Molecular Dynamics Across the Scales

Edward Smith,

David Heyes and Daniele Dini

02/10/19

Multi-scale and non-continuum flows Special Interest Group

Plan

- Large-scale molecular dynamics (MD)
- Understanding the range of scales
- Molecular structure, the link to stress and viscosity
- Non-equilibrium molecular dynamics (NEMD)

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Section 0

LARGE SCALE MD

Molecular Dynamics

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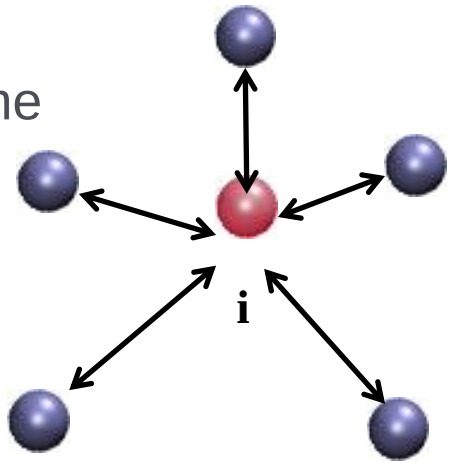
Discrete molecules in continuous space

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

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



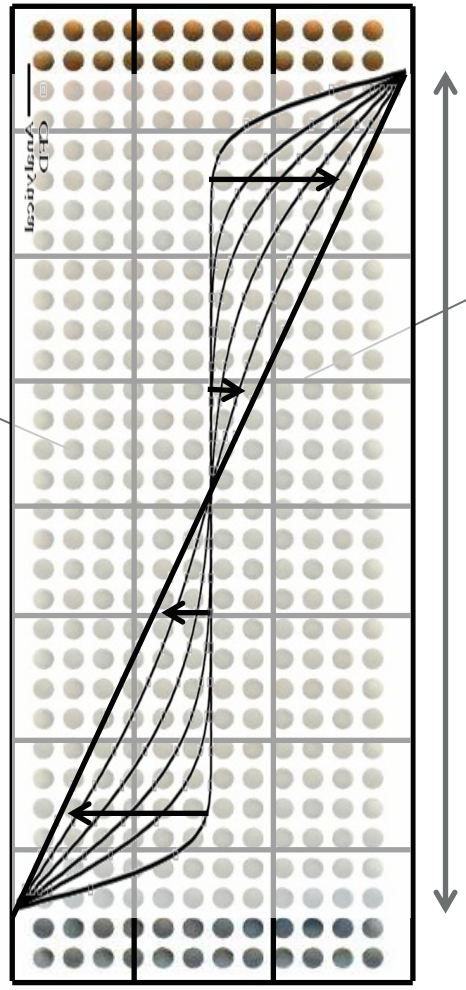
Acceleration obtained from forces

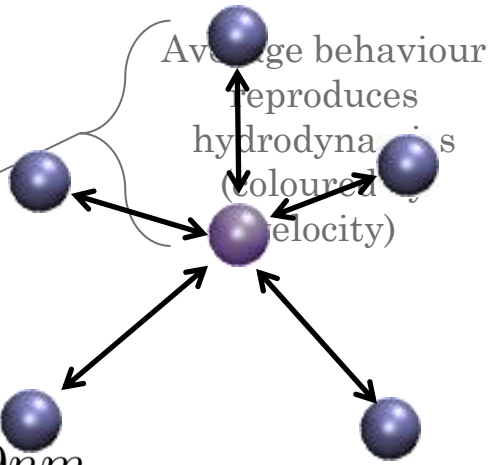
- Governed by Newton's law for an N-body system
- Point particles with pairwise interactions only

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

Molecular Dynamics

Liquid structure





$H \approx 9nm$

Time evolving structure not modelled by other methods

- Continuum Navier Stokes
- Boltzmann (Lattice)
- Smooth particle hydrodynamics
- Monte Carlo
- Classical density functional theory

Reynolds Number

$Re \approx 15$

with

4096 molecules

Molecular Simulation of Turbulence

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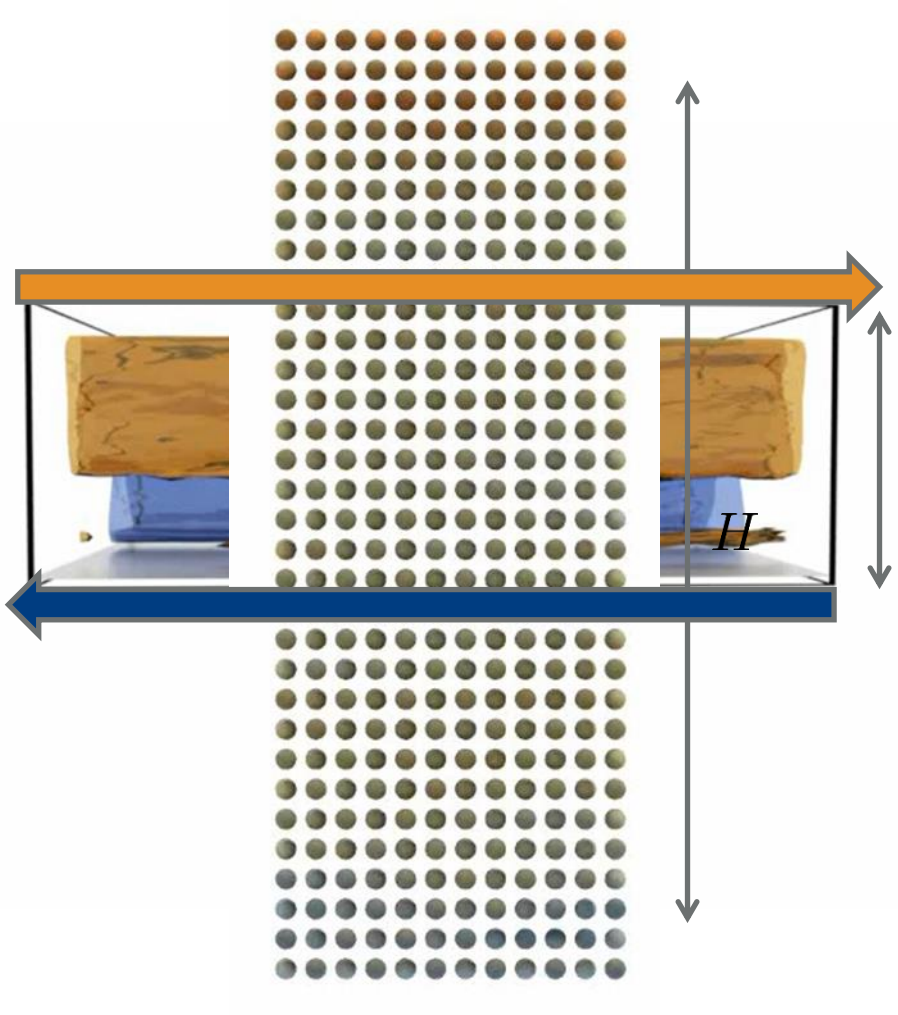


Reynolds Number

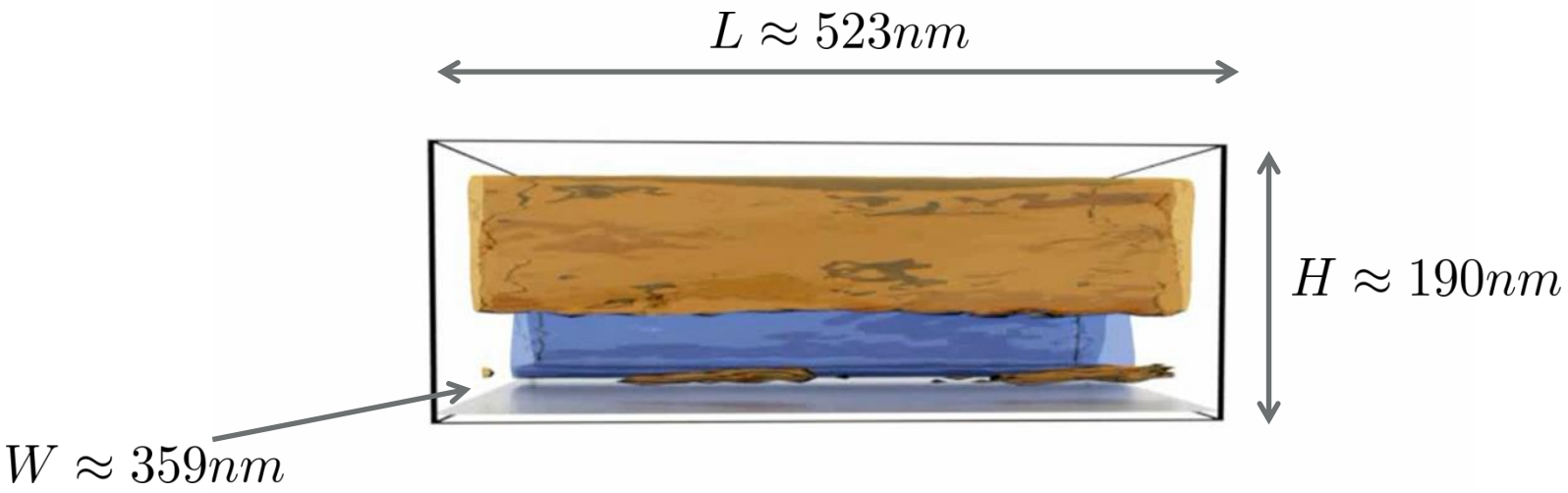
$Re \approx 400$

with

300 million molecules

Molecular Simulation of Turbulence

Minimal channel Couette flow



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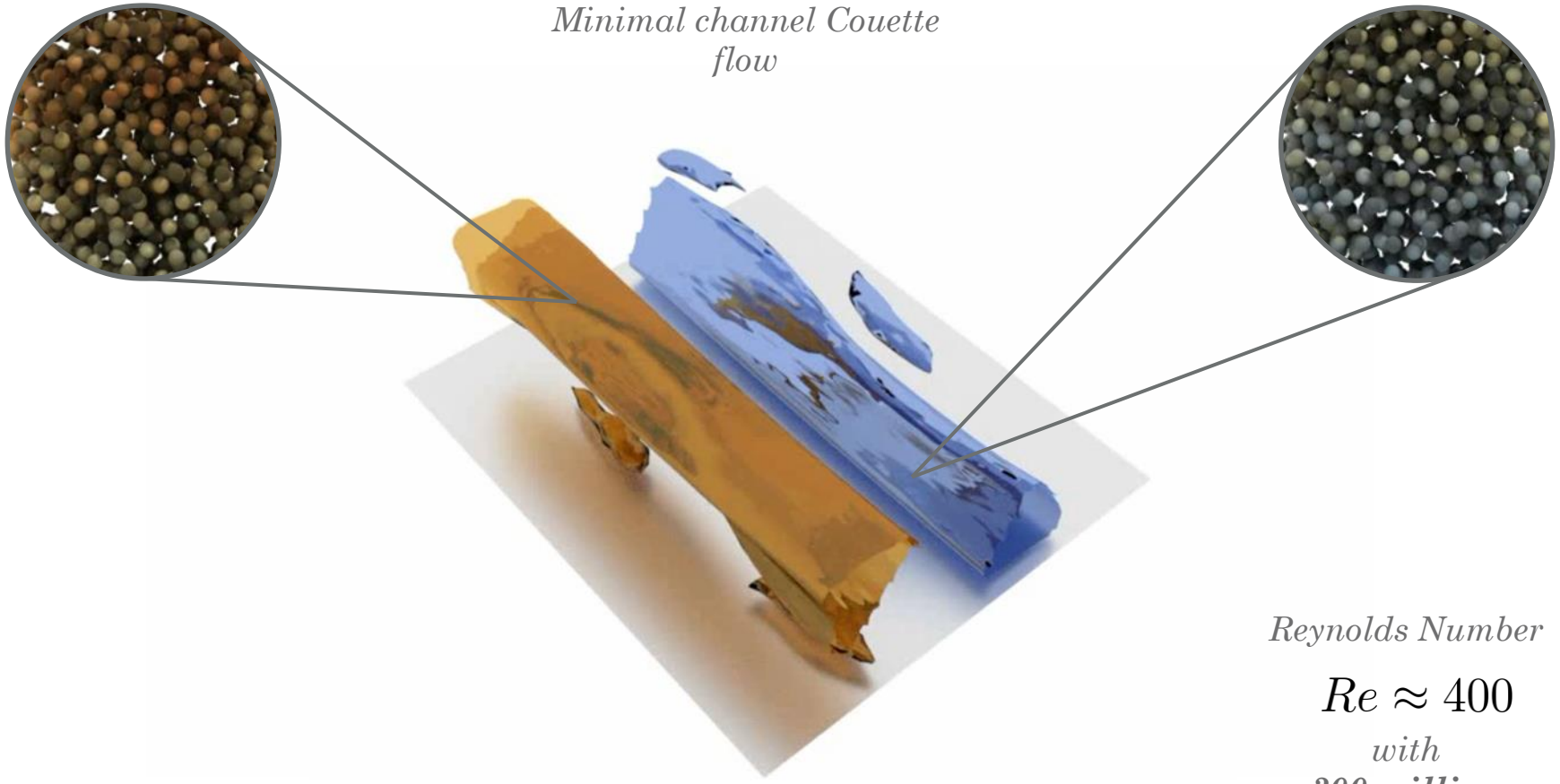

Isosurfaces of turbulent kinetic energy coloured by velocity

Reynolds Number

$Re \approx 400$

with

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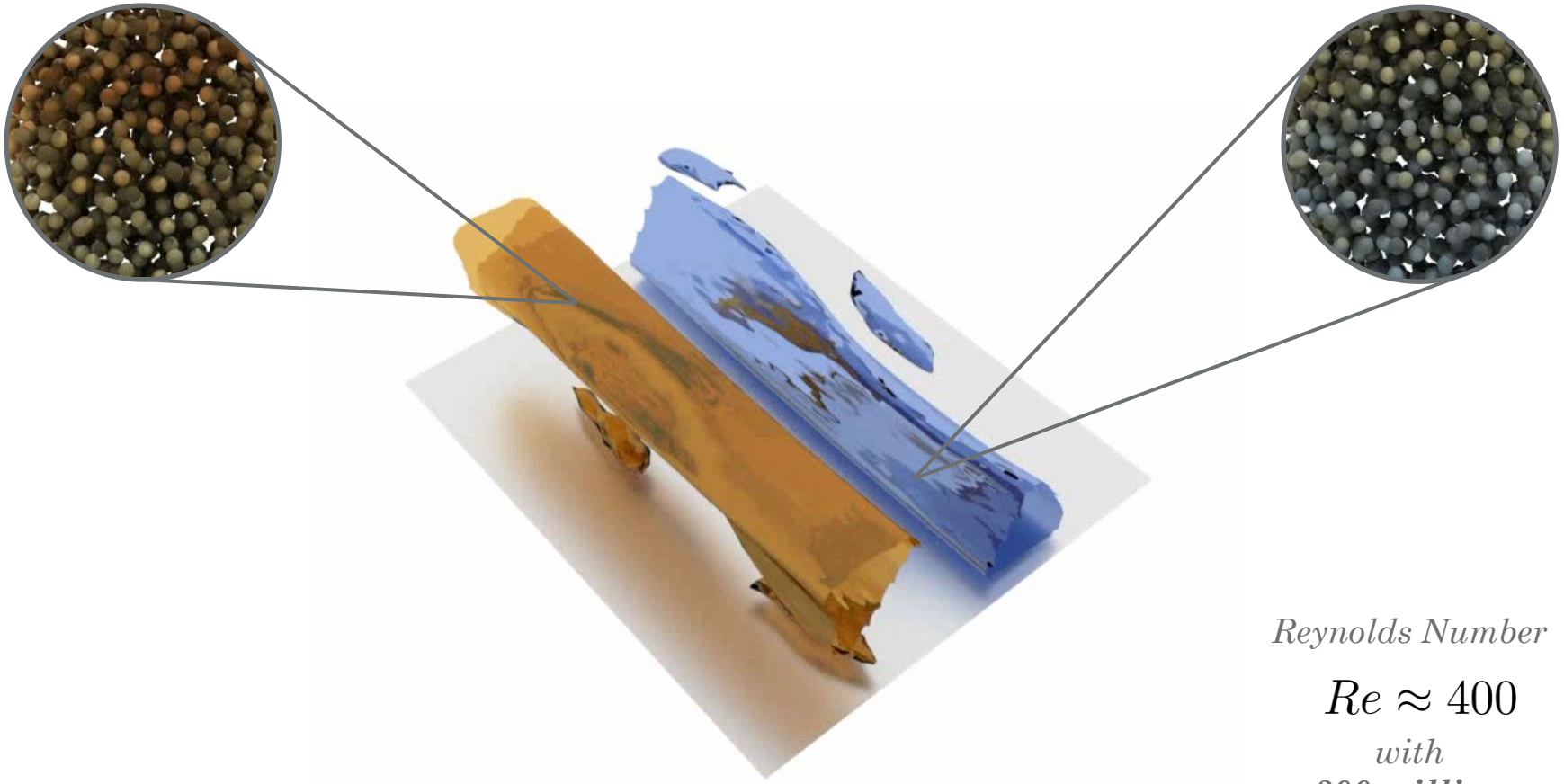
Molecular Simulation of Turbulence



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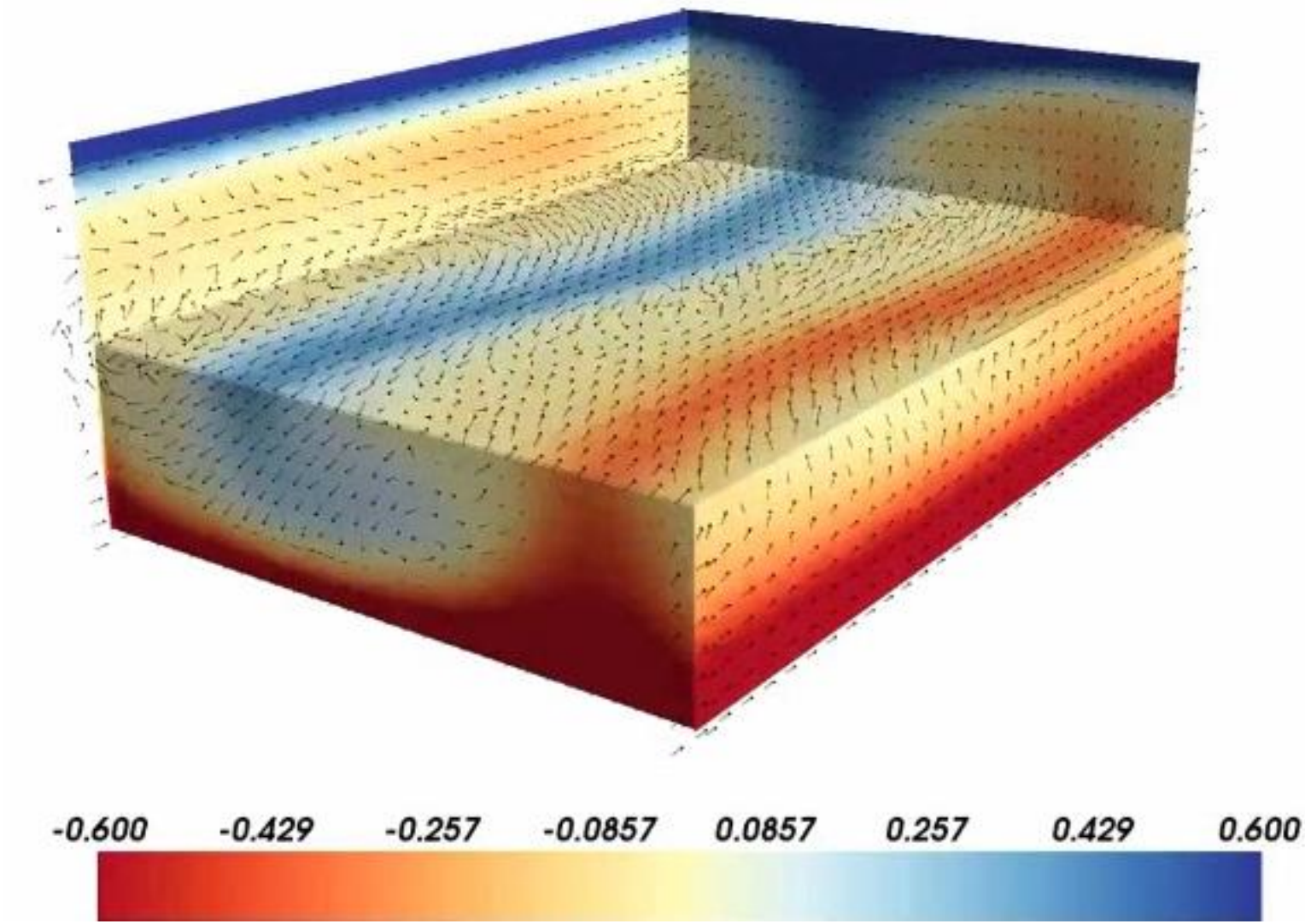
Molecular Turbulent Couette Flow



MD vs CFD

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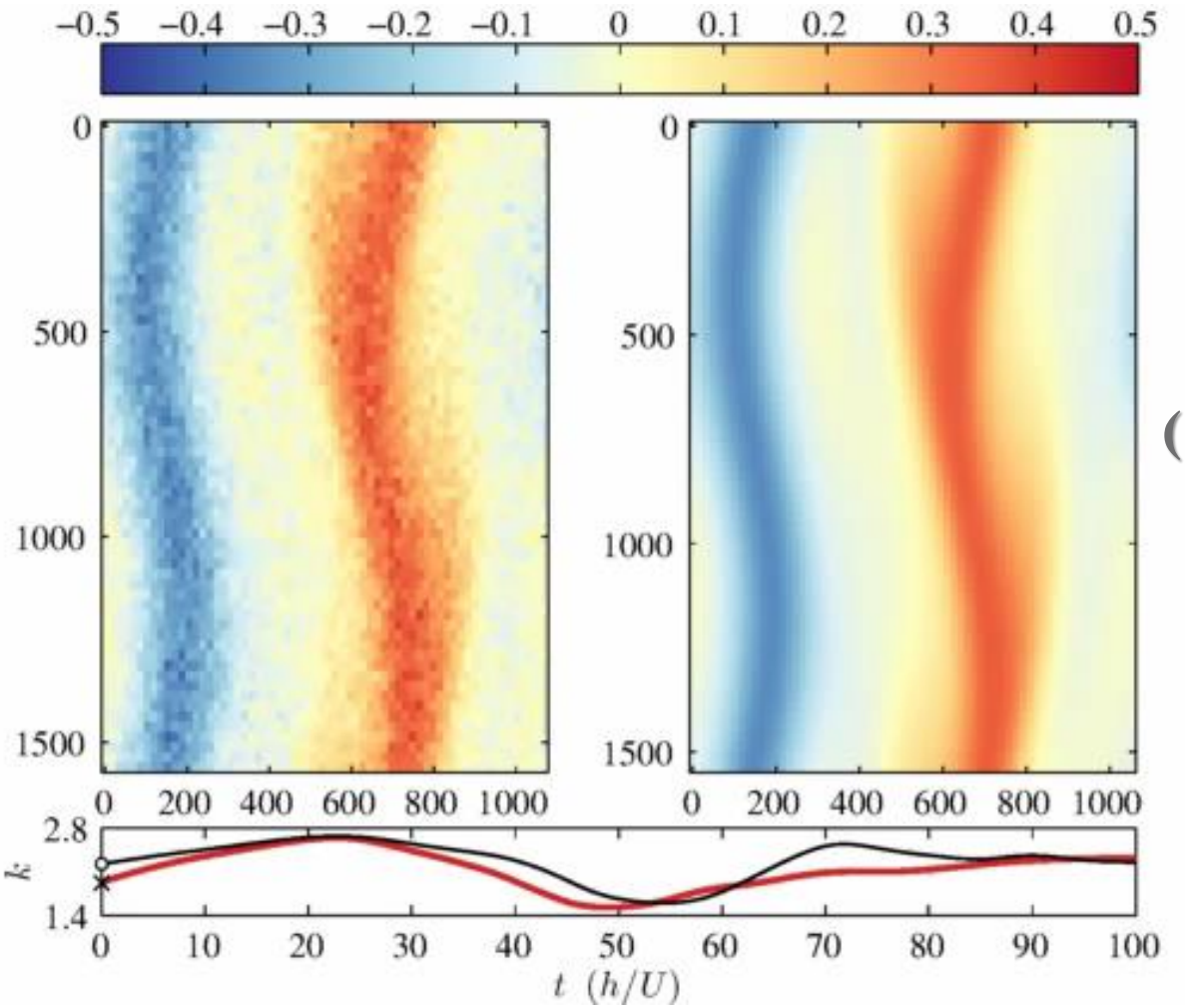
Centre slice velocity



MD

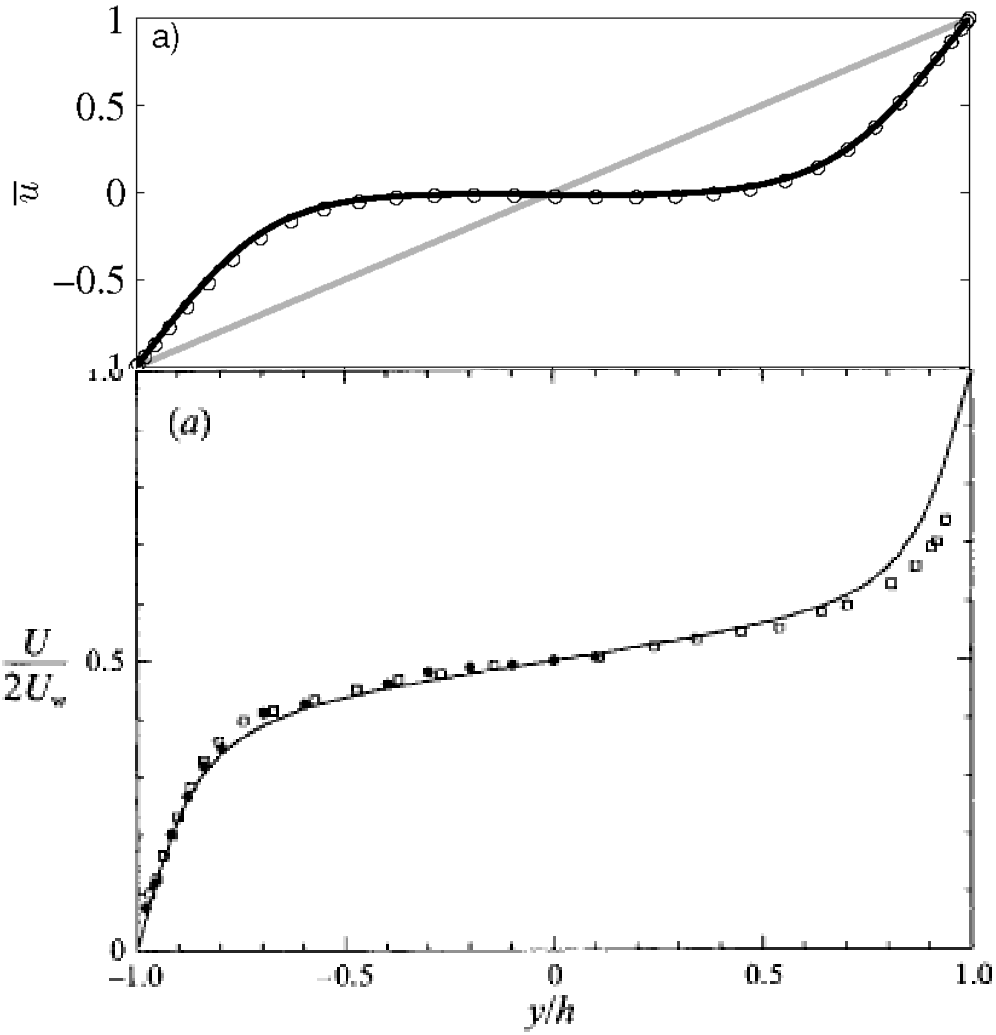
Own code written in Fortran and parallelised using MPI

CFD (Channelflow)

F. Gibson. Channelow: A spectral Navier-Stokes simulator in C++. Technical report, U. New Hampshire, 2012. Channelflow.org.

Statistical Results

- Averaged velocity profile
- No longer Laminar profile across domain
- Good agreement with literature
  - Numerical continuum studies (points)
  - Experimental results from turbulent simulations (bottom graph)

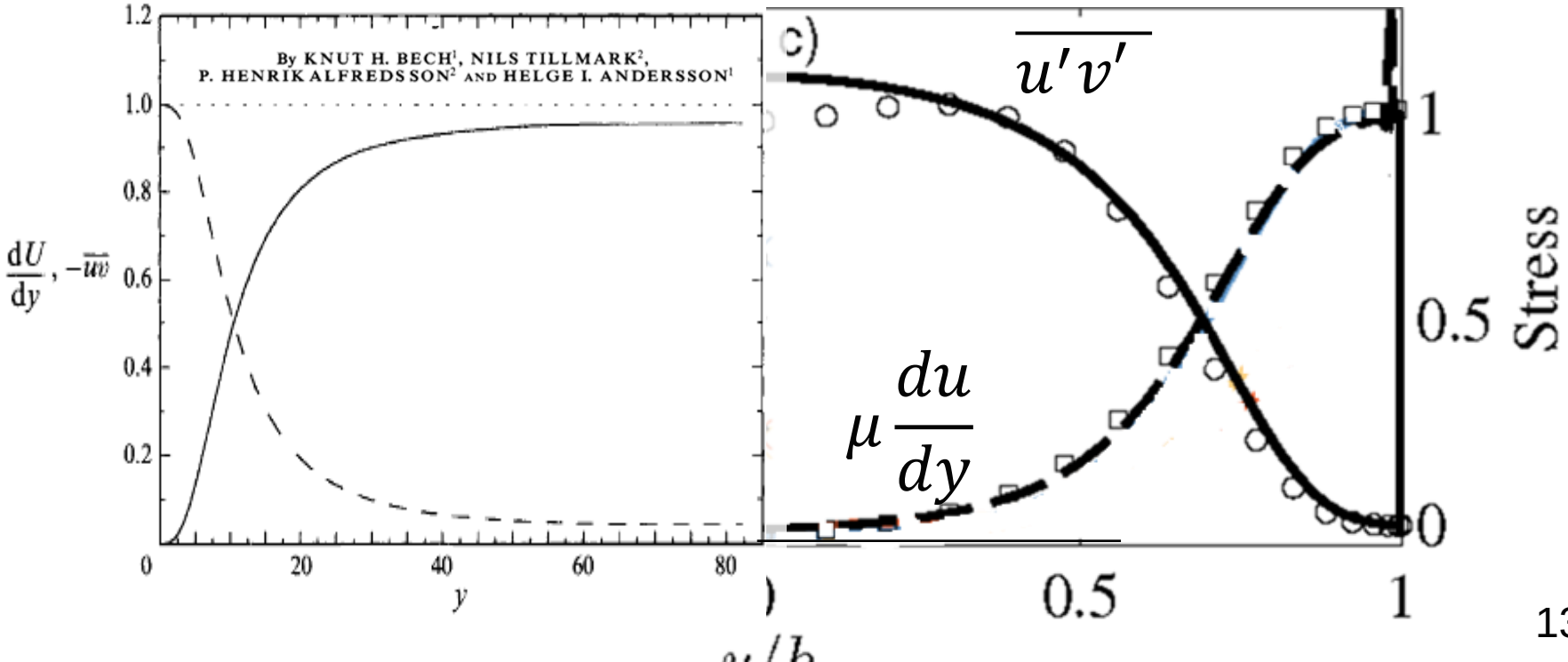


By KNUT H. BECH[1], NILS TILLMARK[2], P. HENRIK ALFREDSSON[2] AND HELGE I. ANDERSSON[1]

Turbulent Stresses & Molecular Stresses

- Turbulent Shear Stress balanced by Viscous Shear Stress

Reynolds shear stress $\overline{u'v'} - \mu\frac{du}{dy} = 1$ Viscous shear stress



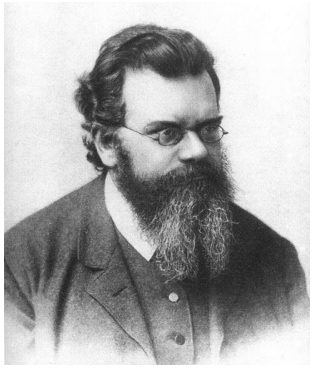
Pressure Tensor in an MD Simulation

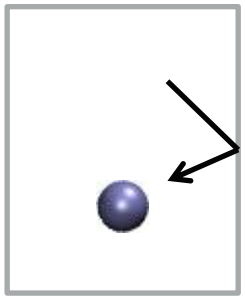
- Pressure definition in a dense molecular system
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

Viscous shear stress $= \underbrace{\sum_{i=1}^{N} \left\langle m_i v_{xi} v_{yi} dS_{yi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left\langle f_{xij} dS_{yij} \right\rangle}_{\text{Configurational}}$

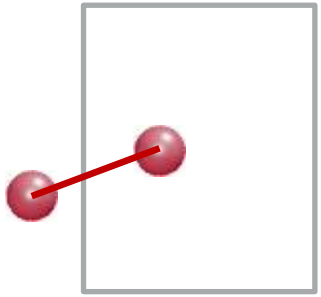
Kinetic theory part

Momentum due to average of molecules crossing a plane and returning





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

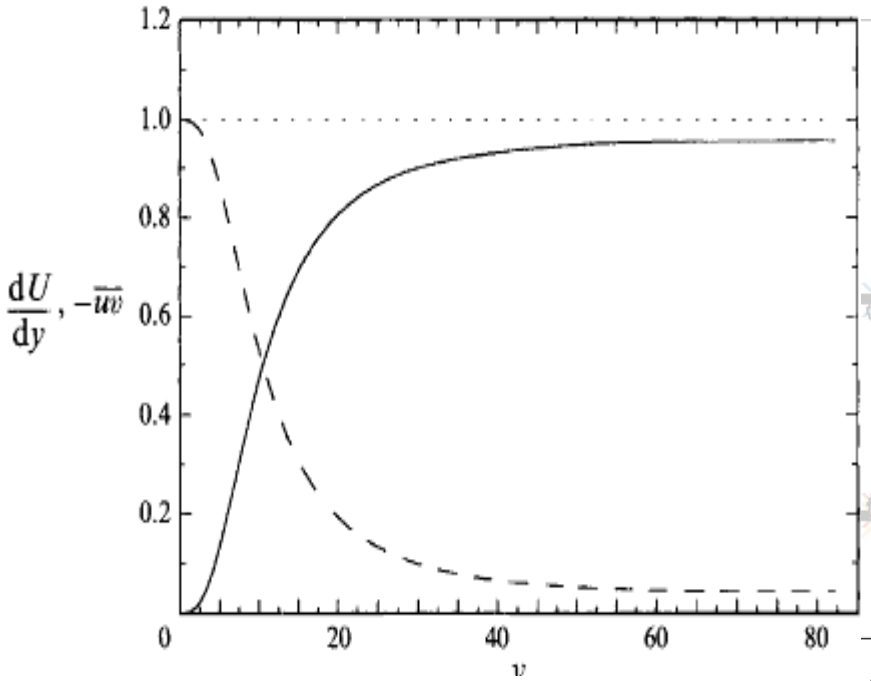


Configurational part

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

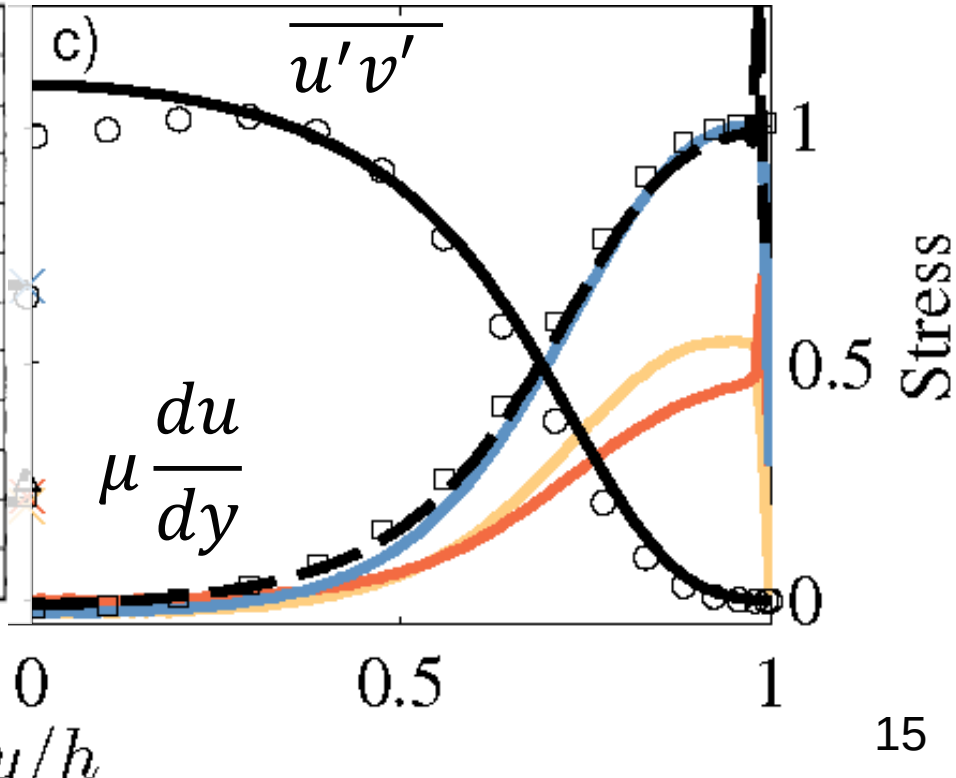
Turbulent Stresses & Molecular Stresses

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



An investigation of turbulent plane Couette flow at low Reynolds numbers

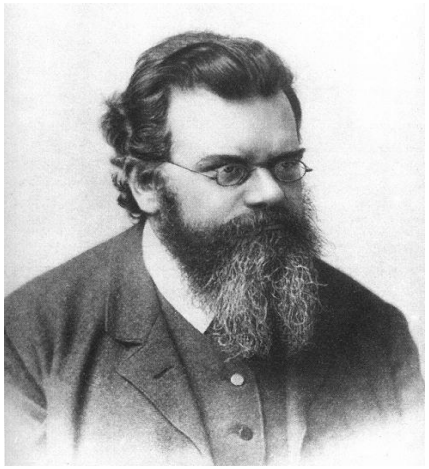
By KNUT H. BECH[1], NILS TILLMARK[2],



Section 1

UNDERSTANDING THE RANGE OF SCALES

Same Concept, Different Scales



Peculiar velocity

$$\dot{r}_i = v_i + u$$

Reynolds' Decomposition

$$u = u' + \bar{u}$$

- Kinetic part of the pressure tensor and Reynolds stress same mathematical quantity averaged over different length/time scales

$$\sum_{i=1}^{N} \overline{\langle \dot{\boldsymbol{r}}_i \dot{\boldsymbol{r}}_i \rangle} = \sum_{i=1}^{N} \overline{\langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle} + \overline{\boldsymbol{u}'\boldsymbol{u}'} + \overline{\boldsymbol{u}\boldsymbol{u}}$$

Molecular average time $\langle \dots \rangle$ Continuum average time $\overline{\dots}$

Continuum Equations

- Right hand side is the divergence of a pressure tensor

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

- Reynold's Decomposition gives us,

$$\frac{\partial}{\partial t}\rho \overline{\boldsymbol{u}} + \boldsymbol{\nabla} \cdot \rho \overline{uv} = -\boldsymbol{\nabla} \cdot \rho \overline{u'v'} - \boldsymbol{\nabla} \cdot \boldsymbol{\Pi}$$

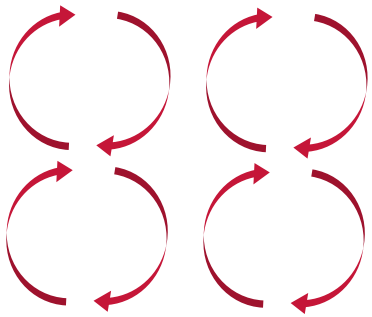
- Where the pressure tensor can be expanded to

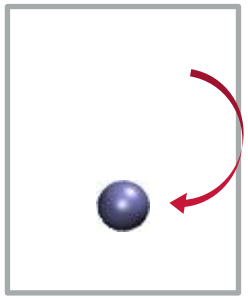
$$\frac{\partial}{\partial t}\rho \overline{\boldsymbol{u}} + \boldsymbol{\nabla} \cdot \rho \overline{uv} = -\boldsymbol{\nabla} \cdot \underbrace{\rho\ \overline{u'\ v'}}_{\text{Reynold's Stress Tensor}} \underbrace{-\sum_{i=1}^{N} \left\langle m_i v_{xi} v_{yi} dS_{yi} \right\rangle}_{\text{Kinetic}} \underbrace{-\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \left\langle f_{xij} dS_{yij} \right\rangle}_{\text{Configurational}}$$

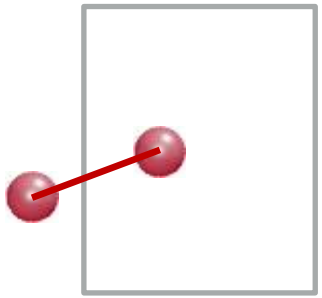
A Hierarchy of Scales

- At least three scales in the problem
  - Turbulent fluctuations
  - Kinetic fluctuations
  - Configurational part due to liquid structure

$$\underbrace{\rho\ \overline{u'\ v'}}_{\text{Reynold's Stress Tensor}} \quad \underbrace{+\sum_{i=1}^{N}\left\langle m_i v_{xi} v_{yi} dS_{yi}\right\rangle}_{\text{Kinetic}} \quad \underbrace{+\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left\langle f_{xij} dS_{yij}\right\rangle}_{\text{Configurational}}$$



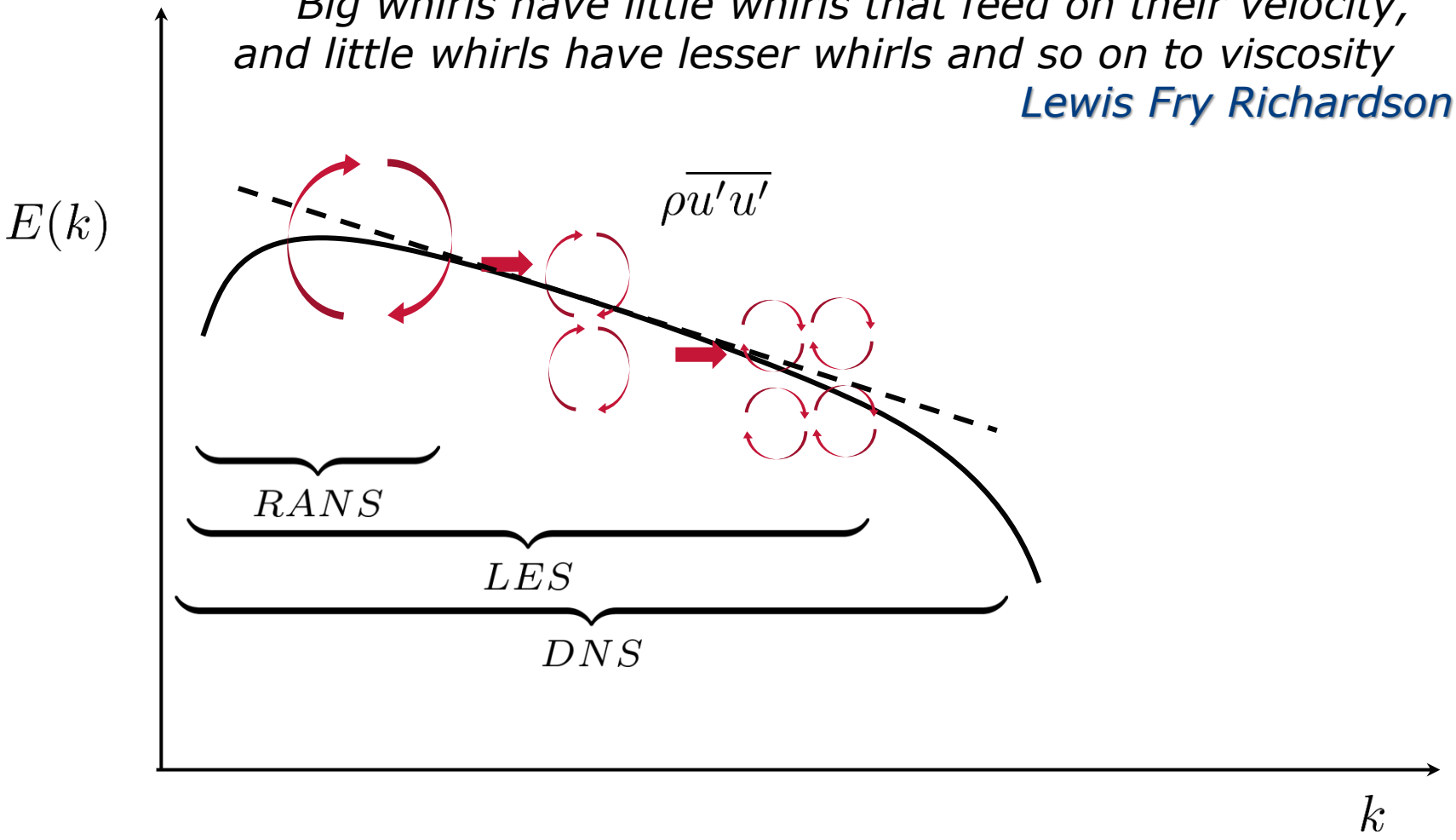




Across the Scales

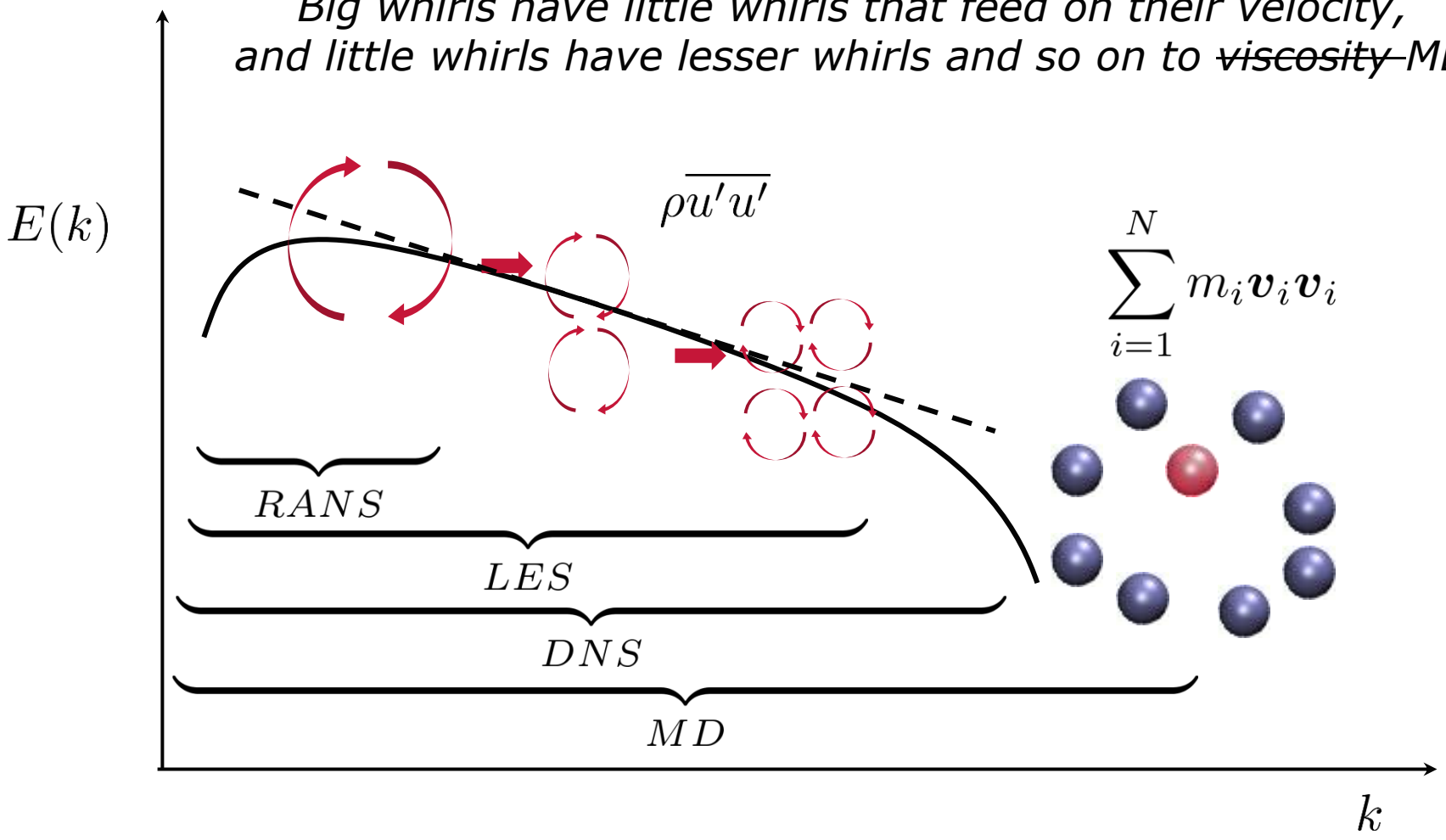
Big whirls have little whirls that feed on their velocity, and little whirls have lesser whirls and so on to viscosity

Lewis Fry Richardson

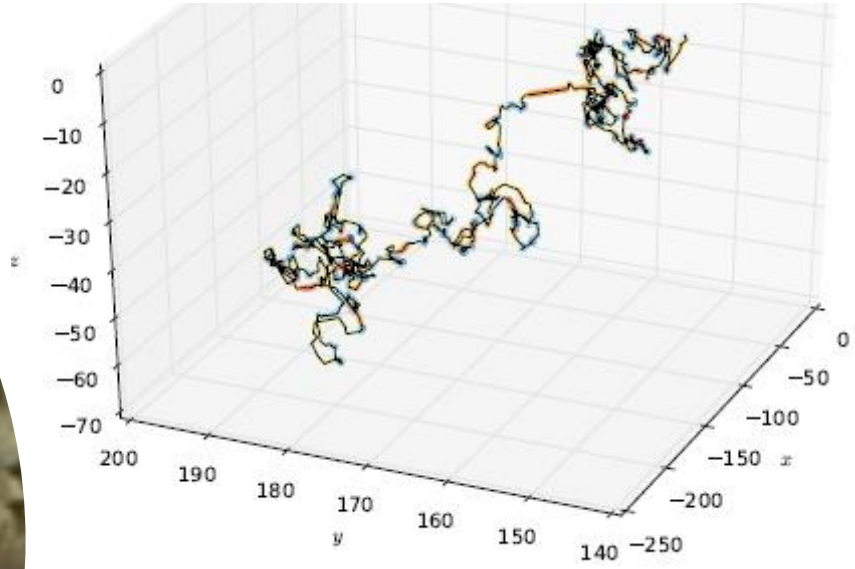


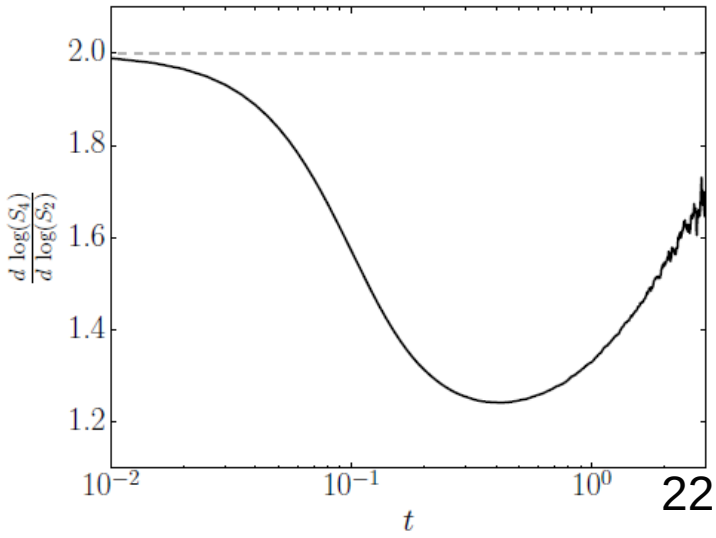
Across the Scales

Big whirls have little whirls that feed on their velocity, and little whirls have lesser whirls and so on to ~~viscosity~~ MD

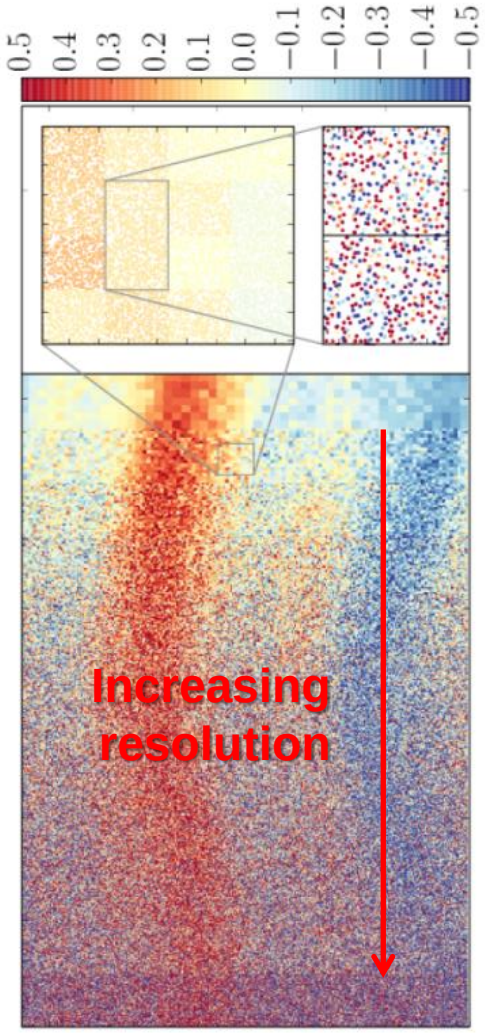


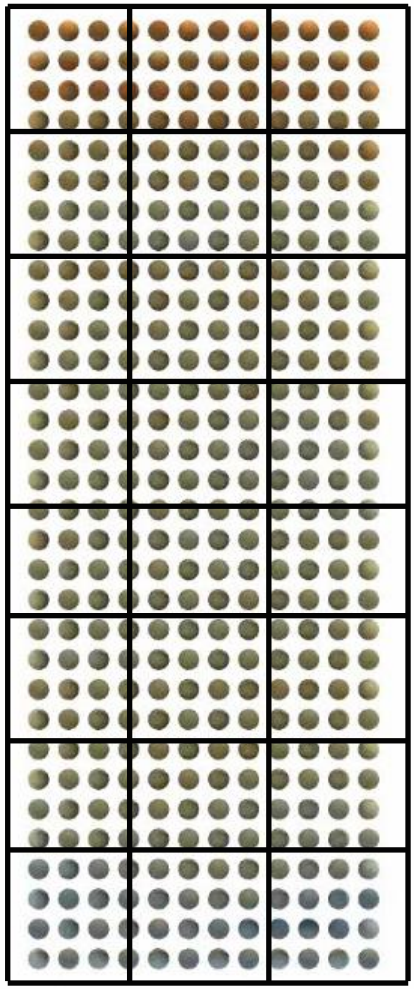
Molecular Structure





Refining our Grid

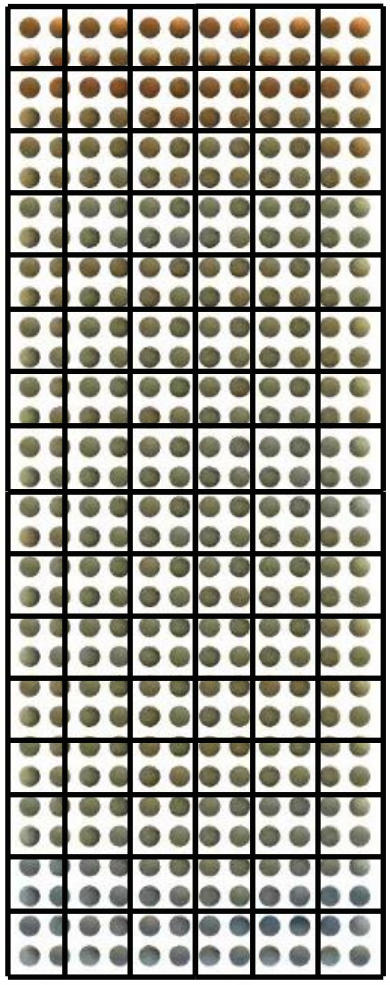




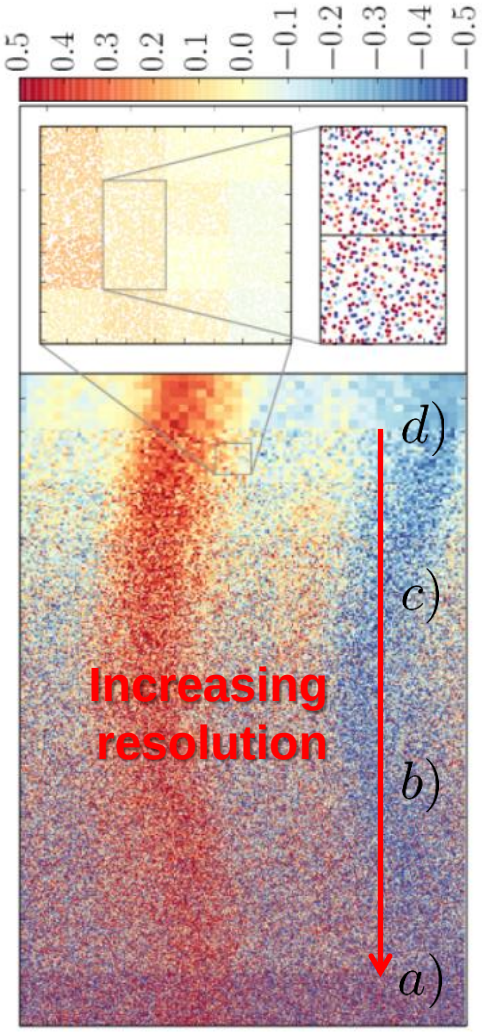
$$\boldsymbol{u} = \frac{1}{N}\sum_{i=1}^{N}\langle \dot{\boldsymbol{r}}_i \rangle$$

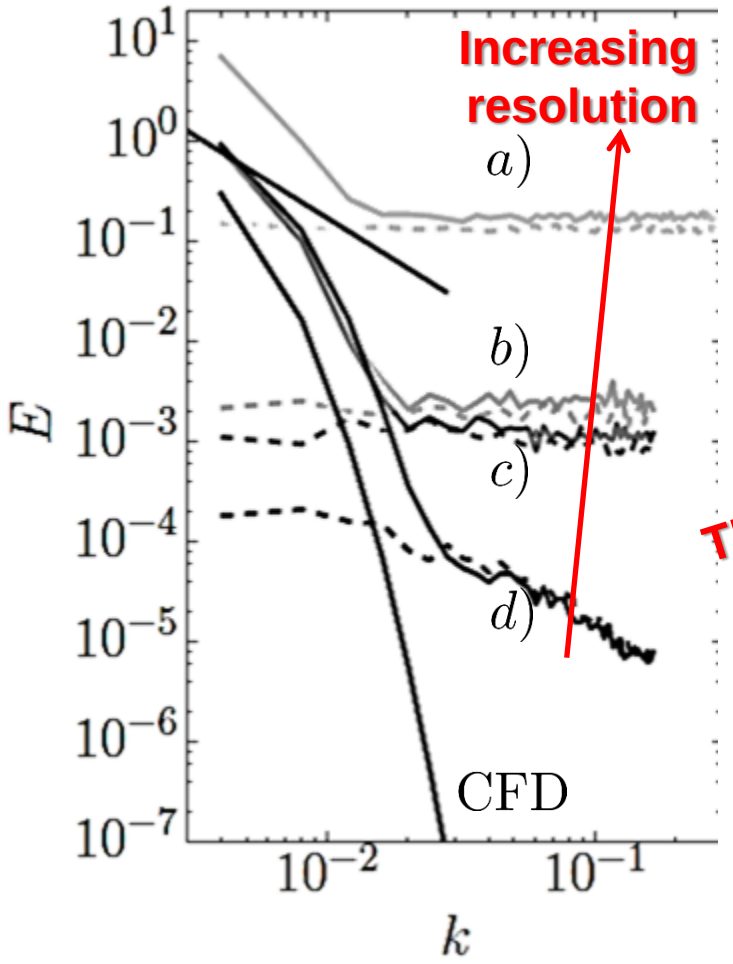
Increasing resolution

$$T = \frac{1}{3N}\sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i^2}{m_i} \right\rangle$$



Spectra





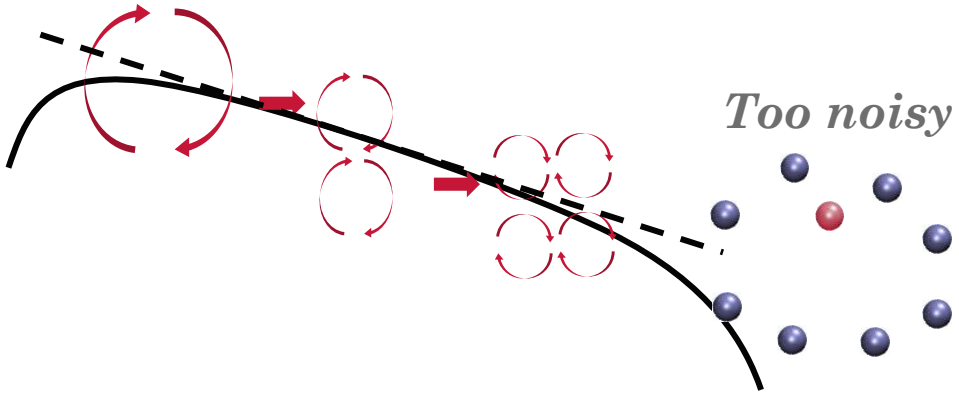
The more we zoom in, the less we can see

Dotted lines - laminar initial condition at same Re

Section 2

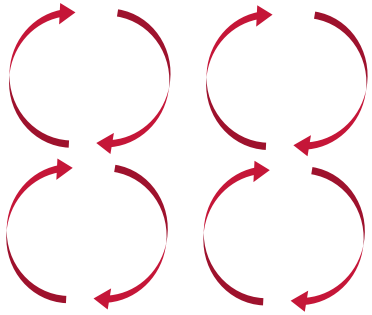
MOLECULAR STRUCTURE AND THE LINK TO VISCOSITY

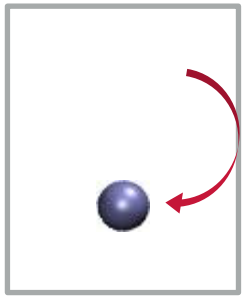
A Hierarchy of Scales

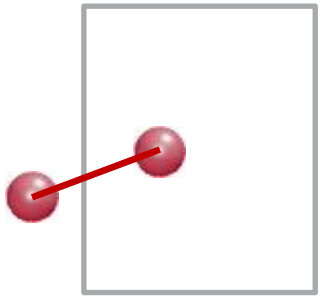


Can we gain insight from the liquid structure?

$$\underbrace{\rho\ \overline{u'\ v'}}_{\text{Reynold's Stress Tensor}} \underbrace{+\sum_{i=1}^{N}\left\langle m_i v_{xi} v_{yi} dS_{yi}\right\rangle}_{\text{Kinetic}} \underbrace{+\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left\langle f_{xij} dS_{yij}\right\rangle}_{\text{Configurational}}$$

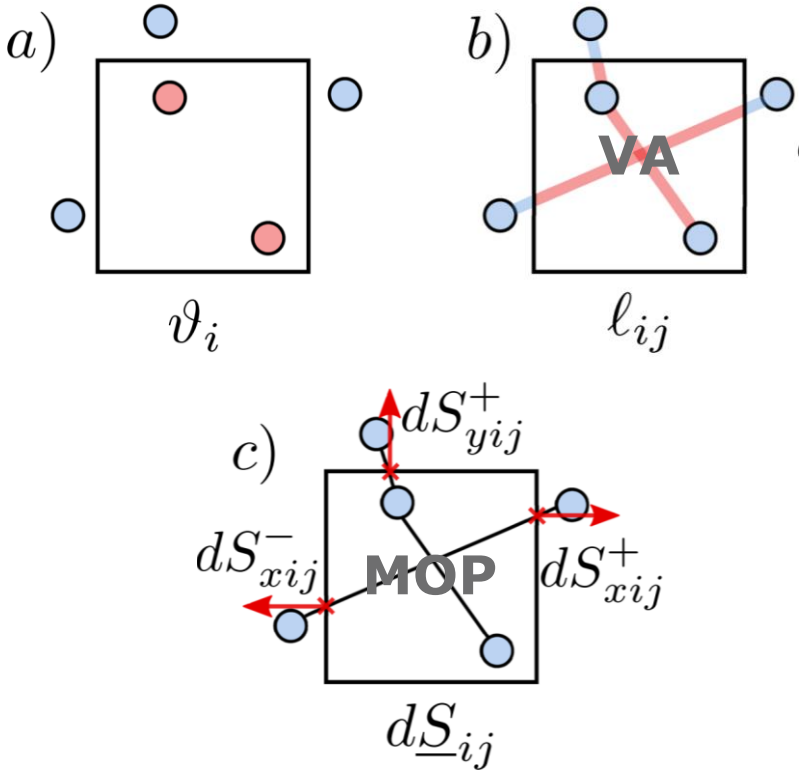


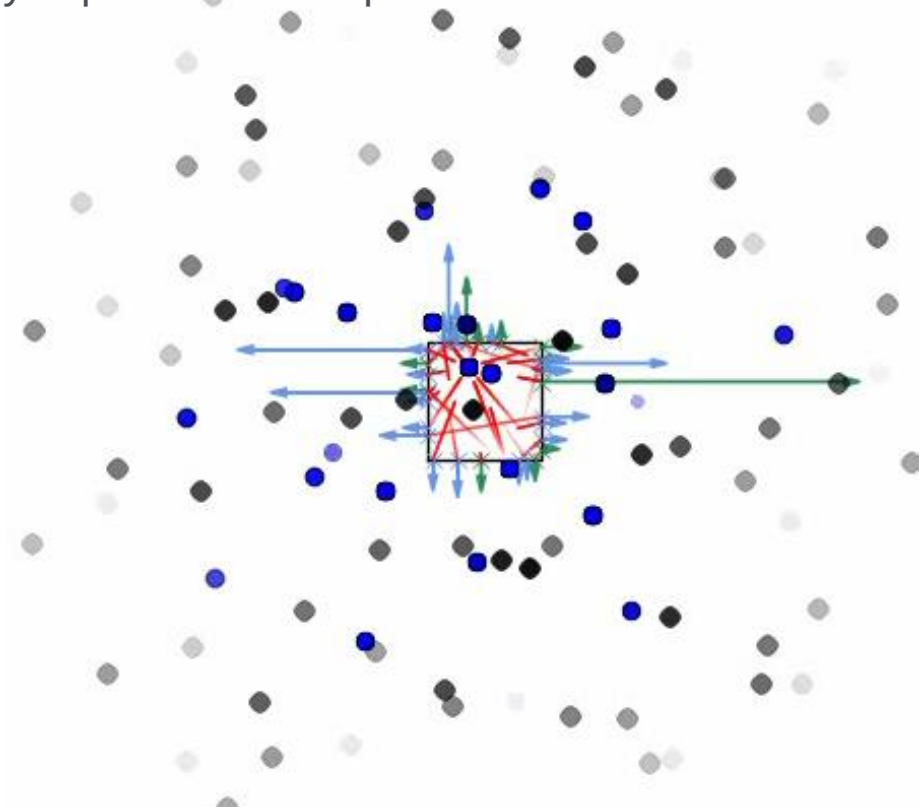




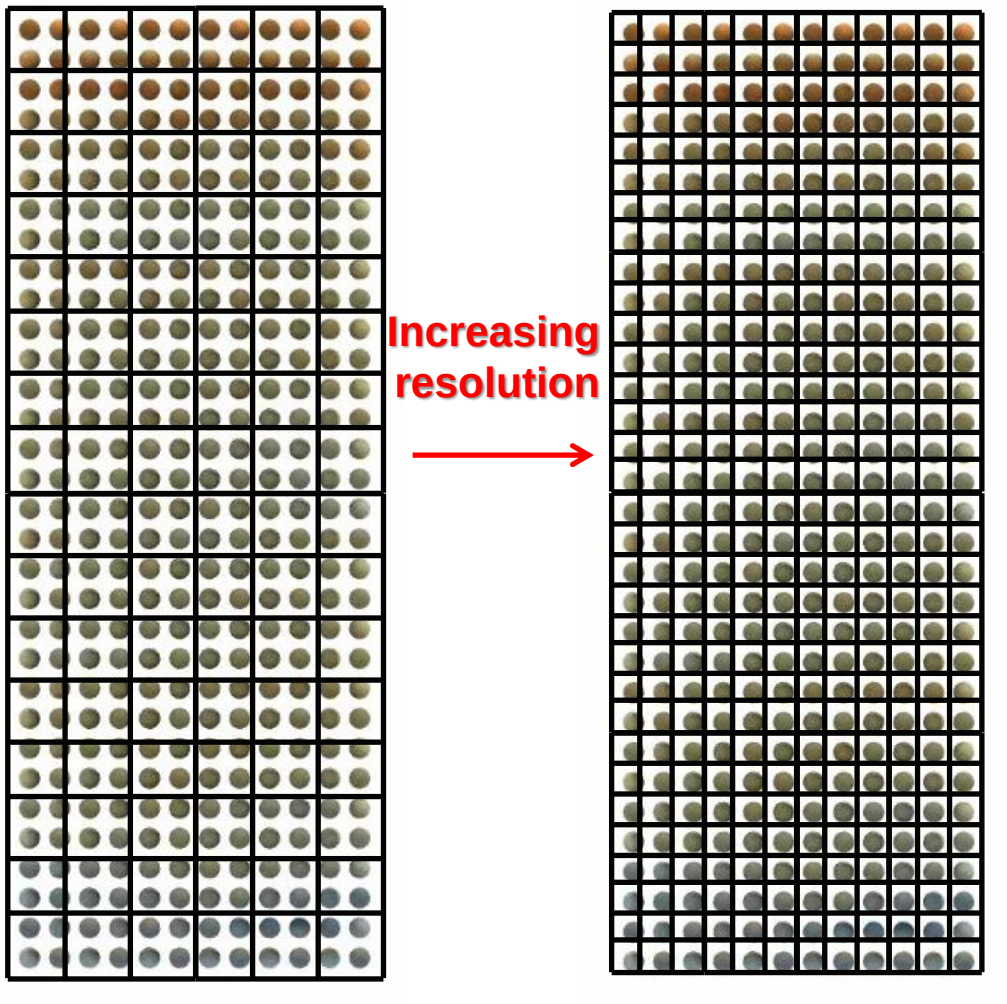
The Stress Tensor

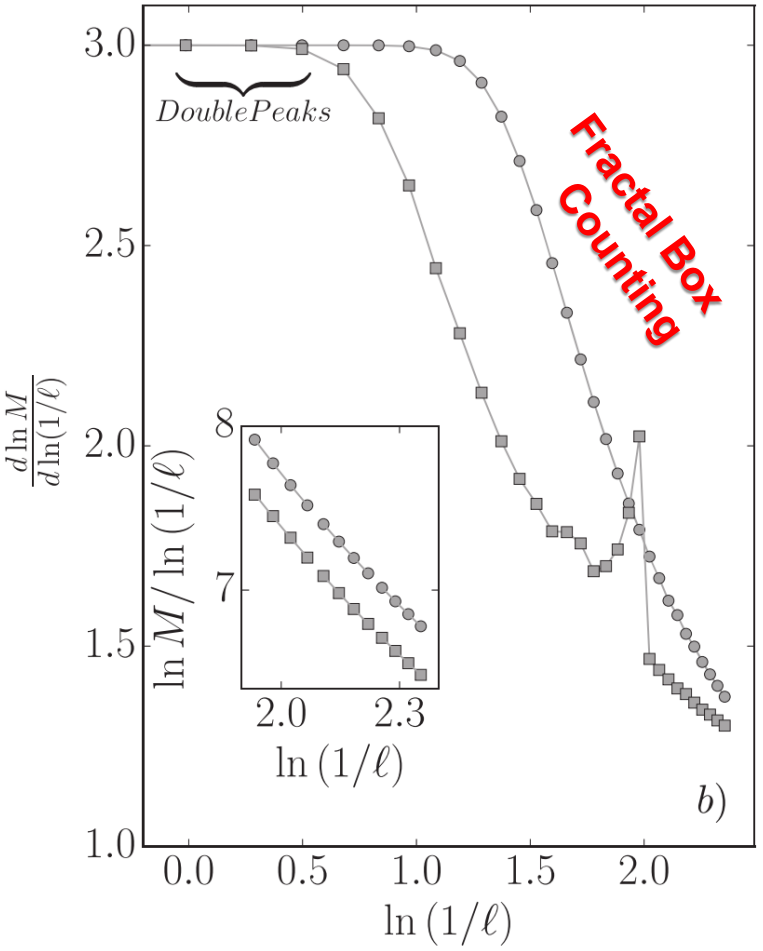
- a) Virial, b) Volume Averaged (VA) and c) Surface (MOP) Stresses
  - Even with one particle in a cell, very complex physics
  - Stress is the right hand side so fully captures the complex fluid behaviour





Taking the Zero Volume Limit





Configuration Stress PDF

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VA (blue) and MOP (red)

Skewed Gaussian PDFs

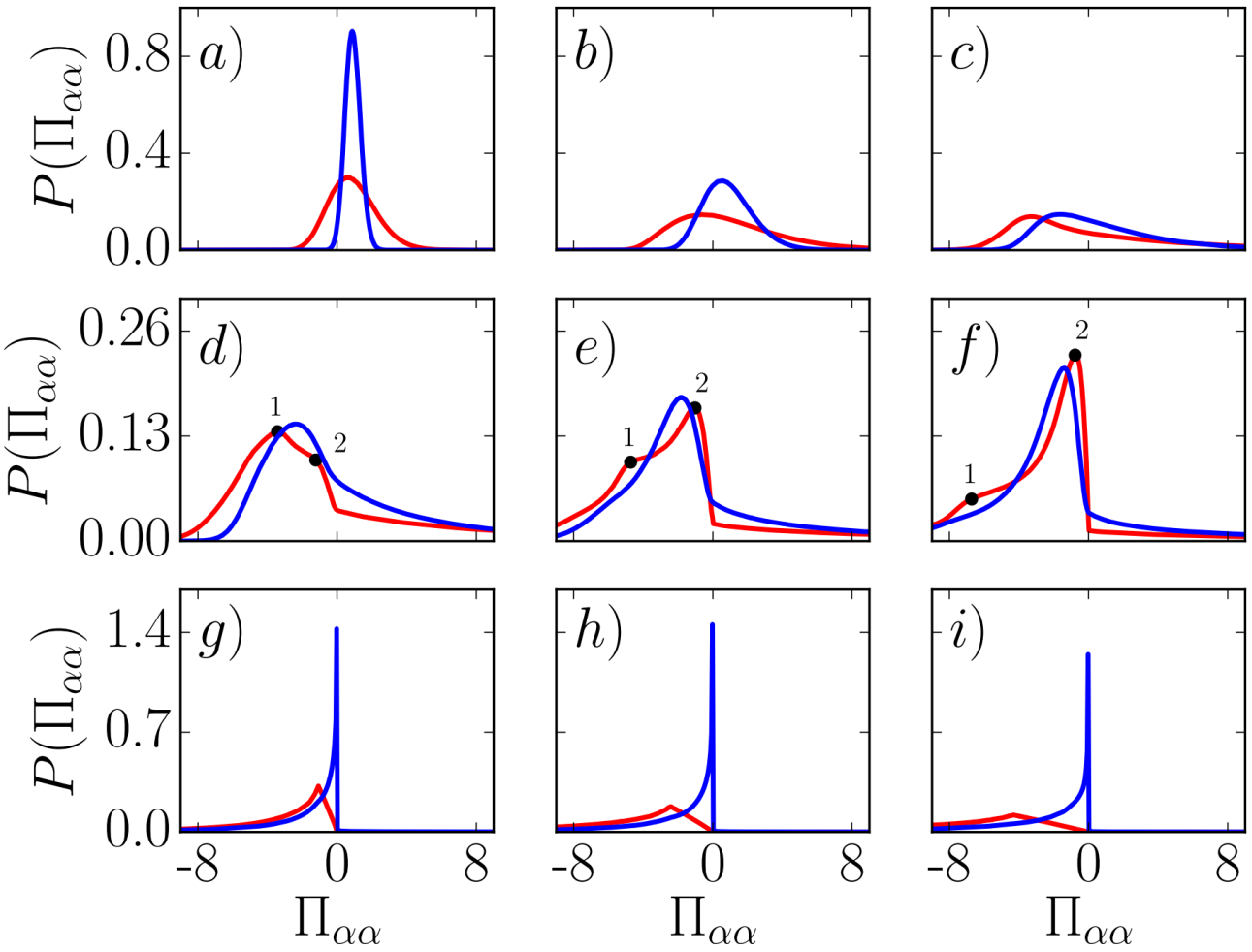
ℓ=6.84, 3.04, 1.52

Two peak region

ℓ=1.01,0.76,0.61

Limiting cases PDF

ℓ=0.19,0.127,0.095



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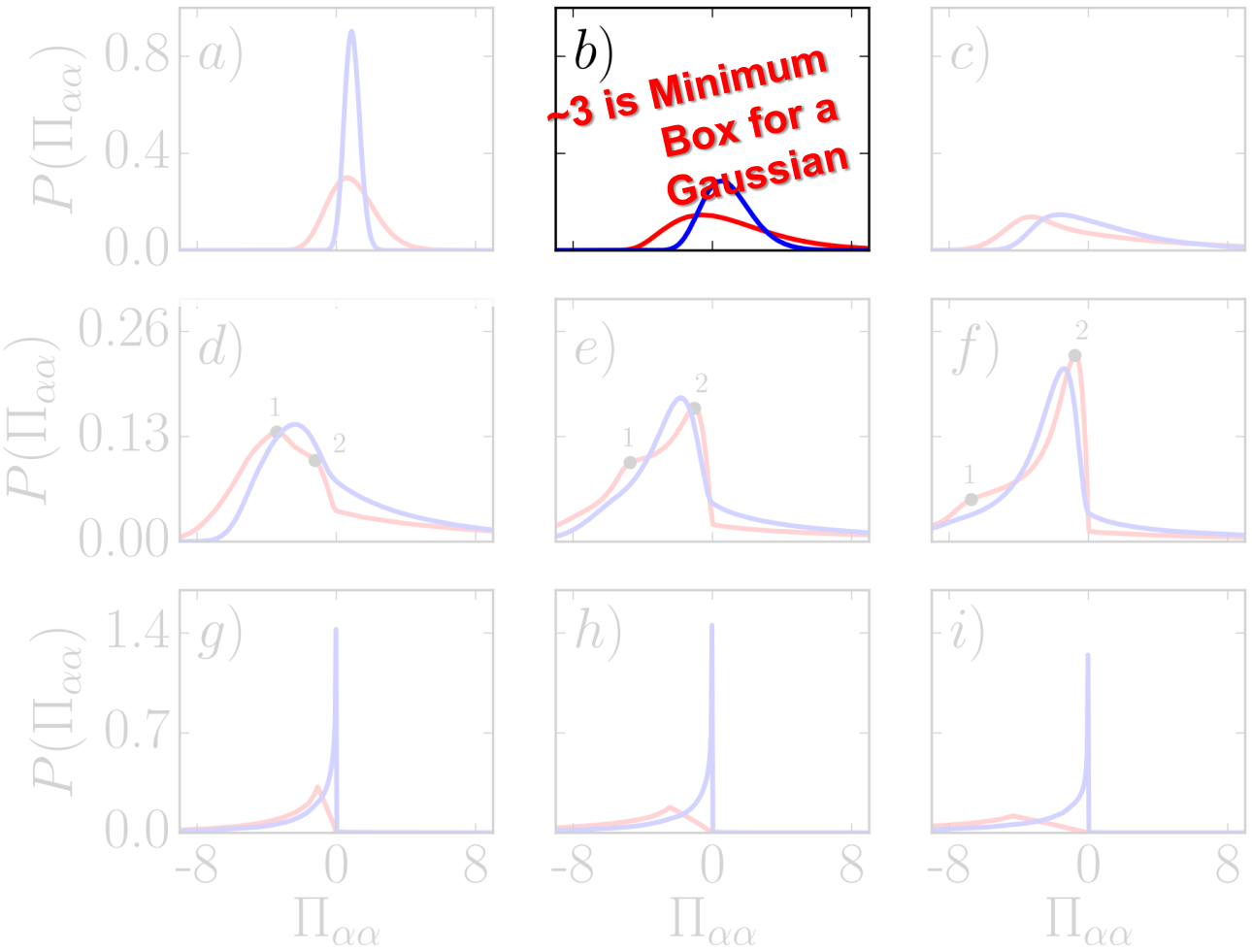

From Stress to Viscosity

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- Approximate stress in terms of viscosity

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

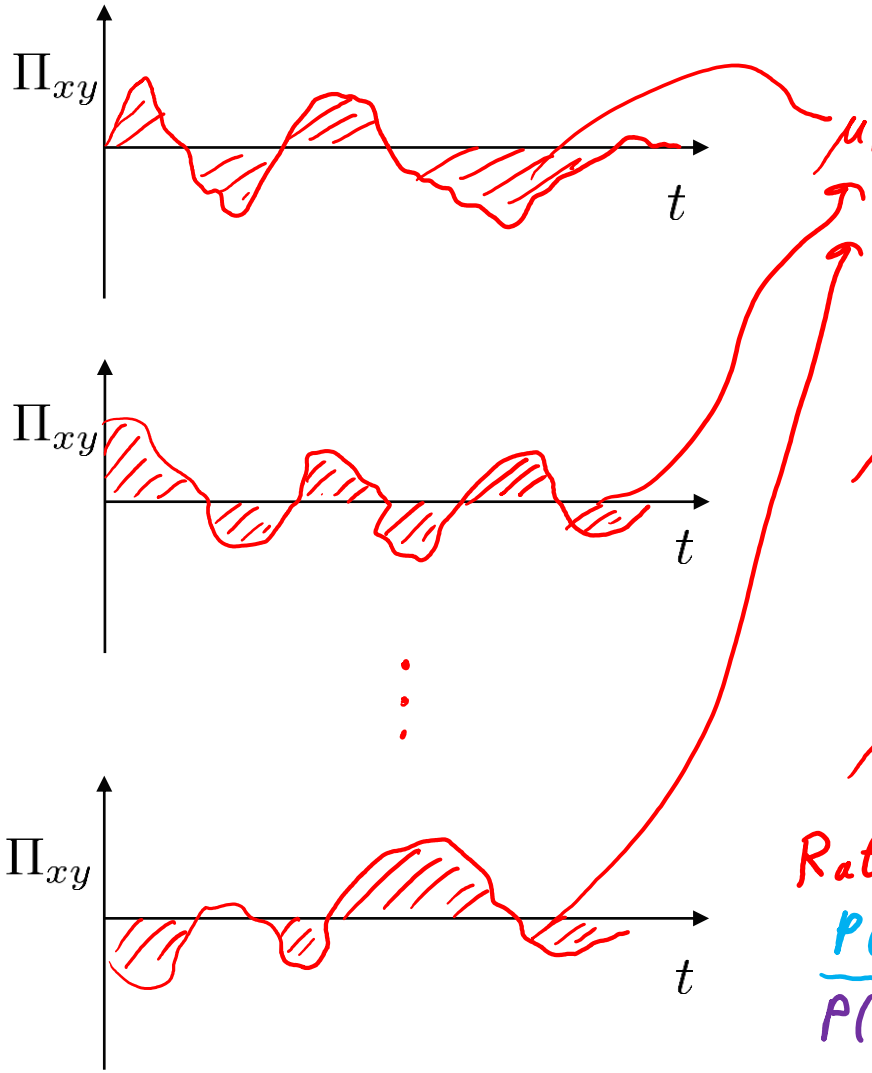
- Viscosity from the integral of the ensemble averaged shear-stress correlation (Green Kubo)

$$\mu = \frac{V}{k_B T}\int_0^t \left\langle \Pi_{xy}(\tau)\Pi_{xy}(0) \right\rangle d\tau$$

- We can take **individual stress trajectories** to get the “viscuit” which sum to give the overall viscosity

$$\mu_u = \frac{V}{k_B T}\int_0^t \Pi_{xy}(\tau)\Pi_{xy}(0)\ \ d\tau$$

Viscosity



Viscosity

$$\mu_u = \frac{V}{k_B T} \int_0^t \Pi_{xy}(\tau)\Pi_{xy}(0)\ d\tau$$

$$\mu = \langle \mu_u \rangle$$

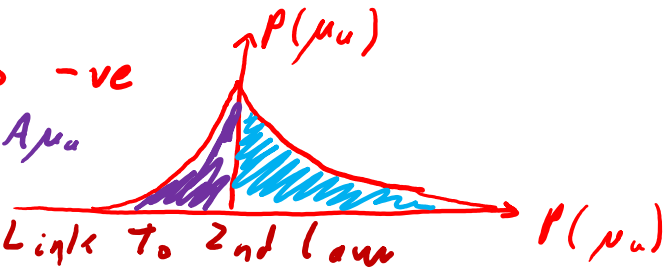
or, taking PDF of μ_u

$$\mu = \int_{-\infty}^{\infty} P(\mu_u)\,\mu_u\, d\mu_u$$

Ratio +ve to -ve

$$\frac{P(\mu_u > 0)}{P(\mu_u < 0)} = e^{-A\mu_u}$$

↳ Link to 2nd law



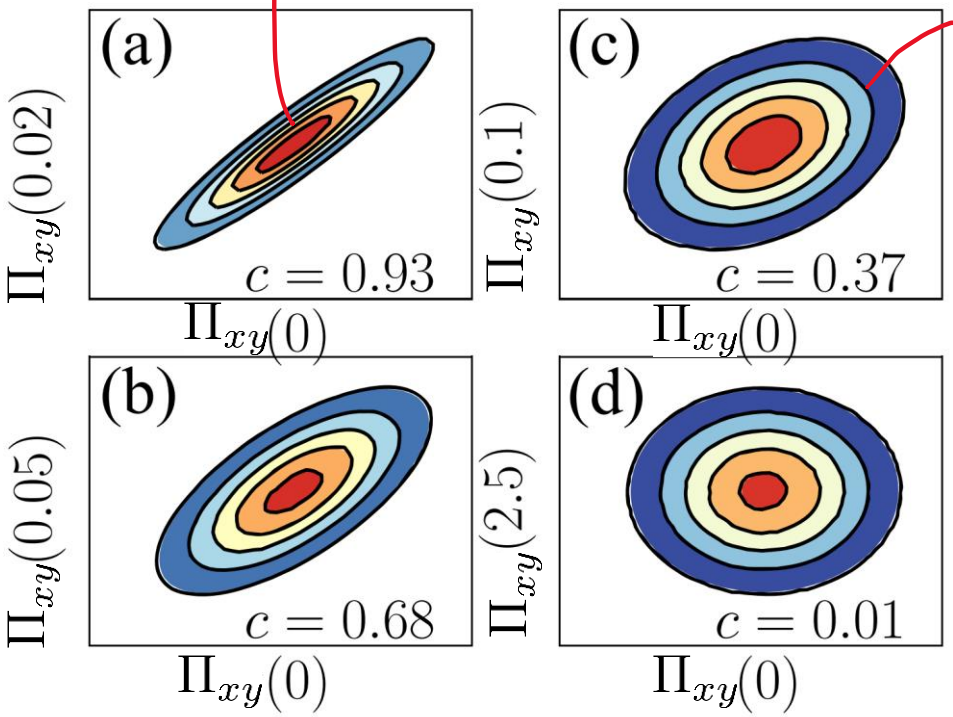
Viscosity

- Correlation used to get viscosity could be used in a stochastic model

$$\mu = \frac{V}{k_B T} \int_0^t \underbrace{\langle \Pi_{xy}(\tau)\Pi_{xy}(0) \rangle}_{c(t)} d\tau$$

lines random model

colour MD data



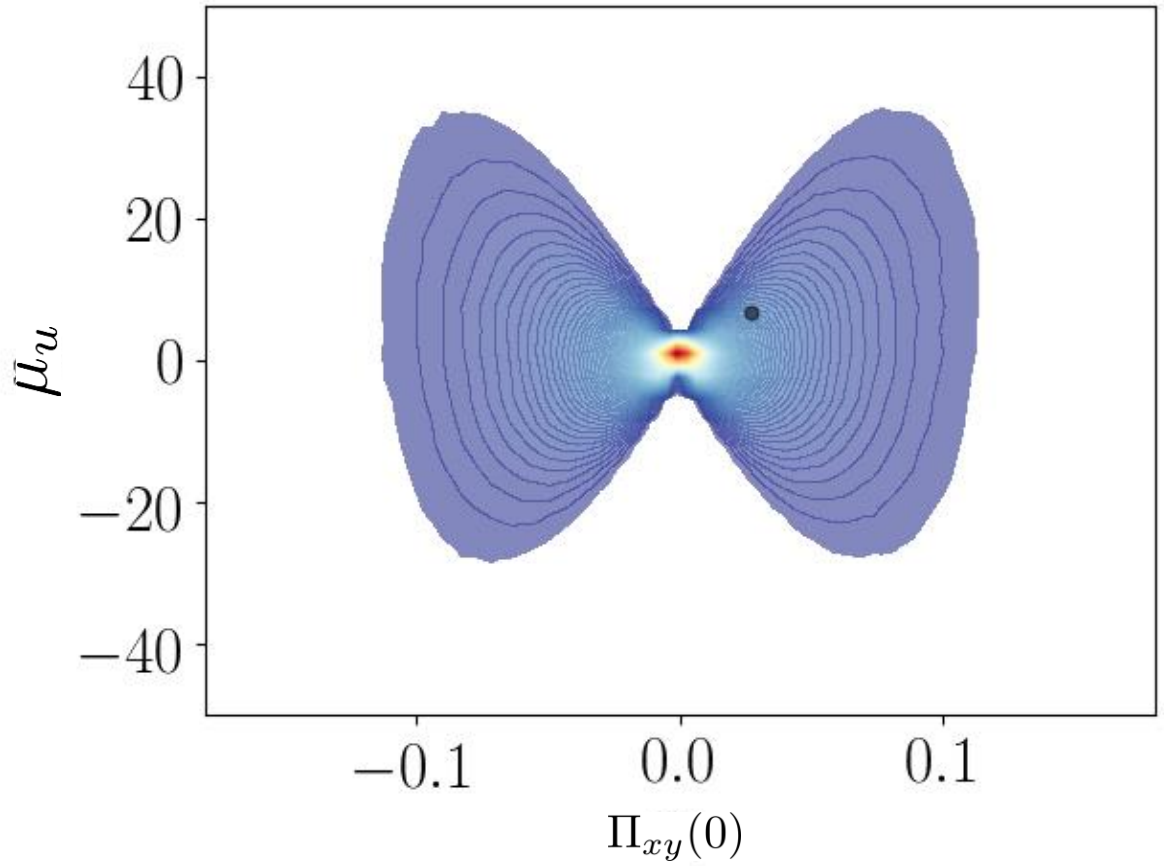
- Initial stress predicts final stress using Gaussian random noise

$$\Pi^S_{xy}(t) = c(t)\Pi^S_{xy}(0) + \xi\sqrt{1 - c(t)^2}$$

- Shown by joint-PDF of initial stresses vs stress at time t

Viscuit

- However, stochastic model does not capture current state of stress – structure determines the evolution, evolution determines the viscosity



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Section 3

NON EQUILIBRIUM MOLECULAR DYNAMICS (NEMD)

Non Equilibrium Molecular Dynamics

- Non Equilibrium Molecular Dynamics (NEMD)
  - Structure of the molecules is the key
  - An MD system is completely described by position $\boldsymbol{r}_i$ and velocity $\boldsymbol{v}_i$ of all N molecules in the system
  - Theoretical underpinning in the form of the Liouville equation – a continuity equation in 6N degrees $f = f(\boldsymbol{r}_i, \boldsymbol{v}_i)$ which gives,

$$\frac{df}{dt} = \sum_{i=1}^{N} \left[\frac{\partial \boldsymbol{r}_i}{\partial t} \frac{\partial f}{\partial \boldsymbol{r}_i} + \frac{\partial \boldsymbol{v}_i}{\partial t} \frac{\partial f}{\partial \boldsymbol{v}_i} \right]$$

- New Special interest group (SIG) on NEMD
  - First meeting **17th January 2020** at Brunel, London, please let me know if you're interested in joining
  - Focus on statistical mechanics, molecular microscopic underpinnings of fluid dynamics and include a wider community in the UKFN
  - Potential applications in a wide range of problems in fluid dynamics

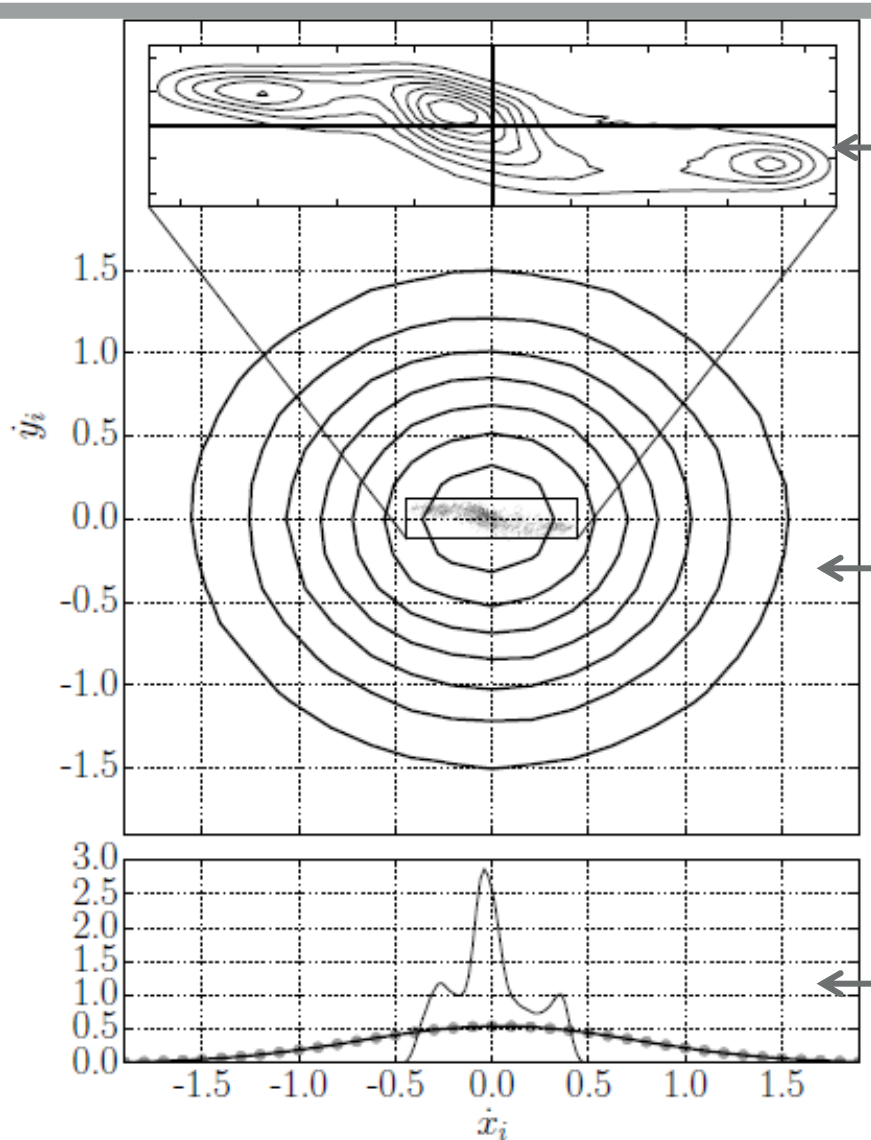
Summary

- Molecular Dynamics (MD) turbulent minimal channel
  - Large scale flow matches continuum simulation of turbulent flow
  - MD can model the full range of scales, below the Kolmogorov length scale, down to the molecular lattice
- But impossible to get a picture of these small scales due to molecular fluctuations or “noise”
  - Instead of noisy velocity, we measure stresses and viscosity
  - Taking PDF of stress and “viscuit” provides further insights
- Non-equilibrium molecular dynamics (NEMD)
  - The study of fluids phenomena from molecular structure
  - New SIG to explore fundamental MD fluid simulation

Section 4

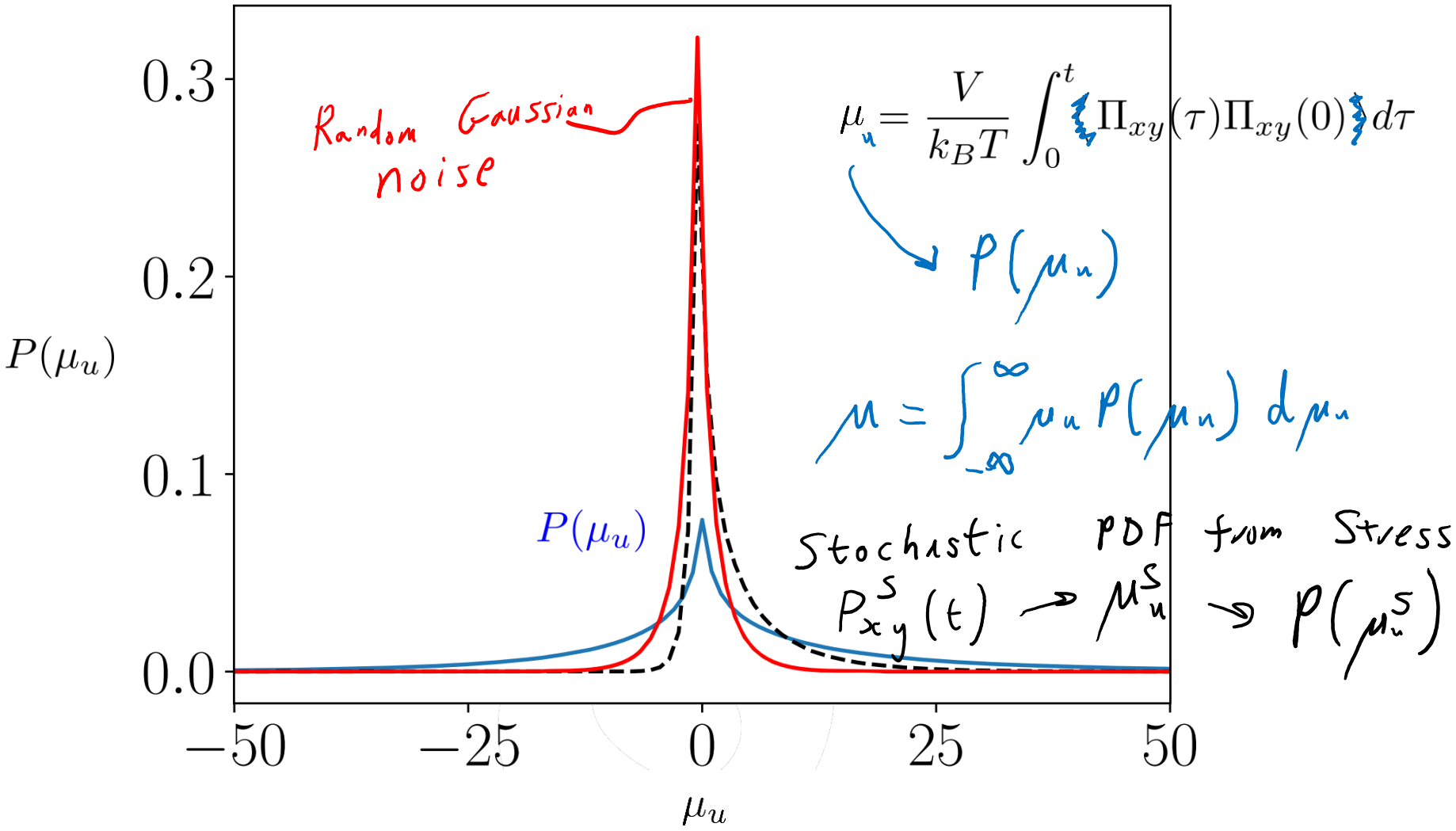
BONUS SLIDES

Probability density functions (PDF)

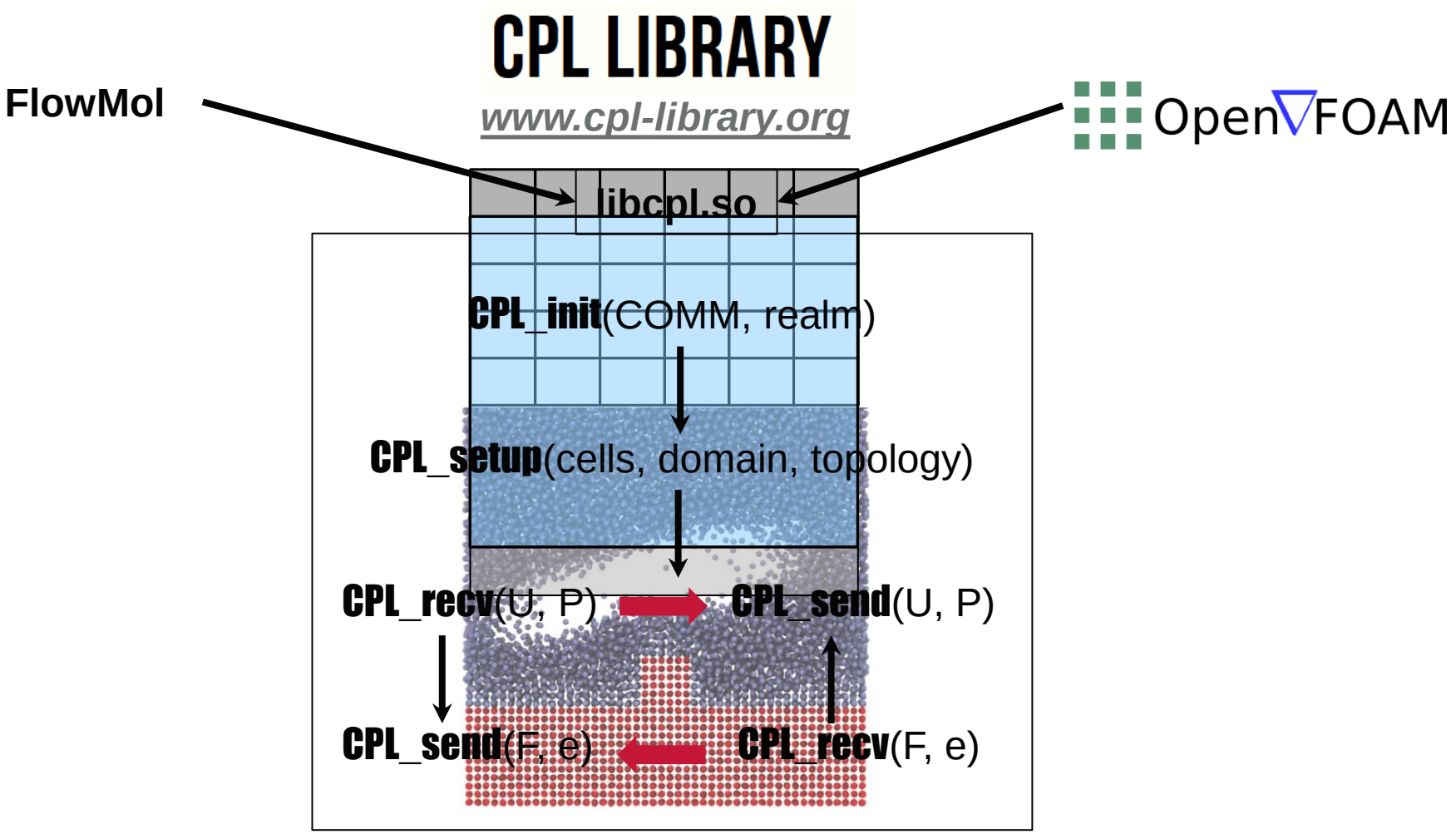


- PDF of average velocity shows sweeps and ejections
  - Seen in near wall turbulence
  - Isolates signal from the noise
- PDF of molecular velocities show Gaussian behaviour
  - Much wider range of velocities
  - Symmetrical in x and y
  - No observable flow
- Side view of PDFs
  - Projection of x

Viscuit


0.3
0.2
0.1
0.0
$P(\mu_u)$
−50
−25
0
25
50
μ_u
Random Gaussian noise
$P(\mu_u)$
$\mu_u = \frac{V}{k_B T} \int_0^t \langle \Pi_{xy}(\tau)\Pi_{xy}(0) \rangle d\tau$
$P(\mu_u)$
$\mu = \int_{-\infty}^{\infty} \mu_u P(\mu_u)\, d\mu_u$
Stochastic PDF from Stress
$P_{xy}^S(t) \rightarrow \mu_u^S \rightarrow P(\mu_u^S)$

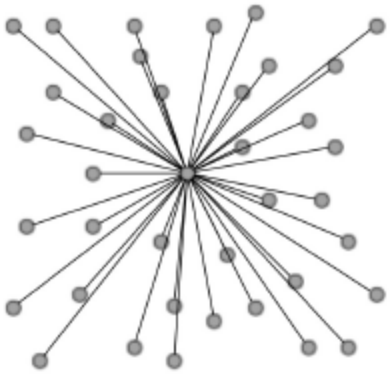
Coupled Simulation Software

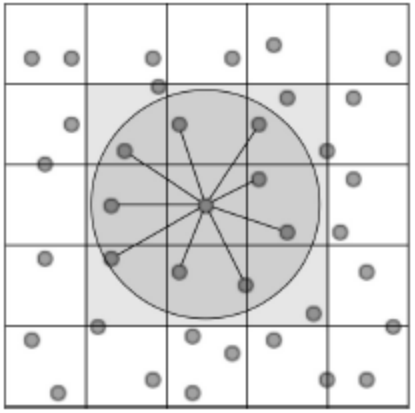


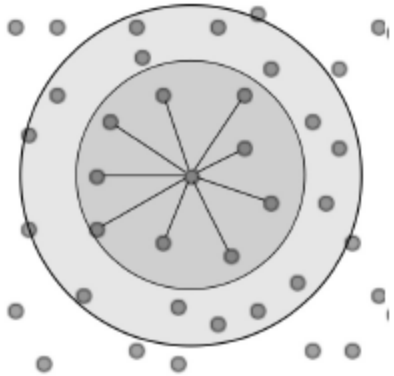
MD Computing

- 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)

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

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

MD Computing – Parallel optimisations

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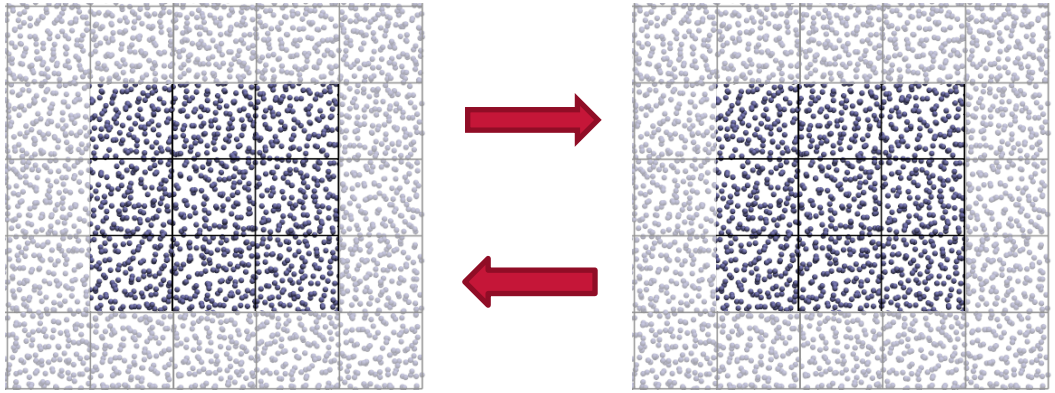
Localisations lends itself to parallel computing using MPI

- Spatial decomposition employed as in CFD
- Halo cells (ghost molecules) are used to link adjacent regions



Halo exchange of variable amounts of data

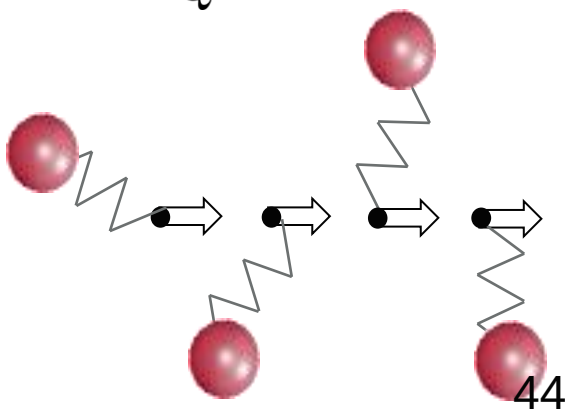
- MPI_Send
- MPI_Probe and MPI_Recv

NEMD - Tethering and Thermostatting

- 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)
- We induce temperature gradients and flows
  - Thermostats (e.g. Nosé Hoover)
    - Remove heat from system
  - Tethered molecules
    - (An)harmonic spring to tether site
  - With sliding
    - Slide site and (optionally) molecules

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

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



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