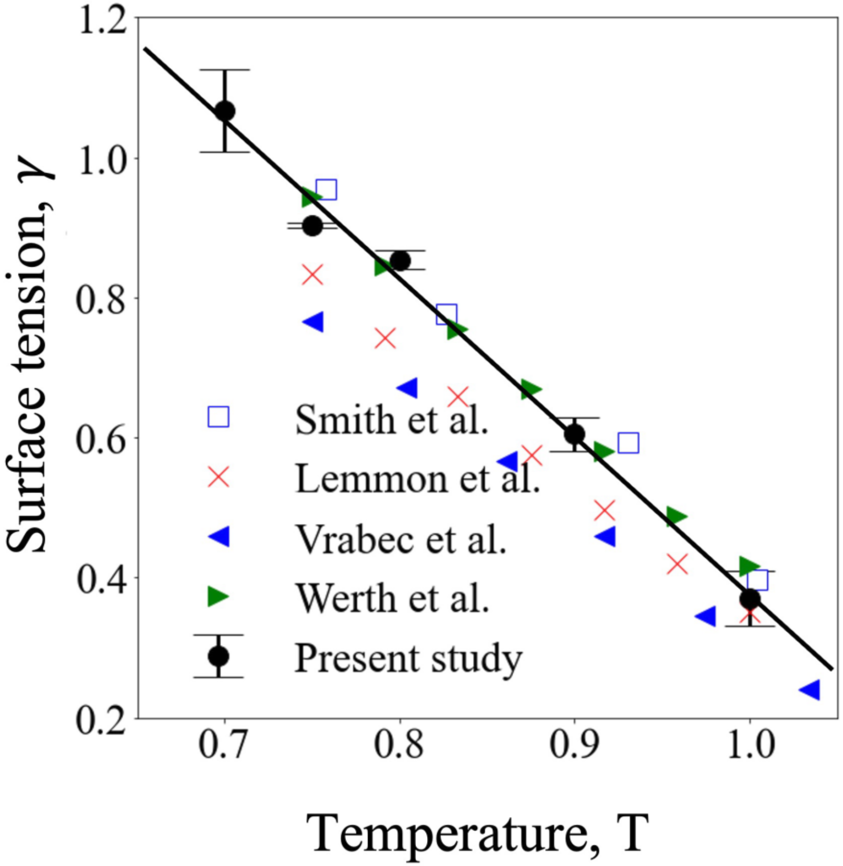
Integrate difference between normal and tangential pressure over liquid-vapour interface(s)

Tangential Pressure and Surface Tension

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

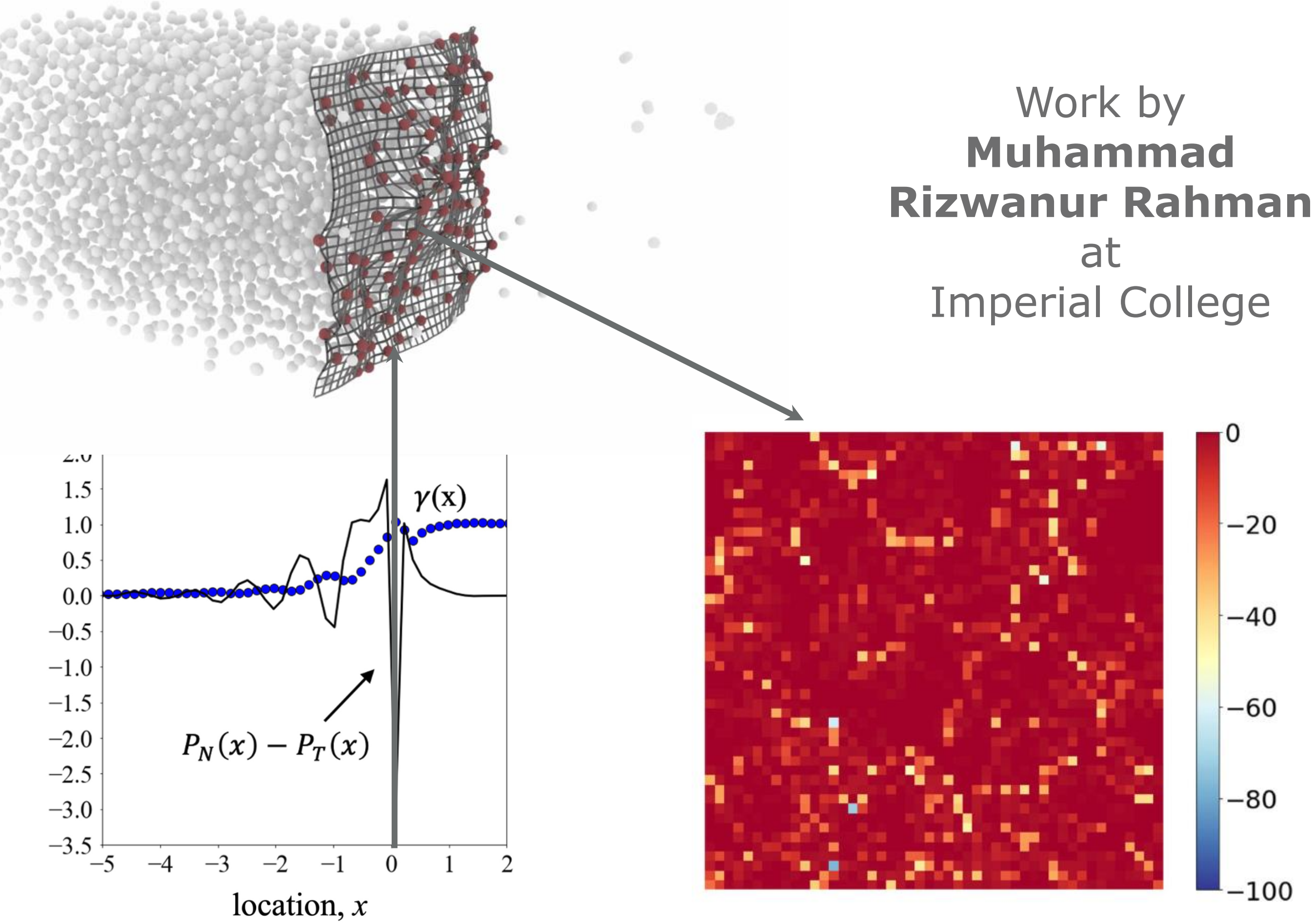
$$\gamma = \int_{-2^{\frac{1}{6}}}^{2^{\frac{1}{6}}} \left[\Pi_N - \Pi_T\right] dx$$



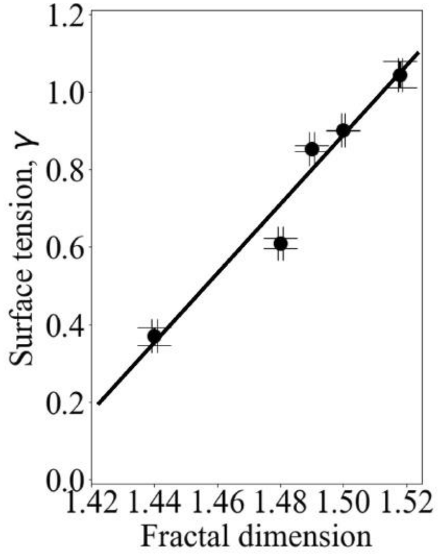


Stress Networks

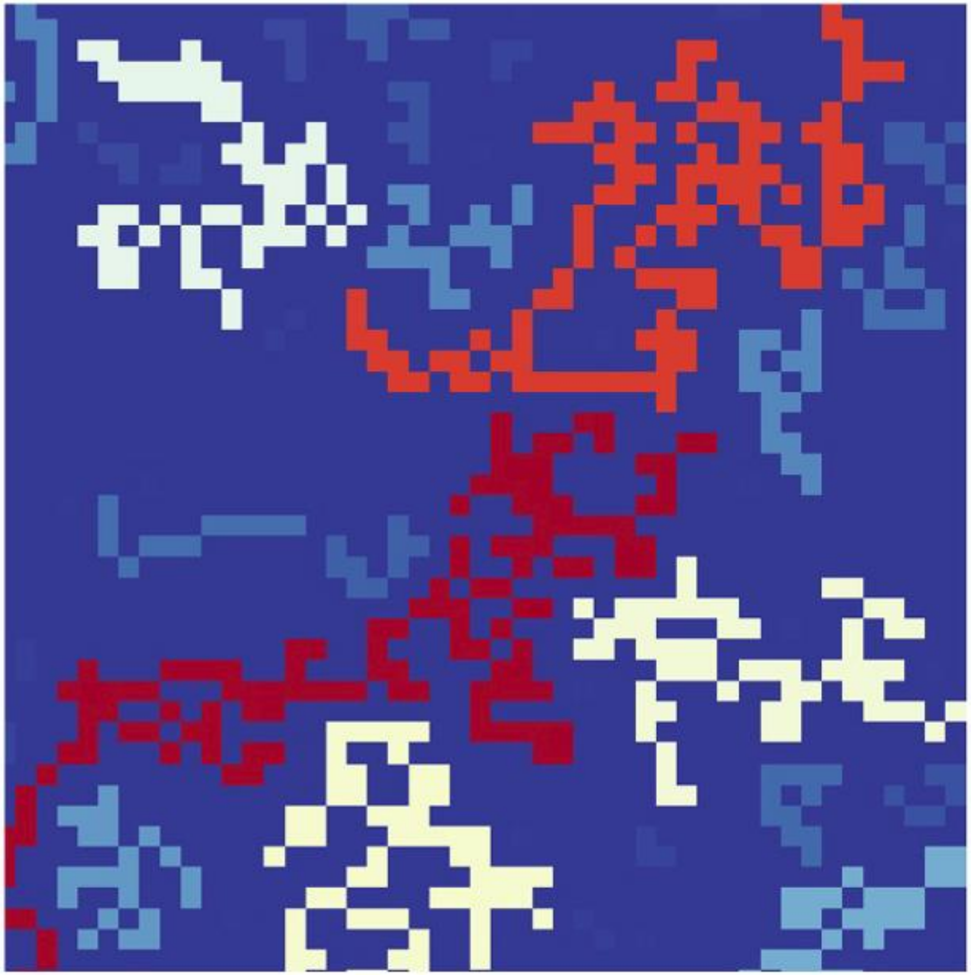
- Taking the instant Tangential Pressures on the intrinsic interface itself



Work by
Muhammad Rizwanur Rahman
at
Imperial College



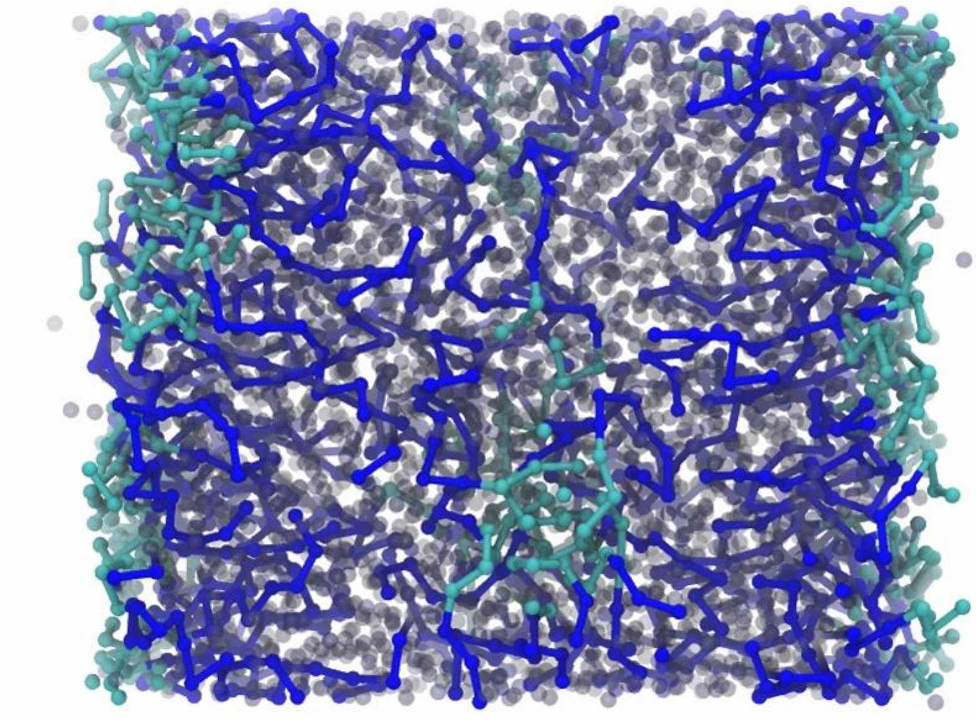
Percolating Cluster



Applications

Marangoni flows

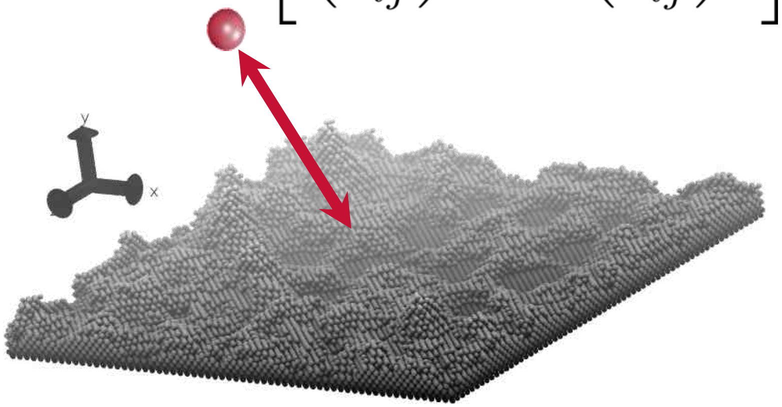
- Formation of concentrations gradients linked to surface

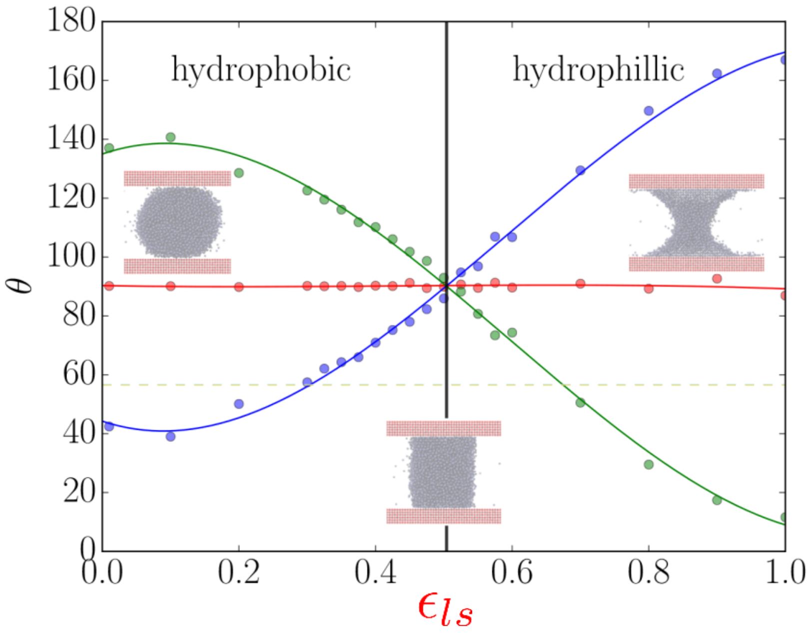


Surface Wettability

- 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

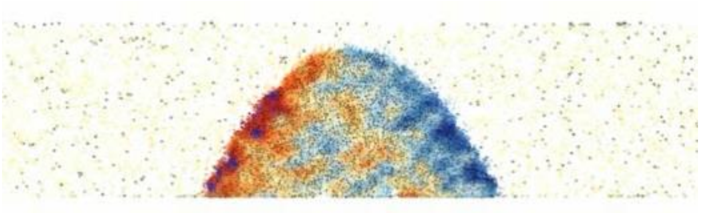
$$\phi(r_{ij}) = 4\epsilon_{ls}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$



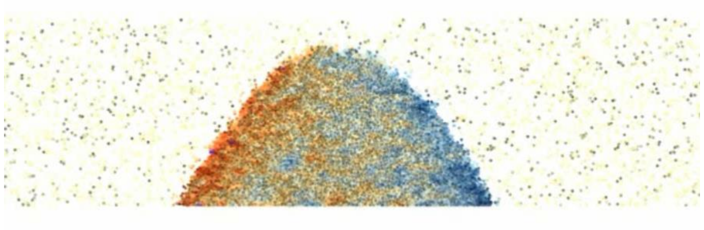


MD Simulation of Droplets

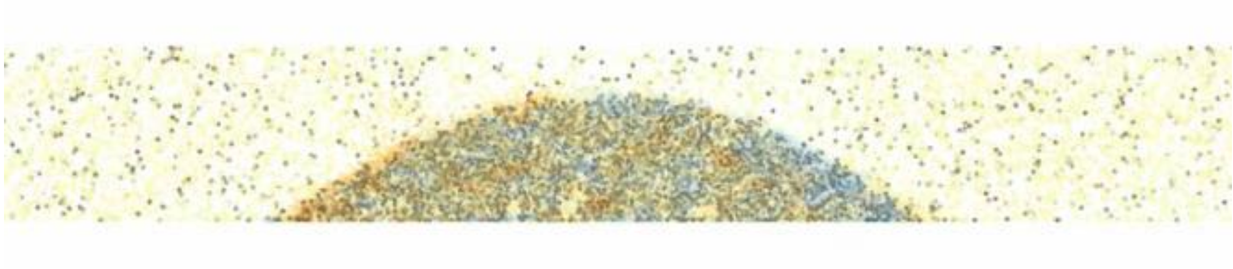
- Low Wettability



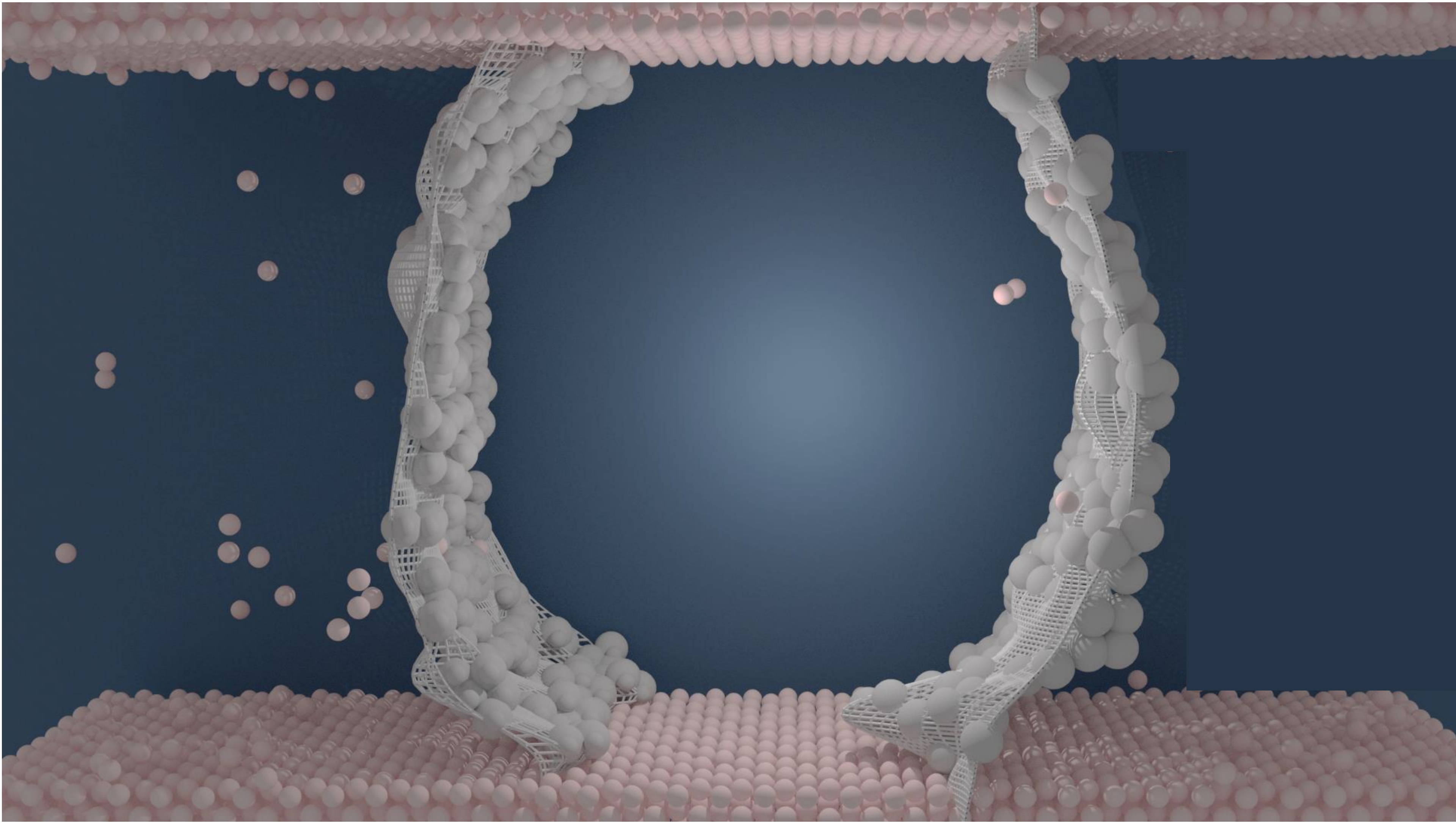
- Intermediate Wettability



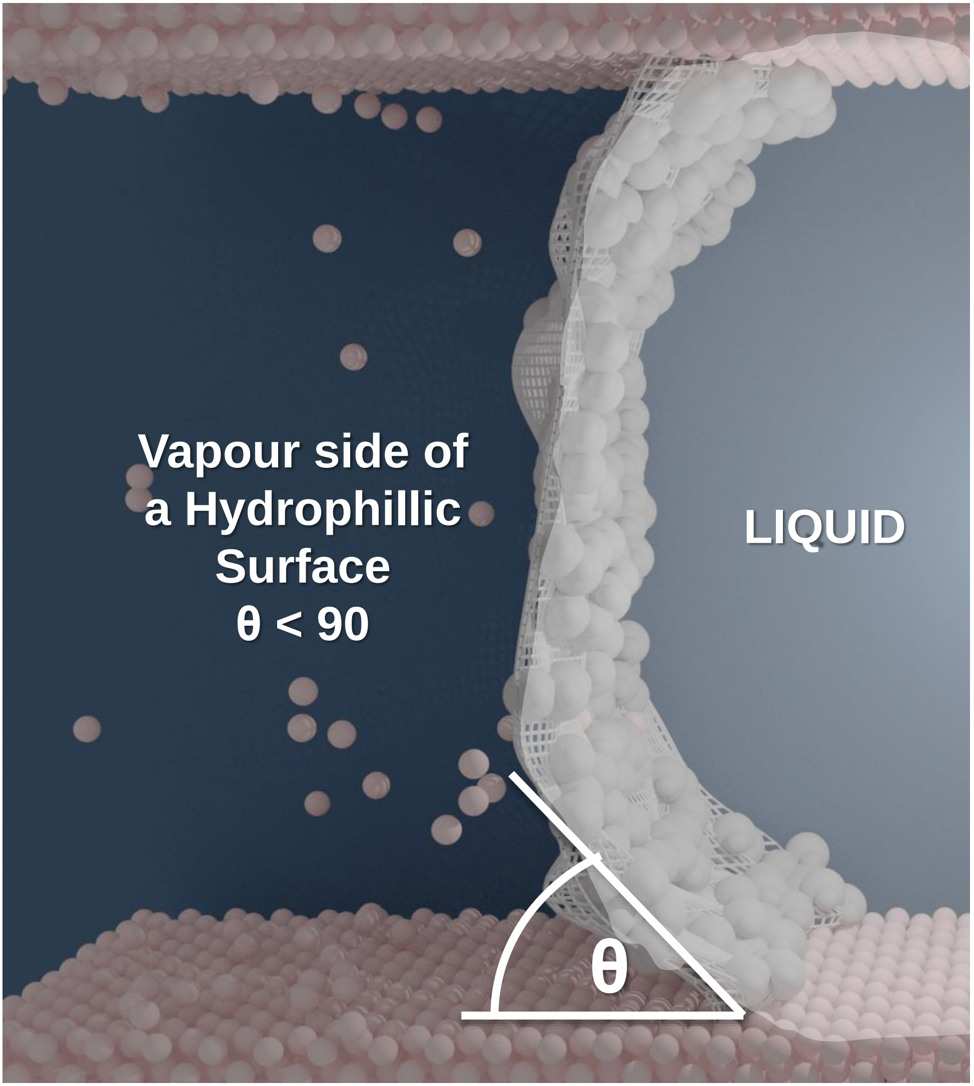
- High Wettability



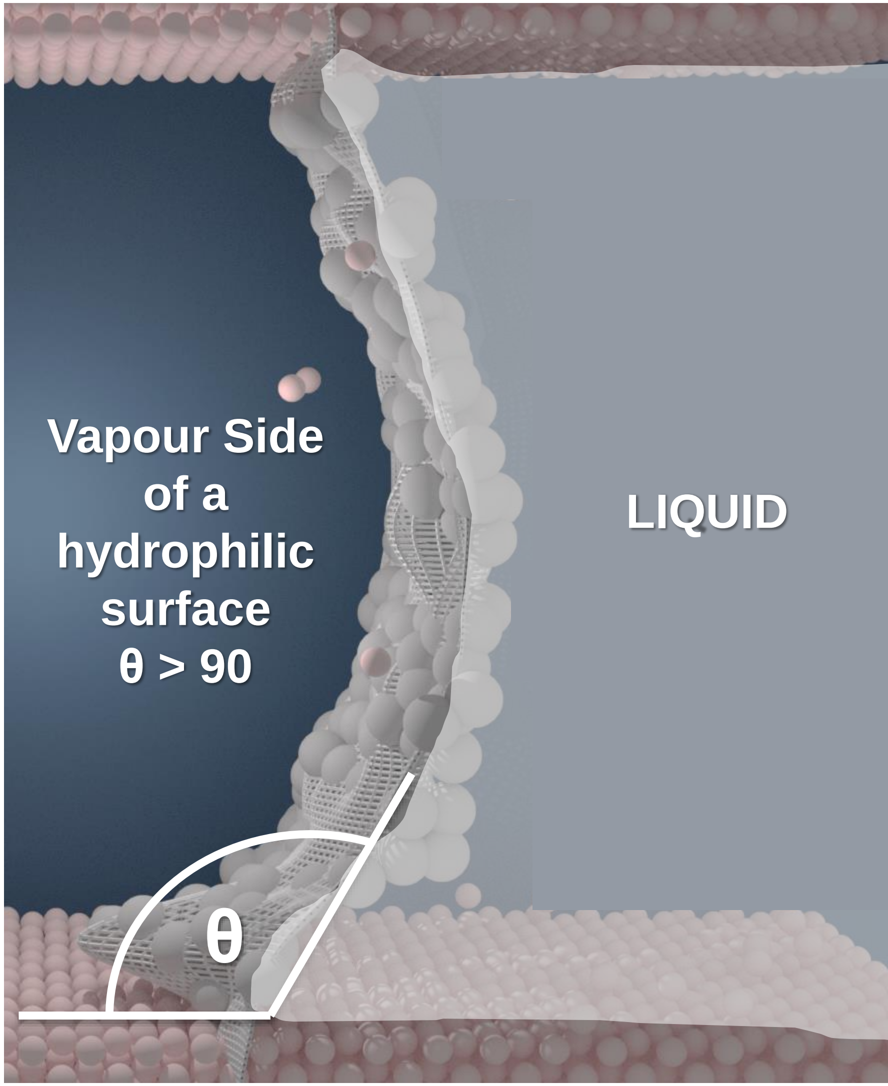
The Static Contact Line



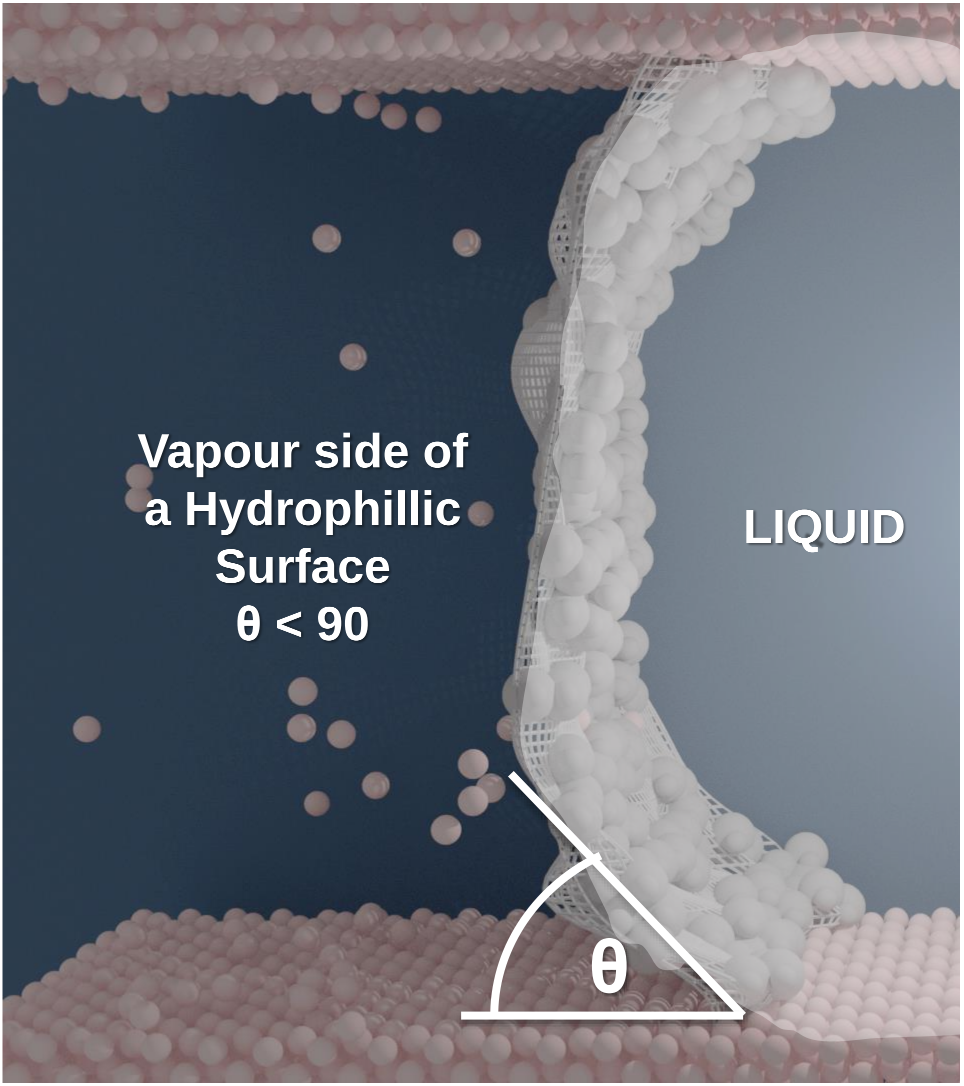
The Static Contact Line

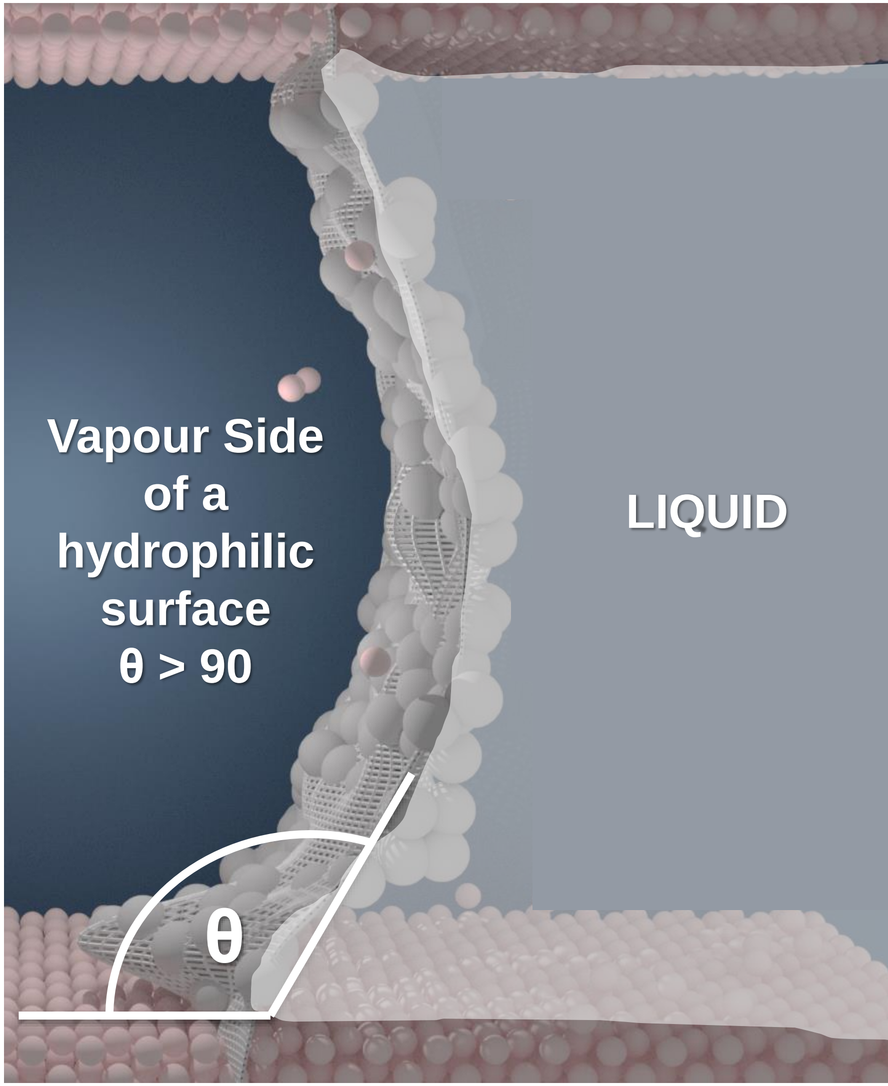


The Static Contact Line

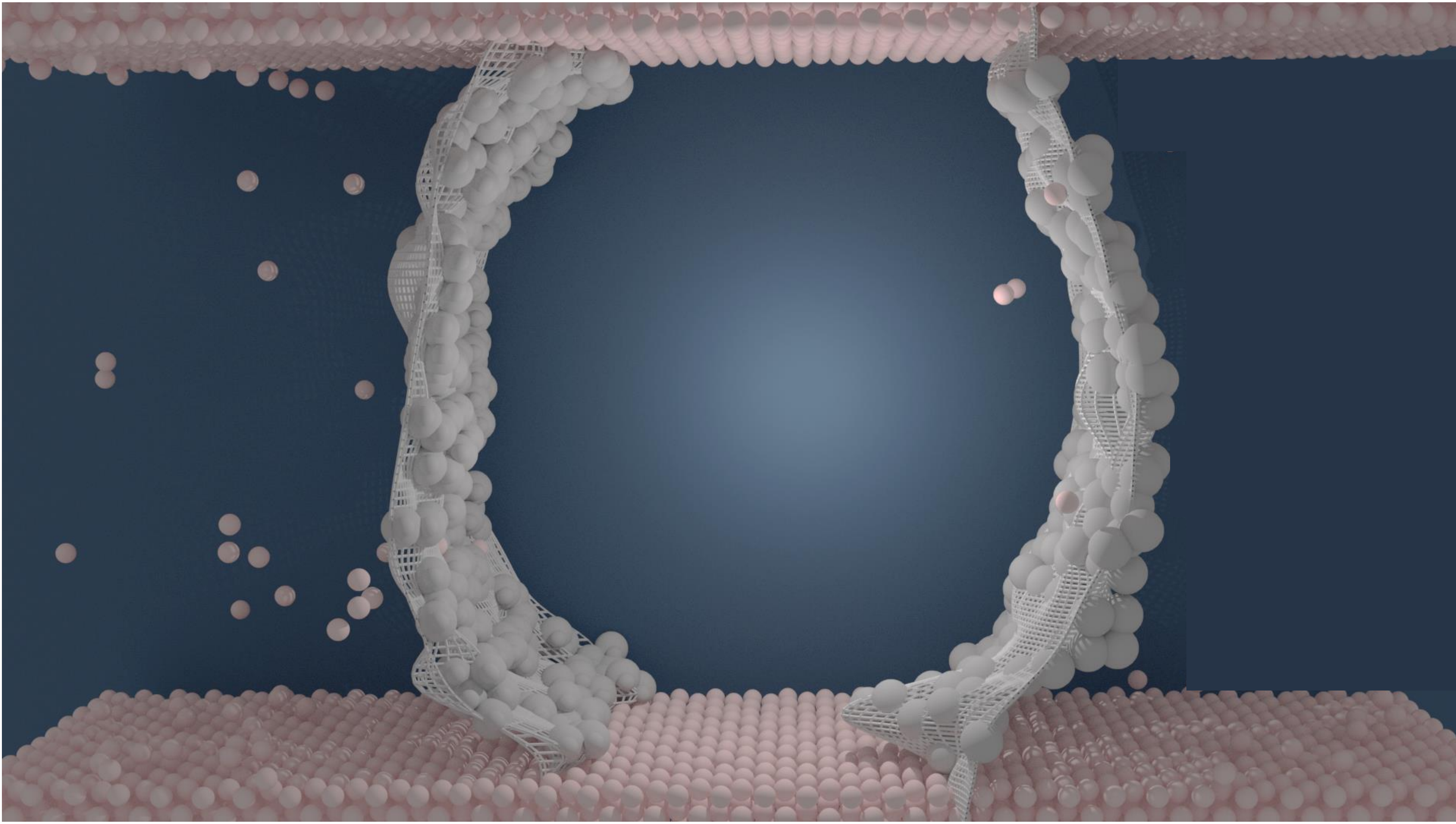


The Static Contact Line



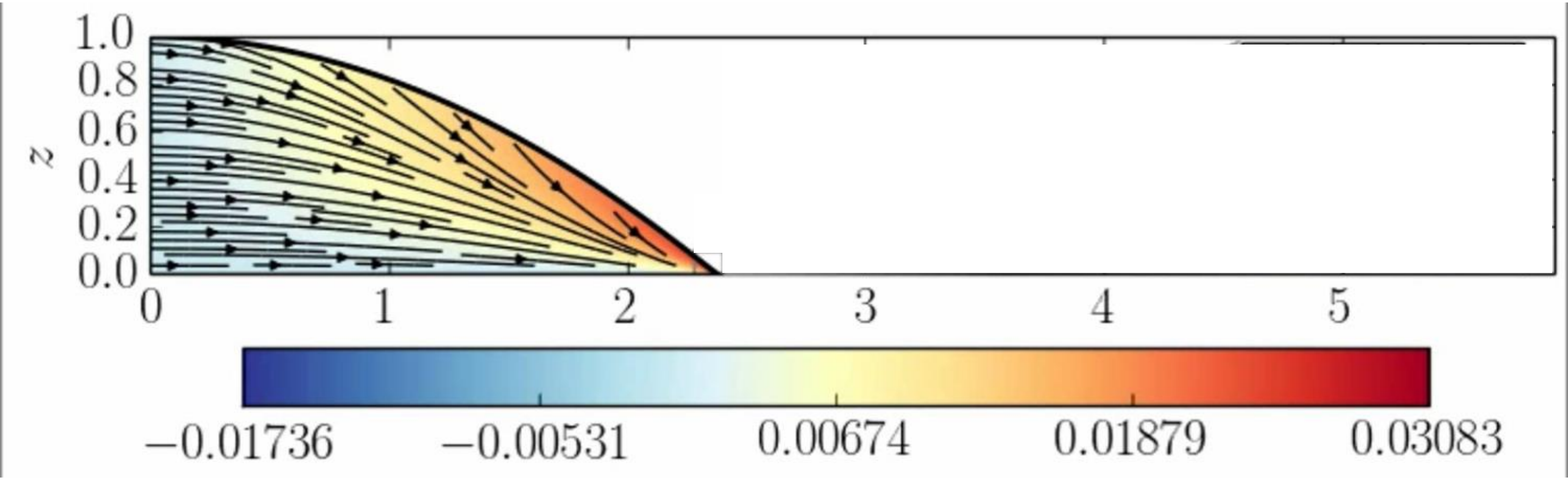


The Static Contact Line



Work with Omar Matar, Erich Muller and Richard Craster

Dynamic Contact Line



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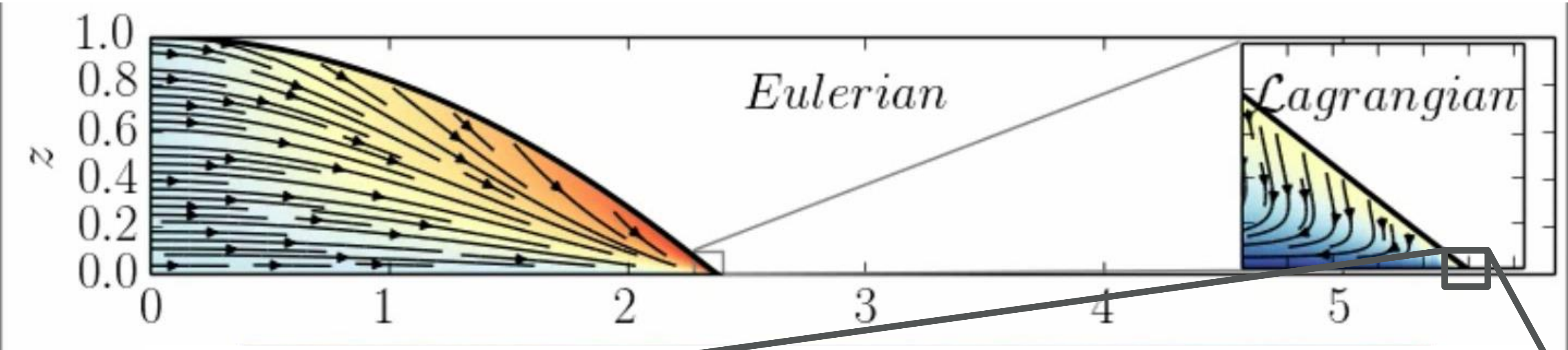
Dynamic Contact Line



- Model the moving contact line with MD

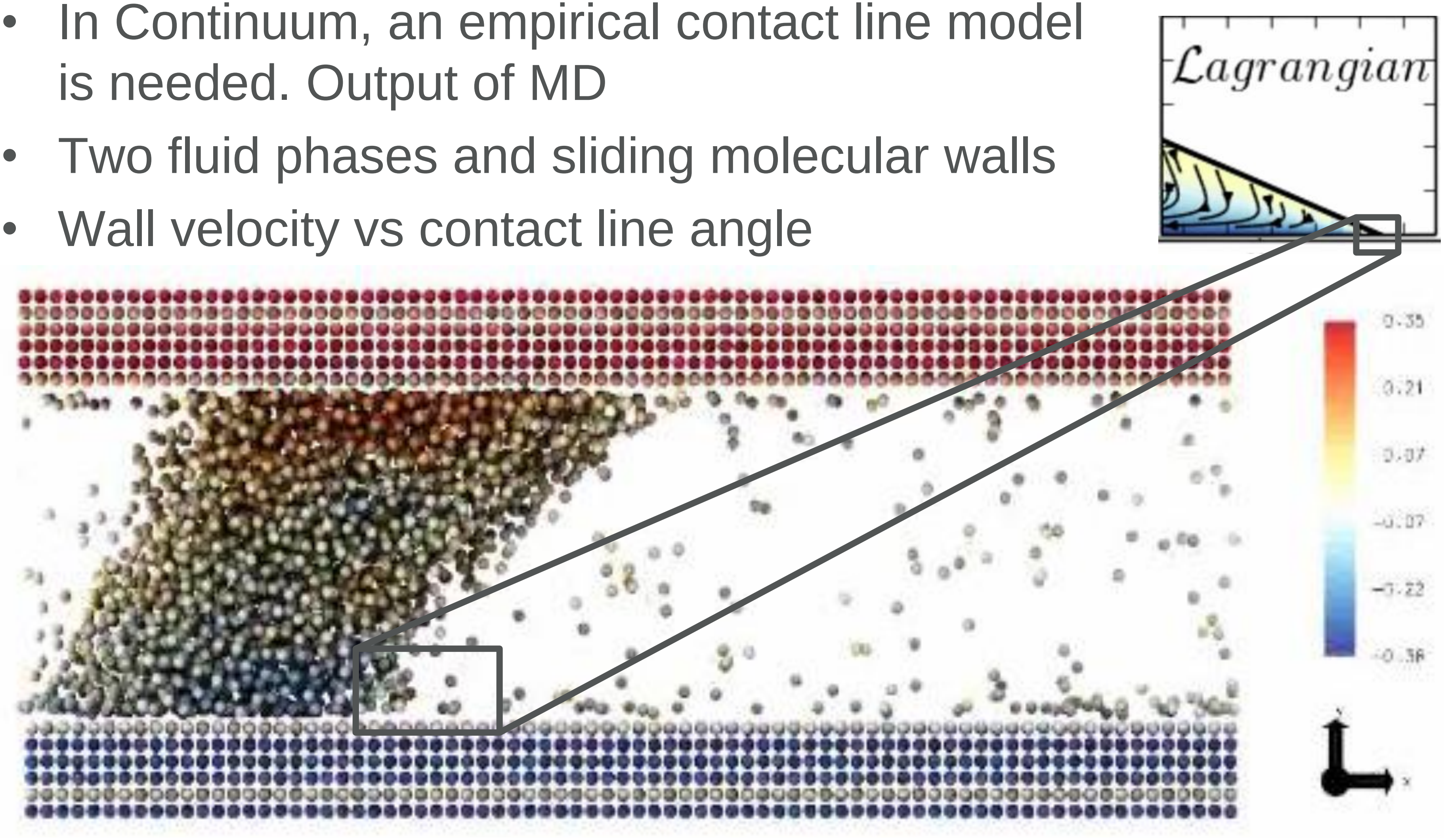
- We want contact line speed as a function of continuum contact angle

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

Work with Omar Matar, Erich Muller and Richard Craster

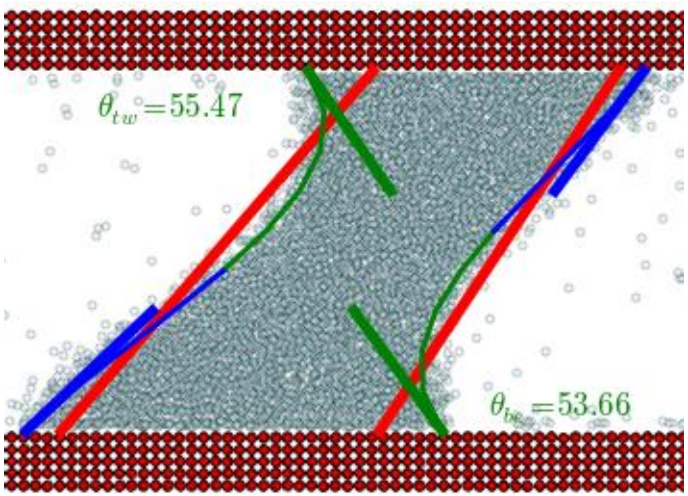
Dynamic Contact Line

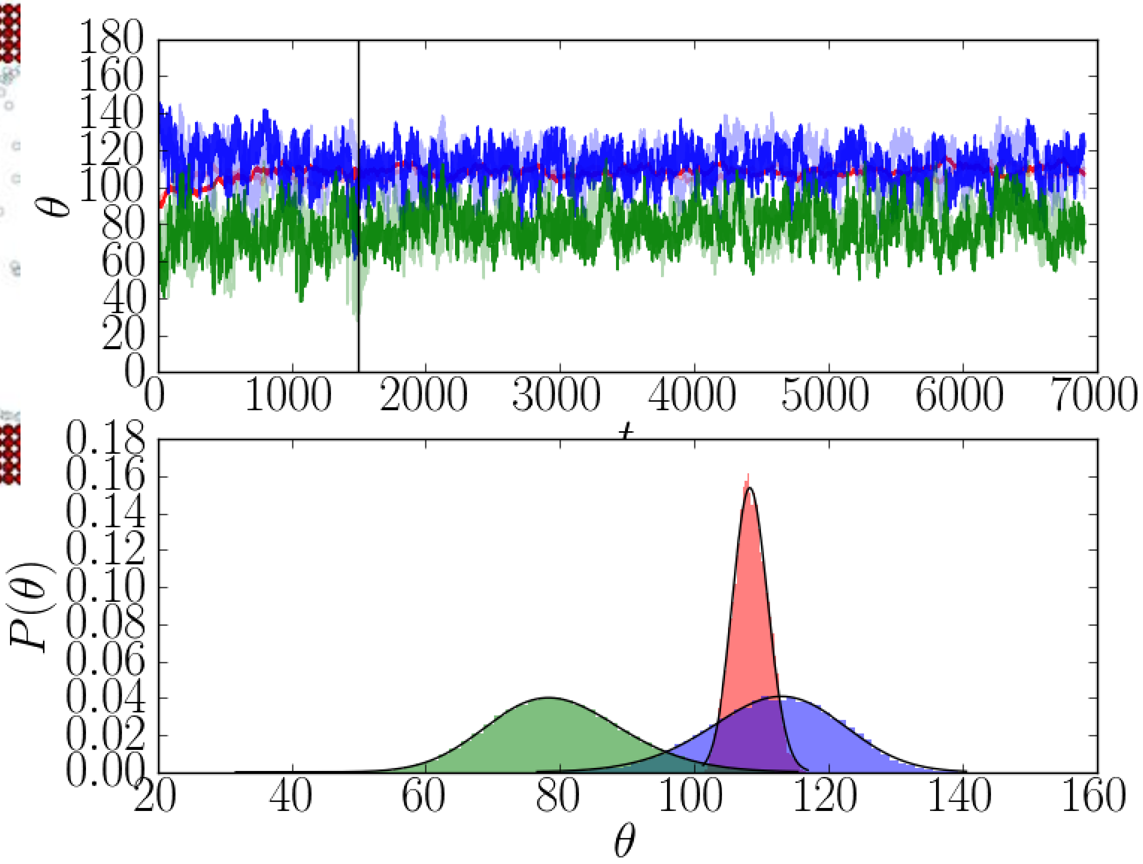
- In Continuum, an empirical contact line model is needed. Output of MD
- Two fluid phases and sliding molecular walls
- Wall velocity vs contact line angle



Time Evolution of Contact Angle

- Linear and Cubic Fitting angles fluctuates over time





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

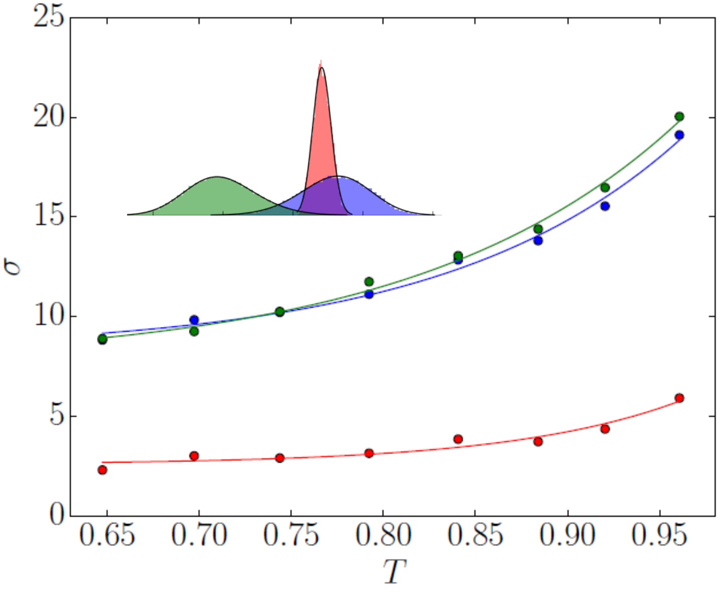
- *Linear, Advancing and Receding angles*

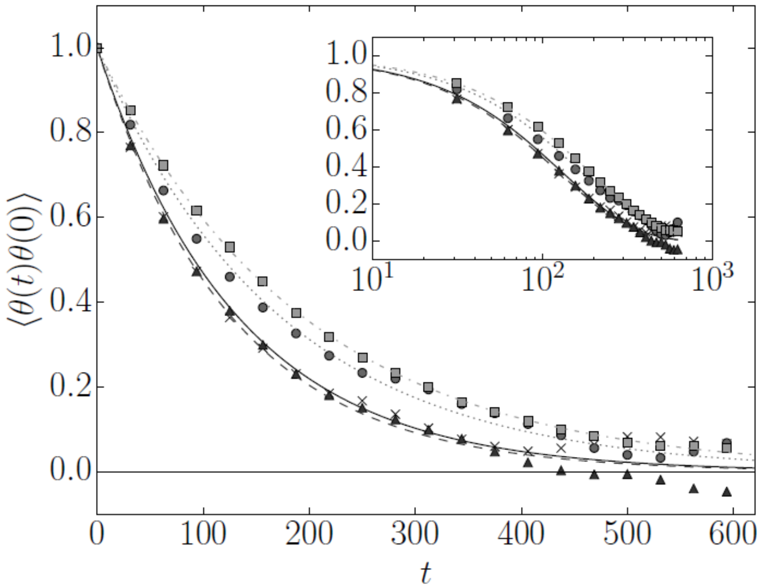
Building this into the Continuum Model

- 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.





Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

Molecular Dynamics - Nucleation

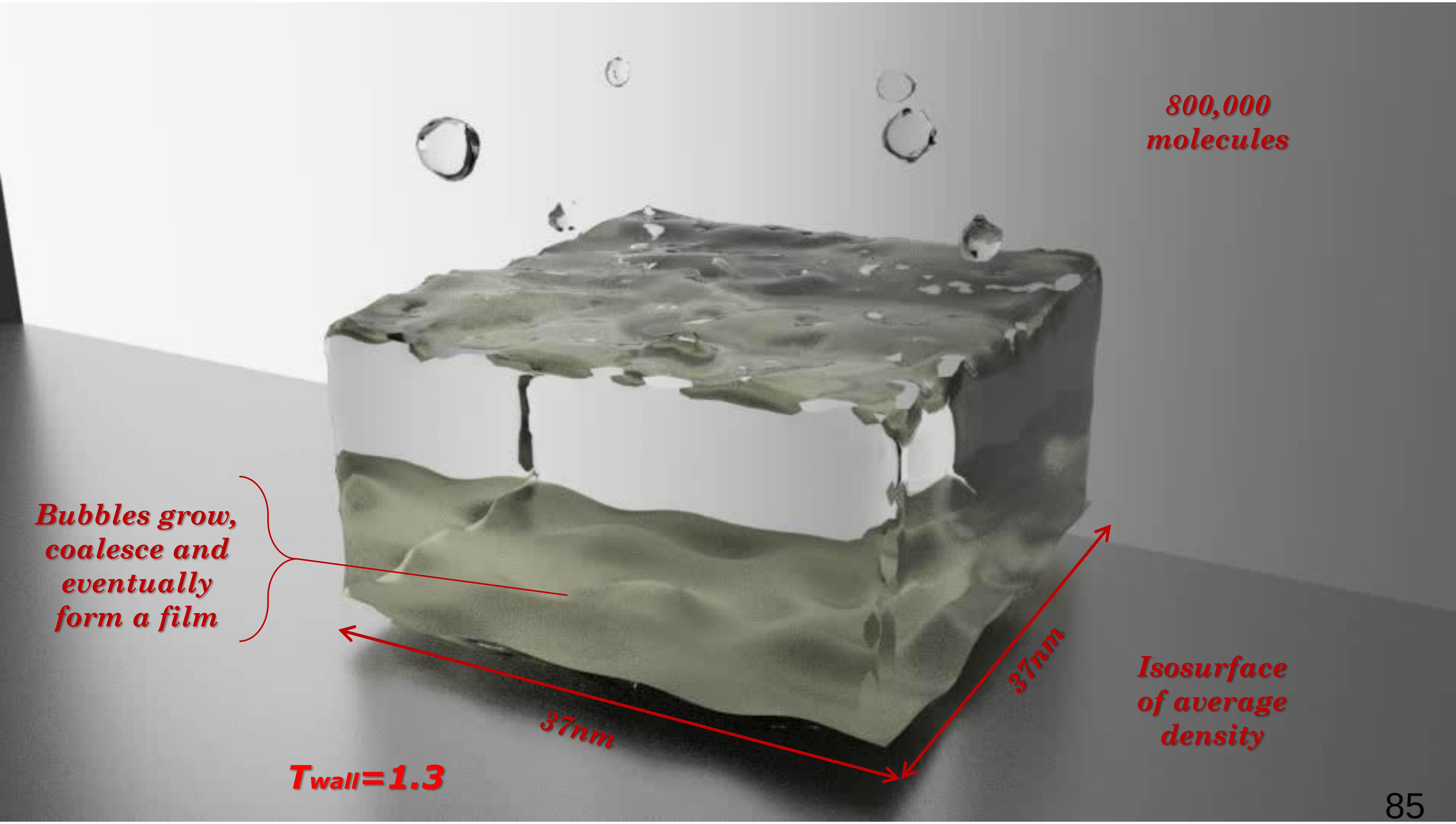
Wall w
mo
rou

800,000 molecules

Isosurface of average density

Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

Isosurface of Density



800,000 molecules

Bubbles grow, coalesce and eventually form a film

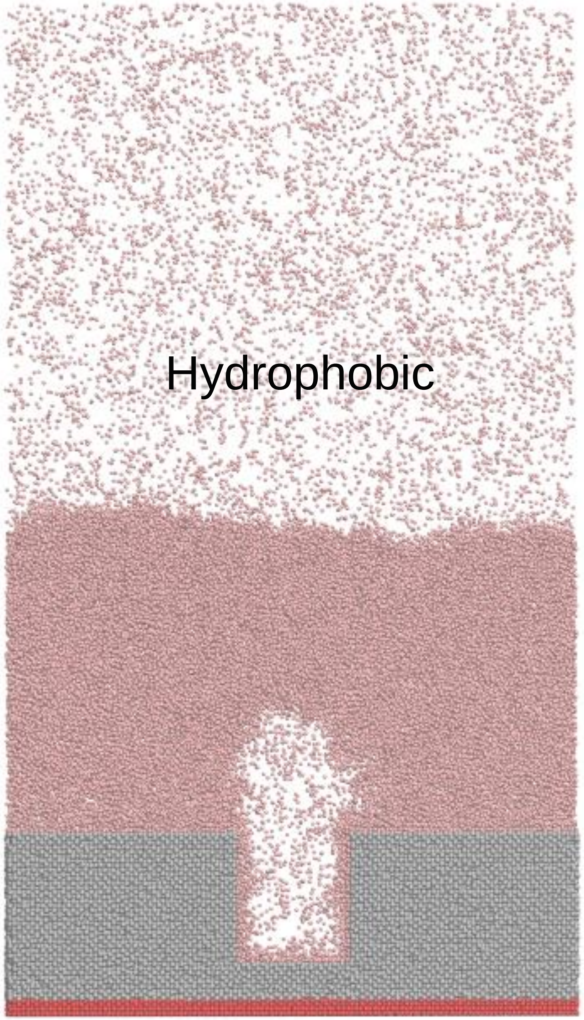
37nm

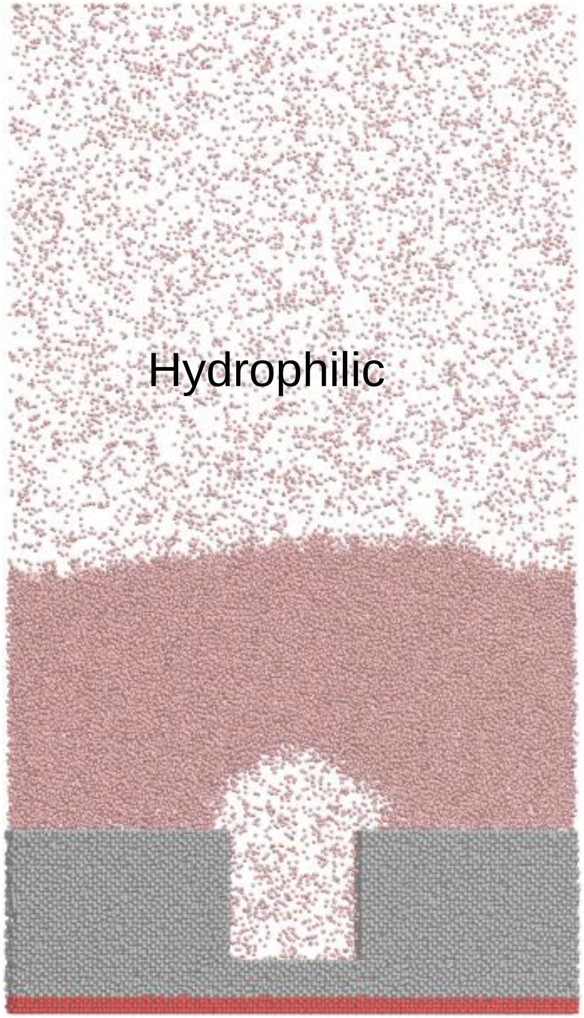
37nm

Isosurface of average density

$T_{wall}=1.3$

Wetting and Nucleation



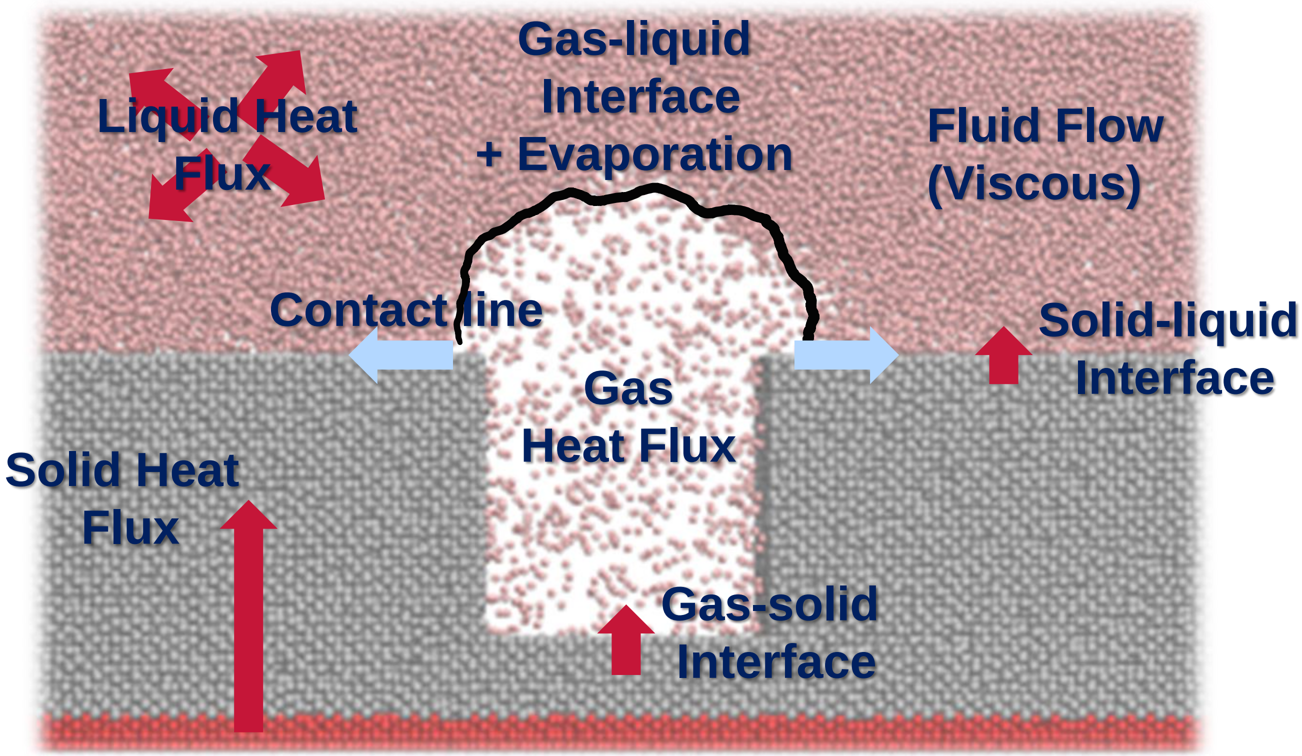


Work by

Alessio Lavino

at Imperial

Factors in Bubble Nucleation

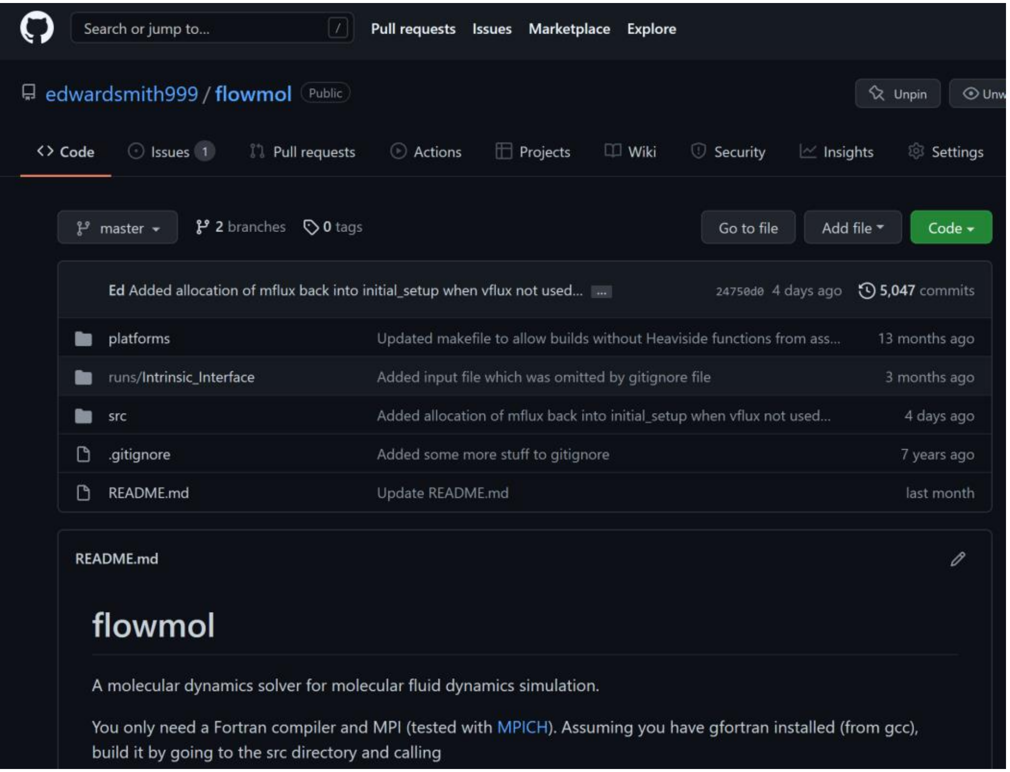


Overview

- An introduction to Molecular Dynamics (MD)
- Molecular Fluid Dynamics and getting quantities from a molecular system
- The liquid-vapour interface
- Defining a Lagrangian reference frame moving with the interface
- Some applications

Questions

Thank you, any questions?



Ed Added allocation of mflux back into initial_setup when vflux not used... 2475ed0 4 days ago 5,047 commits

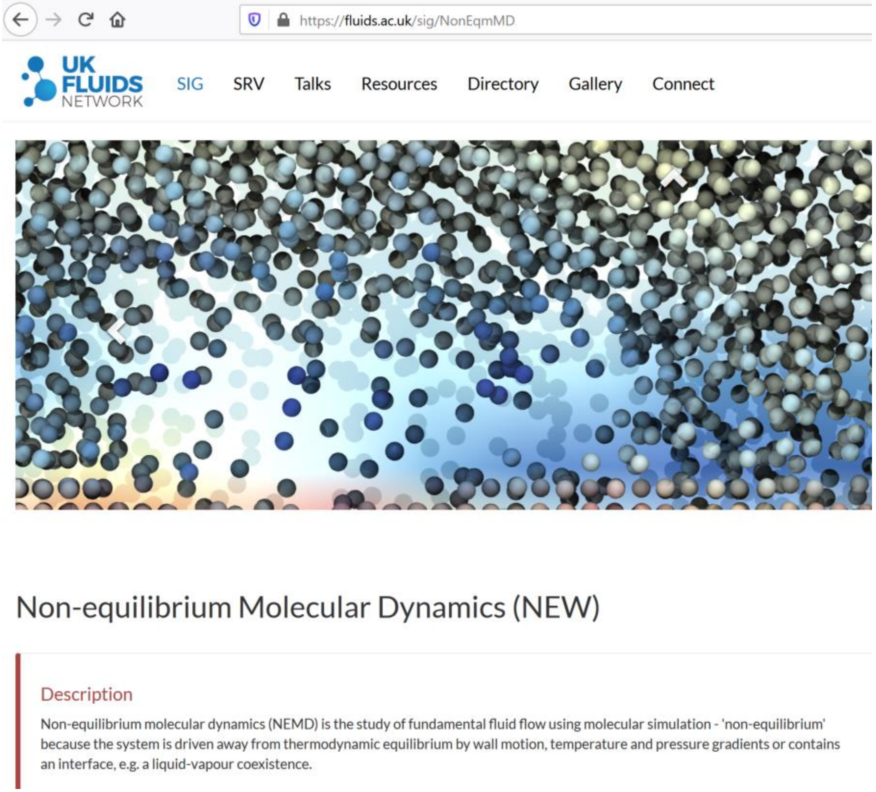
platforms	Updated makefile to allow builds without Heaviside functions from ass...	13 months ago
runs/Intrinsic_Interface	Added input file which was omitted by gitignore file	3 months ago
src	Added allocation of mflux back into initial_setup when vflux not used...	4 days ago
.gitignore	Added some more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



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

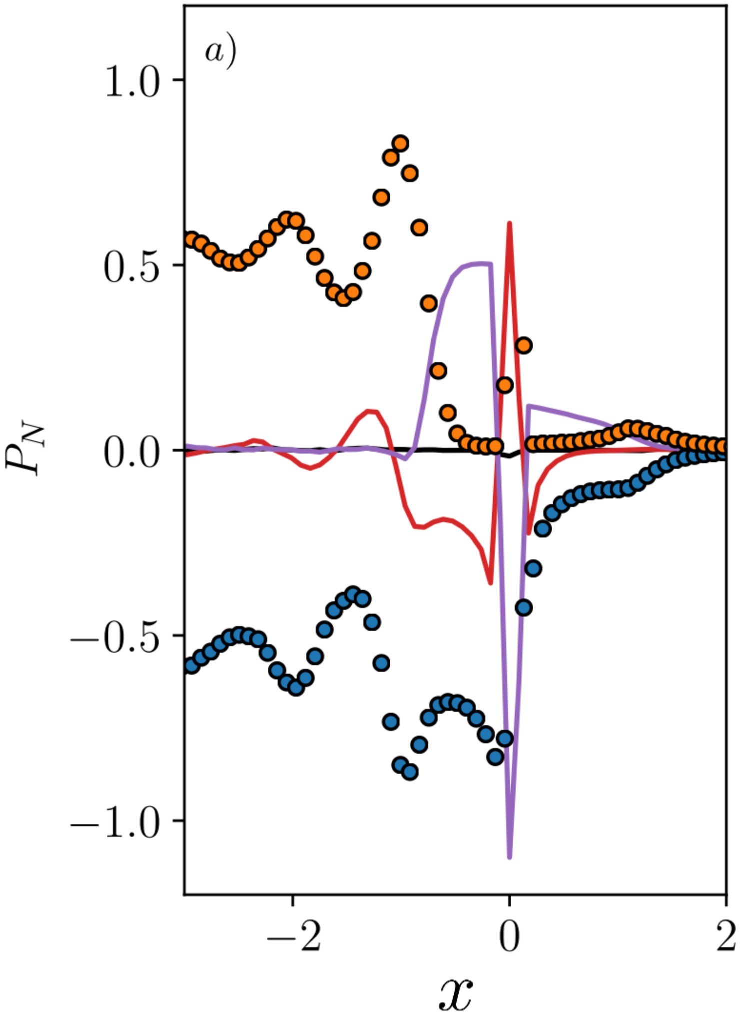
Normal Components Balance

$$\Big[\boxed{\dot{x}_i} + \overbrace{\boxed{\dot{y}_i \frac{\partial \xi_i^{+}}{\partial y_i} + \dot{z}_i \frac{\partial \xi_i^{+}}{\partial z_i}}}^{Kinetic\ Curvature} \ \overbrace{\boxed{\frac{\partial \xi_i^{+}}{\partial t}}}^{Surface\ Evolution}\Big] dS^{+}_{xi}$$

$$\boxed{x_{ij}} + \underbrace{\boxed{y_{ij} \frac{\partial \xi_\lambda^{+}}{\partial y_\lambda} + z_{ij} \frac{\partial \xi_\lambda^{+}}{\partial z_\lambda}}}_{Configurational\ Curvature}\Big] dS^{+}_{x\lambda} d\lambda,$$

- This suggests a new insight into surface tension on a flat surface

$$\boldsymbol{n} \cdot \boldsymbol{\Pi} \cdot \boldsymbol{n} = \gamma \boldsymbol{\nabla} \cdot \boldsymbol{n}$$



Written in terms of normal vector

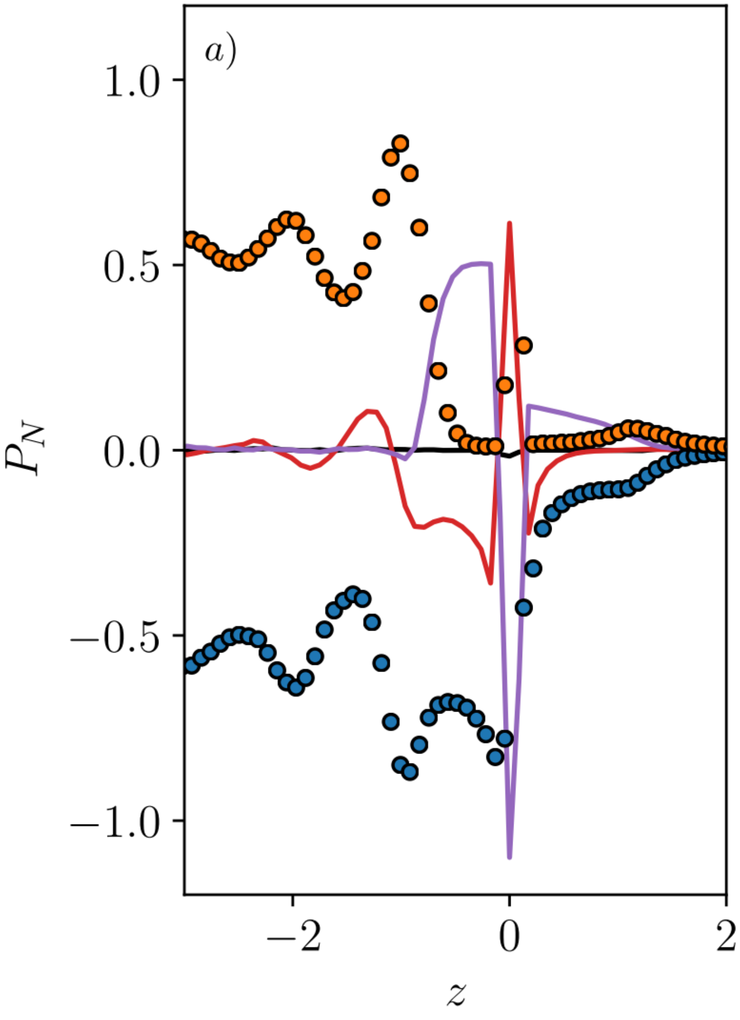
Kinetic Curvature *Surface Evolution*

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

$$\underbrace{\boxed{\boxed{\frac{1}{2\Delta S_z}\sum_{i,j}^{N} \boldsymbol{f}_{ij} \frac{\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z}{|\boldsymbol{r}_{ij}\cdot\boldsymbol{n}_z|} dS^+}}}_{Configurational\ Curvature} \qquad \boldsymbol{n}_x = \frac{\boldsymbol{\nabla}_\alpha(\xi - z_\alpha)}{||\boldsymbol{\nabla}_\alpha(\xi - z_\alpha)||}$$

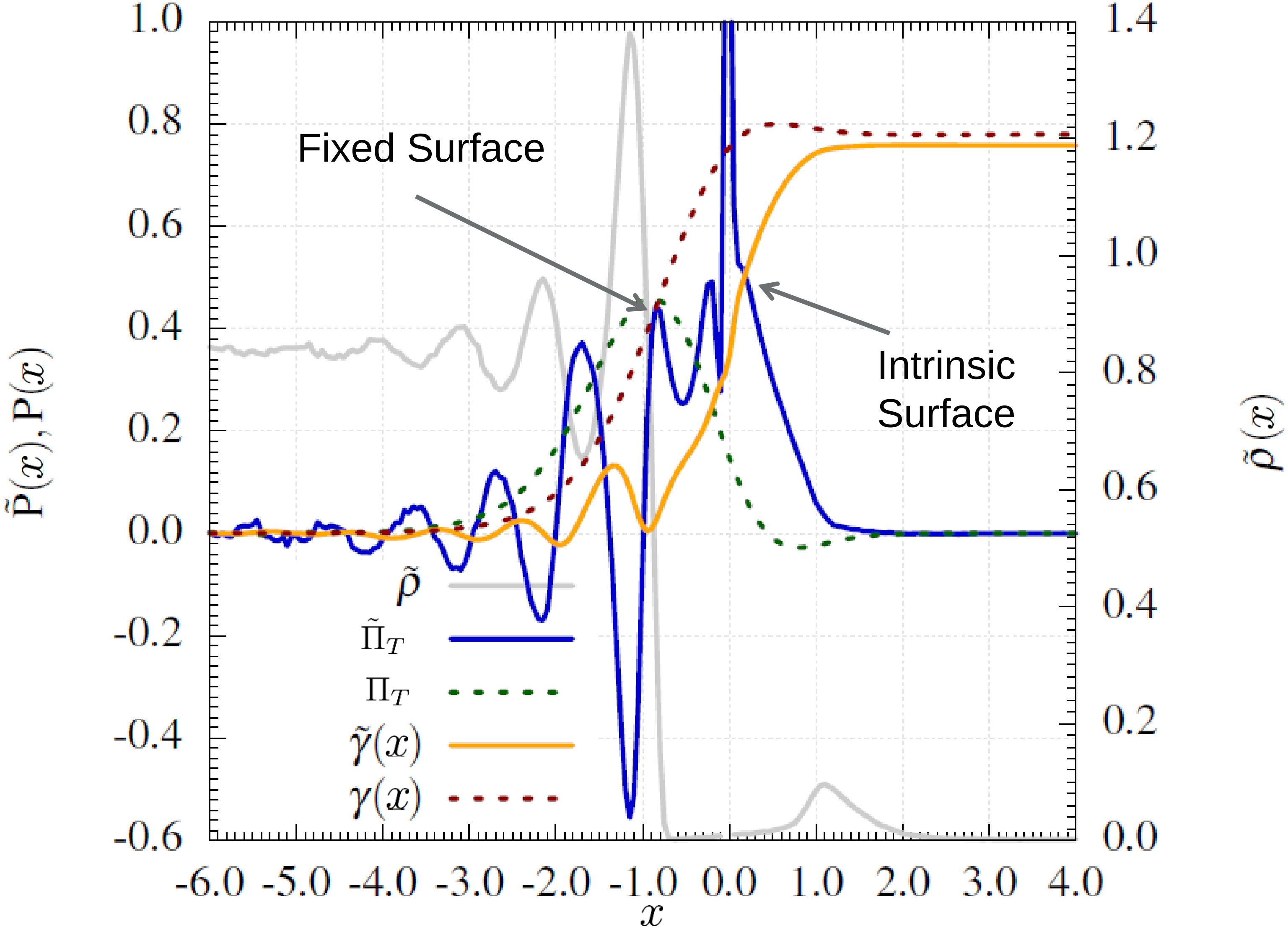
- This suggests a new insight into surface tension on a flat surface

$$\boldsymbol{n}\cdot\boldsymbol{\Pi}\cdot\boldsymbol{n} = \gamma\boldsymbol{\nabla}\cdot\boldsymbol{n}$$



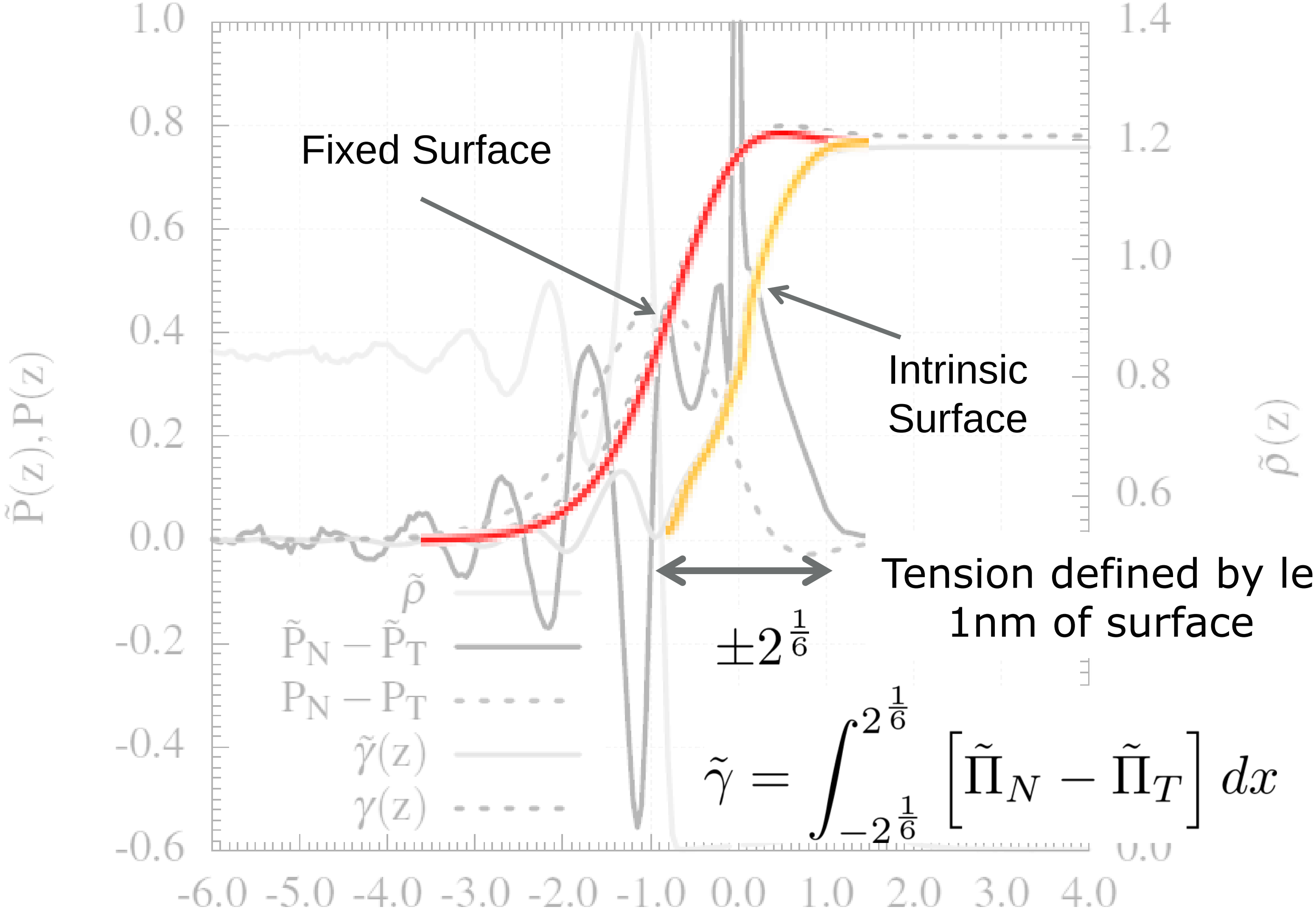
Work with Carlos Braga and Serafim Kalliadasis

Tangential Pressure



Work with Carlos Braga and Serafim Kalliadasis

Results for Surface Tension



Fixed Surface

Intrinsic Surface

Tension defined by less than 1nm of surface

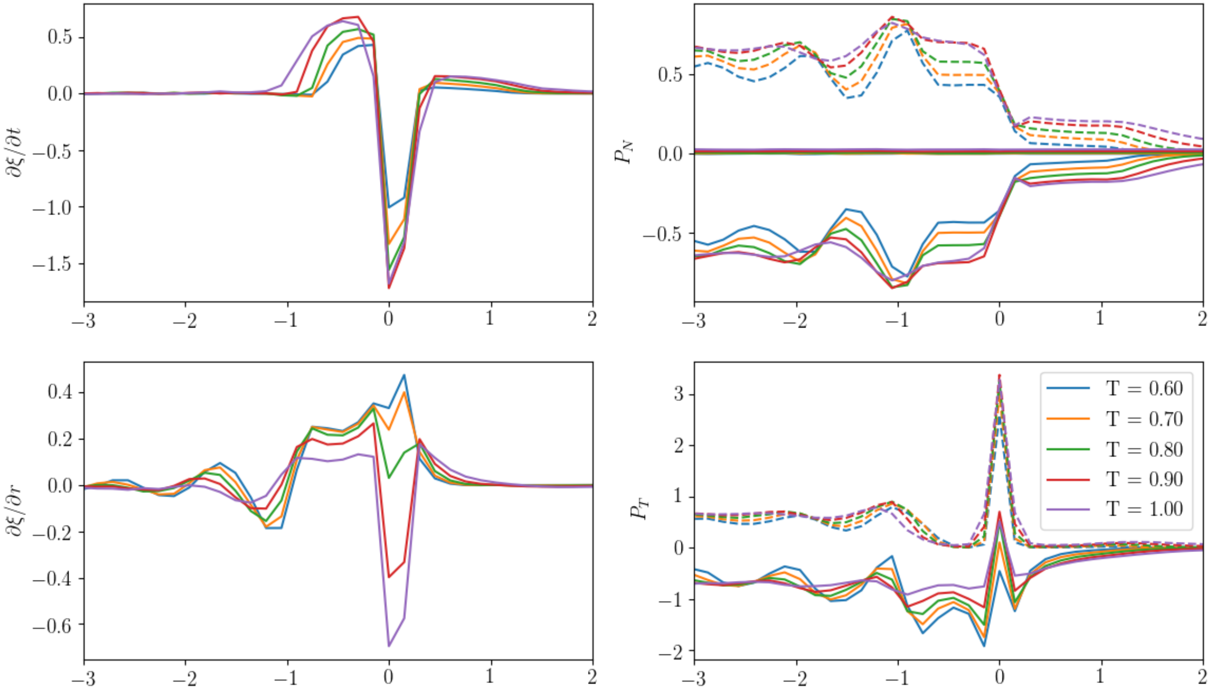
$\pm 2^{\frac{1}{6}}$

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

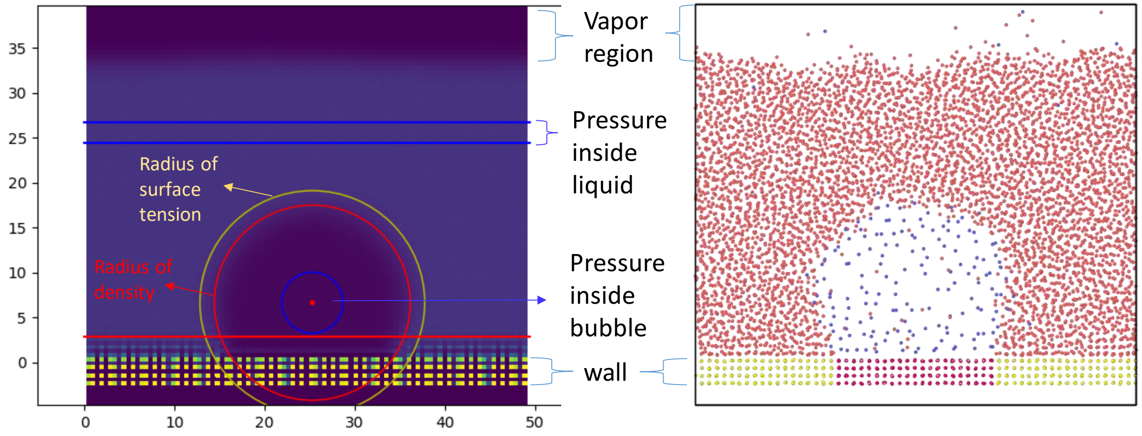
Pressure as a function of Temperature

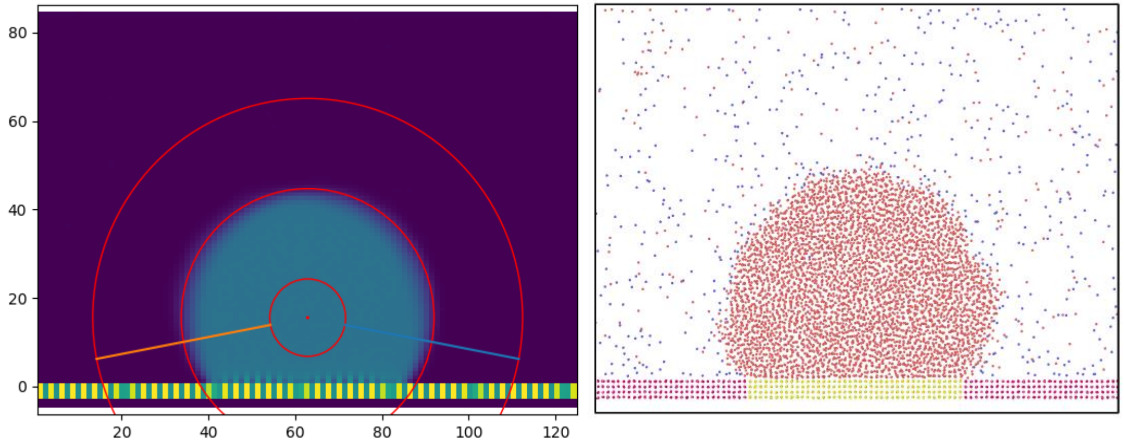
$$\overbrace{\dot{x}_i \frac{\partial \xi_i{}^+}{\partial x_i} + \dot{y}_i \frac{\partial \xi_i{}^+}{\partial y_i}}^{Kinetic\ Curvature} + \dot{z}_i + \overbrace{\frac{\partial \xi_i{}^+}{\partial t}}^{Surface\ Evolution} \Big] dS_{zi}^+$$

$$\underbrace{x_{ij} \frac{\partial \xi_\lambda^+}{\partial x_\lambda} + y_{ij} \frac{\partial \xi_\lambda^+}{\partial y_\lambda}}_{Configurational\ Curvature} + z_{ij} \Big] dS_{z\lambda}^+ d\lambda,$$



Droplet vs. Bubbles





Work by

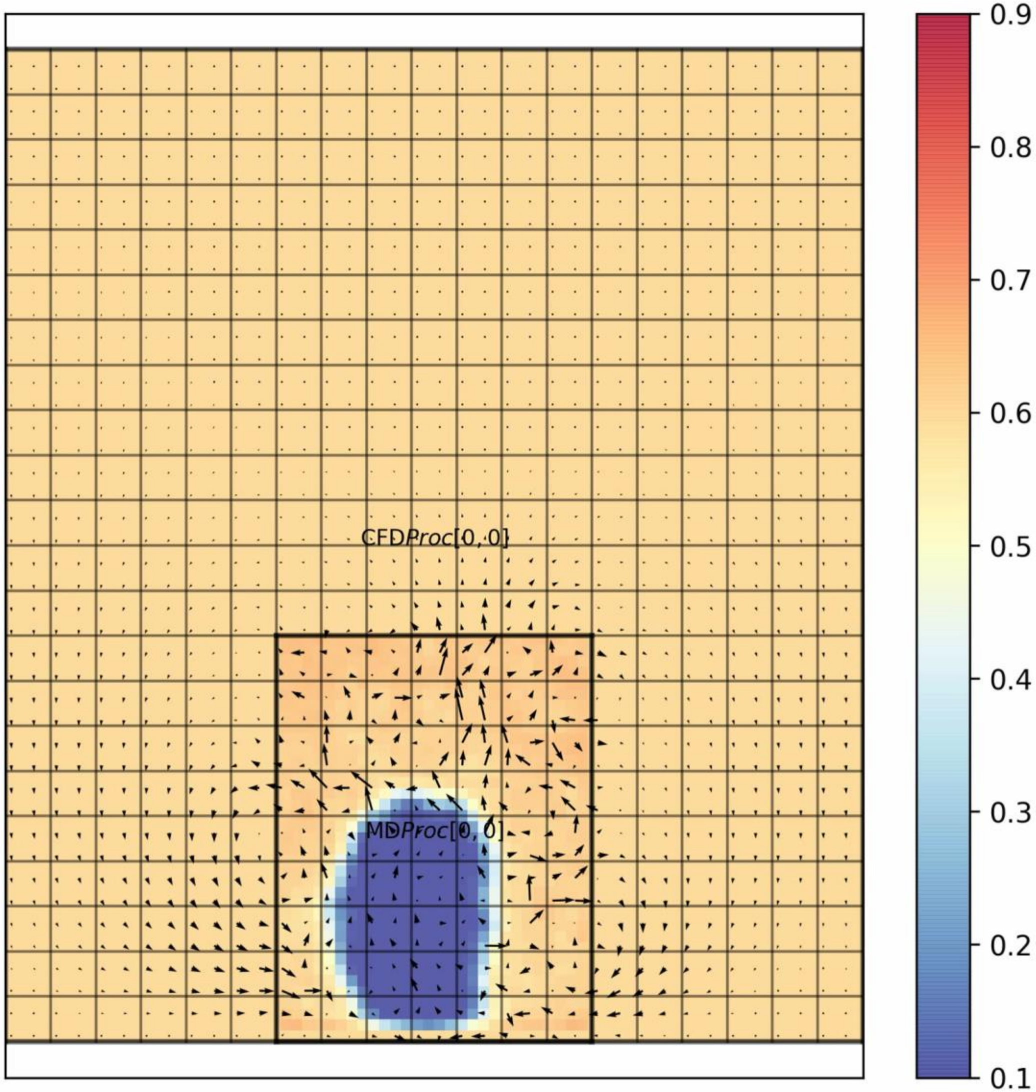
Wen Jun (Sonic)

at Imperial

Coupled Simulation of Boiling

- Bubble nucleation occurs naturally in MD

- Density, velocity and temperature passed as boundary conditions



Getting Quantities from MD

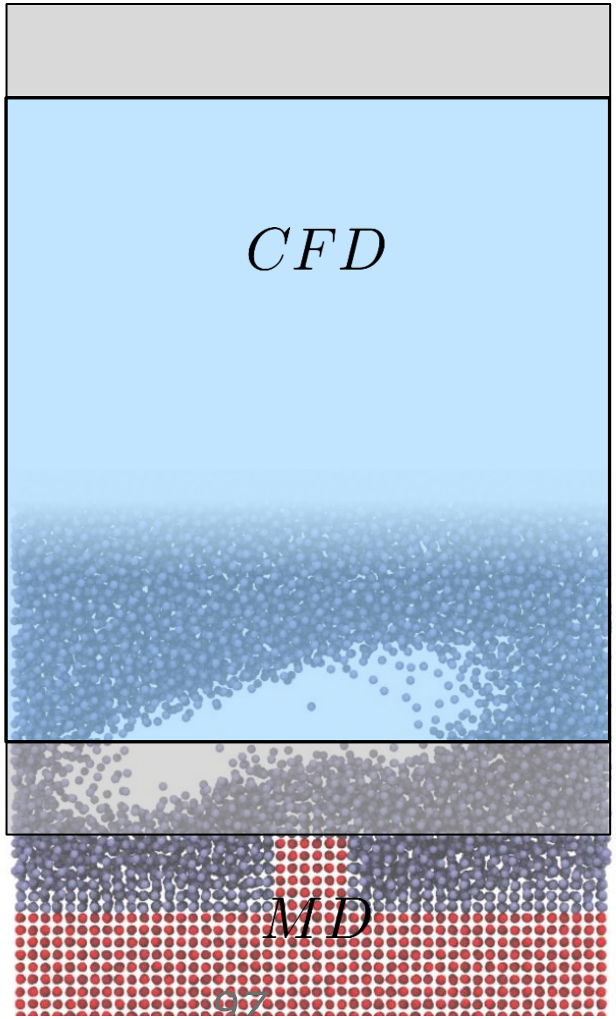
- Density at a point

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

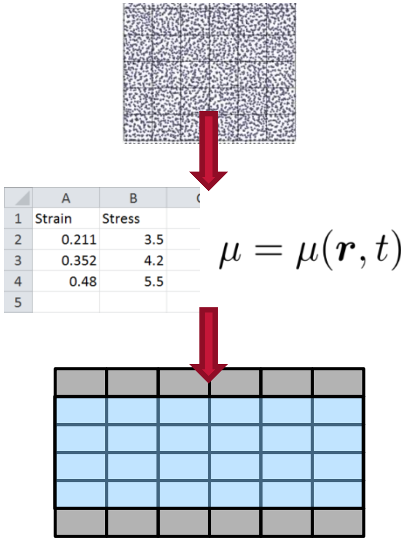
Share the same **time** and **length** scales

- Discrete molecules

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

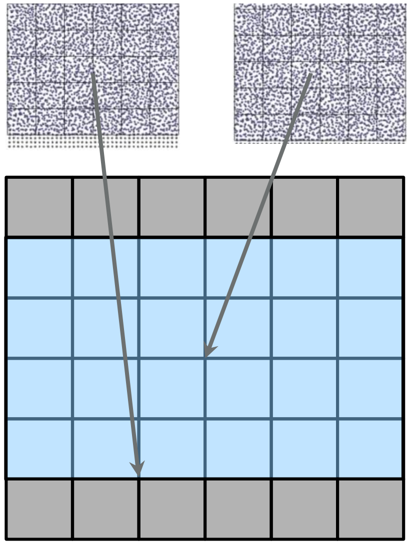


The Link to Continuum Fluid Dynamics



	A	B
1	Strain	Stress
2	0.211	3.5
3	0.352	4.2
4	0.48	5.5
5		

$$\mu = \mu(\boldsymbol{r}, t)$$



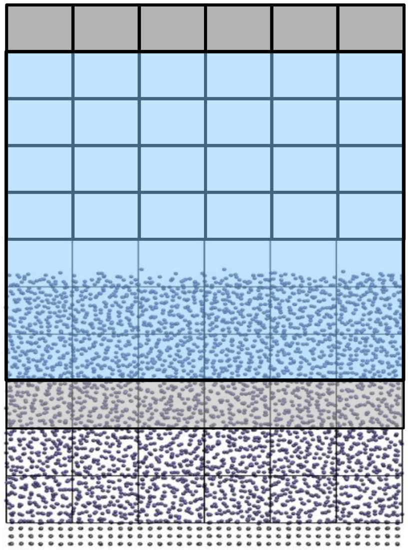


Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

Embedded Models (HMM)

MD – embedded in a CFD simulation 1)

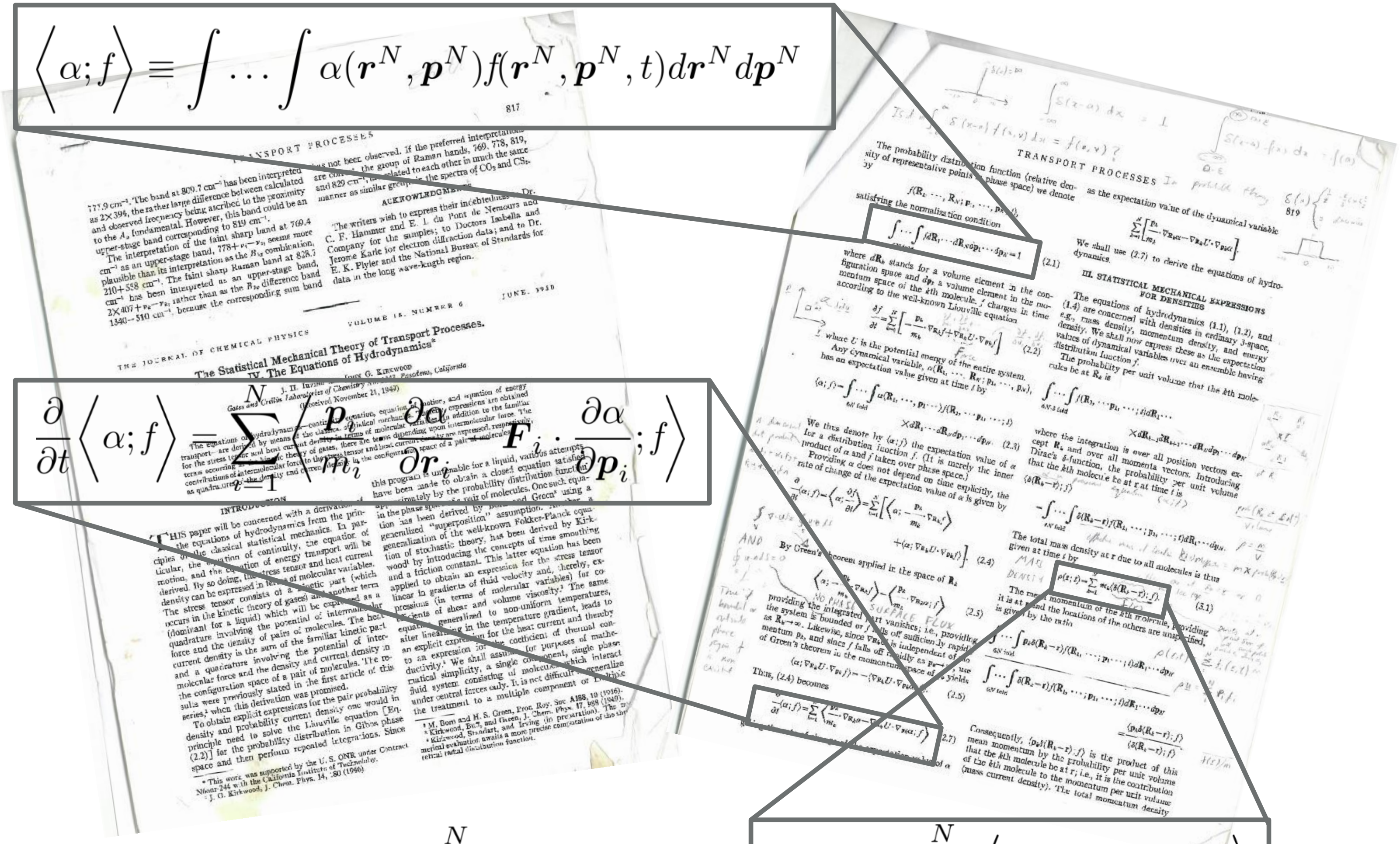
Domain Decomposition

MD –CFD linked along an interface 2)

1) Ren (2007), E et al (2003), Borg et al (2013) 2) O'Connell and Thompson (1995), Flekkøy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni & Coveney, (2003), Mohamed & Mohamad, (2009)

Irving and Kirkwood (1950)

Brunel University London



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

$$\left\langle \alpha; f \right\rangle \equiv \int \dots \int \alpha(\boldsymbol{r}^N, \boldsymbol{p}^N) f(\boldsymbol{r}^N, \boldsymbol{p}^N, t) d\boldsymbol{r}^N d\boldsymbol{p}^N$$

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

$$\alpha = \sum_{i=1}^{N} m_i \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right)$$

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

Irving and Kirkwood (1950) cont.

Density in the molecular system is defined

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

Time evolution from the Irving and Kirkwood procedure

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

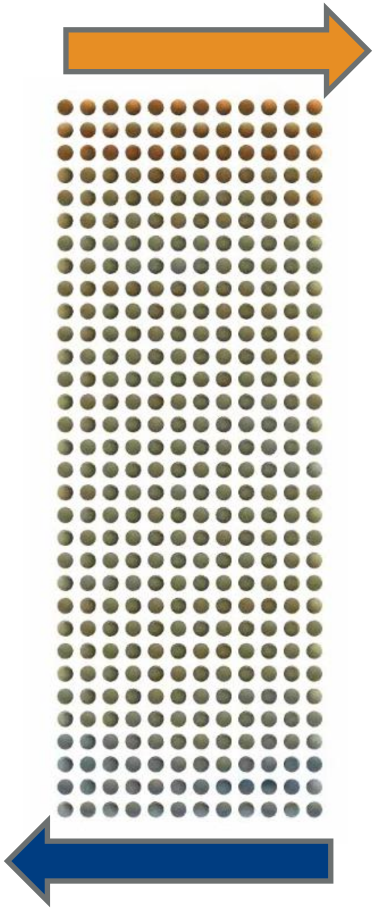
$$\frac{\partial}{\partial t}\sum_{i=1}^{N}\left\langle m_i\delta(\boldsymbol{r}-\boldsymbol{r}_i);f\right\rangle = \sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i}{m_i}\cdot\frac{\partial}{\partial\boldsymbol{r}_i}m_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)\right.$$

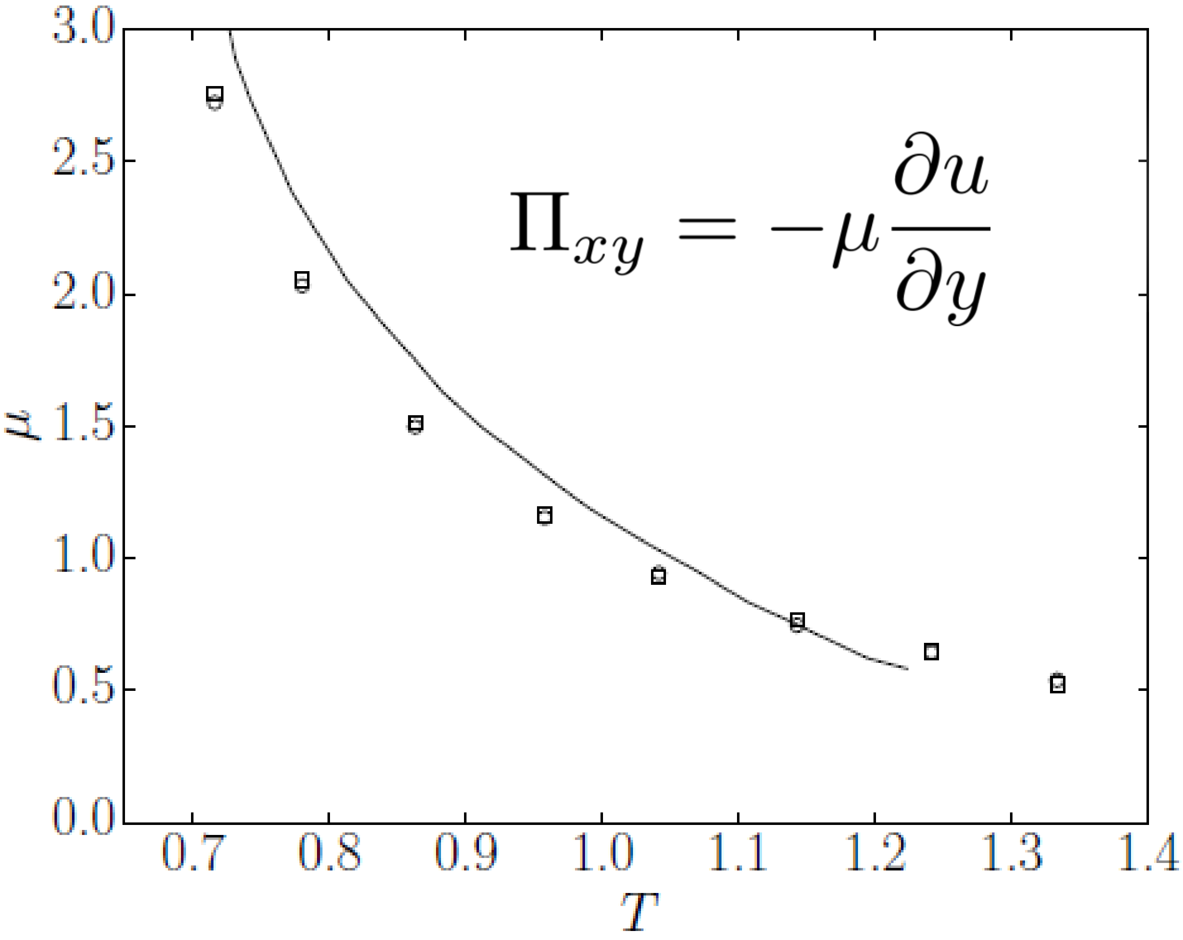
$$\left. -\boldsymbol{F}_i\cdot\cancel{\frac{\partial}{\partial\boldsymbol{p}_i}m_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)};f\right\rangle$$

$$= -\frac{\partial}{\partial\boldsymbol{r}}\cdot\sum_{i=1}^{N}\left\langle \boldsymbol{p}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i);f\right\rangle = -\boldsymbol{\nabla}\cdot\rho\boldsymbol{u}$$

Viscosity

- Good agreement with experiments





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

Heat Conduction

- Good agreement with experiments