Measuring Heat Flux Beyond Fourier's Law

Edward Smith,
Peter Daivis and Billy Todd
15/04/19
Swinburne University

Summary

- Introduction
  - Heat Flux - Fourier’s law and beyond
  - Molecular Dynamics

- Two Cases
  - Temperature-Driven Flow
  - Shear-Driven (Couette) Flow

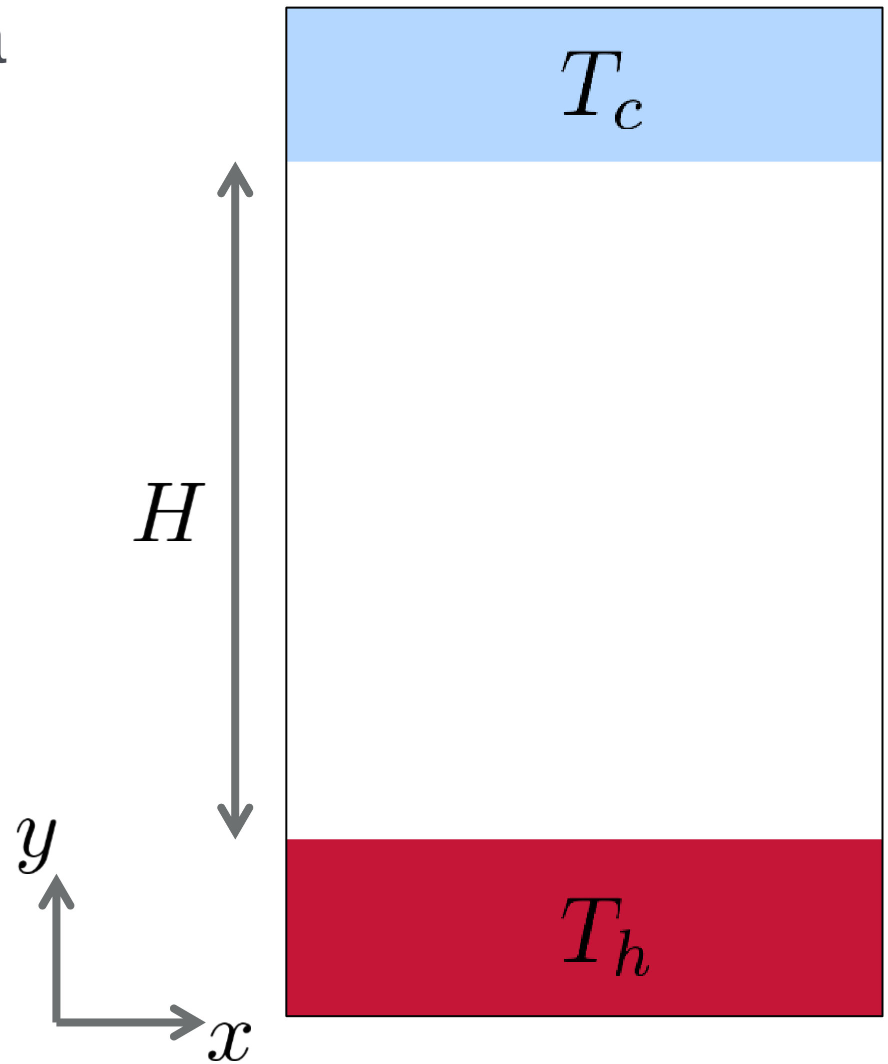
Section 1

INTRODUCTION

Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

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



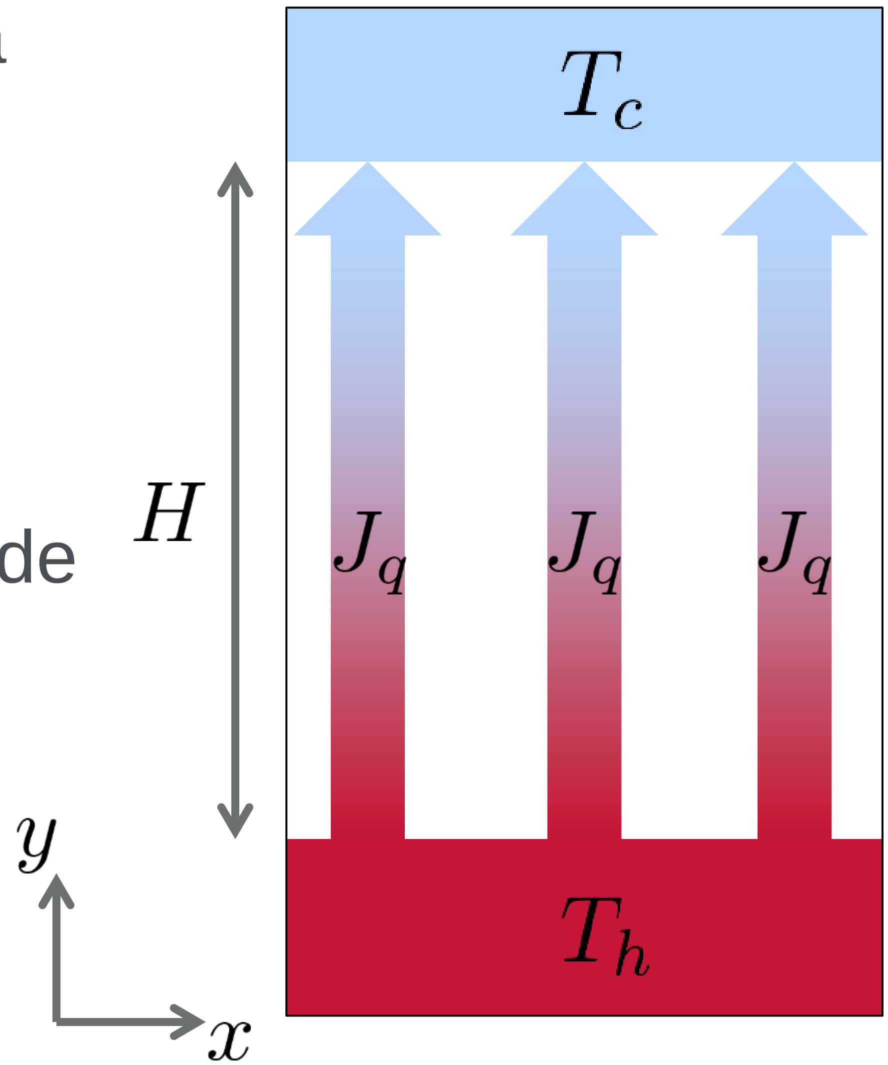
Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

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

- Proportional to magnitude of temperature gradient

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



Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

$$\boldsymbol{J}_q(\boldsymbol{\nabla} T, \boldsymbol{\nabla} \boldsymbol{u}) \approx \boldsymbol{\nabla} T \frac{\partial \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} T} + \ldots$$

Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

$$\boldsymbol{J}_q(\boldsymbol{\nabla} T, \boldsymbol{\nabla} \boldsymbol{u}) \approx \boldsymbol{\nabla} T \frac{\partial \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} T} + \ldots$$

λ

Fourier's law is first
term in expansion

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

Beyond Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

$$\boldsymbol{J}_q(\boldsymbol{\nabla} T, \boldsymbol{\nabla} \boldsymbol{u}) \approx \boldsymbol{\nabla} T \frac{\partial \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} T} + \dots$$

λ

$$+ \boldsymbol{\nabla} T \boldsymbol{\nabla} \boldsymbol{u} \frac{\partial^2 \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} \boldsymbol{u} \partial \boldsymbol{\nabla} T}$$

- Only temperature gradient and strain cross term is non-zero to 1^{st} order

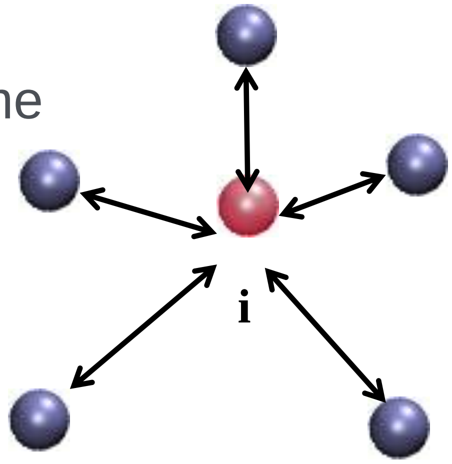
$$\mathbf{J}_q \approx -\boldsymbol{\lambda}_{\text{eff}} \cdot \nabla T$$

Molecular Dynamics

Brunel University London

Discrete molecules in continuous space

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



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

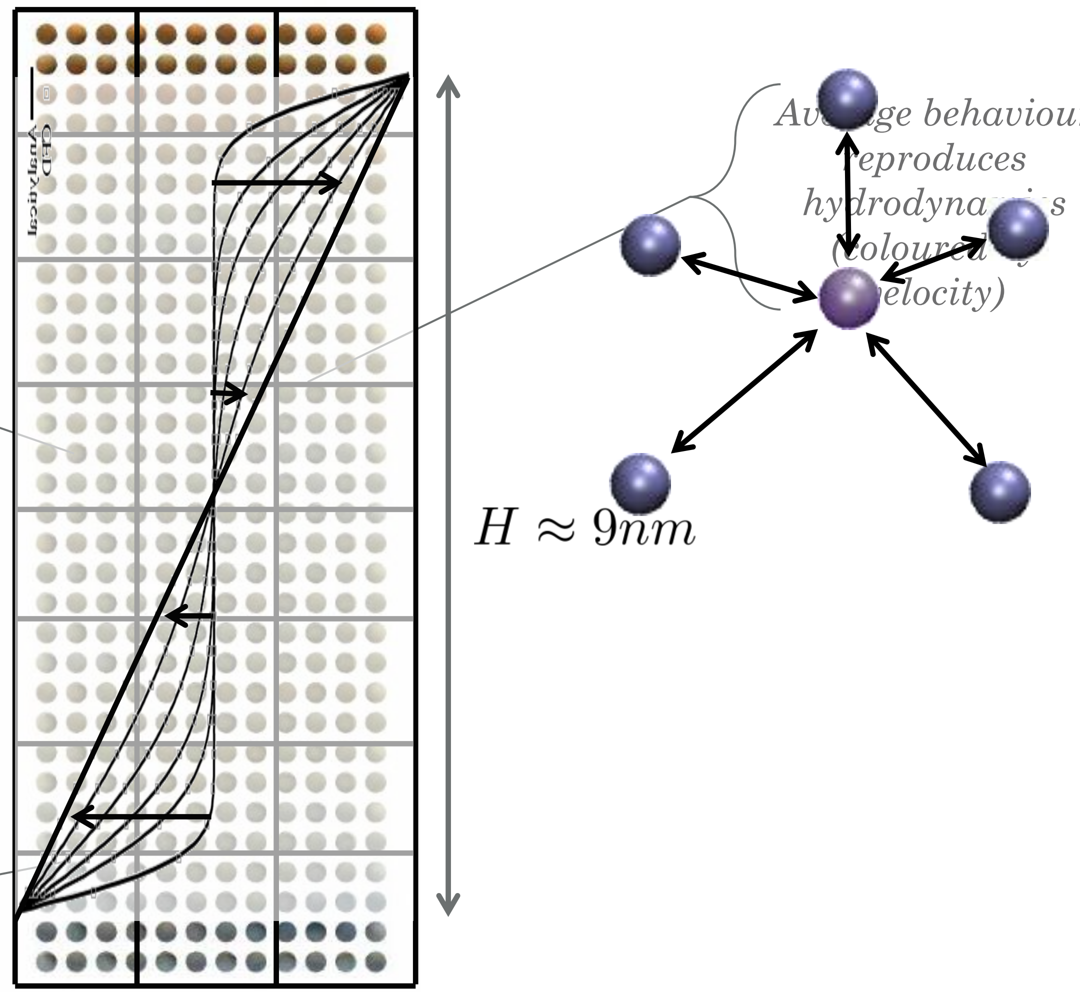
Acceleration obtained from forces

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

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

Molecular Dynamics

Liquid structure causes viscosity and heat conduction



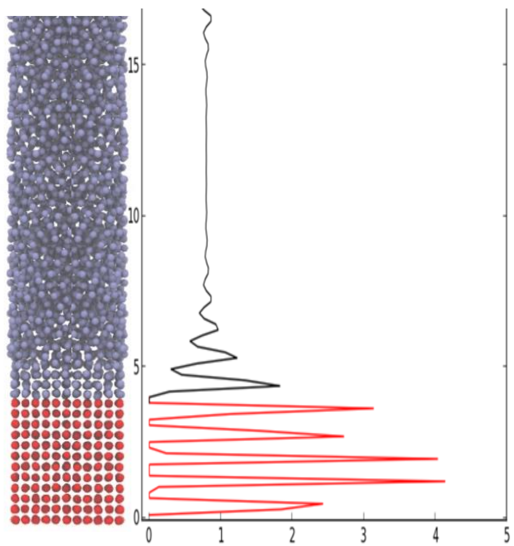
Stick-slip and temperature jumps near walls

Brunel University London

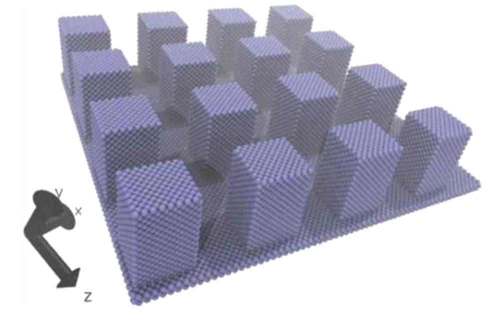
Molecular Dynamics – Complex Walls and Fluids

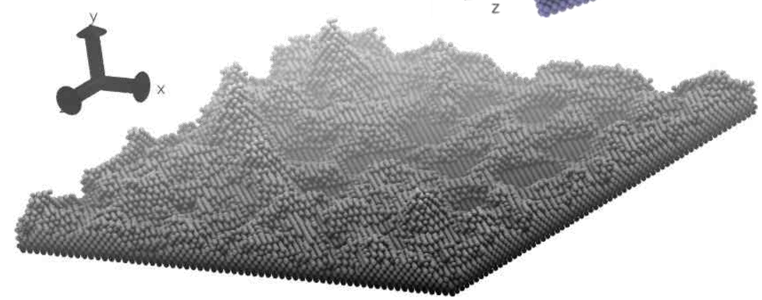
Liquid structure causes viscosity

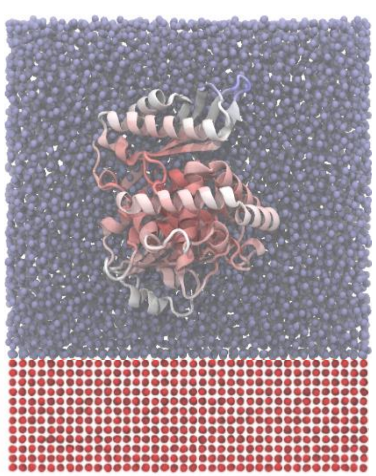
Stick-slip near walls



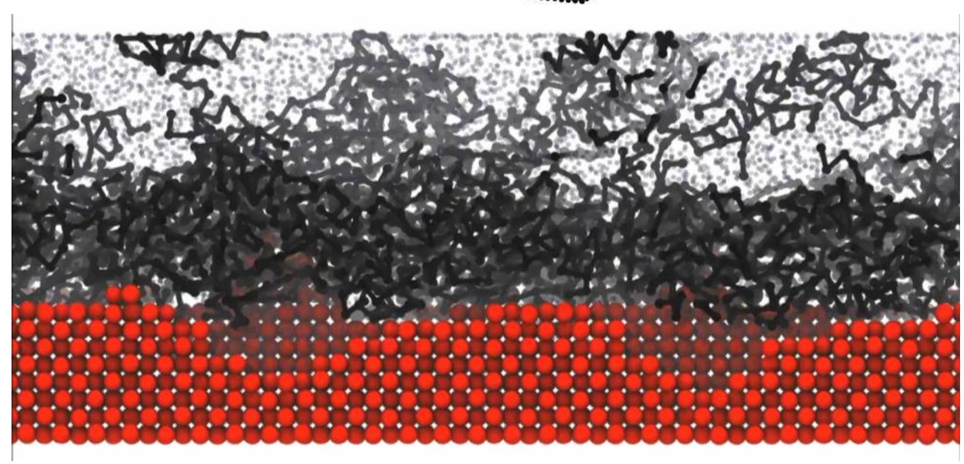
Wall Texture







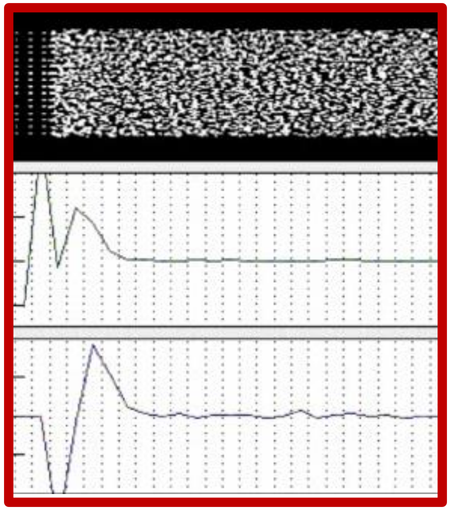
Molecules of arbitrary complexity

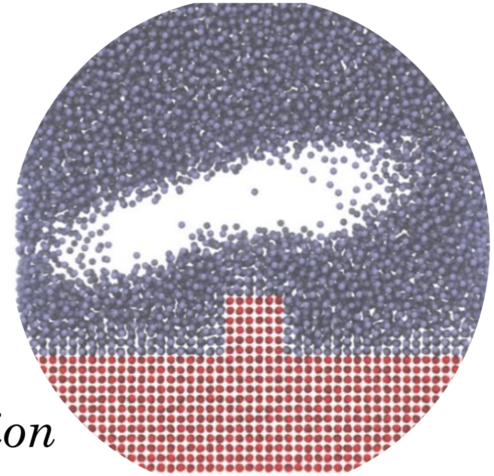


Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

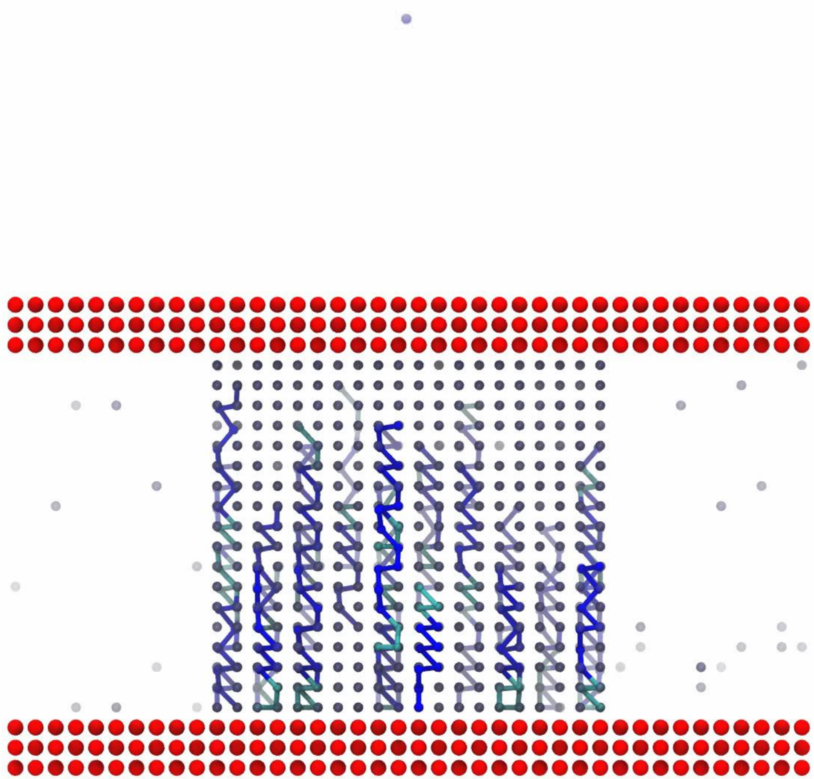
Shockwave





Nucleation

Droplet Formation

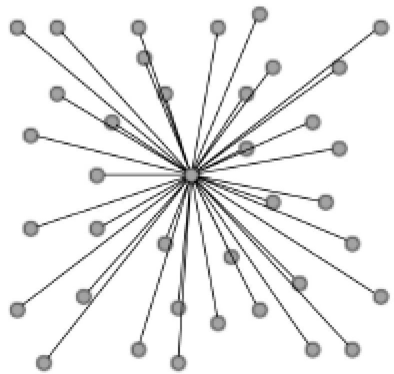


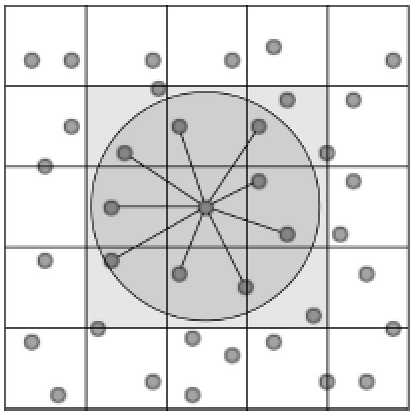
Contact line

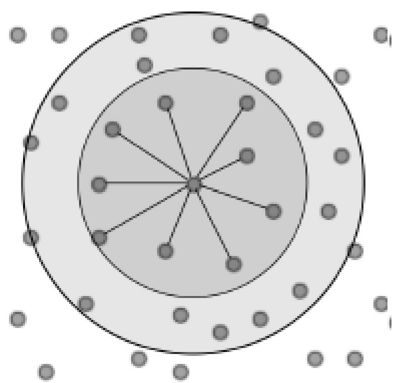
MD Computing

- 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)

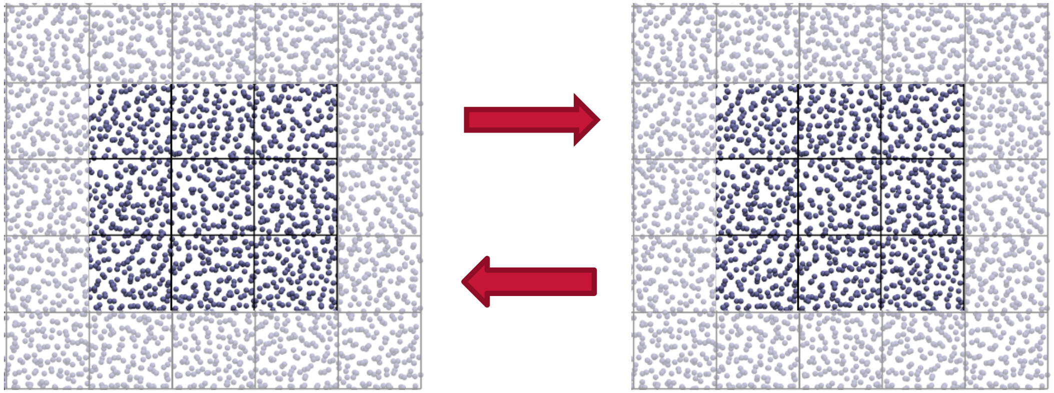
$$m_i \frac{dv_i}{dt} \approx m_i \frac{v_i(t + \Delta t/2) - v_i(t - \Delta t/2)}{\Delta t} = F_i$$

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

MD Computing

Localisations lends itself to parallel computing using MPI

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



Halo exchange of variable amounts of data

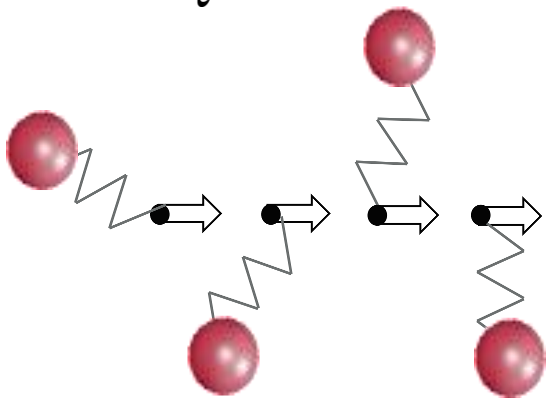
- MPI_Send
- MPI_Probe and MPI_Recv

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

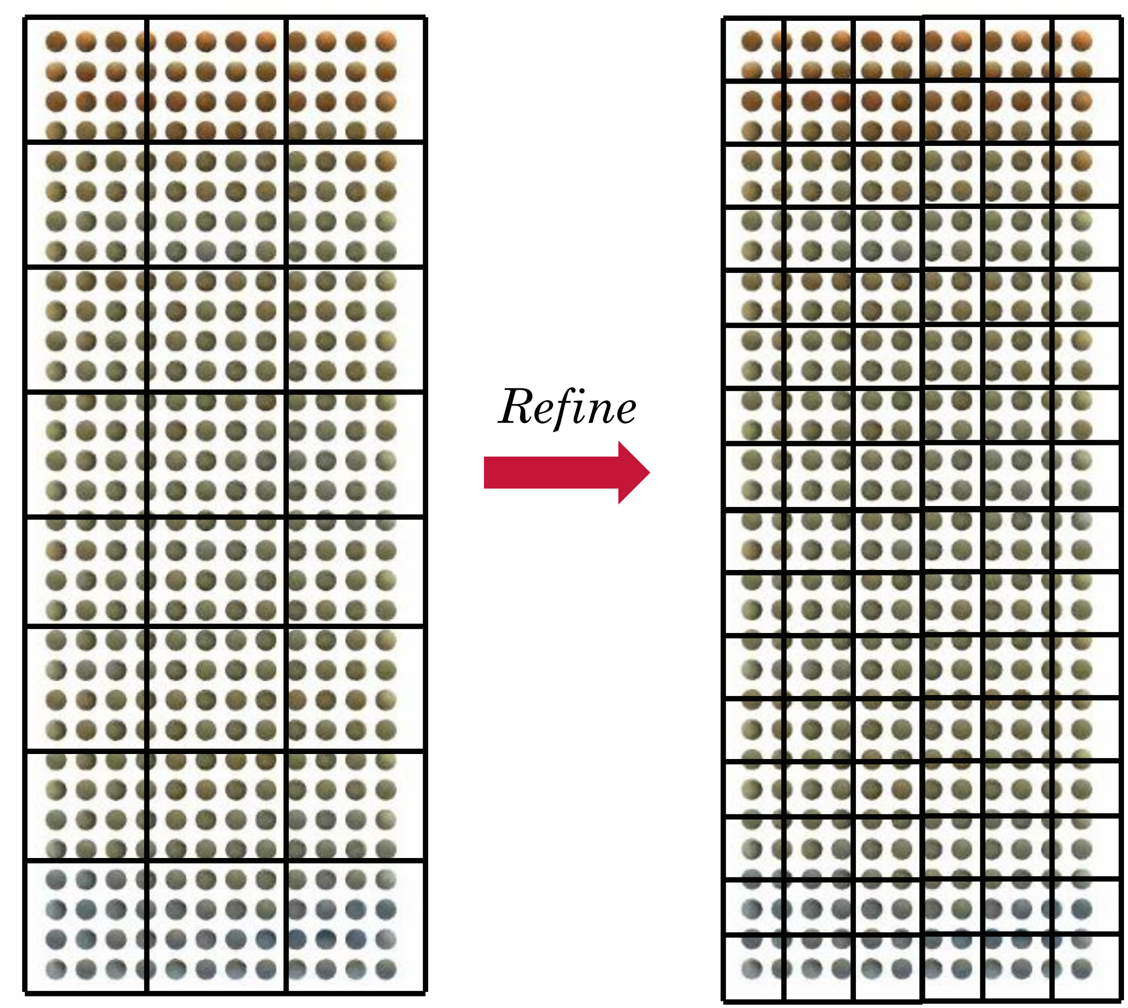
$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{teth} - \psi m_i \boldsymbol{c}_i$$

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



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

Molecular Dynamics - Averaging



- Density in a cell

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

- Momentum in a cell

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

- Temperature in a cell

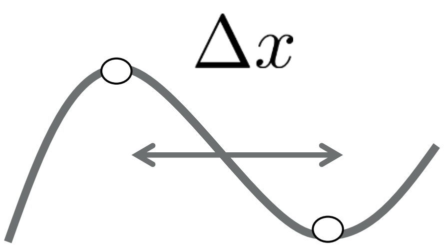
$$T = \frac{1}{3N} \sum_{i=1}^{N_{cell}} \langle \boldsymbol{v}_i^2 \rangle$$

Continuum vs. Discrete

- Consider the pointwise energy equation

$$\underbrace{\frac{\partial}{\partial t}\rho\mathcal{E}}_{Unsteady} = -\boldsymbol{\nabla}\cdot\left[\quad \underbrace{\rho\mathcal{E}\boldsymbol{u}}_{\text{Advection}} \quad + \quad \underbrace{\boldsymbol{\Pi}\cdot\boldsymbol{u}}_{\text{Stress Work}} \quad + \quad \underbrace{\boldsymbol{J_q}}_{\text{Heat Flux}} \quad\right]$$

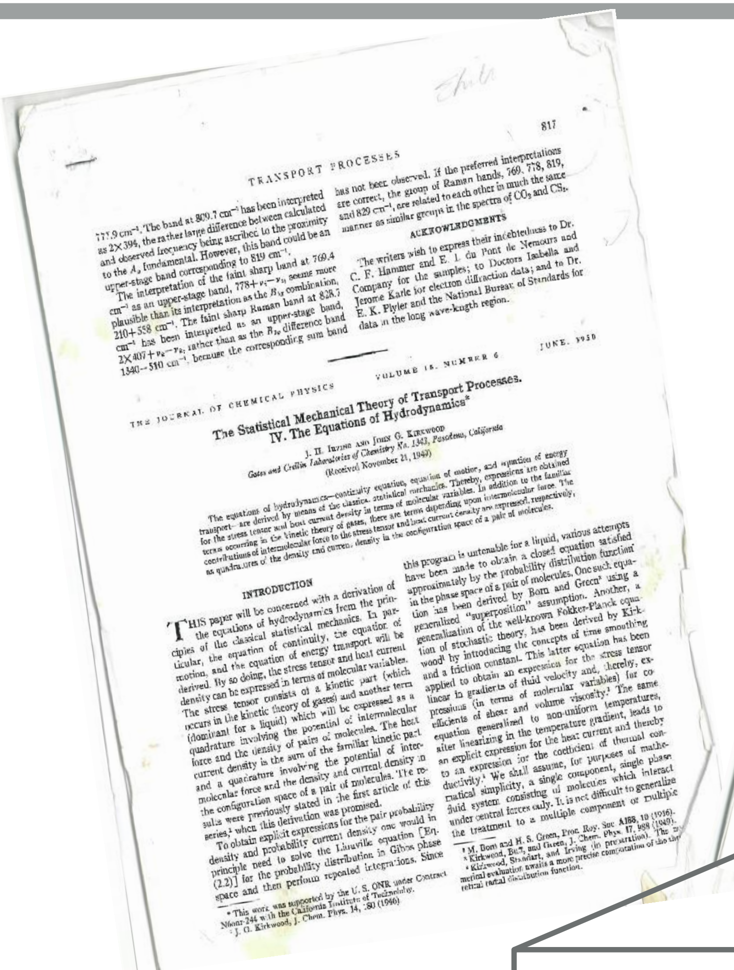
- Based on the continuum hypothesis
  - Describes fields
  - Valid at every point in space
  - Uses the calculus



$$\frac{df}{dx} = \lim_{\Delta x \to \infty} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

Irving and Kirkwood (1950)

Brunel University London



TRANSPORT PROCESSES

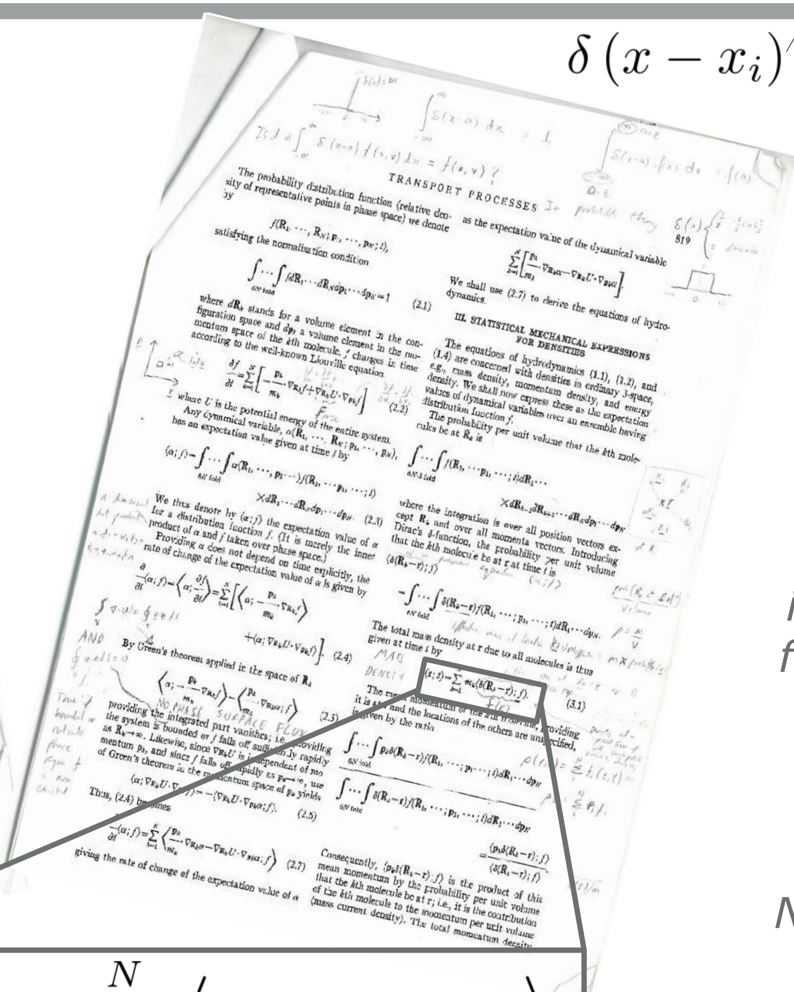
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 18, NUMBER 6 JUNE, 1950

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

J. H. Irving and John G. Kirkwood

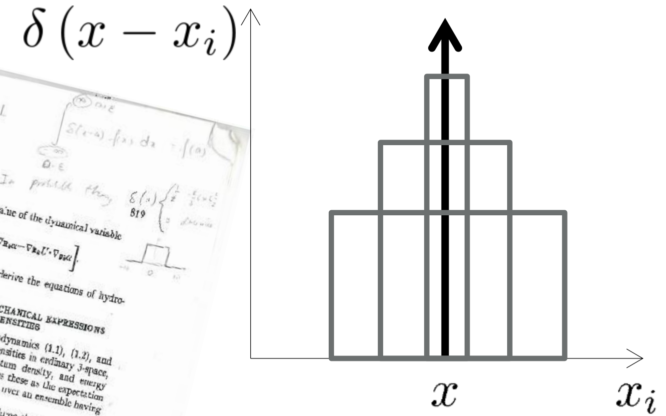
Gates and Crellin Laboratories of Chemistry, Pasadena, California

INTRODUCTION



TRANSPORT PROCESSES

III. STATISTICAL MECHANICAL EXPRESSIONS FOR DENSITIES



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

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

BUT

No molecule is ever exactly at a point

Integrating the Dirac Delta

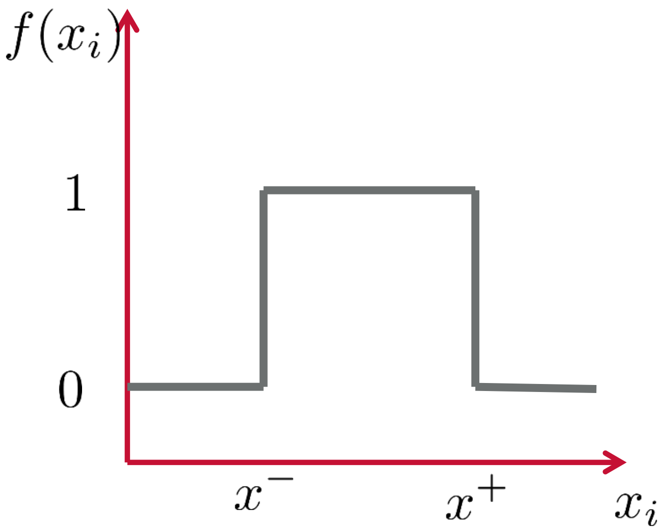
- Much better to write the equations in integrated form

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

- Integrating the Dirac delta function exactly provides a box car function (two Heaviside functions)
  - Consider the 1D case

$$\int_{x^-}^{x^+} \delta(x - x_i) dx = \Big[H(x - x_i) \Big]_{x^-}^{x^+}$$

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



The Control Volume Functional

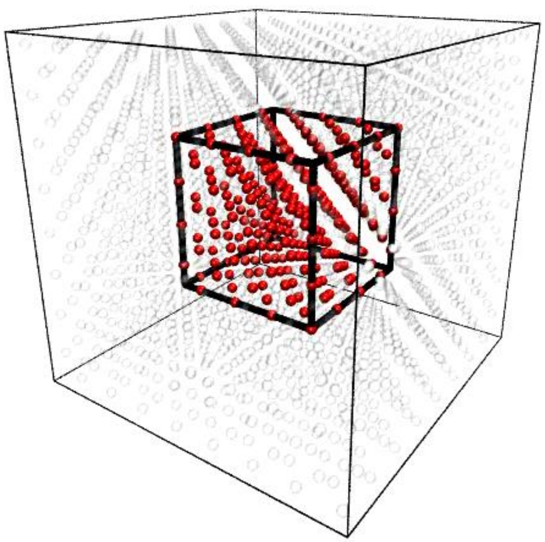
- In three dimensions this integral gives a cube

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

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

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

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



- In words

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

Derivative yields surface fluxes (Method of Planes)

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

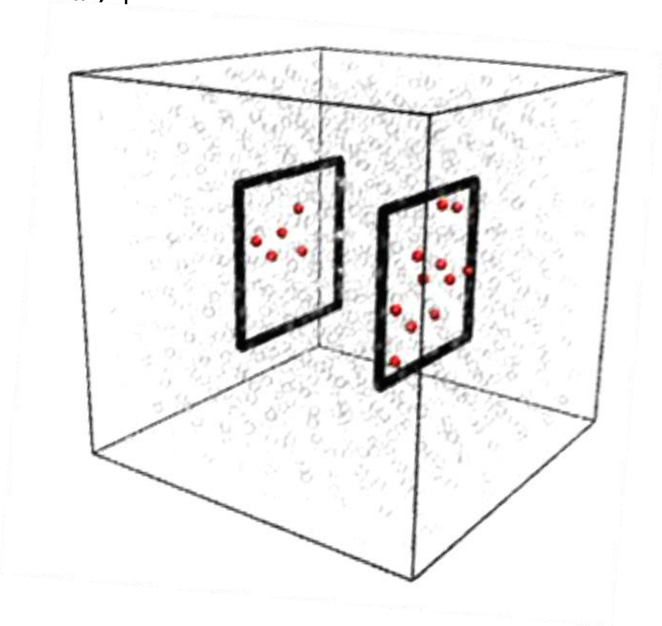
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

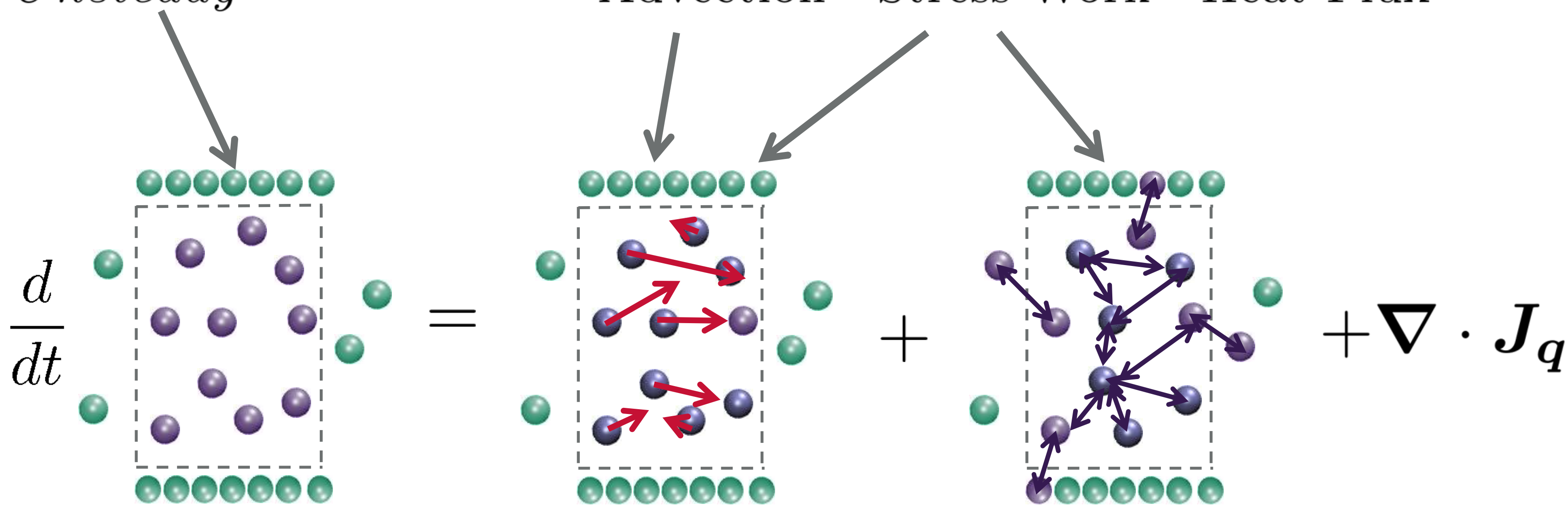
$$d\mathbf{S}_i \equiv \begin{cases} \infty & \text{if molecule on surface} \\ 0 & \text{otherwise} \end{cases}$$



Control Volume Form

- Integrate to get the control volume energy equation

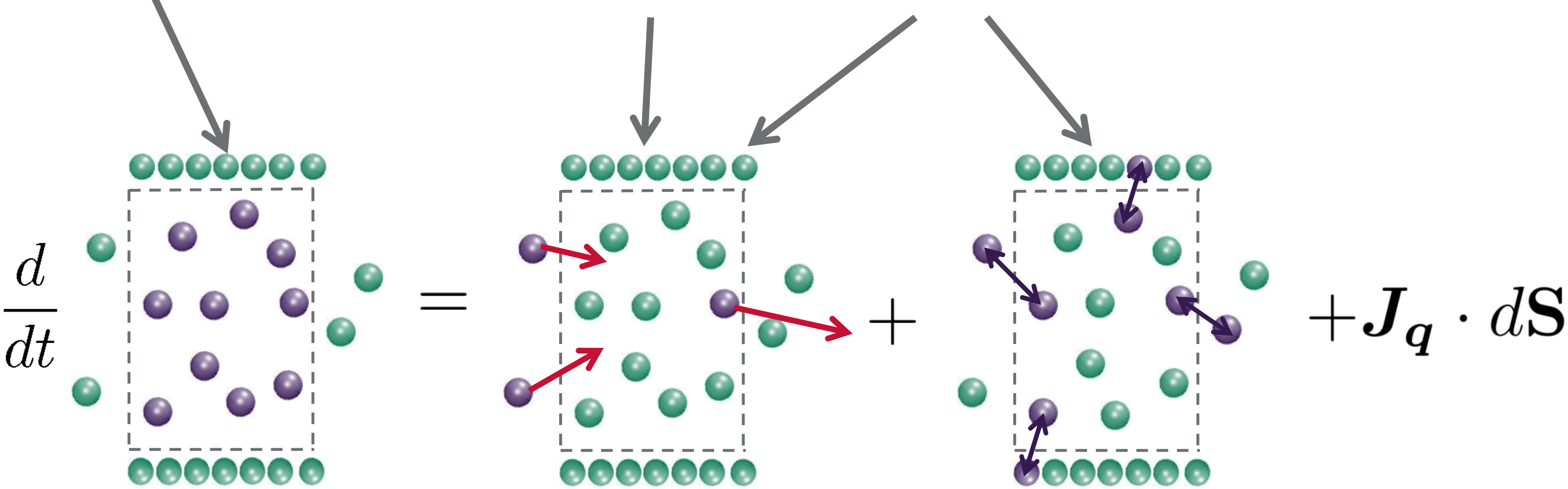
$$\underbrace{\int_V \frac{\partial}{\partial t}\rho \mathcal{E} dV}_{Unsteady} = -\int_V \boldsymbol{\nabla} \cdot \left[\underbrace{\rho \mathcal{E} \boldsymbol{u}}_{\text{Advection}} + \underbrace{\boldsymbol{\Pi} \cdot \boldsymbol{u}}_{\text{Stress Work}} + \underbrace{\boldsymbol{J_q}}_{\text{Heat Flux}} \right] dV$$



Control Volume (surface flux) Form

- Or can be expressed in terms of surface fluxes

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



Key Points

- Molecular dynamics captures the full structure of a fluid and models complex non-equilibrium behaviour
- Continuum differential equations are problematic in MD as they result in a Dirac delta function
- Integrated form is better, and the integral of the Dirac delta function provides a useful function
- This function is used to measure the heat flux in an MD system as,
  - Volume Average
  - Surface Flux - Method of Planes (MOP) form

Section 2

TEMPERATURE-DRIVEN FLOW

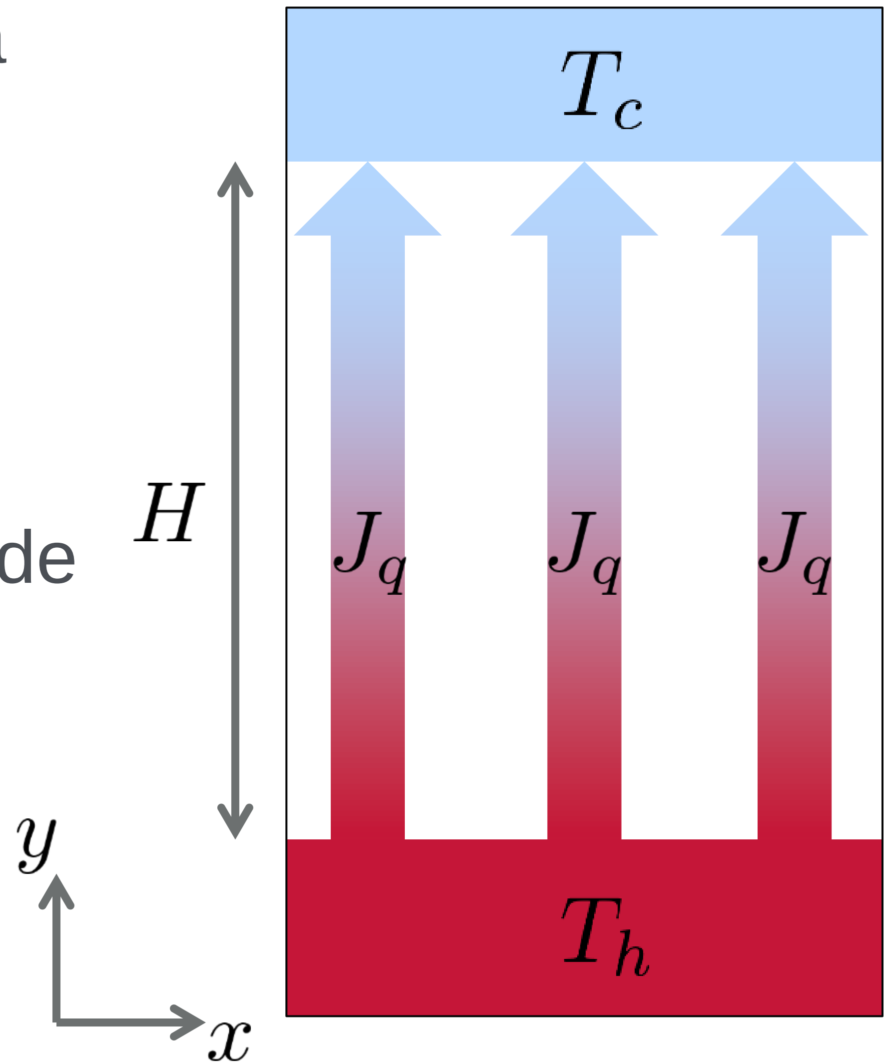
Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

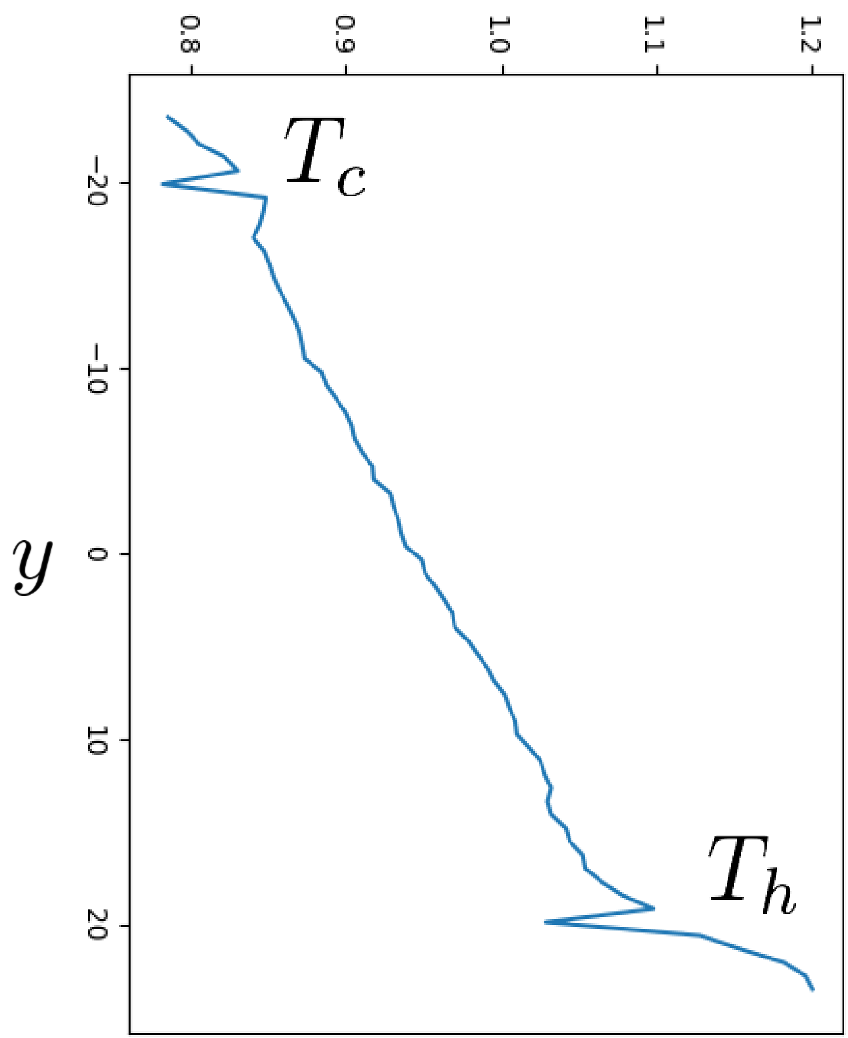
$$\frac{\partial T}{\partial y} \approx \frac{T_c - T_h}{H}$$

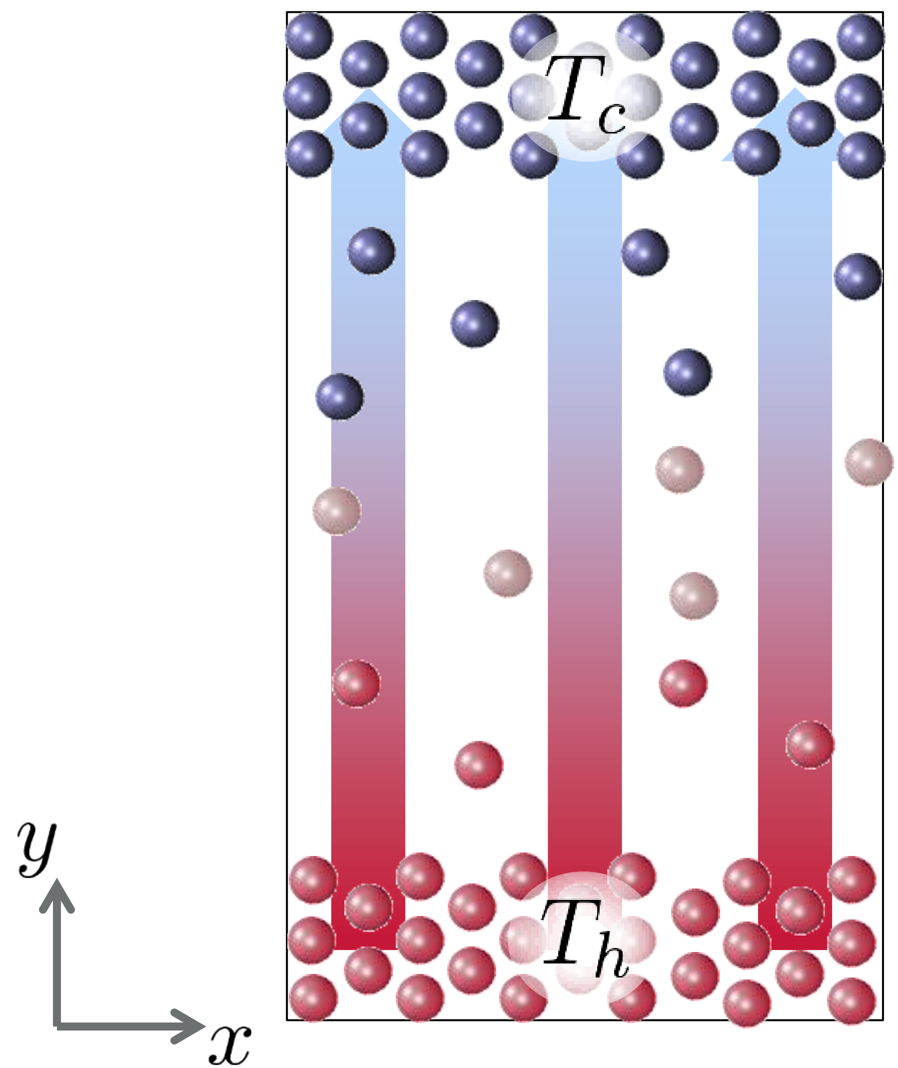
- Proportional to magnitude of temperature gradient

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



Fourier's law of Heat Conduction

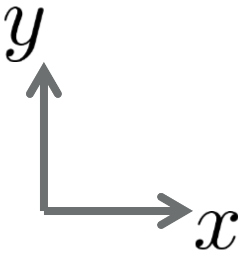


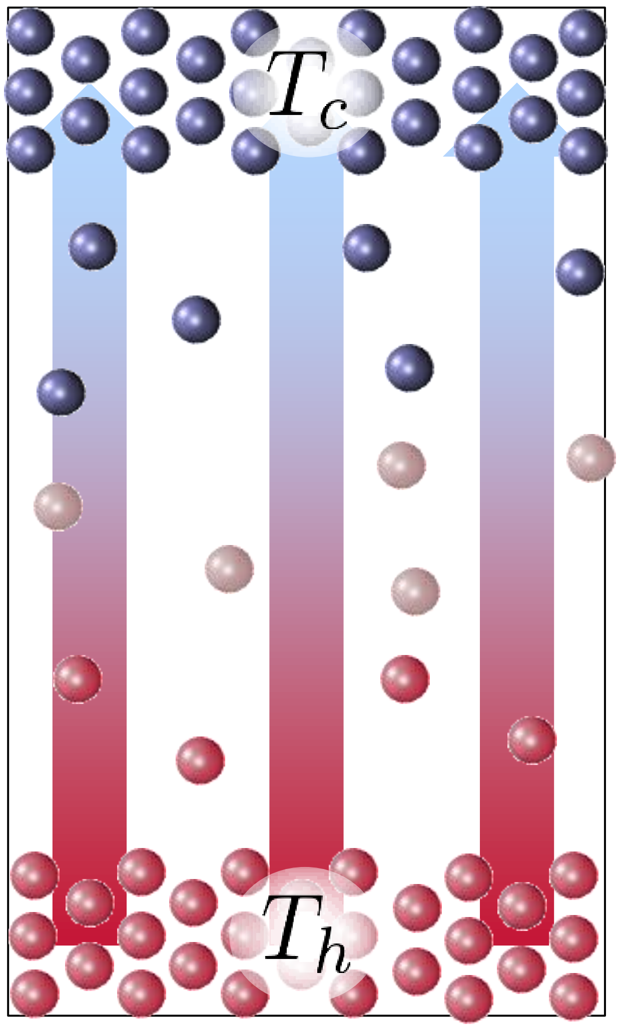


Fourier's law of Heat Conduction

- Thermostat tethered walls to different temperatures
- Linear temperature gradient between walls
- We need a way of measuring J_q from MD

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



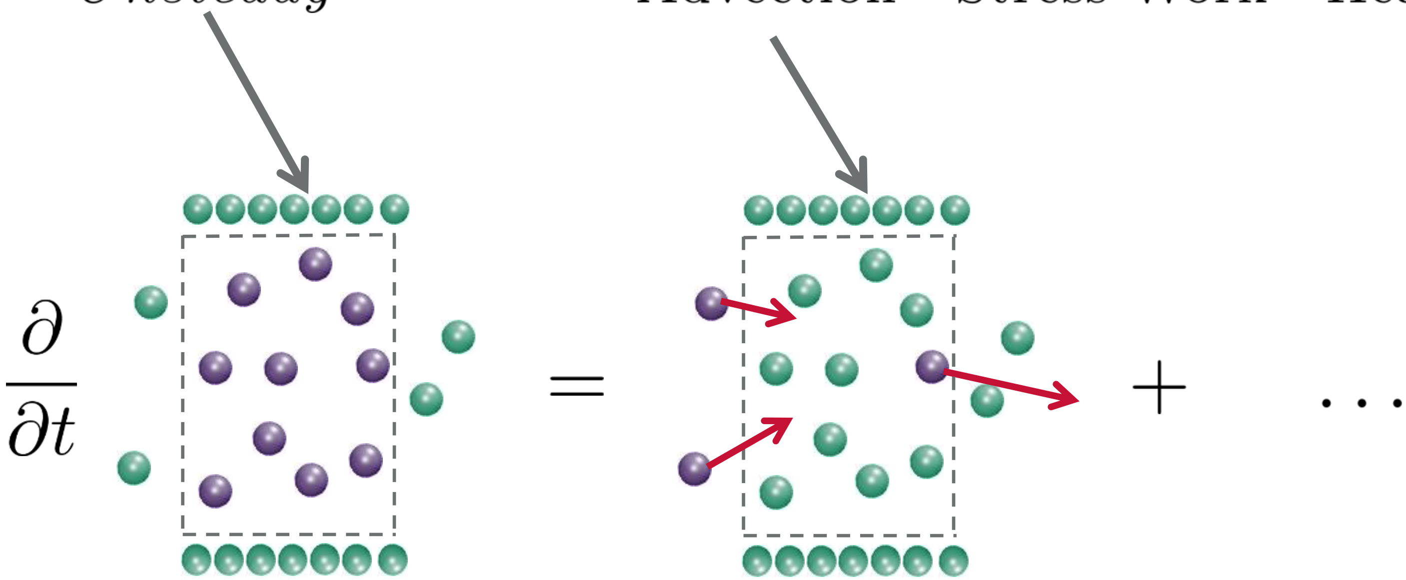


Measuring Heat Flux in MD

Brunel University London

- Consider the energy equation

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



Pressure (Stress) in an MD Simulation

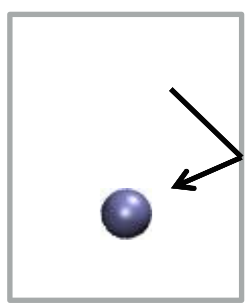
Brunel University London

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

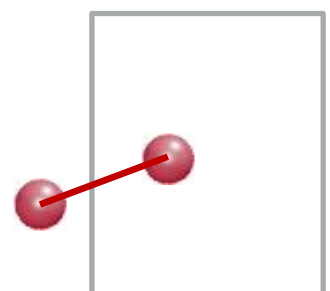
$$\Pi_{xy} = \underbrace{\sum_{i=1}^{N} \left\langle m_i c_{xi} c_{yi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2}\sum_{i=1}^{N} \sum_{j\neq i}^{N} \left\langle f_{xij} r_{yij} \right\rangle}_{\text{Configurational}}$$

Kinetic theory part

Momentum due to average of molecules crossing a plane and returning



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



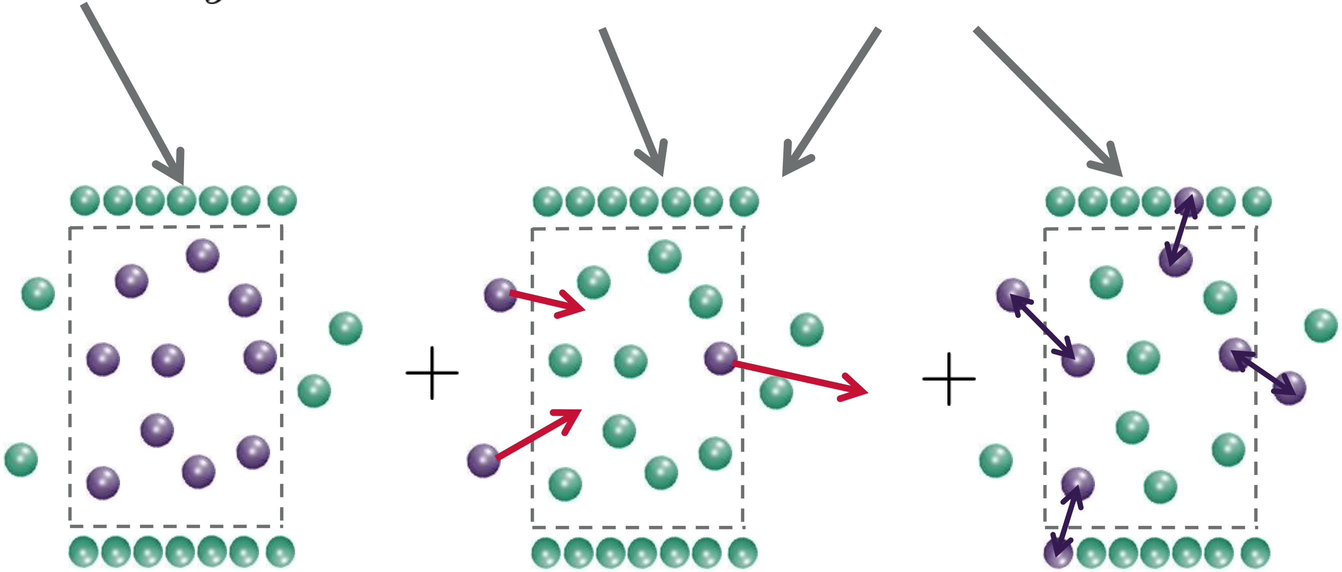
Configurational part

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

Measuring Heat Flux in MD

- Consider the energy equation

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



$$= \oint_S \boldsymbol{J_q}\cdot d\mathbf{S}$$

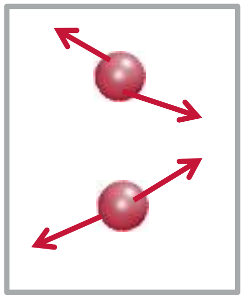
Volume Average Heat Flux

Brunel University London

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^{\phi}$

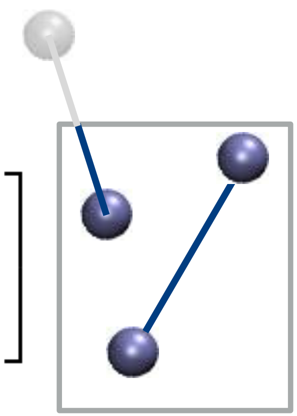
Kinetic

$$\mathbf{J}_{qV}^{K}\left(\mathbf{r}_m, t\right) = \frac{1}{\Delta V}\left[\sum_{i=1}^{N} e_i \mathbf{v}_i \vartheta_i - \bar{\mathbf{v}}\left(\mathbf{r}_m, t\right)\sum_{i=1}^{N} e_i \vartheta_i\right]$$



Configurational

$$\mathbf{J}_{qV}^{\phi}\left(\mathbf{r}_m, t\right) = -\frac{1}{\Delta V}\frac{1}{2}\left[\sum_{i,j}^{N} \mathbf{r}_{ij}\mathbf{F}_{ij} \cdot \mathbf{v}_i \ell_{ij} - \left(\sum_{i,j}^{N} \mathbf{r}_{ij}\mathbf{F}_{ij}\ell_{ij}\right) \cdot \bar{\mathbf{v}}\left(\mathbf{r}_m\right)\right]$$

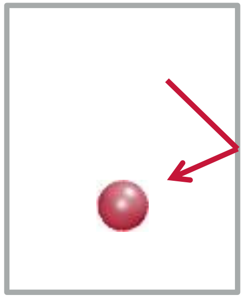


Surface (MOP) Heat Flux

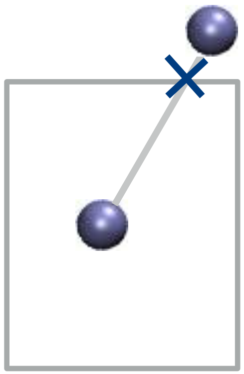
- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$

Kinetic

$$J^K_{qA,x} = \frac{1}{\Delta A_x} \sum_{i=1}^{N} e_i \left(v_{ix} - \bar{v}_x \left(r_m \right) \right) \delta \left(x_i - x_+ \right) S_{xi}$$



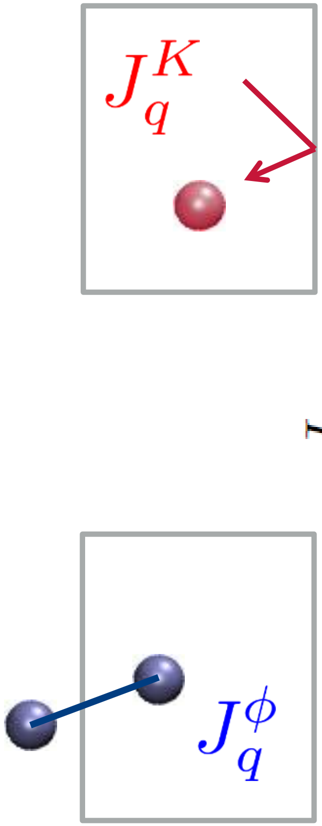
Configurational

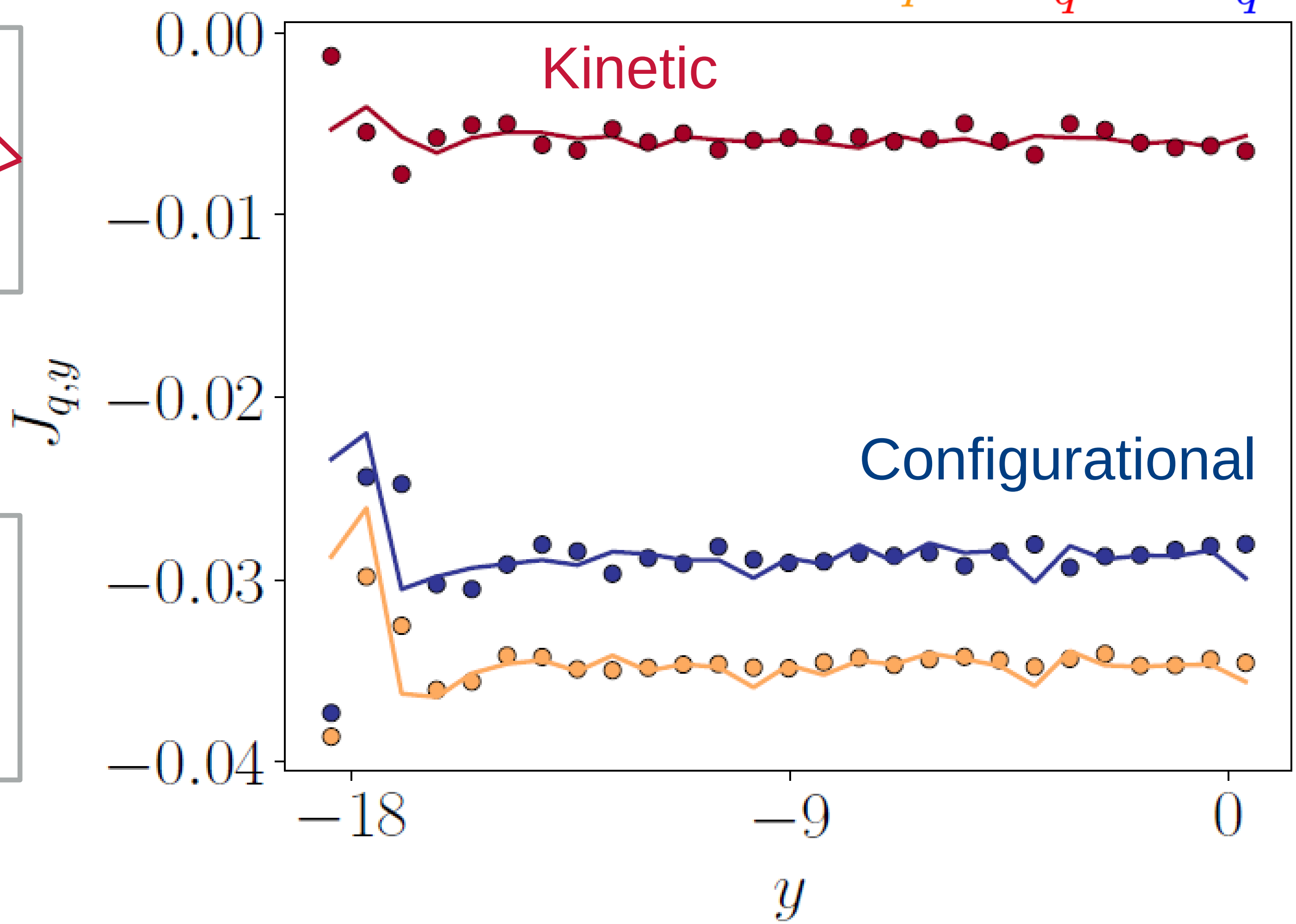


$$J^\phi_{qA,x} = -\frac{1}{\Delta A_{x+}} \frac{1}{2} \sum_{i,j}^{N} \mathbf{F}_{ij} \cdot \left(\mathbf{v}_i - \bar{\mathbf{v}} \left(\mathbf{r}_{x+} \right) \right) S_{ij} \left(x_+ \right)$$

Measuring Heat Flux in MD

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$





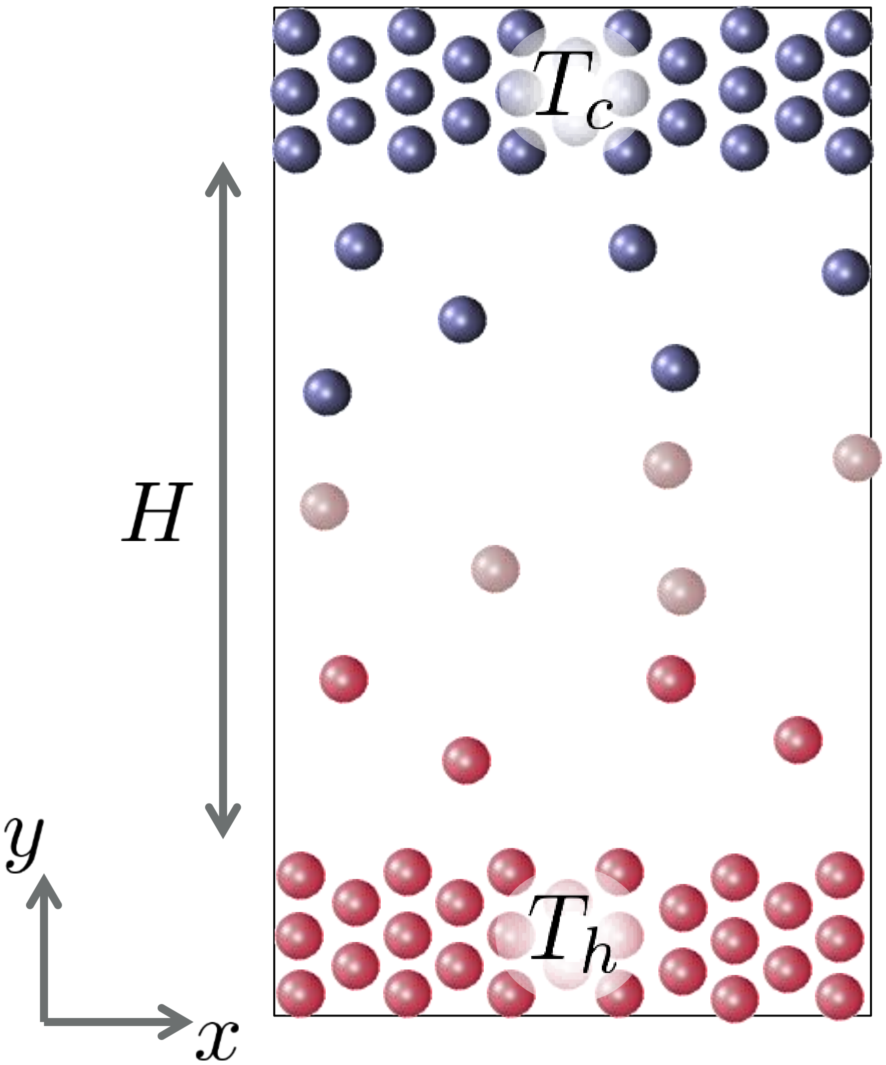
Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

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

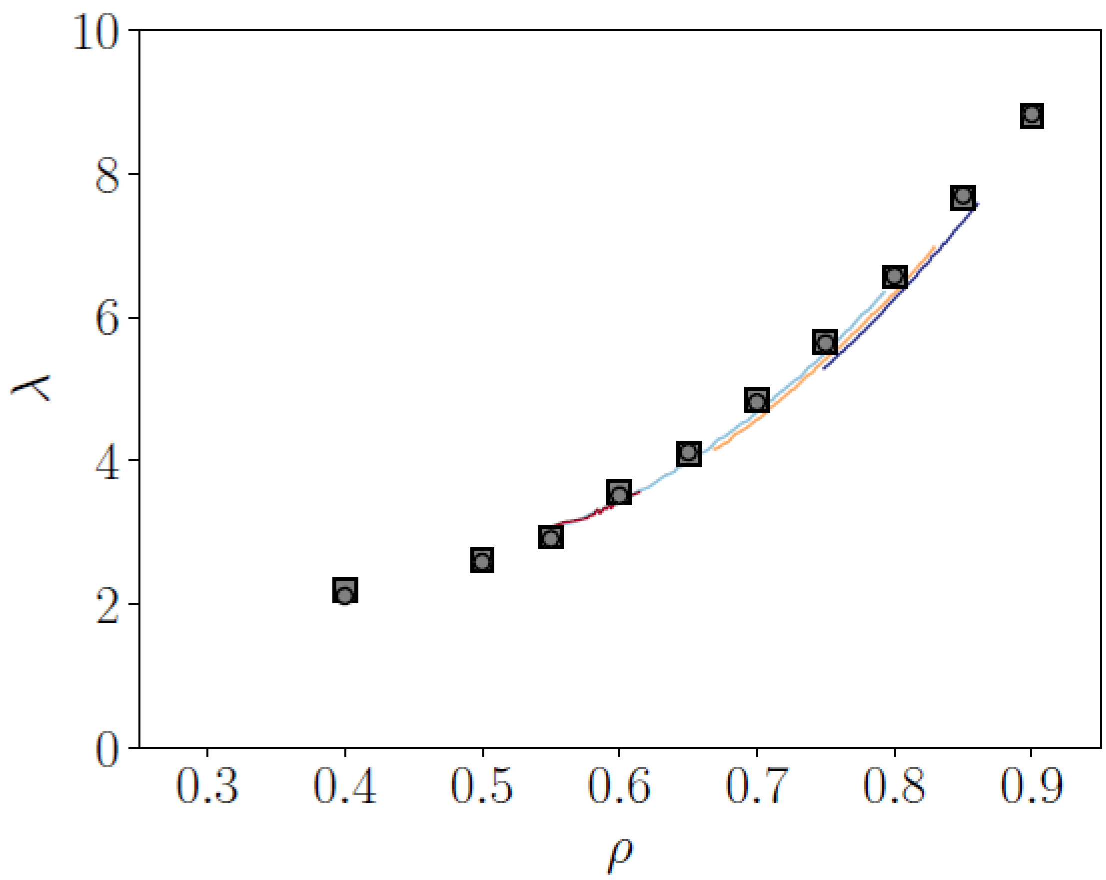
- Using heat flux and temperature gradient,

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



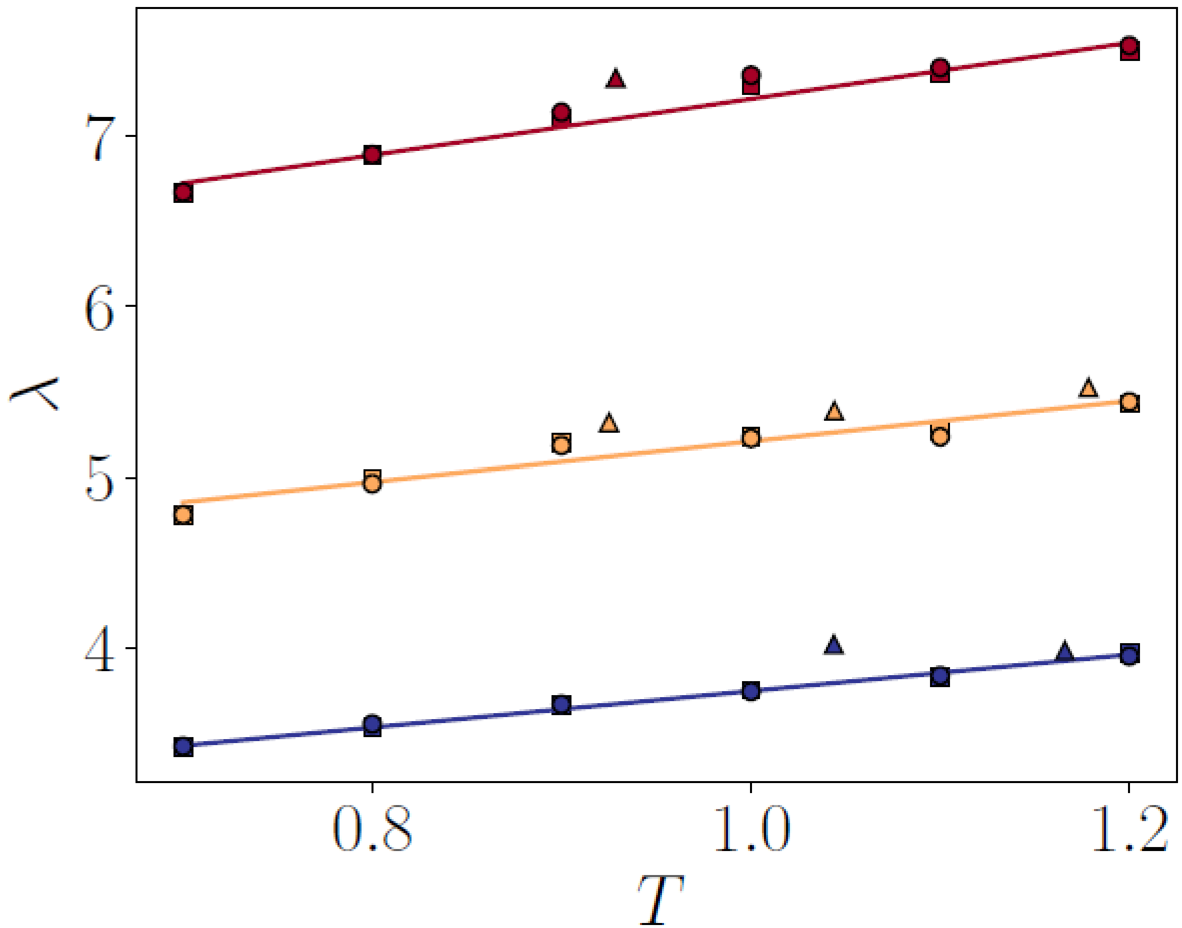
Fourier's law of Heat Conduction

- Run over a range of different density channels
- MD shows good agreement with experimental results



Fourier's law of Heat Conduction

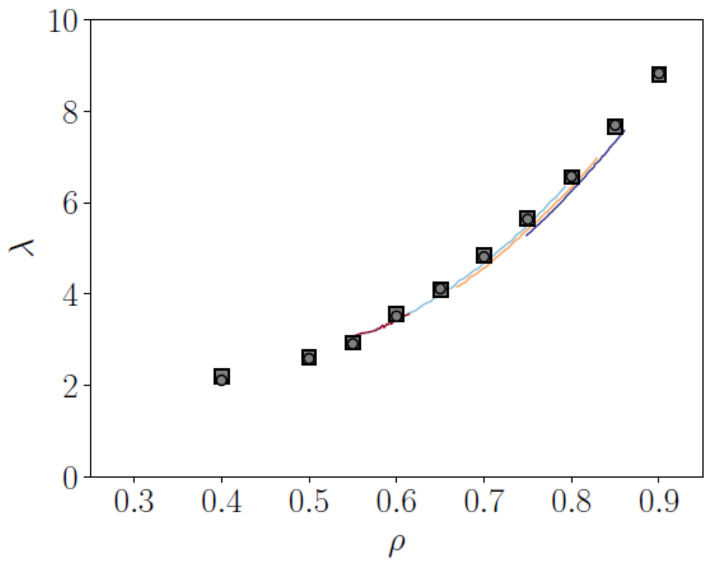
- Run over a range of different temperatures
- Linear variation as a function of temperature

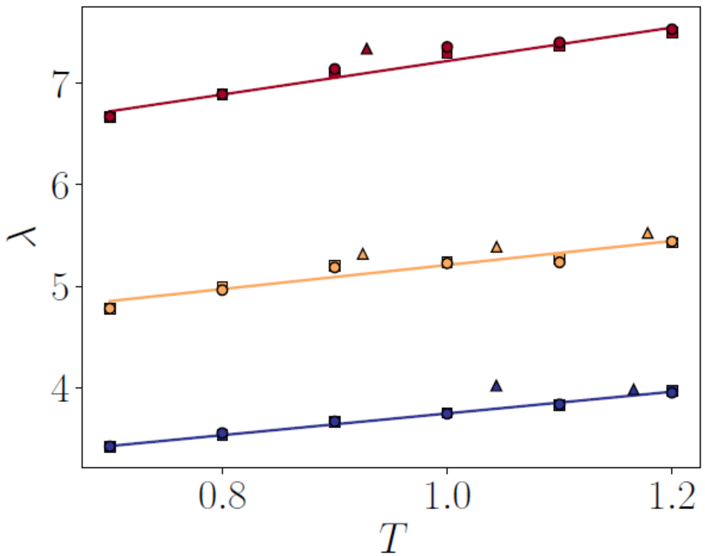


Fourier's law of Heat Conduction

- Using simple fits to both curves we get Fourier's coefficient in terms of density and temperatures

$$\lambda(\rho, T) = 21.3\rho^2 - 14.2\rho + 3.92 + (T-1)\left[13\rho^2 - 17\rho + 6.63\right]$$





Section 3

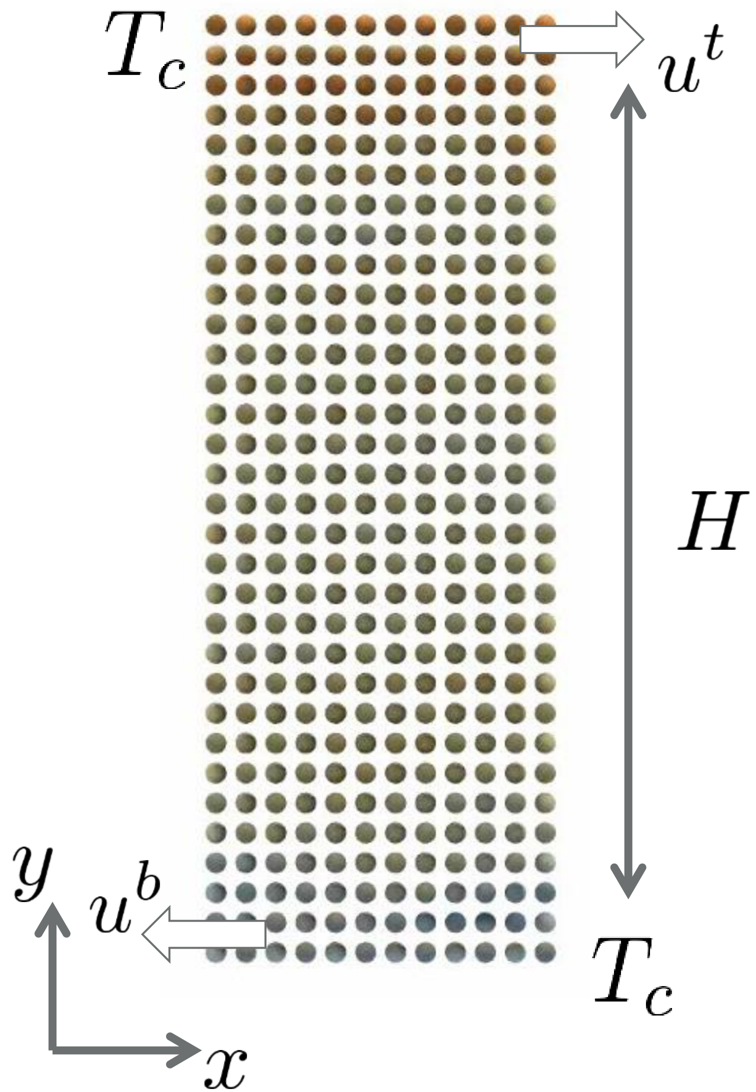
SHEAR-DRIVEN (COUETTE) FLOW

Couette Flow

- Shear flow driven by walls

$$\dot{\gamma} = \frac{\partial u}{\partial y} \approx \frac{u^t - u^b}{H}$$

- Walls are thermostatted

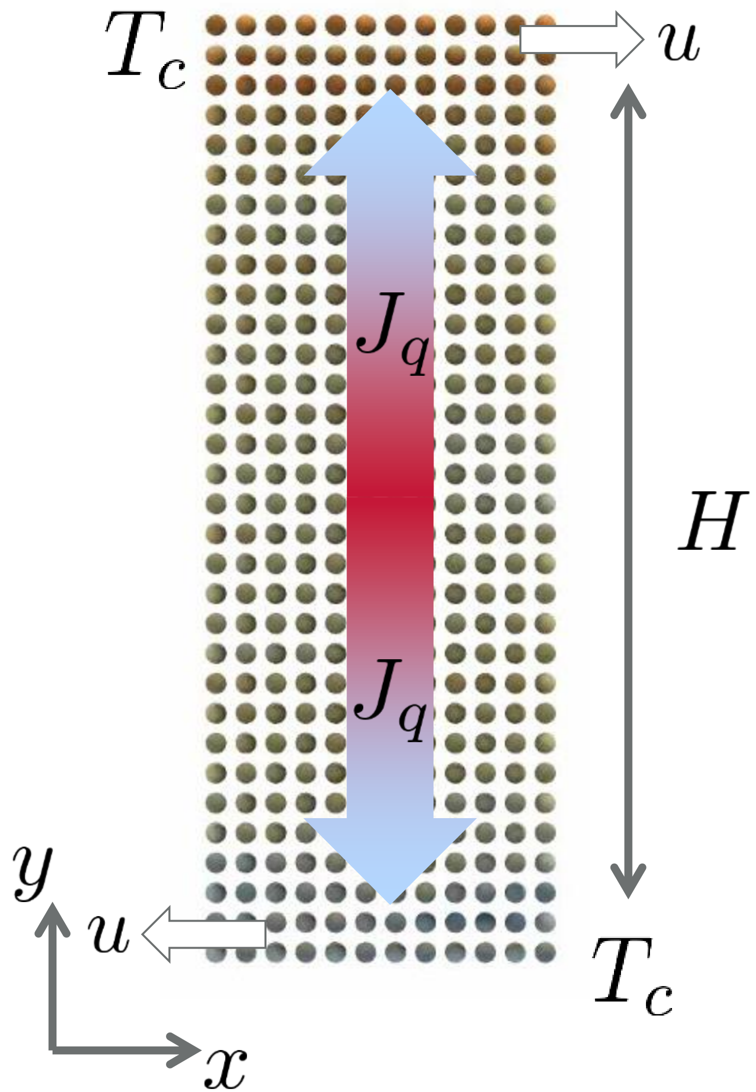


Couette Flow

- Shear flow generates heat

$$\underbrace{\Pi_{xy}\dot{\gamma}}_{\text{Stress Work}} = \underbrace{\frac{\partial J_{q,y}}{\partial y}}_{\text{Heat Flux}}$$

- Walls are thermostatted

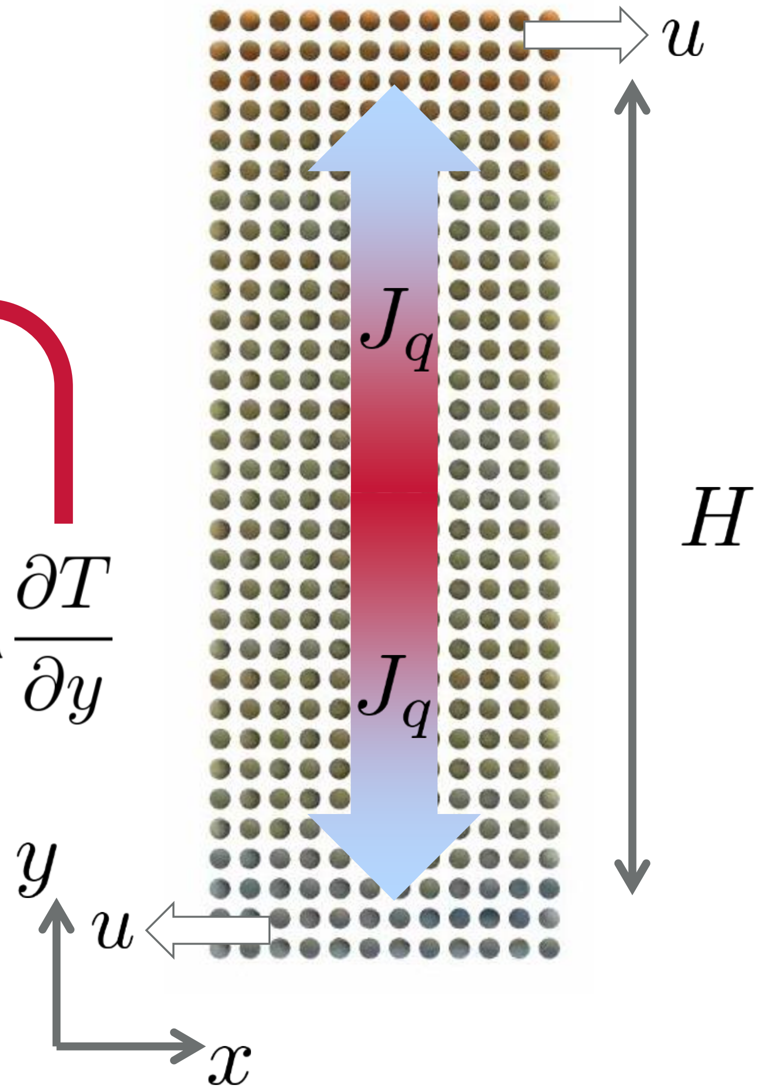


Couette Flow

- Shear flow generates heat

$$\underbrace{\Pi_{xy}\dot{\gamma}}_{\text{Stress Work}} = \underbrace{\frac{\partial J_{q,y}}{\partial y}}_{\text{Heat Flux}}$$

- Insert Fourier's law $J_{q,y} = -\lambda \frac{\partial T}{\partial y}$



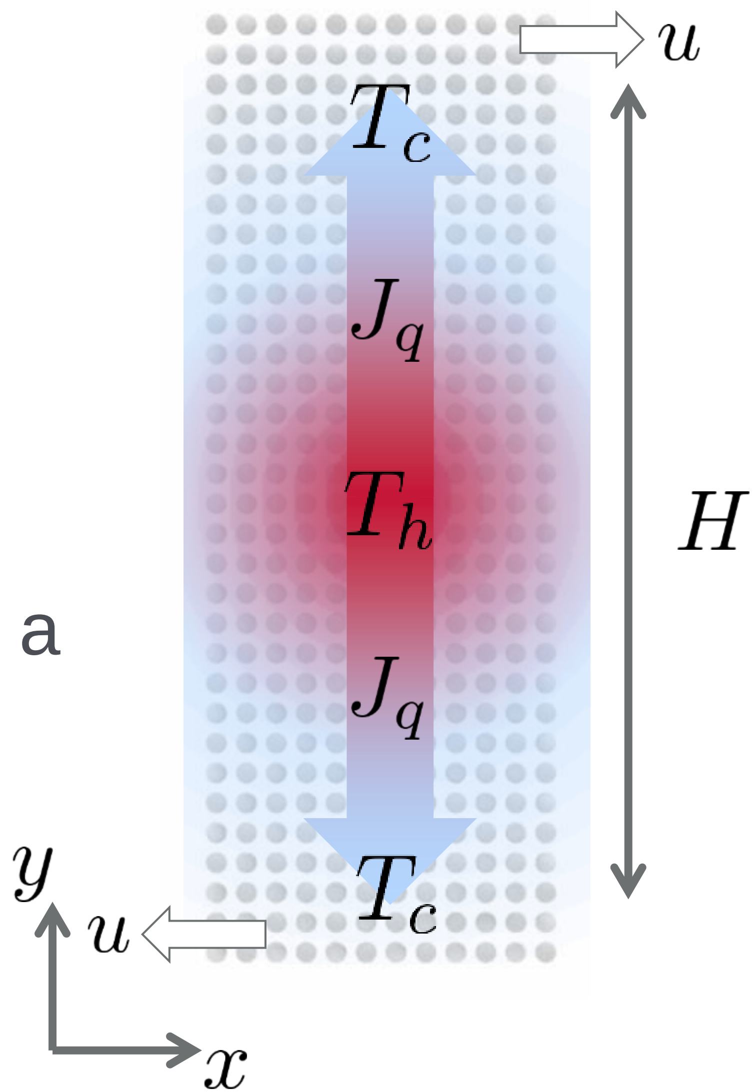
Couette Flow

- Shear flow generates heat

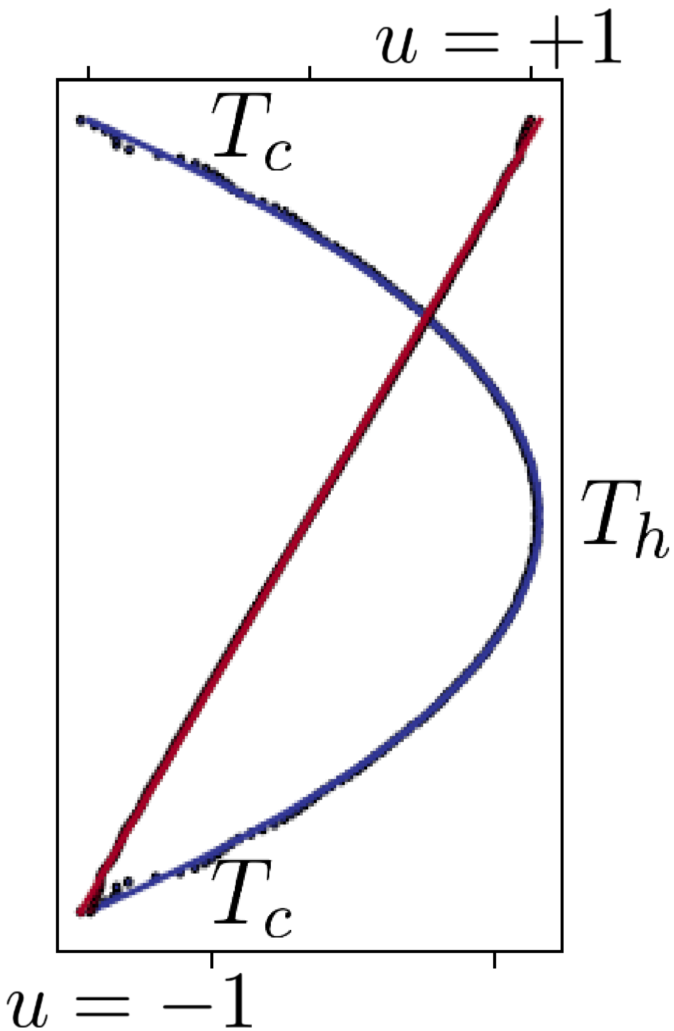
$$\underbrace{\Pi_{xy}\dot{\gamma}}_{\text{Stress Work}} = \underbrace{-\lambda\frac{\partial^2 T}{\partial y^2}}_{\text{Heat Flux}}$$

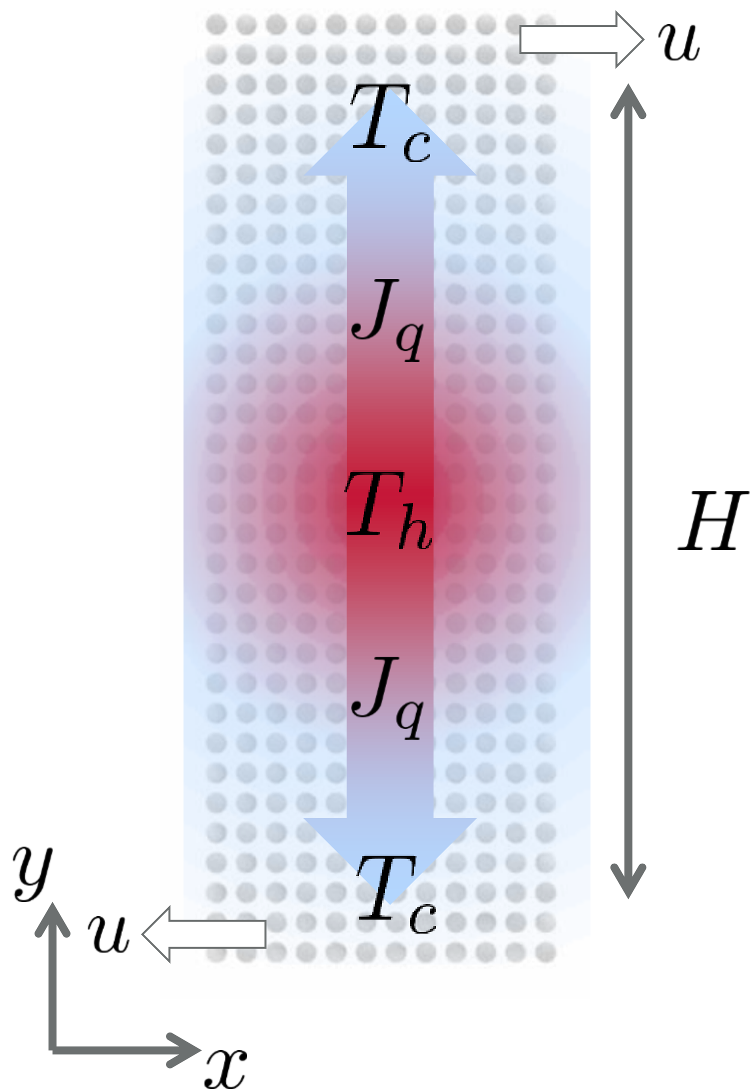
- Walls are thermostatted giving a parabolic temperature profile

$$T(y) = \left[\frac{H^2}{4} - y^2\right]\frac{\Pi_{xy}\dot{\gamma}}{\lambda} + T_c$$



Couette Flow





Couette Flow

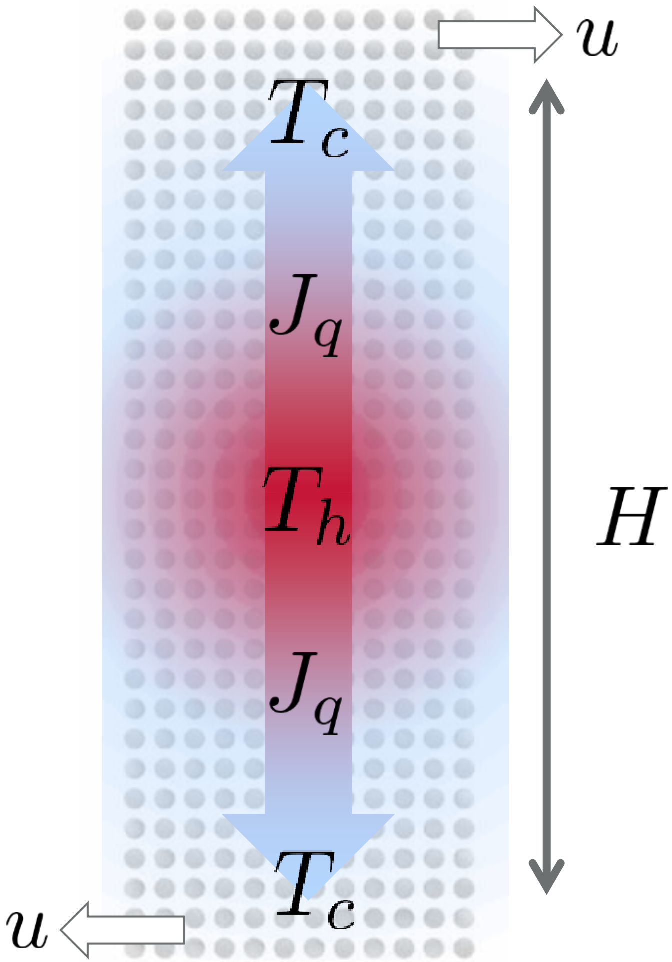
- Heat flux J_q driven by a temperature difference

$$T(y) = \left[\frac{H^2}{4} - y^2\right]\frac{\Pi_{xy}\dot{\gamma}}{\lambda} + T_c$$

- Use heat flux and temperature gradient, we could evaluate,

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

- But missing the strain-rate coupling predicted by theory…



Beyond Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

$$\boldsymbol{J}_q(\boldsymbol{\nabla} T, \boldsymbol{\nabla} \boldsymbol{u}) \approx \boldsymbol{\nabla} T \frac{\partial \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} T} + \dots$$

λ

$$+ \boldsymbol{\nabla} T \boldsymbol{\nabla} \boldsymbol{u} \frac{\partial^2 \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} \boldsymbol{u} \partial \boldsymbol{\nabla} T}$$

- Only temperature gradient and strain cross term is non-zero to 1st order

$$\mathbf{J}_q \approx -\boldsymbol{\lambda}_{\text{eff}} \cdot \nabla T$$

Beyond Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

$$\boldsymbol{J}_q(\boldsymbol{\nabla} T, \boldsymbol{\nabla} \boldsymbol{u}) \approx \boldsymbol{\nabla} T \frac{\partial \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} T} + \dots$$

$$\lambda$$

$$-\lambda_1 \dot{\gamma} \boldsymbol{i} + 3\lambda_2 \dot{\gamma}^2 \boldsymbol{j}$$

$$+ \boldsymbol{\nabla} T \boldsymbol{\nabla} \boldsymbol{u} \frac{\partial^2 \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} \boldsymbol{u} \partial \boldsymbol{\nabla} T}$$

- Only temperature gradient and strain cross term is non-zero to 1st order

$$\mathbf{J}_q \approx -\boldsymbol{\lambda}_{\text{eff}} \cdot \nabla T$$

$$\boldsymbol{\lambda}_{\text{eff}} = \begin{bmatrix} \lambda + 3\lambda_2\dot{\gamma}^2 & -\lambda_1\dot{\gamma} & 0 \\ -\lambda_1\dot{\gamma} & \lambda + 3\lambda_2\dot{\gamma}^2 & 0 \\ 0 & 0 & \lambda + \lambda_2\dot{\gamma}^2 \end{bmatrix}$$

Beyond Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

$$\boldsymbol{J}_q(\boldsymbol{\nabla} T, \boldsymbol{\nabla} \boldsymbol{u}) \approx \boldsymbol{\nabla} T \frac{\partial \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} T} + \dots$$

$$\lambda$$

$$+ \boldsymbol{\nabla} T \boldsymbol{\nabla} \boldsymbol{u} \frac{\partial^2 \boldsymbol{J}_q}{\partial \boldsymbol{\nabla} \boldsymbol{u} \partial \boldsymbol{\nabla} T}$$

$$-\lambda_1 \dot{\gamma} \boldsymbol{i} + 3\lambda_2 \dot{\gamma}^2 \boldsymbol{j}$$

- Only temperature gradient and strain cross term is non-zero to 1st order

$$J_{q,x} = \lambda_1 \dot{\gamma} \frac{\partial T}{\partial y}$$

$$J_{q,y} = -\lambda \frac{\partial T}{\partial y} - 3\lambda_2 \dot{\gamma}^2 \frac{\partial T}{\partial y}$$

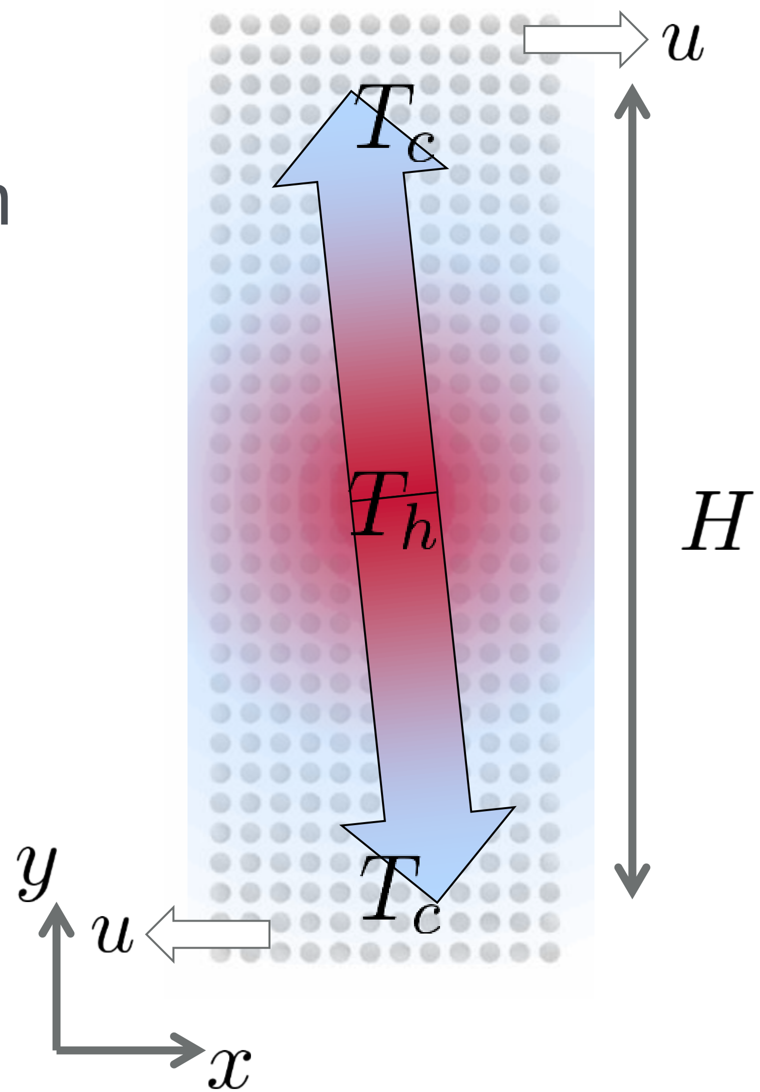
Beyond Fourier's law of Heat Conduction

- Strong shear flow generates heat flux in the flow x direction

$$J_{q,x} = \lambda_1 \dot{\gamma} \frac{\partial T}{\partial y}$$

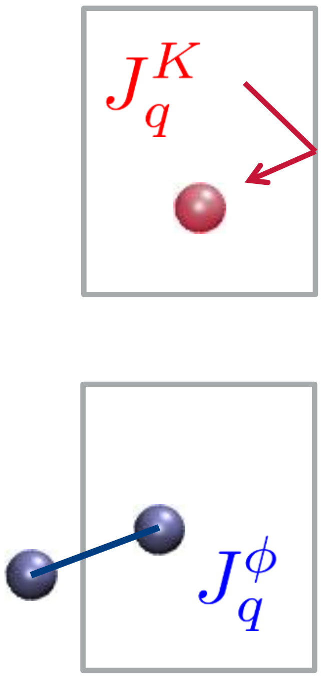
- An extra term in addition to Fourier's coefficient

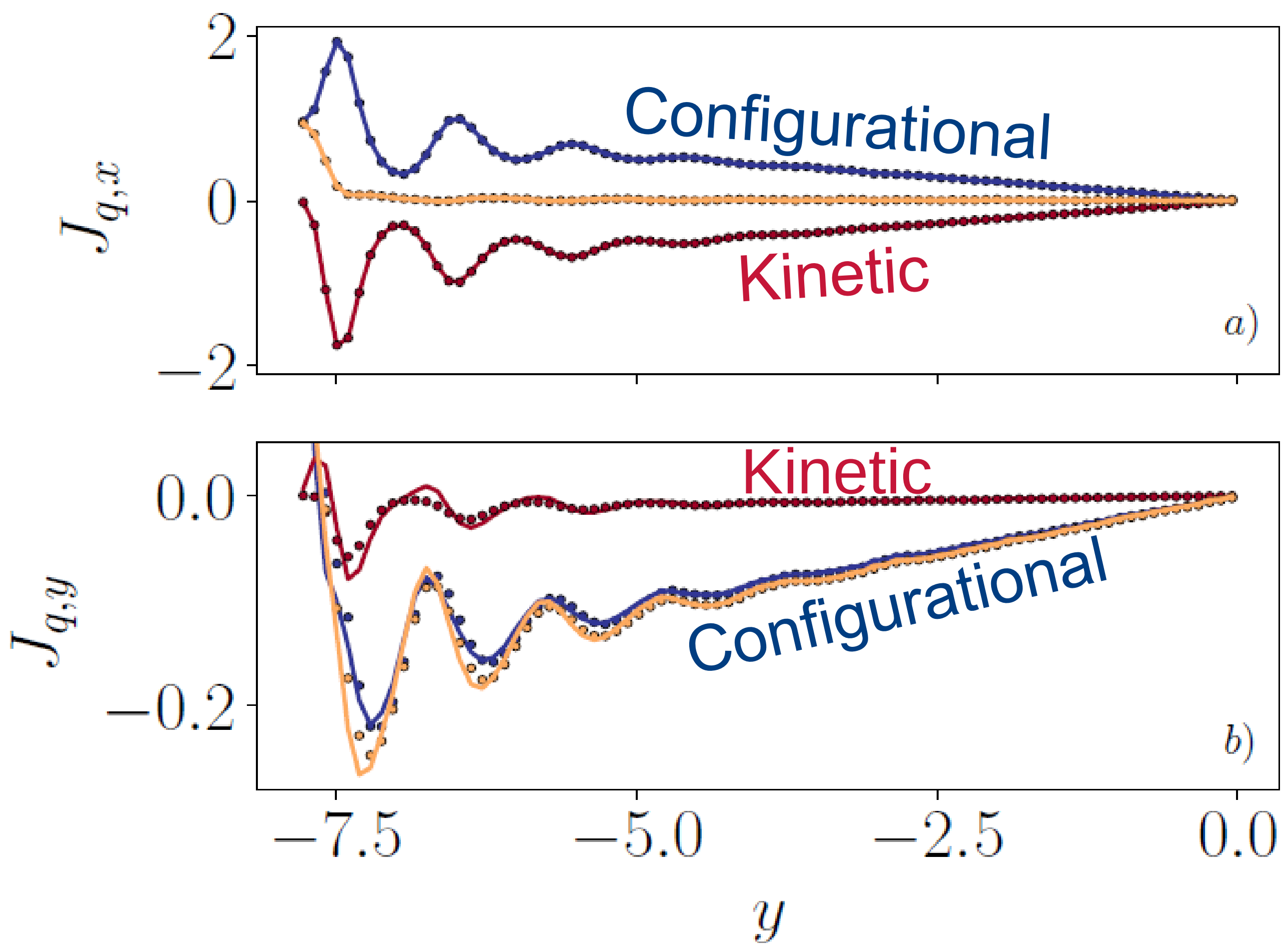
$$J_{q,y} = -\lambda \frac{\partial T}{\partial y} - 3\lambda_2 \dot{\gamma}^2 \frac{\partial T}{\partial y}$$



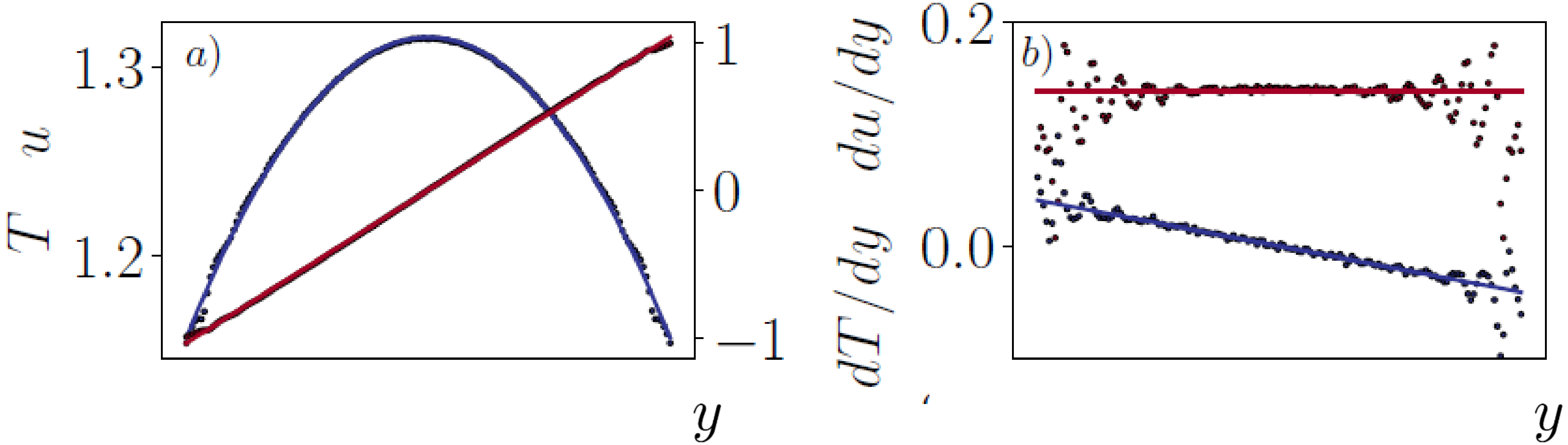
Heat Flux Components

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$





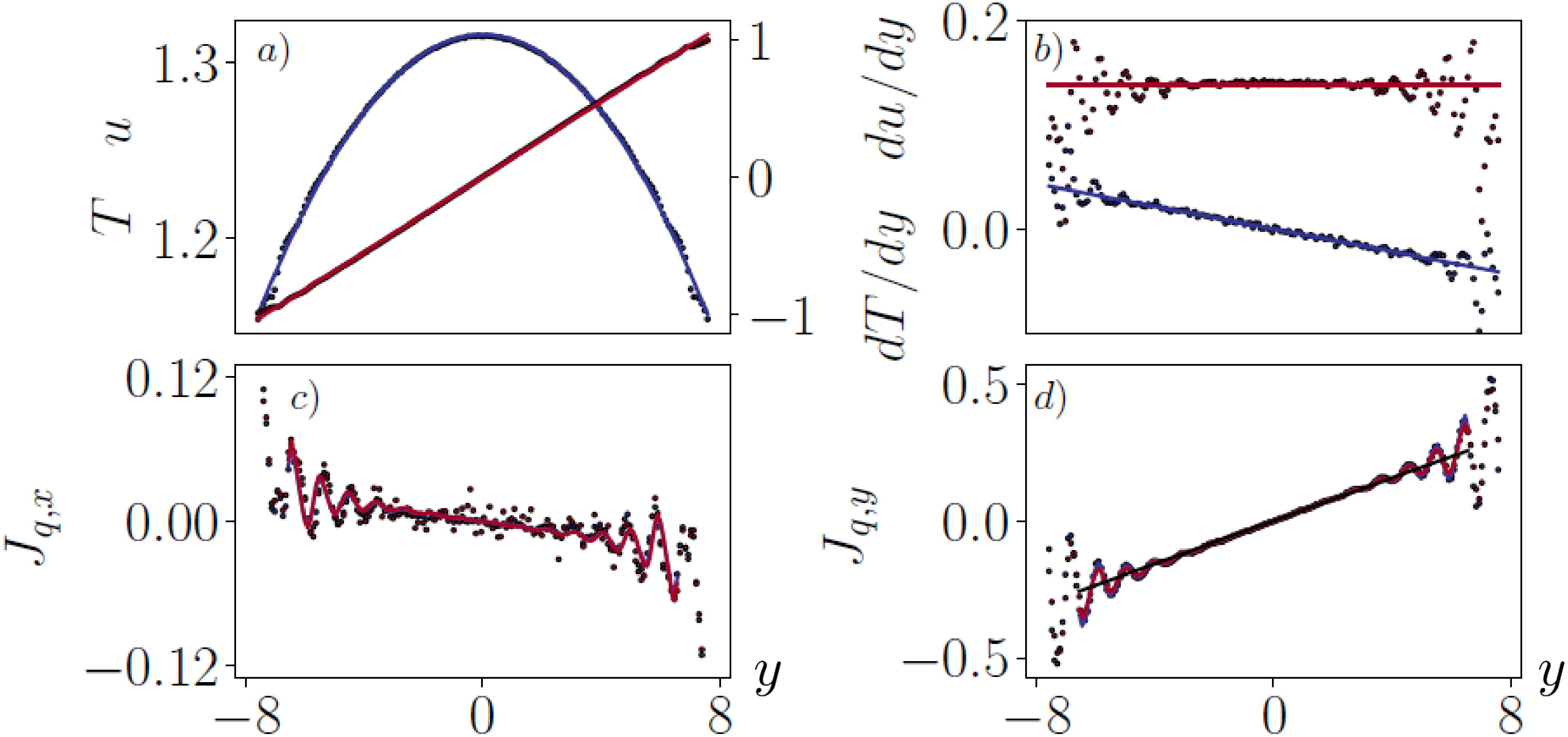
Fitting MD Channel to Get Coefficients



- Fitting to measured MD velocity and temperature
  - Velocity to straight line $u(y) = ay$
  - Temperature to parabolic $T(y) = by^2 + c$
- Derivative obtained from these fits $\dot{\gamma} = \frac{\partial u}{\partial y} = a$
- Correction for density stacking

$$\frac{\partial T}{\partial y} = 2b$$

Fitting MD Channel to Get Coefficients



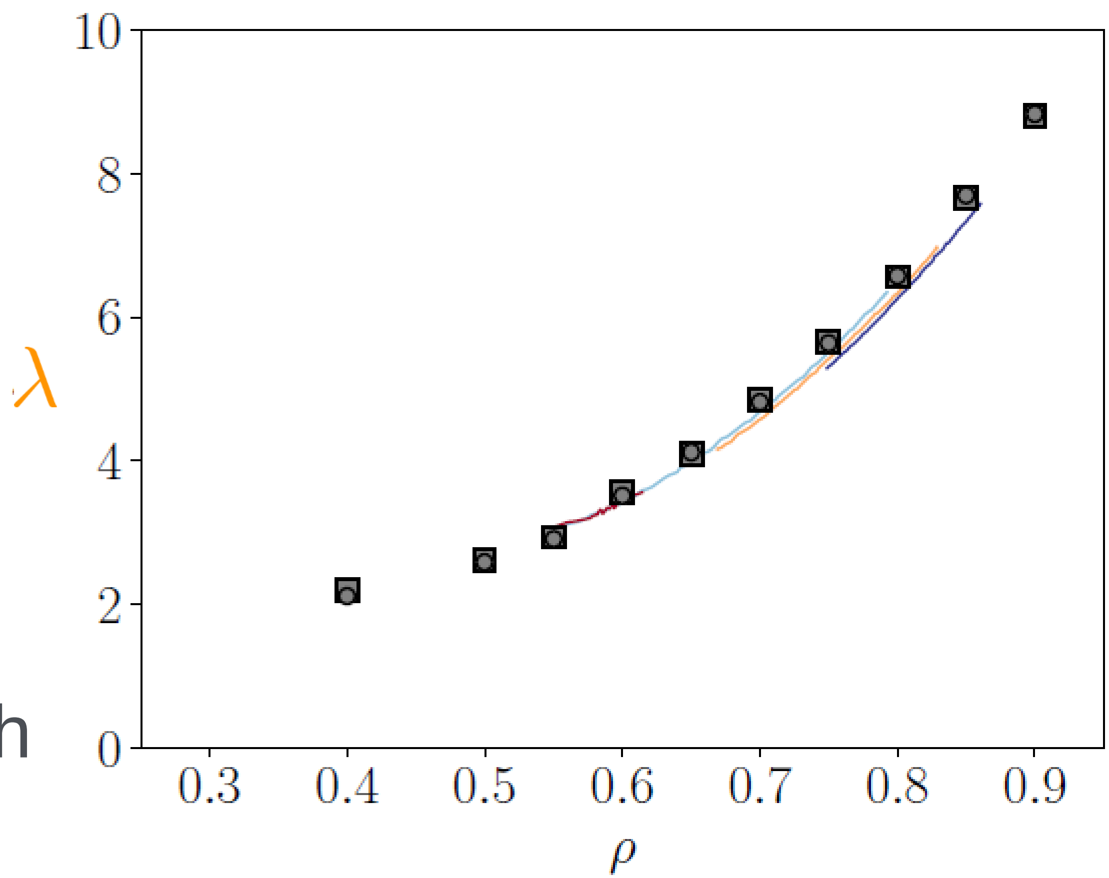
$$J_{q,x} = \lambda_1 \dot{\gamma} \frac{\partial T}{\partial y}$$

$$J_{q,y} = -\lambda \frac{\partial T}{\partial y} - 3\lambda_2 \dot{\gamma}^2 \frac{\partial T}{\partial y}$$

Recall Fourier's law of Heat Conduction

- Run over a range of different density channels

$$q_y = -\lambda \frac{\partial T}{\partial y}$$



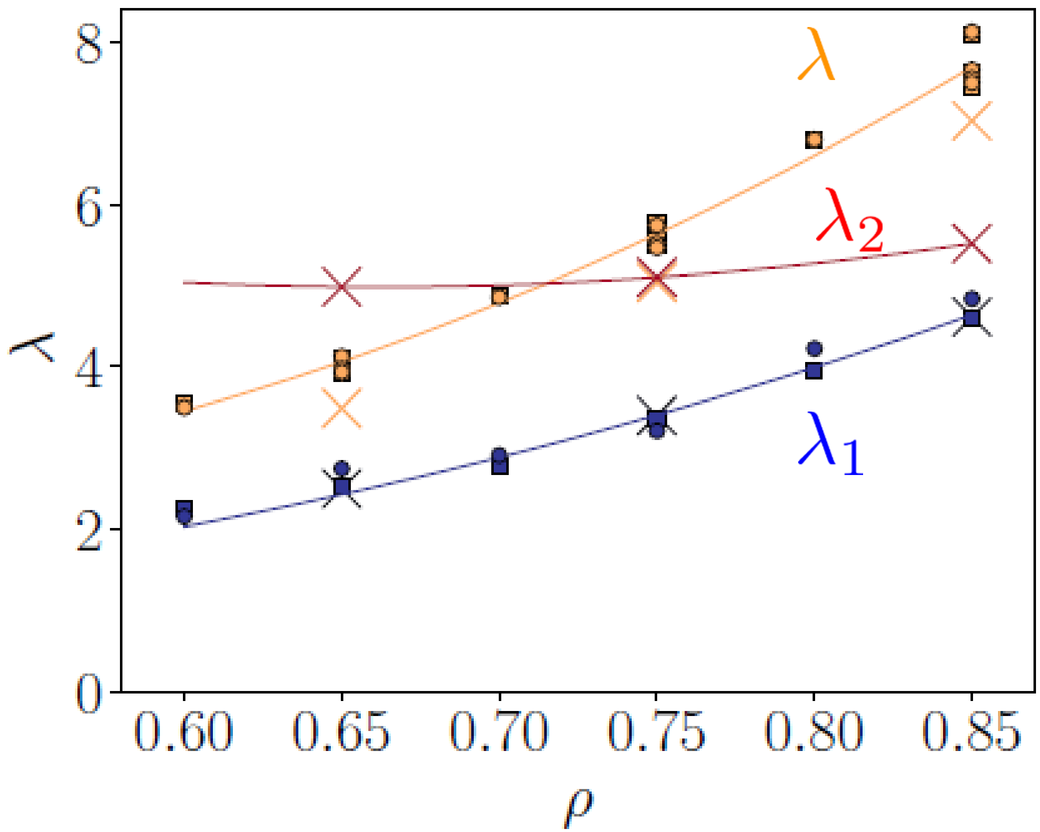
- Fourier's law shows good agreement with experimental results

Beyond Fourier's law of heat conduction

- Run over a range of different density channels

$$q_x = \lambda_1 \dot{\gamma} \frac{\partial T}{\partial y}$$

$$q_y = -\lambda \frac{\partial T}{\partial y} - 3\lambda_2 \dot{\gamma}^2 \frac{\partial T}{\partial y}$$

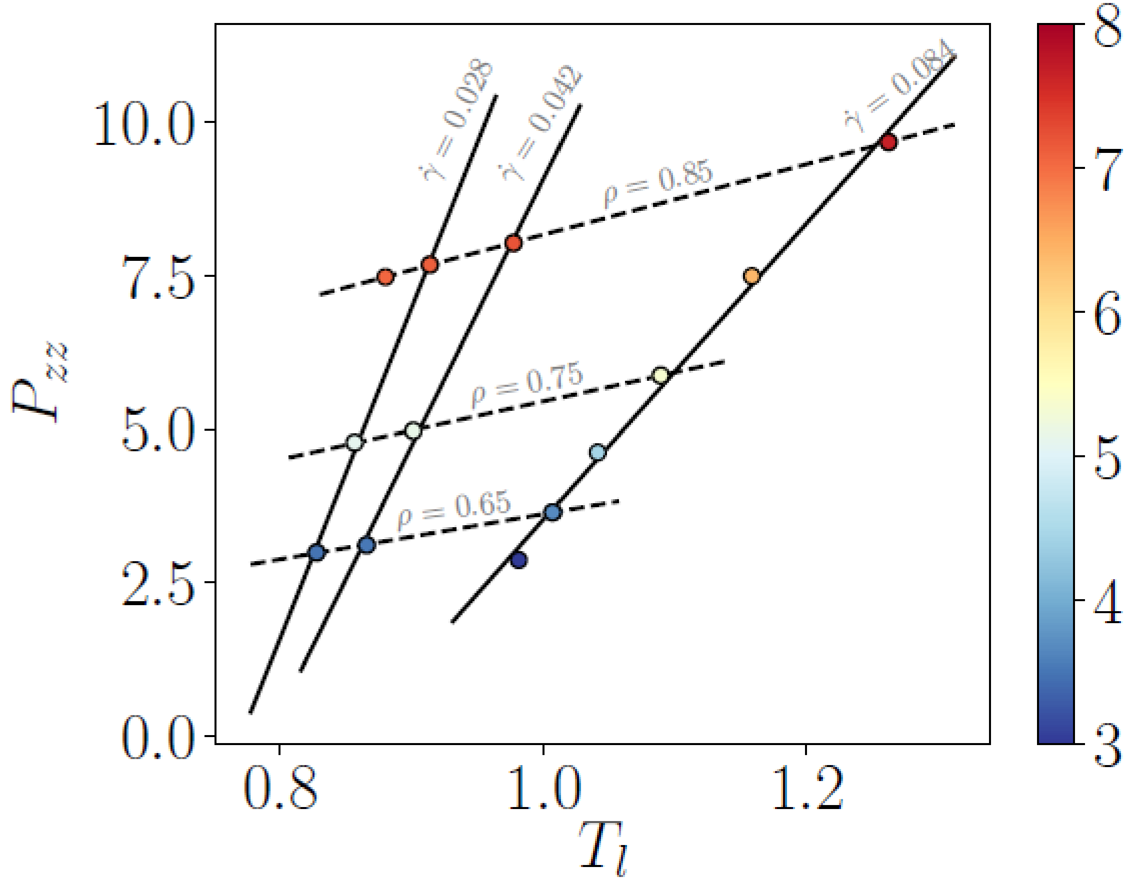


- Fourier's law shows good agreement with experimental results
- Additional coefficients **experimentally testable**

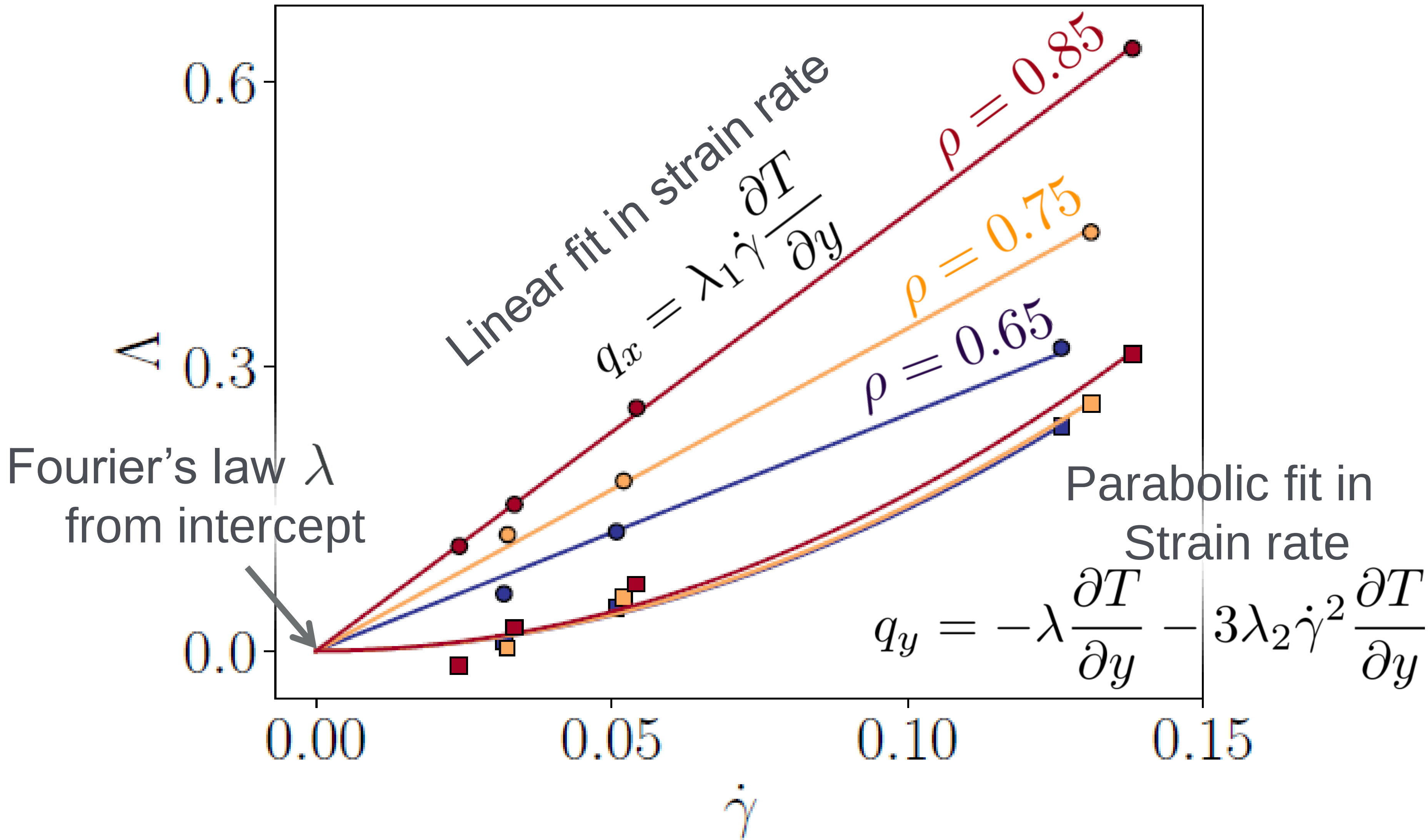
Range of Strain Rates

- Run over a range of systems with varying
  - Strain rate
  - Density
- Temperature varies depending on these values
- Use Fourier's law from part 2

$$\lambda(\rho, T)$$



Coefficients Vs. Strain Rate

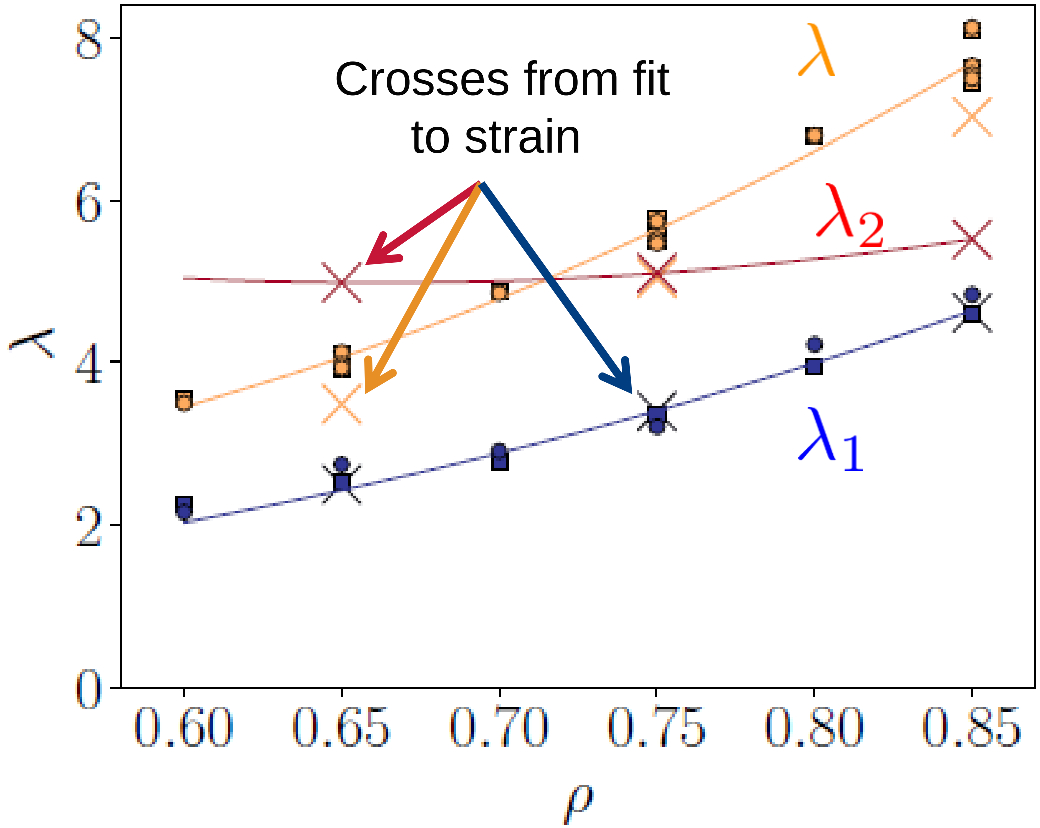


Beyond Fourier's law of heat conduction

- Run over a range of different density channels

$$q_x = \lambda_1 \dot{\gamma} \frac{\partial T}{\partial y}$$

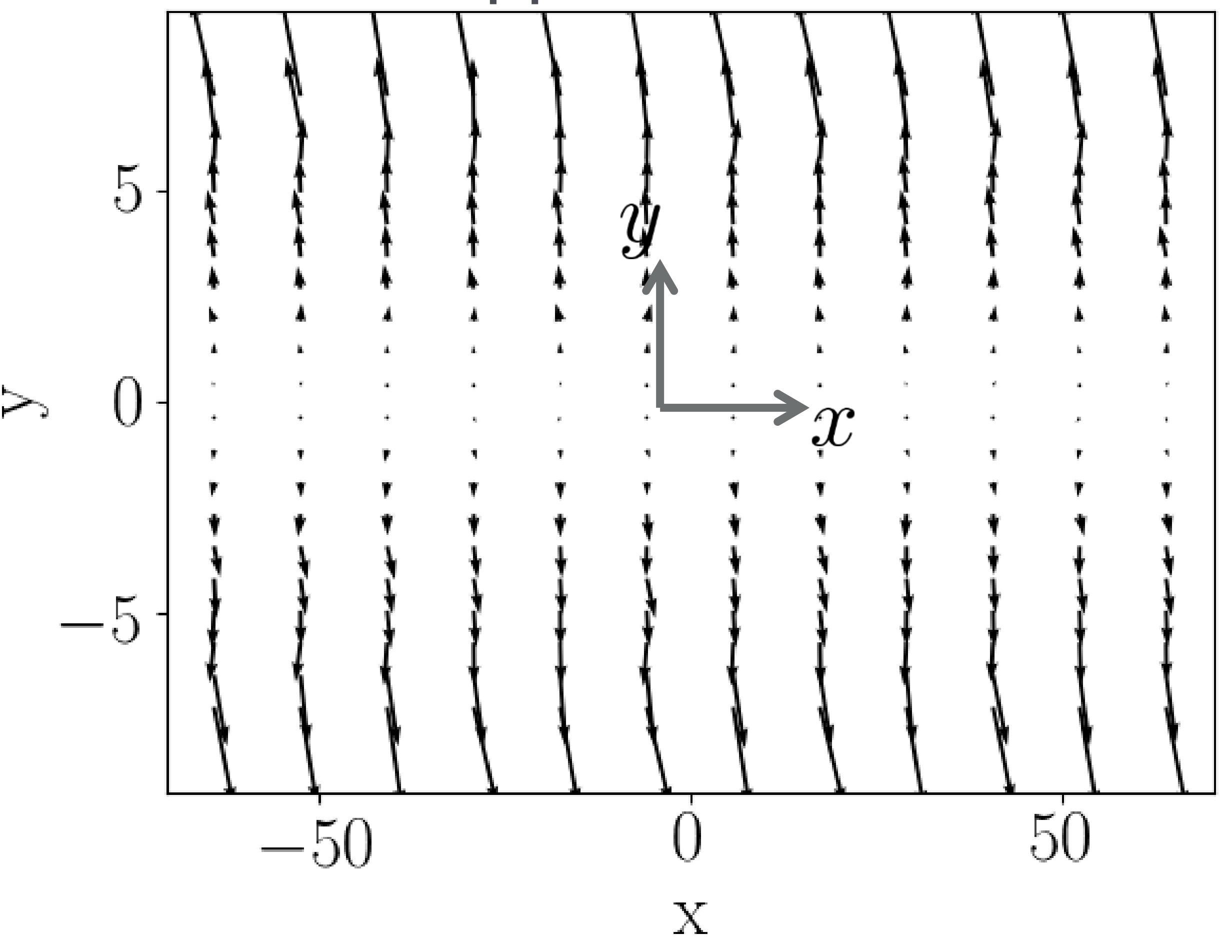
$$q_y = -\lambda \frac{\partial T}{\partial y} - 3\lambda_2 \dot{\gamma}^2 \frac{\partial T}{\partial y}$$

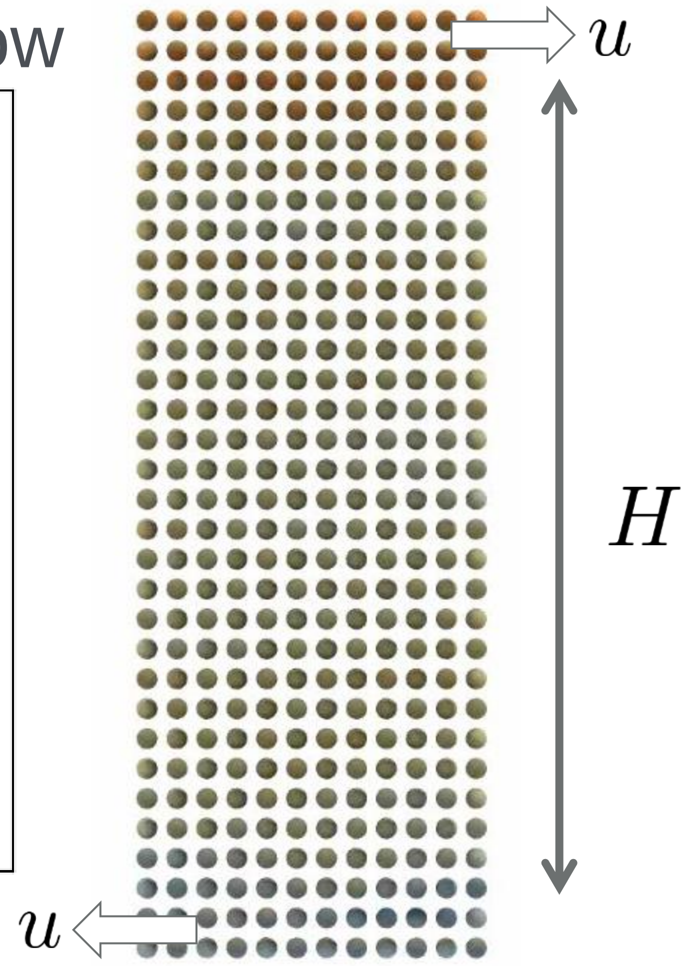


- Fourier's law shows good agreement with experimental results
- Additional coefficients **experimentally testable**

Vector Plot of Heat Flux

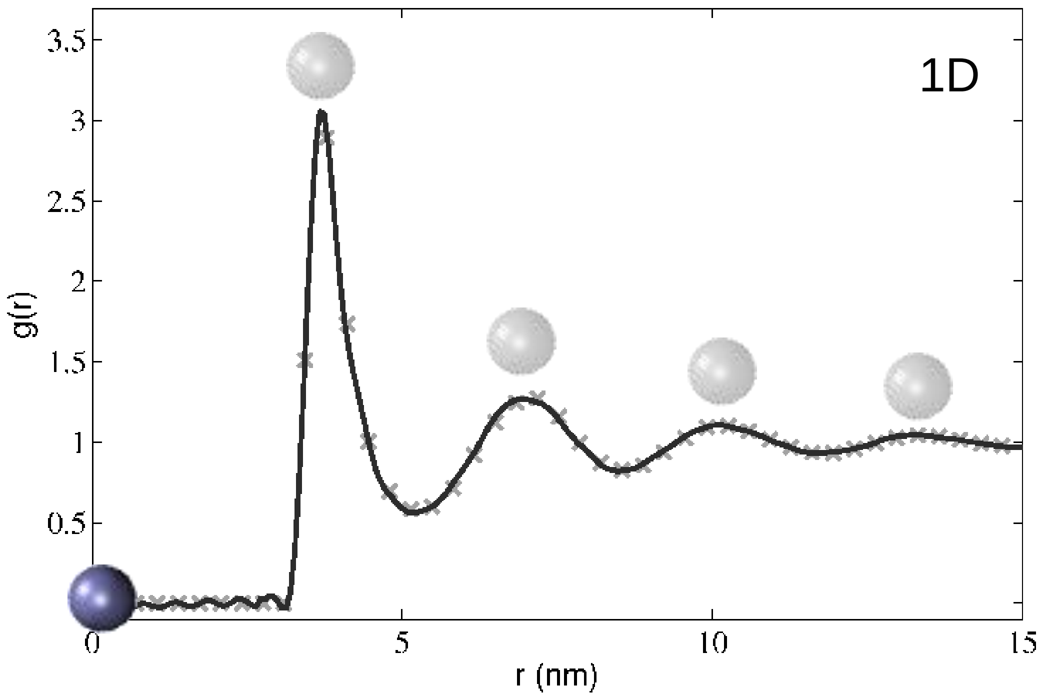
- Heat flux opposite direction to flow

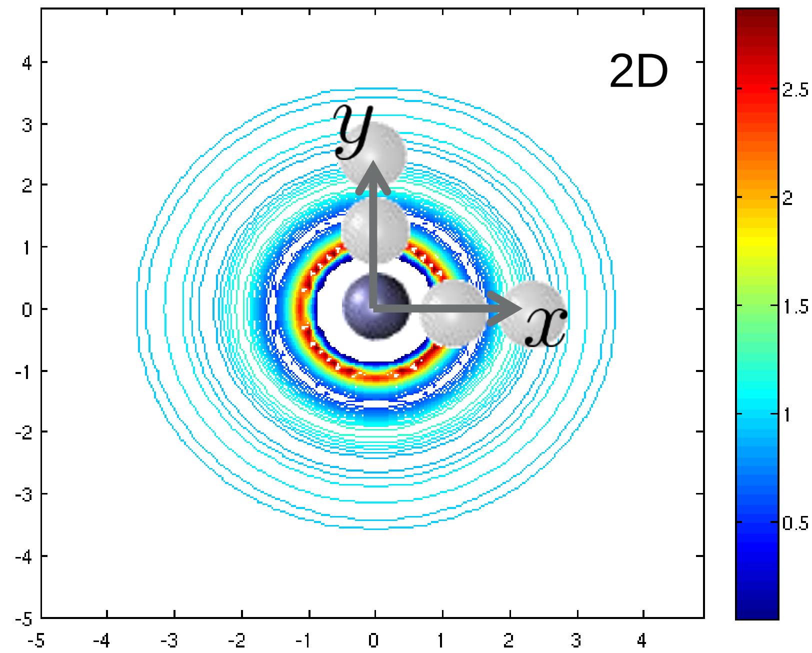




Proposed Mechanism

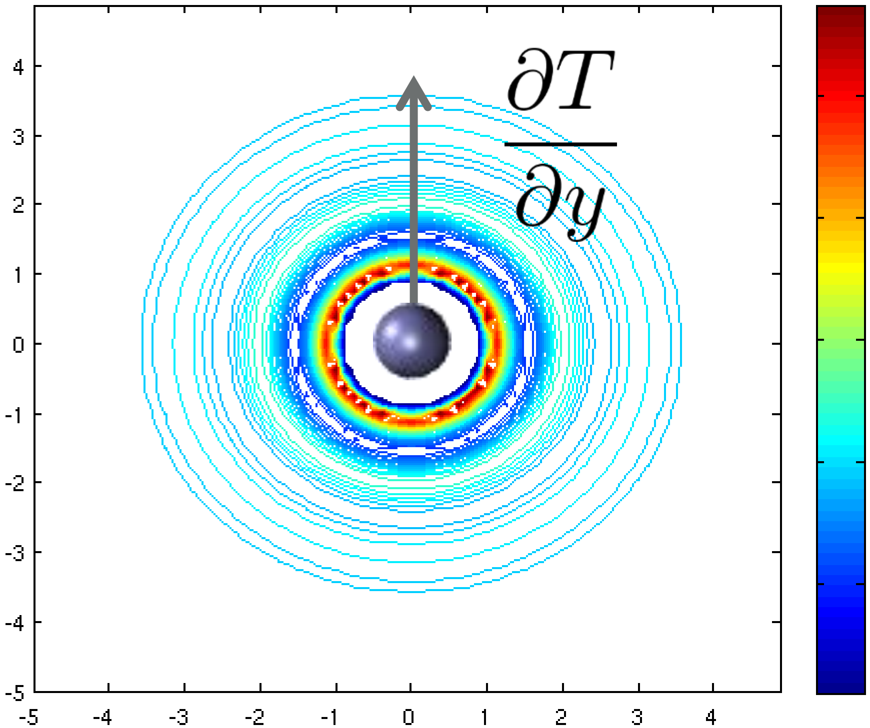
- Consider the Radial Distribution function



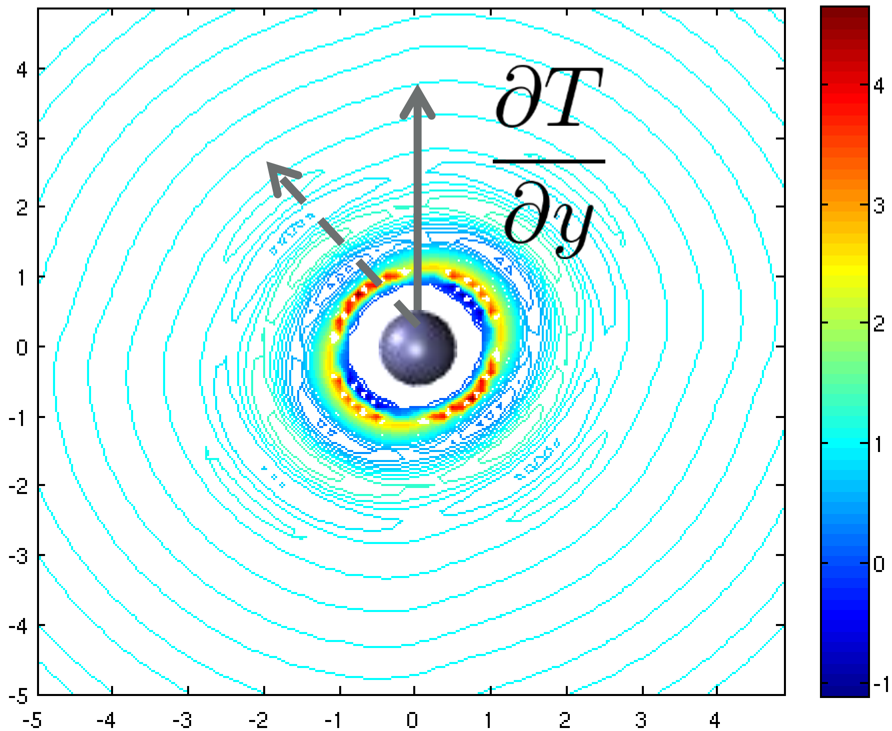


Proposed Mechanism

- Shearing distorts the molecular structure



Unsheared RDF



Sheared RDF

Conclusions

- Molecular dynamics captures the full structure of a fluid and allows non-equilibrium heat flux measurements
- In temperature driven flow, values for Fourier's law coefficient match experiments
- Applying a shear flow results in strain-temperature couplings
- A heat flux occurs in the direction of flow
- Coefficients measured over a range of densities could be compared to experiments

Summary

- Introduction
  - Heat Flux with Fourier's law and beyond
  - Molecular Dynamics

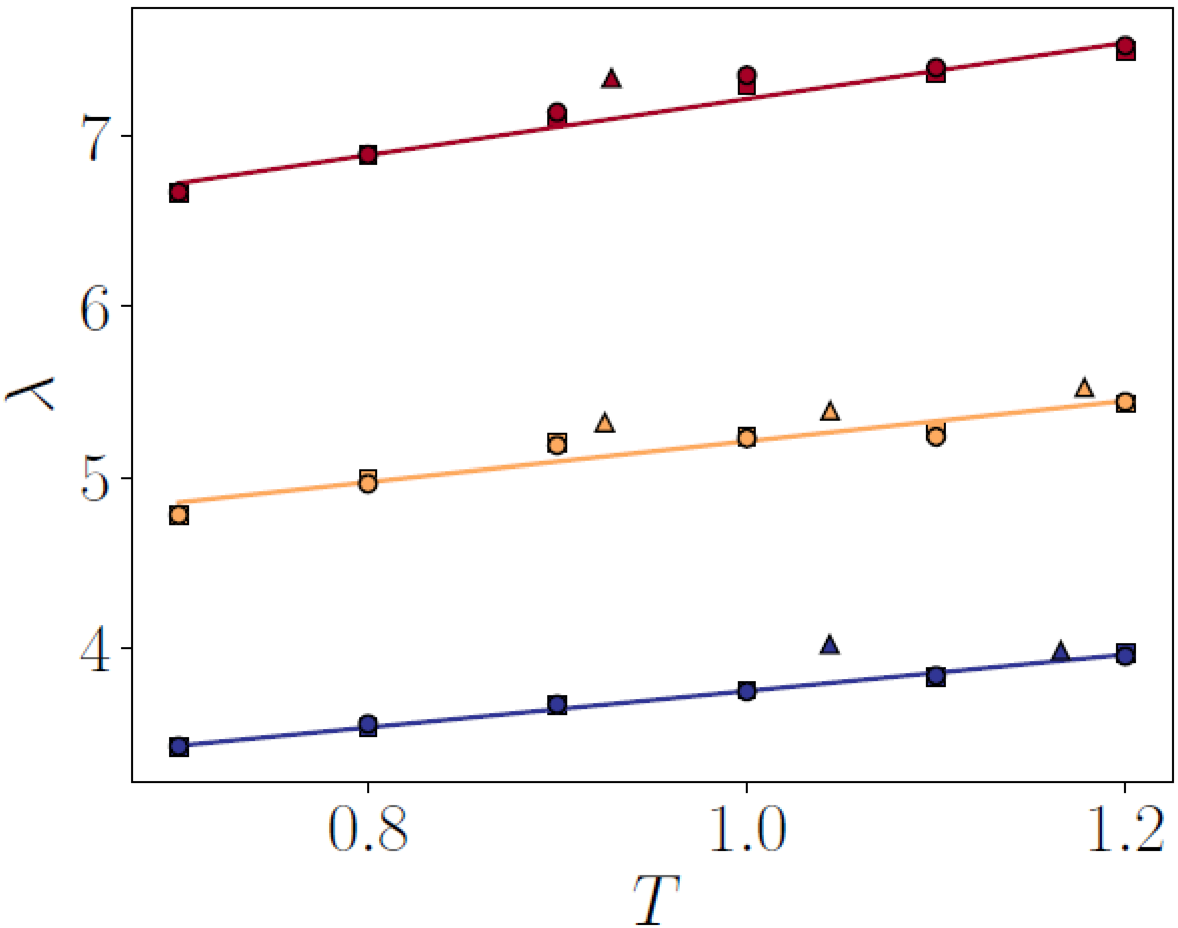
- Two Cases
  - Temperature-Driven Flow
  - Shear-Driven (Couette) Flow

Questions

- Any Questions?

Fourier's law of Heat Conduction

- Run over a range of different temperature channels
- Linear variation as a function of temperature

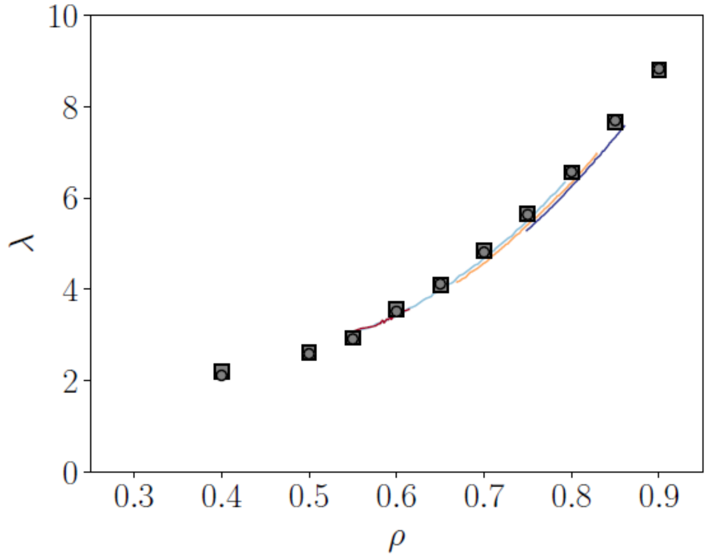


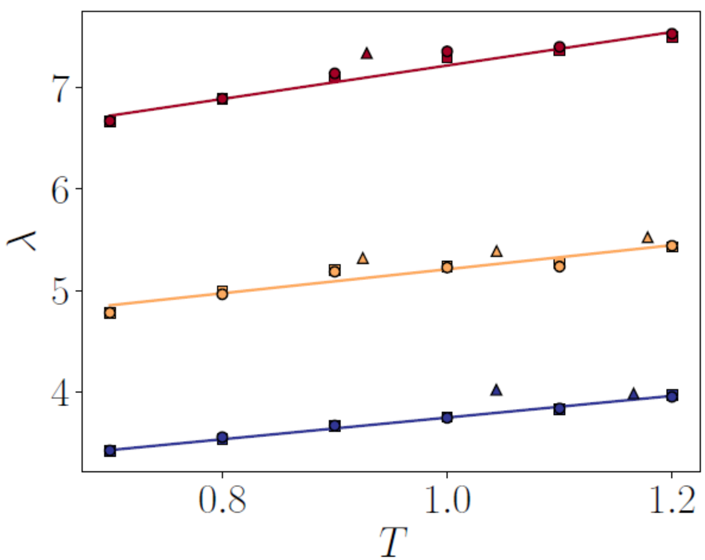
Fourier's law of Heat Conduction

Brunel University London

- Using simple fits to both curves, we can predict Fourier's coefficient for density and temperatures

$$\lambda(\rho, T) = 21.3\rho^2 - 14.2\rho + 3.92 + (T-1)\left[13\rho^2 - 17\rho + 6.63\right]$$





Predictions from Both Systems

- Fourier's law from system 1

$$\lambda_f(\rho_l, T_l) = \lambda'_f(\rho_l) + m_T(\rho_l)\,(T_l - 1)$$

$$\lambda'_f(\rho_l) = 21.3\rho_l^2 - 14.2\rho_l + 3.92$$

$$m_T(\rho_l) = 13.0\rho_l^2 - 17.0\rho_l + 6.63$$

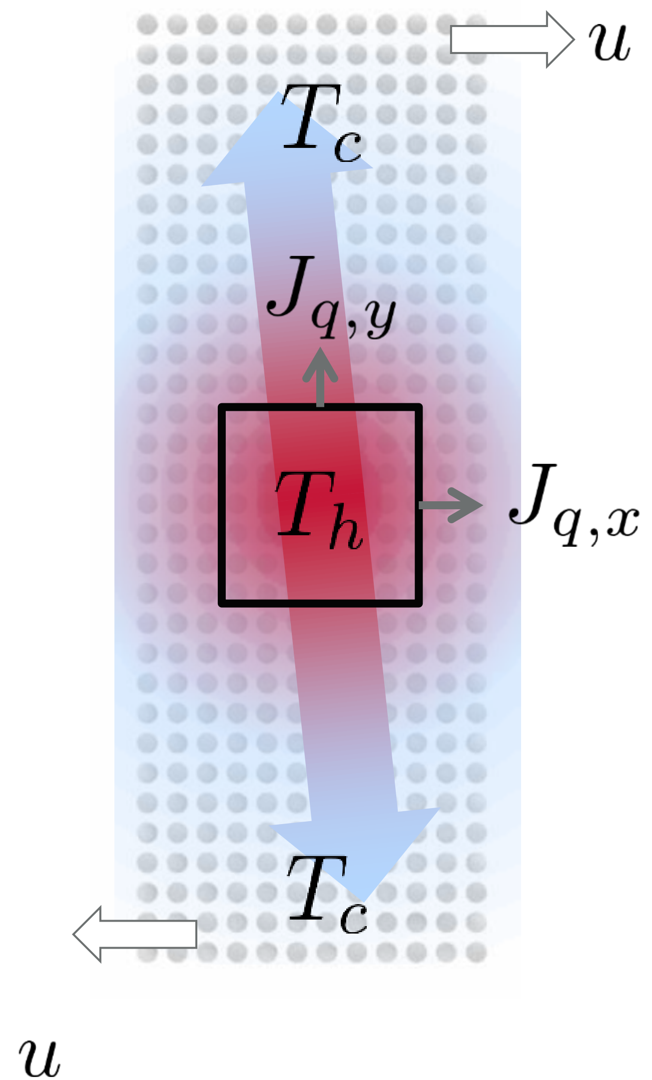
ρ_l	T_l	System 2 intercept	Eq. (51) $\lambda(\rho_l, T_l)$	Eq. (51) $\lambda(\rho_l, T_{wall})$
0.65	0.9	3.50	4.00	3.37
0.75	0.95	5.04	5.60	4.89
0.85	1.0	7.03	7.65	6.77

- We need to measure heat flux in
  - The parallel (x) direction
  - The wall-normal (y) direction
- Define a volume to measure the heat flux either
  - Inside the volume

$$\int_V \boldsymbol{J_q} dV$$

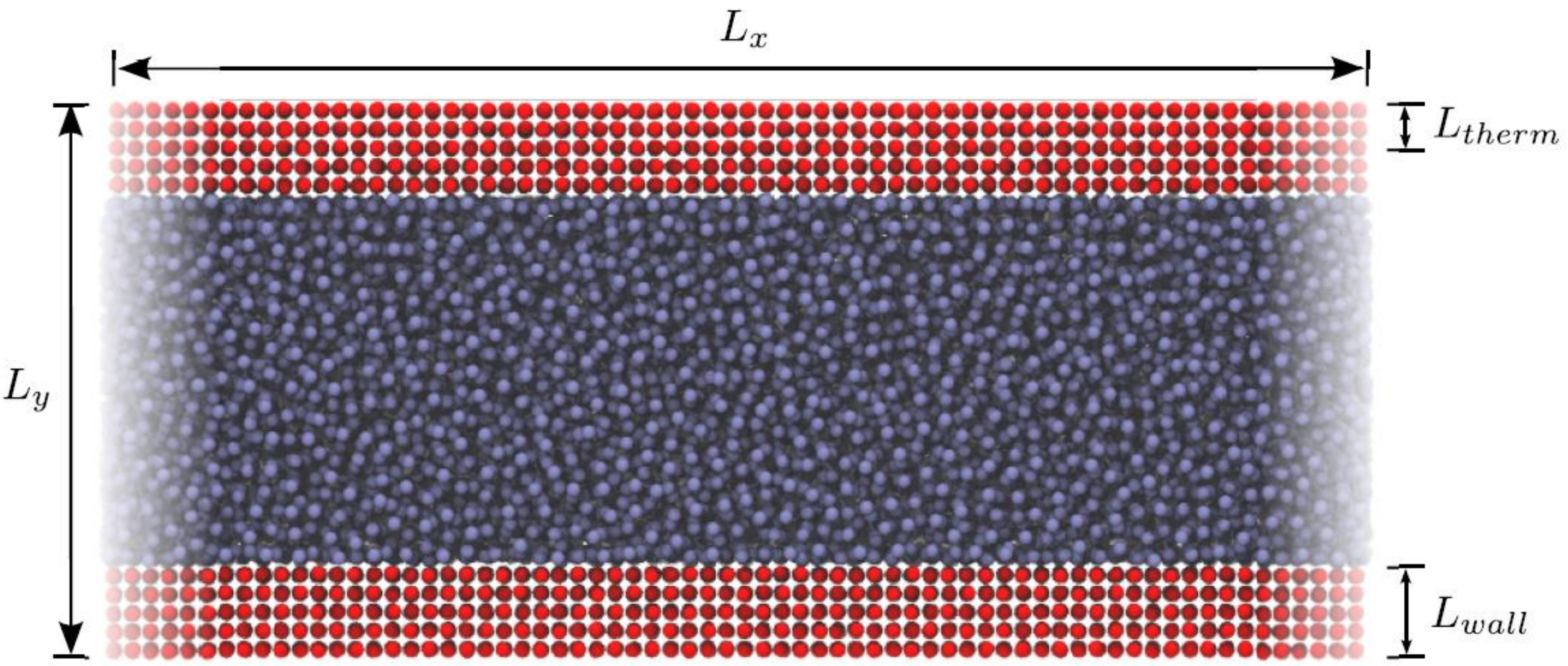
  - Over the surfaces

$$\oint \boldsymbol{J_q} \cdot d\mathbf{S}$$



Channel Dimensions

- The MD channels L_y=15.8, L_{wall}=4, L_{therm}=2
- L_x and L_z large for statistics ~half a million molecules



Integrating the Dirac delta functional gives a combination of Heaviside functionals, which can:

- *Be mathematically manipulated to give fluxes and forces*
- *Be implemented directly in MD codes*
- *Be linked to the continuum control volume.*

The Control Volume Functional

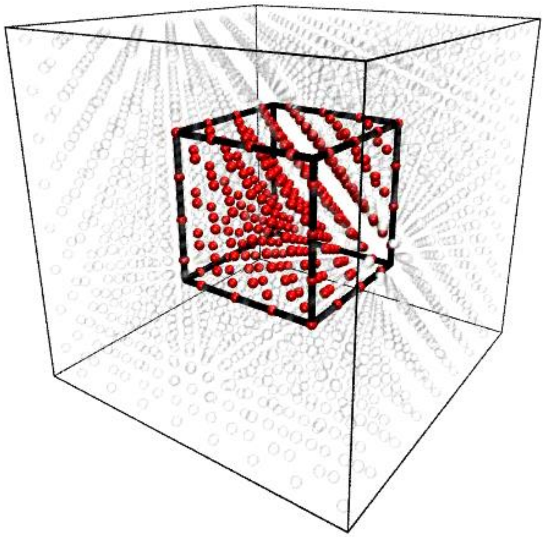
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

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



- 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 Functional

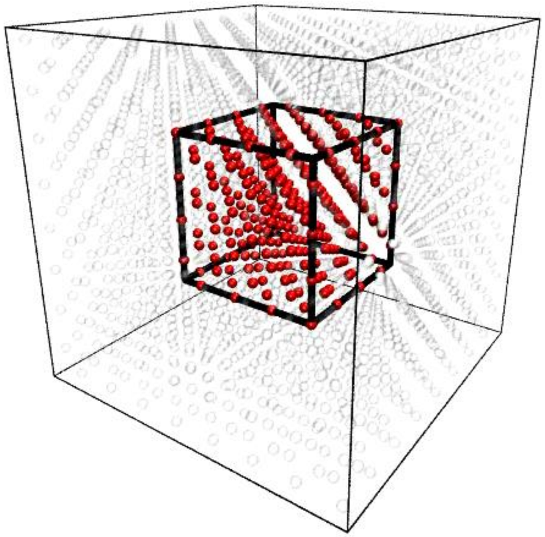
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

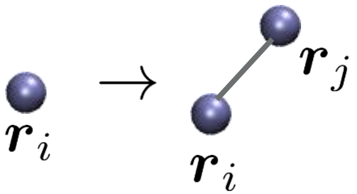
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

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



- Replace molecules with line of inter - molecular interaction

$$\boldsymbol{r}_i \rightarrow \boldsymbol{r}_i - s\boldsymbol{r}_{ij}$$



The Control Volume Functional

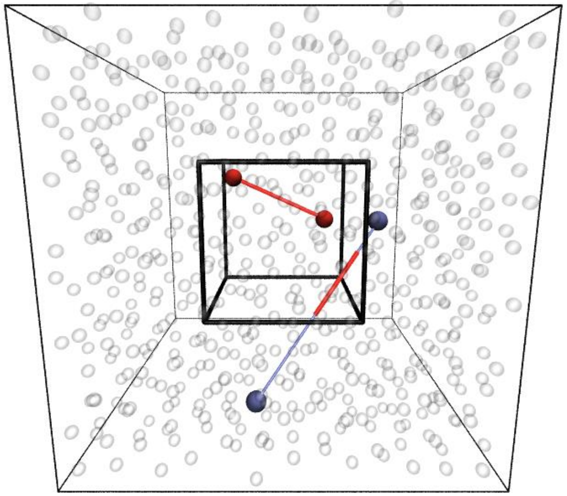
- The Control volume function is the integral of the Dirac delta function in 3 dimensions

$$\vartheta_s \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij}) dV =$$

$$\left[H(x^+ - x_i + sx_{ij}) - H(x^- - x_i + sx_{ij})\right]$$

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

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



- Length of interaction inside the CV

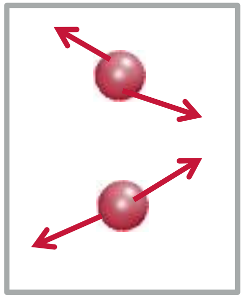
$$\ell_{ij} = \int_0^1 \vartheta_s ds$$

Volume Average Heat Flux

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$

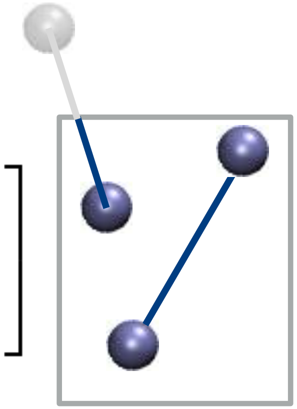
Kinetic

$$\mathbf{J}_{qV}^{K}\left(\mathbf{r}_m, t\right) = \frac{1}{\Delta V}\left[\sum_{i=1}^{N} e_i \mathbf{v}_i \vartheta_i - \bar{\mathbf{v}}\left(\mathbf{r}_m, t\right)\sum_{i=1}^{N} e_i \vartheta_i\right]$$



Configurational

$$\mathbf{J}_{qV}^{\phi}\left(\mathbf{r}_m, t\right) = -\frac{1}{\Delta V}\frac{1}{2}\left[\sum_{i,j}^{N} \mathbf{r}_{ij}\mathbf{F}_{ij}\cdot\mathbf{v}_i \ell_{ij} - \left(\sum_{i,j}^{N} \mathbf{r}_{ij}\mathbf{F}_{ij}\ell_{ij}\right)\cdot\bar{\mathbf{v}}\left(\mathbf{r}_m\right)\right]$$



Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

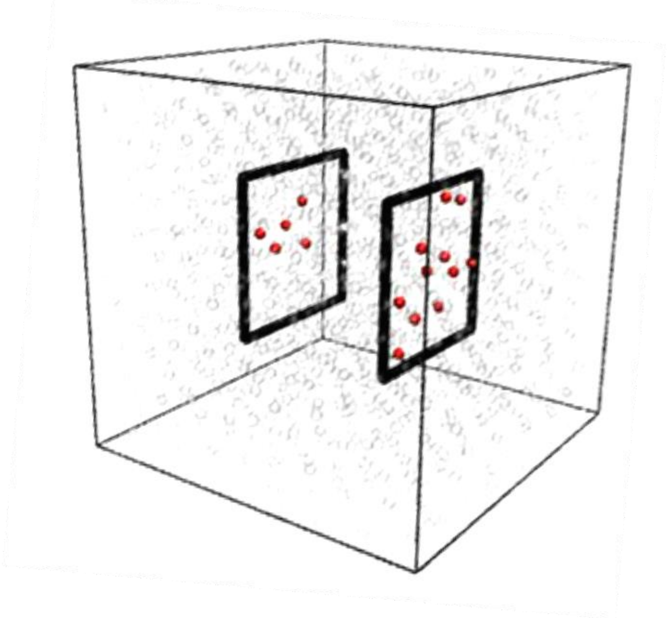
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right]$$
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$
$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

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

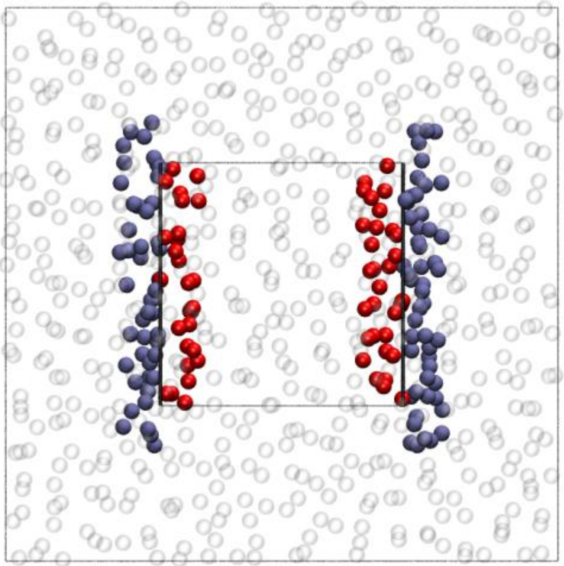


Derivative yields surface fluxes and stresses

Brunel University London

- Taking the Derivative of the CV function

$$\frac{\partial \vartheta_s}{\partial x} \equiv \left[\delta(x^+ - x_i + s x_{ij}) - \delta(x^- - x_i + s x_{ij}) \right]$$
$$\times \left[H(y^+ - y_i + s y_{ij}) - H(y^- - y_i + s y_{ij}) \right]$$
$$\times \left[H(z^+ - z_i + s z_{ij}) - H(z^- - z_i + s z_{ij}) \right]$$



- Surface fluxes over the top and bottom surface

$$dS_{xij} \equiv \int_0^1 \frac{\partial \vartheta_s}{\partial x} ds = dS_{xij}^+ - dS_{xij}^-$$

$$dS_{xij}^+ = \frac{1}{2} \underbrace{\left[sgn(x^+ - x_i) - sgn(x^+ - x_j) \right]}_{MOP} \boxed{S_{xij}}$$

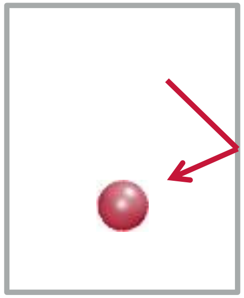
Surface (MOP) Heat Flux

Brunel University London

- Total = Kinetic + Configurational $J_q = J_q^K + J_q^\phi$

Kinetic

$$J^K_{qA,x} = \frac{1}{\Delta A_x} \sum_{i=1}^{N} e_i \left(v_{ix} - \bar{v}_x \left(r_m \right) \right) \delta \left(x_i - x_+ \right) S_{xi}$$



Configurational

$$J^\phi_{qA,x} = -\frac{1}{\Delta A_{x+}} \frac{1}{2} \sum_{i,j}^{N} \mathbf{F}_{ij} \cdot \left(\mathbf{v}_i - \bar{\mathbf{v}} \left(\mathbf{r}_{x+} \right) \right) S_{ij} \left(x_+ \right)$$