

Measuring Heat Flux Beyond Fourier's Law

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Summary

- Introduction
 - Heat Flux - Fourier's law and beyond
 - Molecular Dynamics
- Two Cases
 - Temperature-Driven Flow
 - Shear-Driven (Couette) Flow

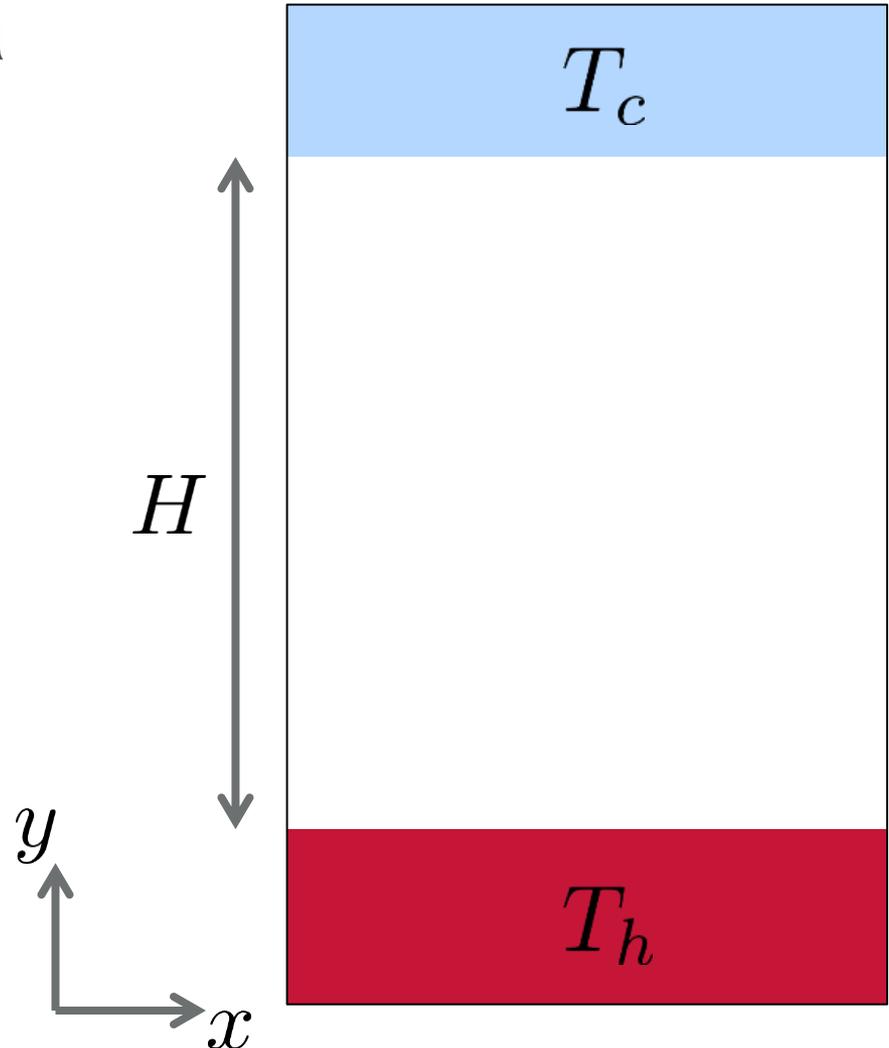
Section 1

INTRODUCTION

Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

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



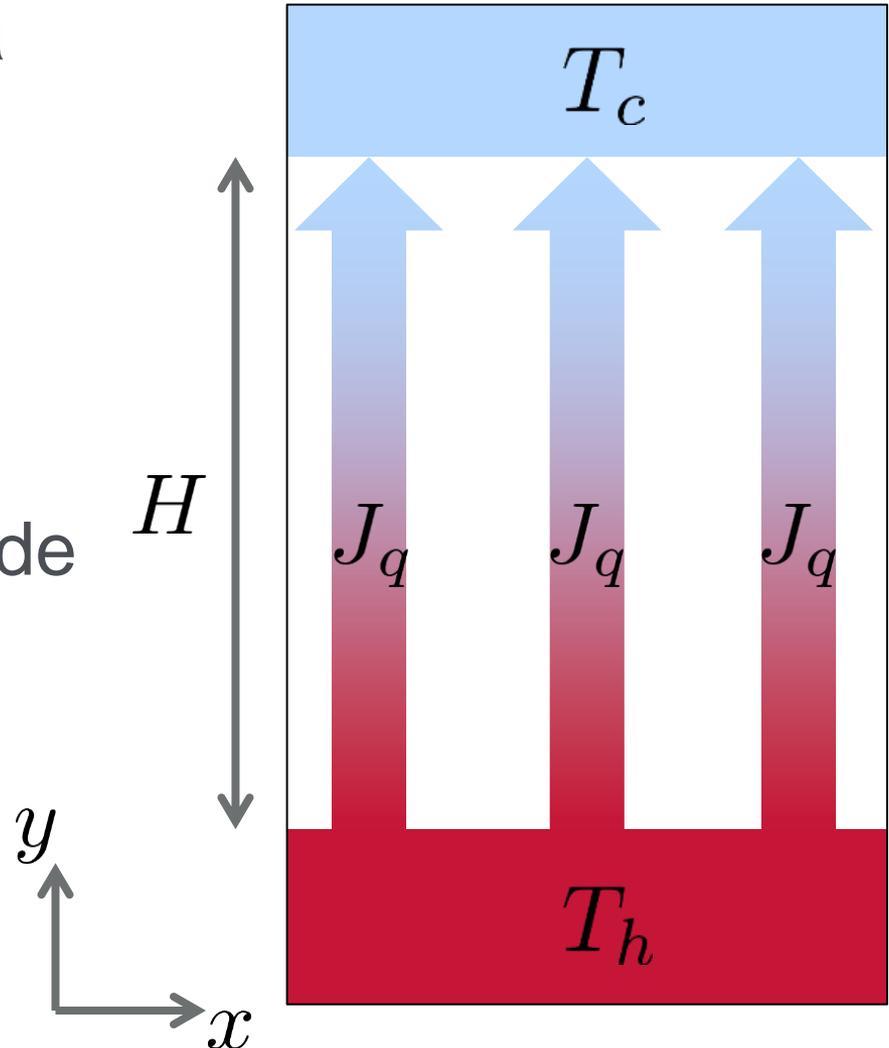
Fourier's law of Heat Conduction

- 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

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

Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

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

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

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

$$\lambda \quad + \nabla T \nabla \mathbf{u} \frac{\partial^2 \mathbf{J}_q}{\partial \nabla \mathbf{u} \partial \nabla T}$$

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

$$\mathbf{J}_q \approx -\lambda_{\text{eff}} \cdot \nabla T$$

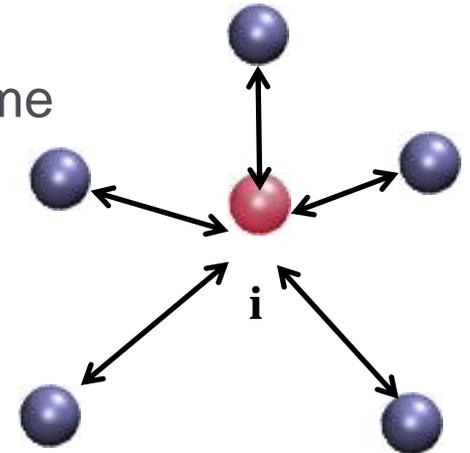
Molecular Dynamics

Discrete molecules in continuous space

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

$$\ddot{\mathbf{r}}_i \rightarrow \dot{\mathbf{r}}_i$$

$$\dot{\mathbf{r}}_i \rightarrow \mathbf{r}_i(t)$$

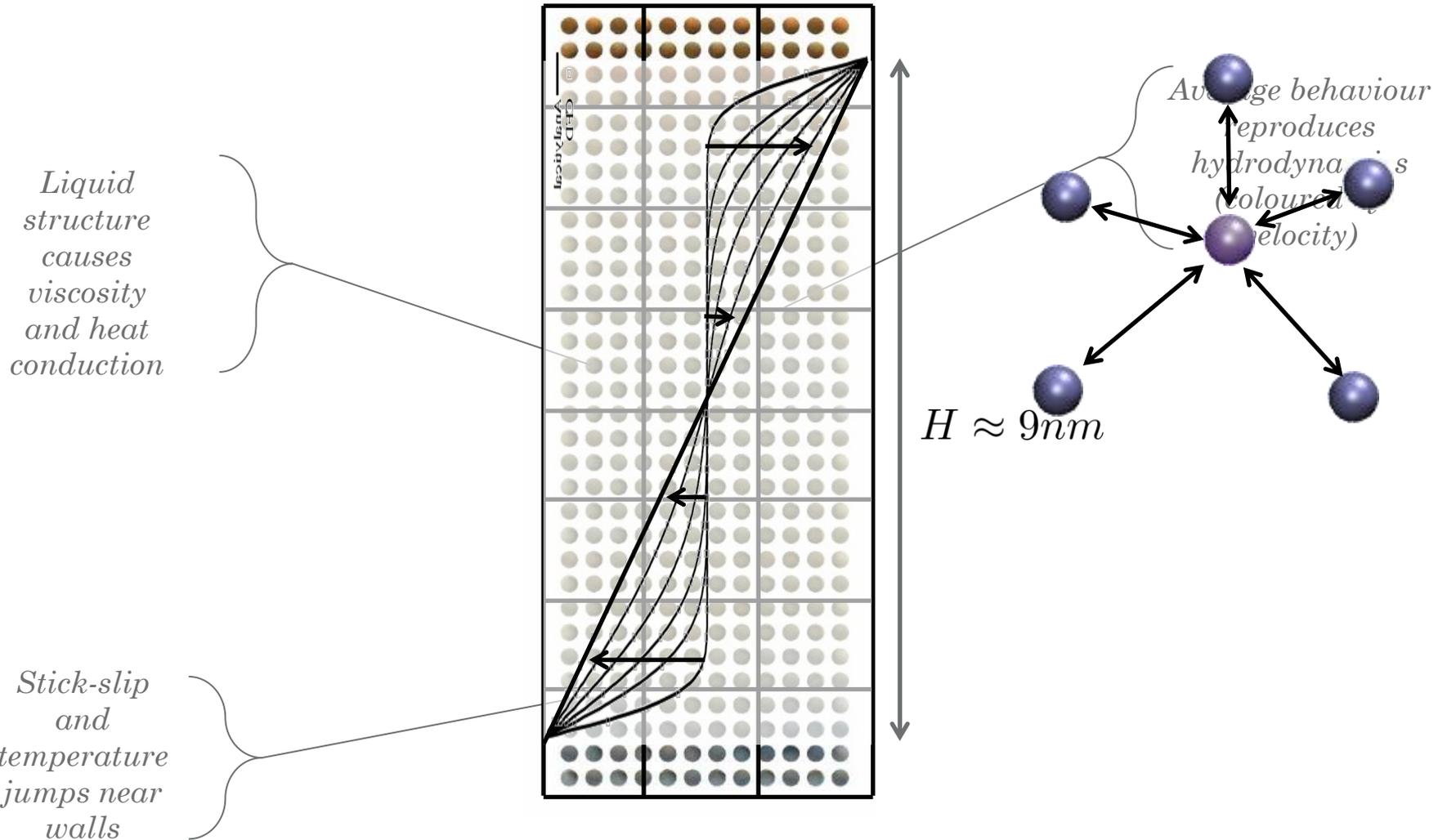


Acceleration obtained from forces

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

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

Molecular Dynamics

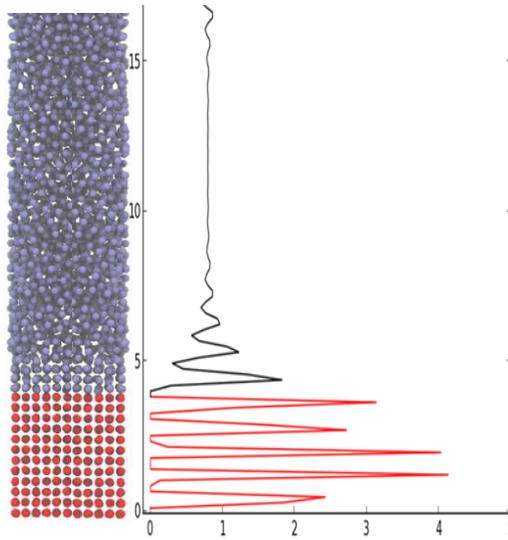




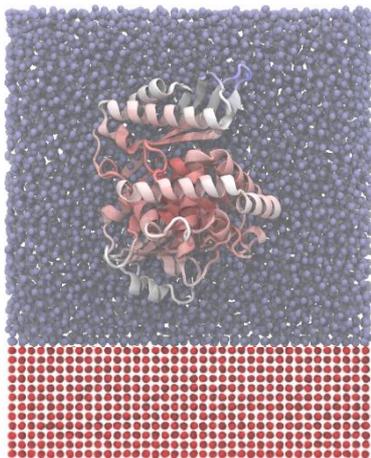
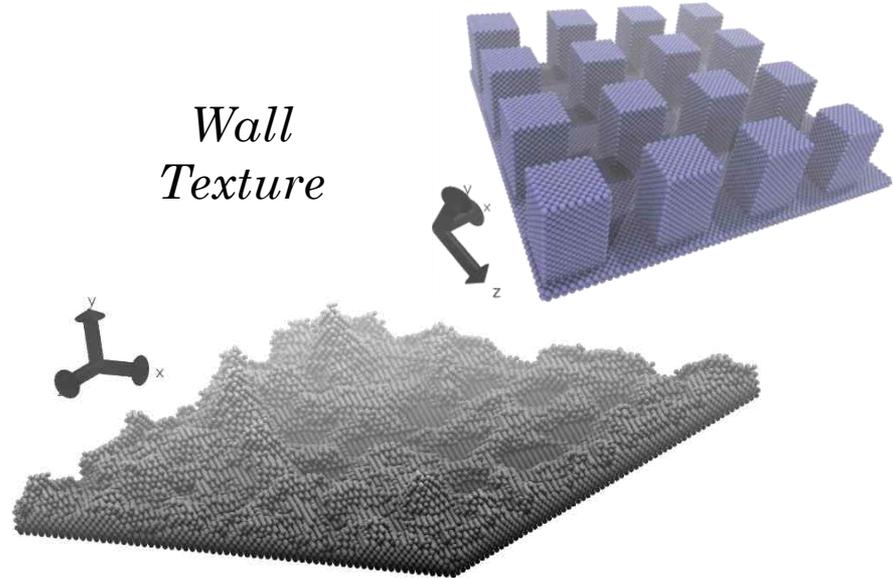
Molecular Dynamics – Complex Walls and Fluids

Liquid structure causes viscosity

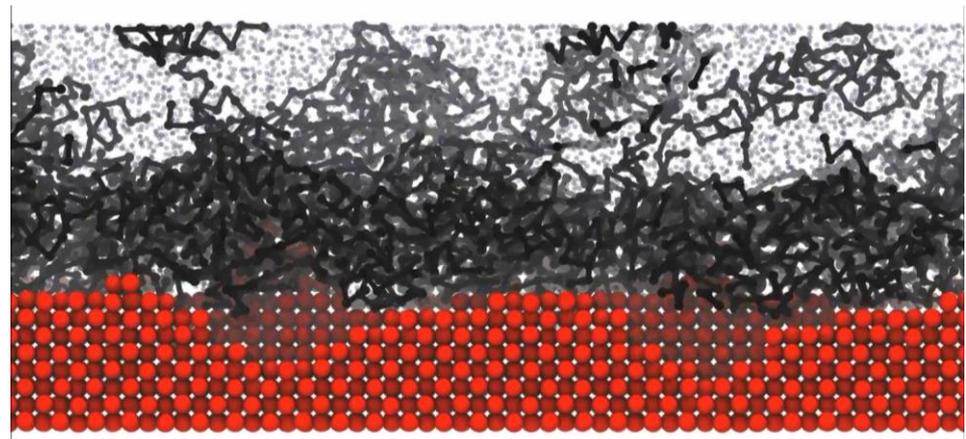
Stick-slip near walls



Wall Texture



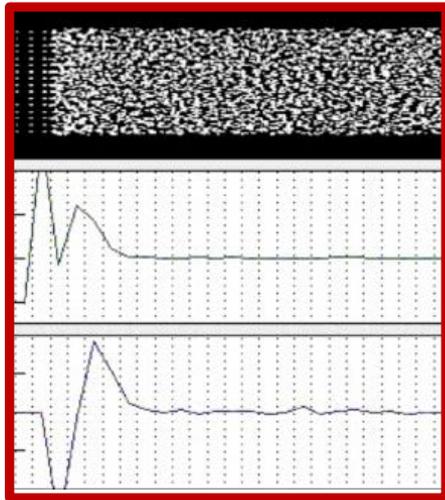
Molecules of arbitrary complexity



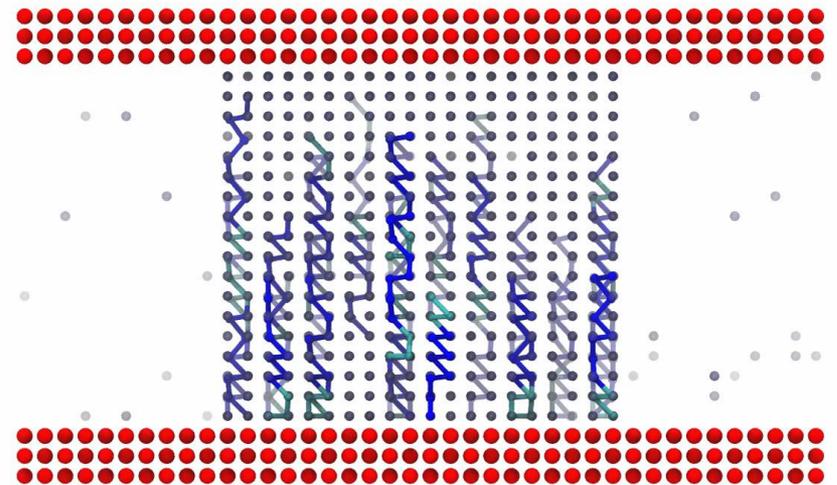
Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

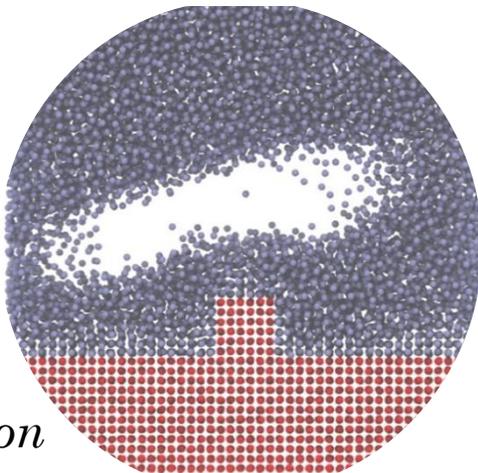
Shockwave



Droplet Formation



Nucleation



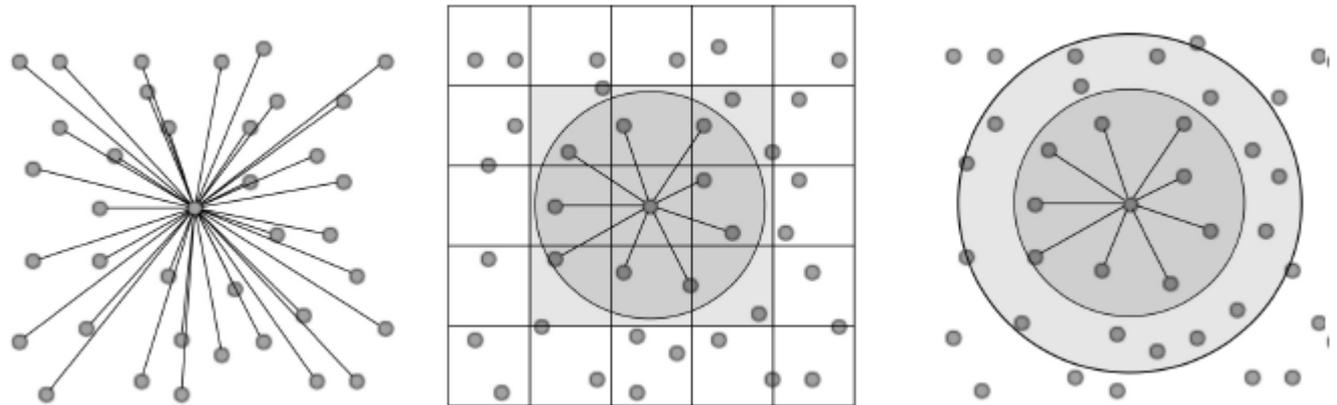
Contact line

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)

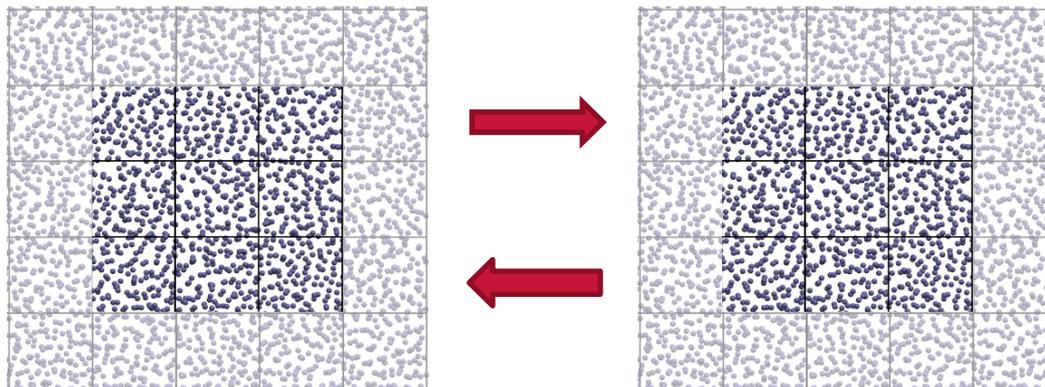
$$m_i \frac{dv_i}{dt} \approx m_i \frac{v_i(t + \Delta t/2) - v_i(t - \Delta t/2)}{\Delta t} = F_i$$

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

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)

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

- Remove heat from system

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

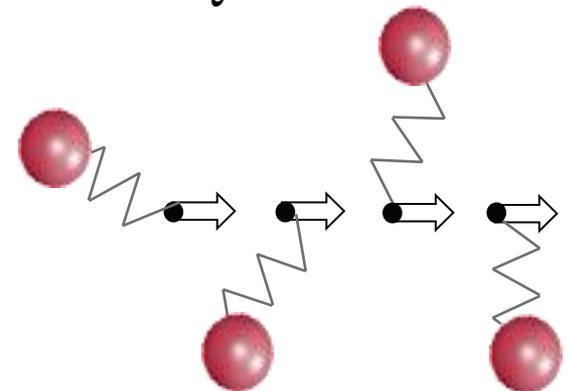
- Tethered molecules

- (An)harmonic spring to tether site

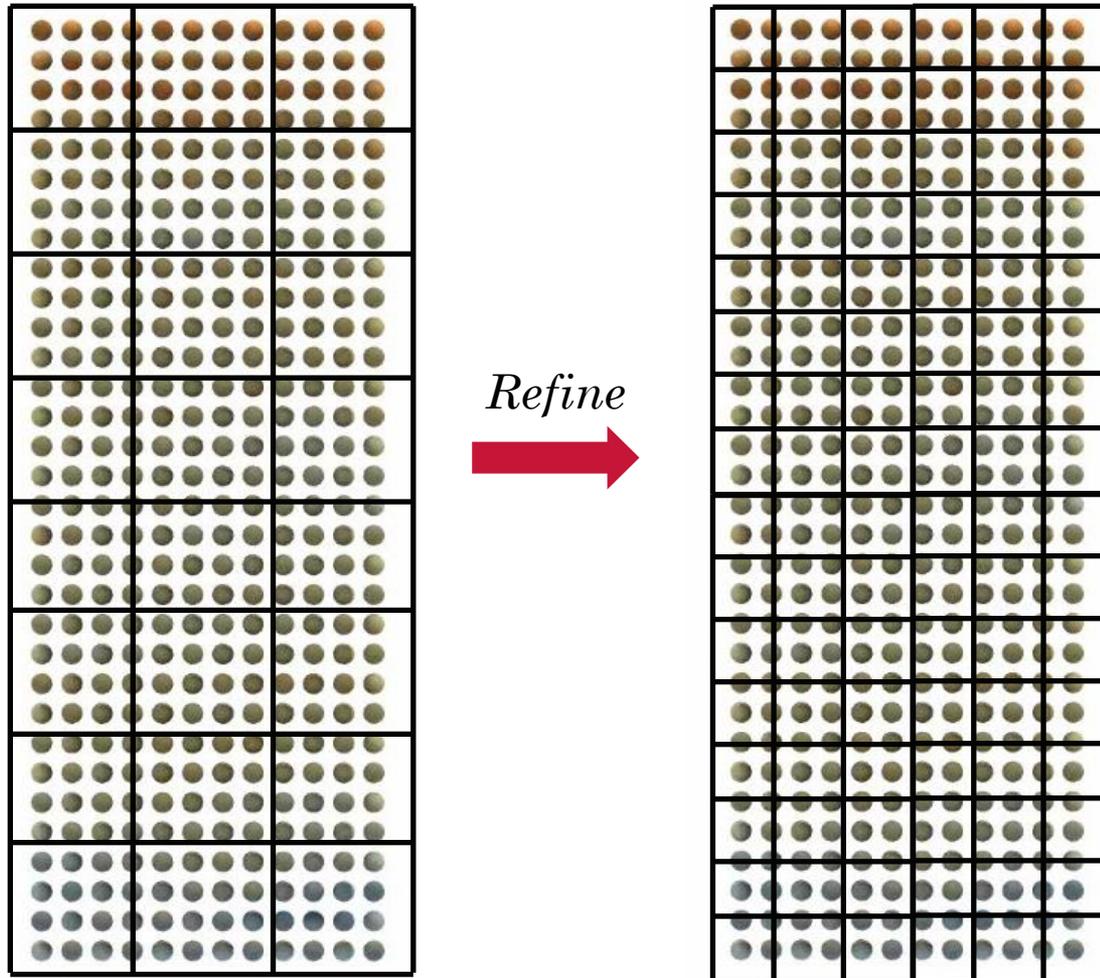
- With sliding

- Slide site and (optionally) molecules

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



Molecular Dynamics - Averaging



- Density in a cell

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

- Momentum in a cell

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

- Temperature in a cell

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

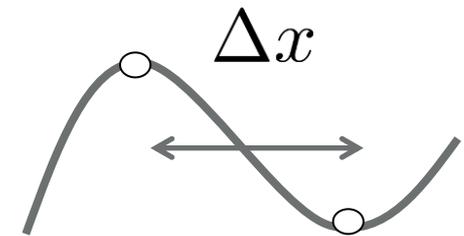
Continuum vs. Discrete

- Consider the pointwise energy equation

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

- Based on the continuum hypothesis

- Describes fields
- Valid at every point in space
- Uses the calculus



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



Irving and Kirkwood (1950)

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777.9 cm². The band at 809.7 cm⁻¹ has been interpreted as 2N₂O, the rather large difference between calculated and observed frequency being ascribed to the proximity of the A₁ fundamental. However, this band could be an upper-stage band corresponding to the R₁₂ combination, as an interpretation as the R₁₂ combination, 2104-558 cm⁻¹. The faint sharp Raman band at 838 cm⁻¹ has been interpreted as an upper-stage band 2X 407 + ν₂ - ν₂, rather than as the R₁₂ difference band 1561 - 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 CO₂ and CS₂.

ACKNOWLEDGMENTS

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JUNE, 1950

THE JOURNAL OF CHEMICAL PHYSICS

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

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 (Received November 11, 1949)

The equations of hydrodynamics—continuity equation of number, equation of energy transport—are derived by means of the classical statistical mechanics. They are obtained for the stress tensor and heat current density in terms of molecular variables. In addition to the familiar terms according to the kinetic theory of gases, there are terms depending upon intermolecular forces. The contributions of intermolecular forces to the stress tensor and heat current density are represented, 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 separation of energy transport will be treated, 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 (analogous for a liquid) which will be expressed as a quadrature involving the potential of interaction between a pair of molecules. The heat current density is the sum of the familiar kinetic part and a quadratic involving the potential of interaction between a pair of molecules. The equations of hydrodynamics for the stress tensor and heat current density in the first article of this series were previously stated in a preliminary form. To obtain explicit expressions for the pair probability density and the density and current density one would use the Boltzmann equation. The Boltzmann equation is used to solve the Liouville equation in this paper, and then previous repeated integrations. This work was supported by the U. S. ONR under Contract No. 49(52)-ONR-100, and by the California Institute of Technology. J. G. Kirkwood, J. Chem. Phys., 14, 30 (1946).

This program is suitable 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 Grestel using a generalized "superposition" assumption. Another, a generalization of the well-known Fokker-Planck equation of stochastic theory, has been derived by Kirkwood by introducing the concepts of time smoothing and a friction constant. This latter equation has been used to obtain an expression for the stress tensor and a friction constant of fluid viscosity and, thereby, applied to problems of molecular variables for the linear (in terms of volume viscosity) and nonlinear (in terms of volume viscosity) and theory of sound. The generalization of the Boltzmann equation to non-uniform gradient leads to an explicit expression for the heat current and thereby an expression for the coefficient of thermal conductivity. We shall assume, for purposes of 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 interaction forces.

*M. Born and H. S. Green, Proc. Roy. Soc. A, 189, 10 (1945).
 J. G. Kirkwood, J. Chem. Phys., 17, 109 (1949).
 J. G. Kirkwood, J. Chem. Phys., 14, 30 (1946).
 J. G. Kirkwood, J. Chem. Phys., 14, 30 (1946).

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

$$\rho(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t)$$

satisfying the normalization condition

$$\int \dots \int \rho(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t) d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{p}_1 \dots d\mathbf{p}_N = 1$$

where $d\mathbf{R}_i$ stands for a volume element in the configuration space and $d\mathbf{p}_i$ a volume element in the momentum space of the i th molecule. Changes in time according to the well-known Liouville equation

$$\frac{d\rho}{dt} + \sum_{i=1}^N \left[\frac{\partial \rho}{\partial \mathbf{p}_i} \cdot \frac{\partial U}{\partial \mathbf{R}_i} + \frac{\partial \rho}{\partial \mathbf{R}_i} \cdot \left(\frac{\partial U}{\partial \mathbf{p}_i} + \mathbf{V}_i \right) \right] = 0$$

where U is the potential energy of the entire system. Any dynamical variable, $\mathcal{A}(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t)$, has an expectation value given at time t by

$$\langle \mathcal{A} \rangle = \int \dots \int \mathcal{A}(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t) \rho(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t) d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{p}_1 \dots d\mathbf{p}_N$$

We then denote by $\langle \mathcal{A} \rangle$ the expectation value of a product of a and f taken over phase space. Providing a does not depend on time explicitly, the rate of change of the expectation value of a is given by

$$\frac{d}{dt} \langle \mathcal{A} \rangle = \langle \dot{\mathcal{A}} \rangle = \left\langle \sum_{i=1}^N \left[\frac{\partial \mathcal{A}}{\partial \mathbf{p}_i} \cdot \frac{\partial U}{\partial \mathbf{R}_i} + \frac{\partial \mathcal{A}}{\partial \mathbf{R}_i} \cdot \left(\frac{\partial U}{\partial \mathbf{p}_i} + \mathbf{V}_i \right) \right] \right\rangle$$

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

$$\frac{d}{dt} \langle \mathcal{A} \rangle = \left\langle \sum_{i=1}^N \left[\frac{\partial \mathcal{A}}{\partial \mathbf{p}_i} \cdot \frac{\partial U}{\partial \mathbf{R}_i} + \frac{\partial \mathcal{A}}{\partial \mathbf{R}_i} \cdot \left(\frac{\partial U}{\partial \mathbf{p}_i} + \mathbf{V}_i \right) \right] \right\rangle$$

providing the integrated part vanishes at $\mathbf{R}_i = \pm \infty$. Likewise, since \mathbf{V}_i is independent of momentum \mathbf{p}_i , and since f falls off rapidly as $\mathbf{p}_i \rightarrow \pm \infty$, the integral of Green's theorem in the momentum space of \mathbf{p}_i yields

$$\frac{d}{dt} \langle \mathcal{A} \rangle = \left\langle \sum_{i=1}^N \left[\frac{\partial \mathcal{A}}{\partial \mathbf{p}_i} \cdot \frac{\partial U}{\partial \mathbf{R}_i} + \frac{\partial \mathcal{A}}{\partial \mathbf{R}_i} \cdot \left(\frac{\partial U}{\partial \mathbf{p}_i} + \mathbf{V}_i \right) \right] \right\rangle$$

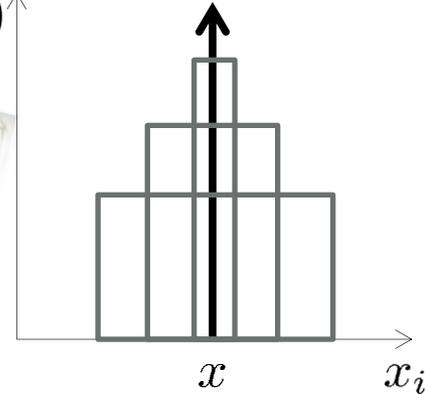
Thus, (2.4) becomes

$$\frac{d}{dt} \langle \mathcal{A} \rangle = \left\langle \sum_{i=1}^N \left[\frac{\partial \mathcal{A}}{\partial \mathbf{p}_i} \cdot \frac{\partial U}{\partial \mathbf{R}_i} + \frac{\partial \mathcal{A}}{\partial \mathbf{R}_i} \cdot \left(\frac{\partial U}{\partial \mathbf{p}_i} + \mathbf{V}_i \right) \right] \right\rangle$$

giving the rate of change of the expectation value of \mathcal{A}

Consequently, $\langle \mathcal{A} \rangle$ is the product of this that the i th molecule is at \mathbf{r}_i , i.e., it is the distribution (mass current density). The local momentum density

$$\delta(x - x_i)$$



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

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

Integrating the Dirac Delta

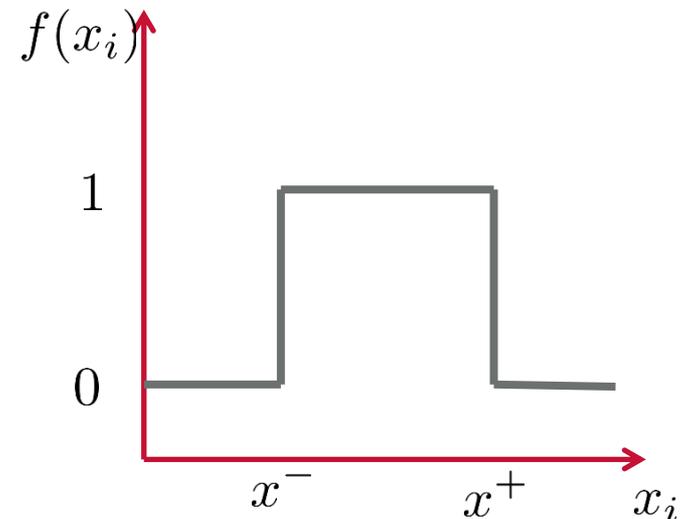
- Much better to write the equations in integrated form

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

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

- Consider the 1D case

$$\begin{aligned} \int_{x^-}^{x^+} \delta(x - x_i) dx &= \left[H(x - x_i) \right]_{x^-}^{x^+} \\ &= H(x^+ - x_i) - H(x^- - x_i) \end{aligned}$$



The Control Volume Functional

- In three dimensions this integral gives a cube

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

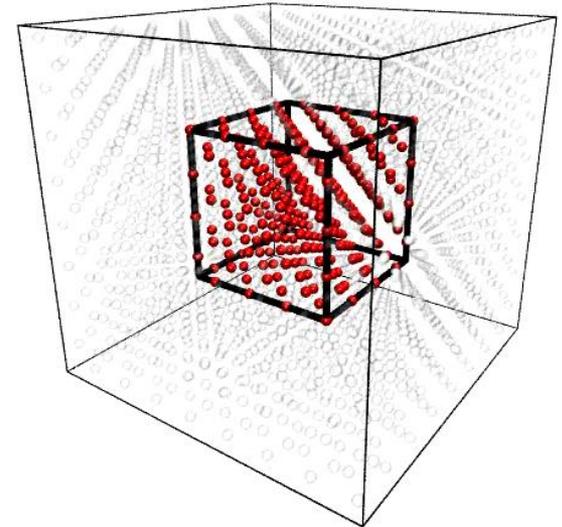
$$= [H(x^+ - x_i) - H(x^- - x_i)]$$

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

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

- 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

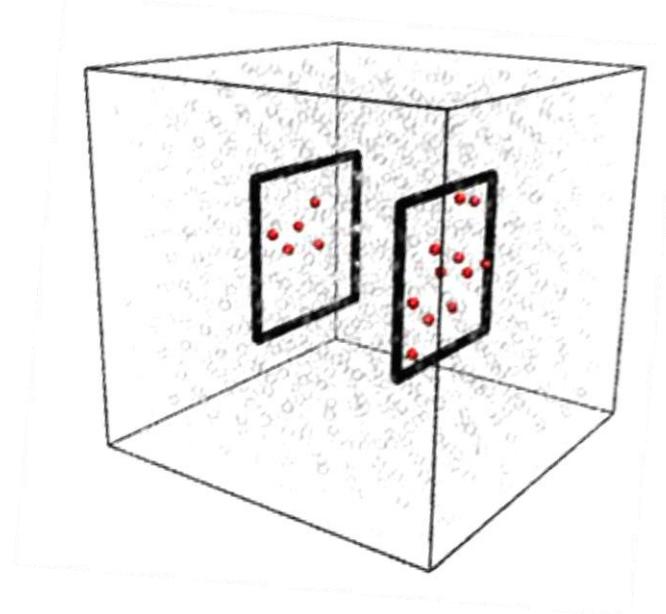
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = [\delta(x^+ - x_i) - \delta(x^- - x_i)] \\ \times [H(y^+ - y_i) - H(y^- - y_i)] \\ \times [H(z^+ - z_i) - H(z^- - z_i)]$$

- Vector form defines six surfaces

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

- Or in words

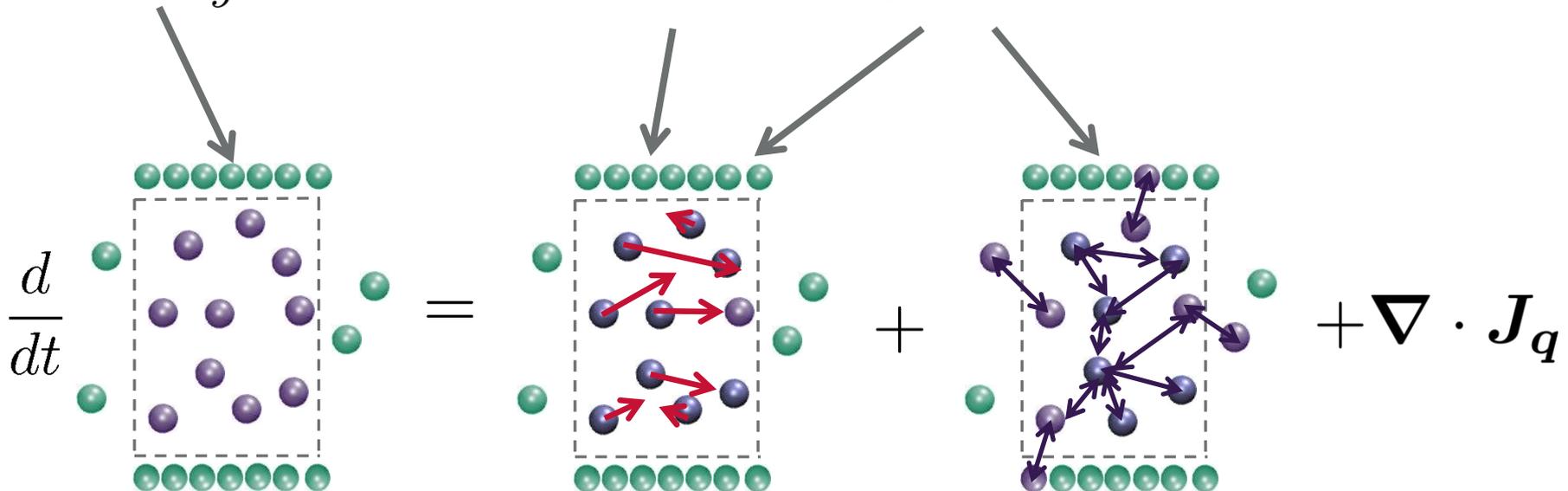
$$d\mathbf{S}_i \equiv \begin{cases} \infty & \text{if molecule on surface} \\ 0 & \text{otherwise} \end{cases}$$



Control Volume Form

- Integrate to get the control volume energy equation

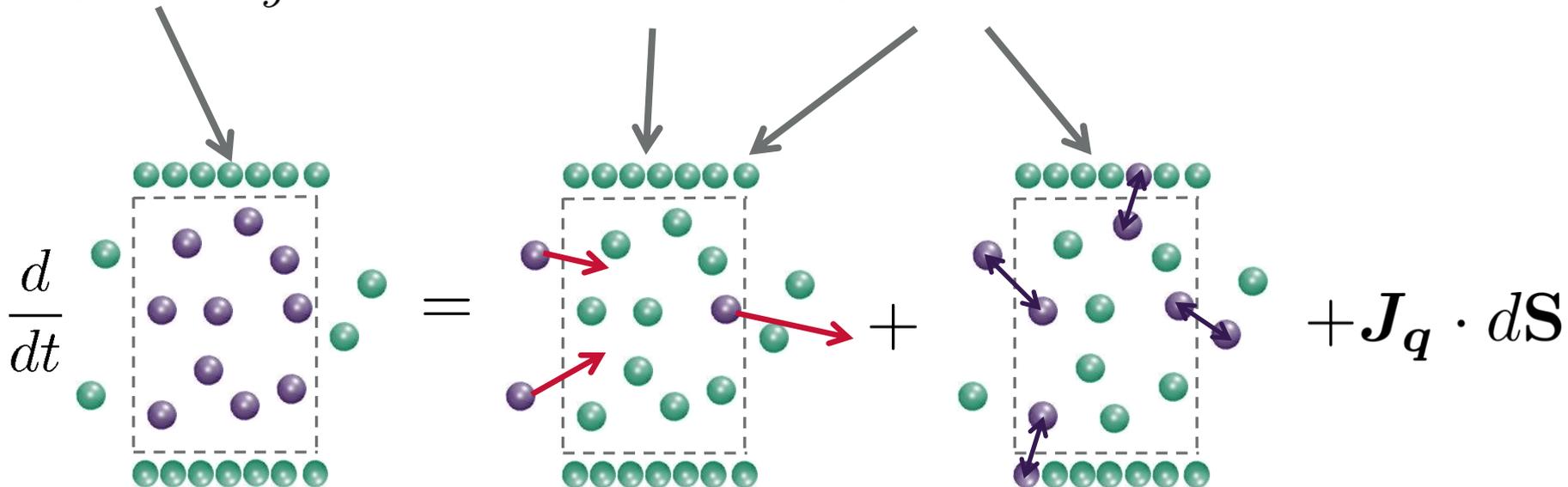
$$\underbrace{\int_V \frac{\partial}{\partial t} \rho \mathcal{E} dV}_{\text{Unsteady}} = - \int_V \nabla \cdot \left[\underbrace{\rho \mathcal{E} \mathbf{u}}_{\text{Advection}} + \underbrace{\boldsymbol{\Pi} \cdot \mathbf{u}}_{\text{Stress Work}} + \underbrace{\mathbf{J}_q}_{\text{Heat Flux}} \right]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



Control Volume (surface flux) Form

- Or can be expressed in terms of surface fluxes

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



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

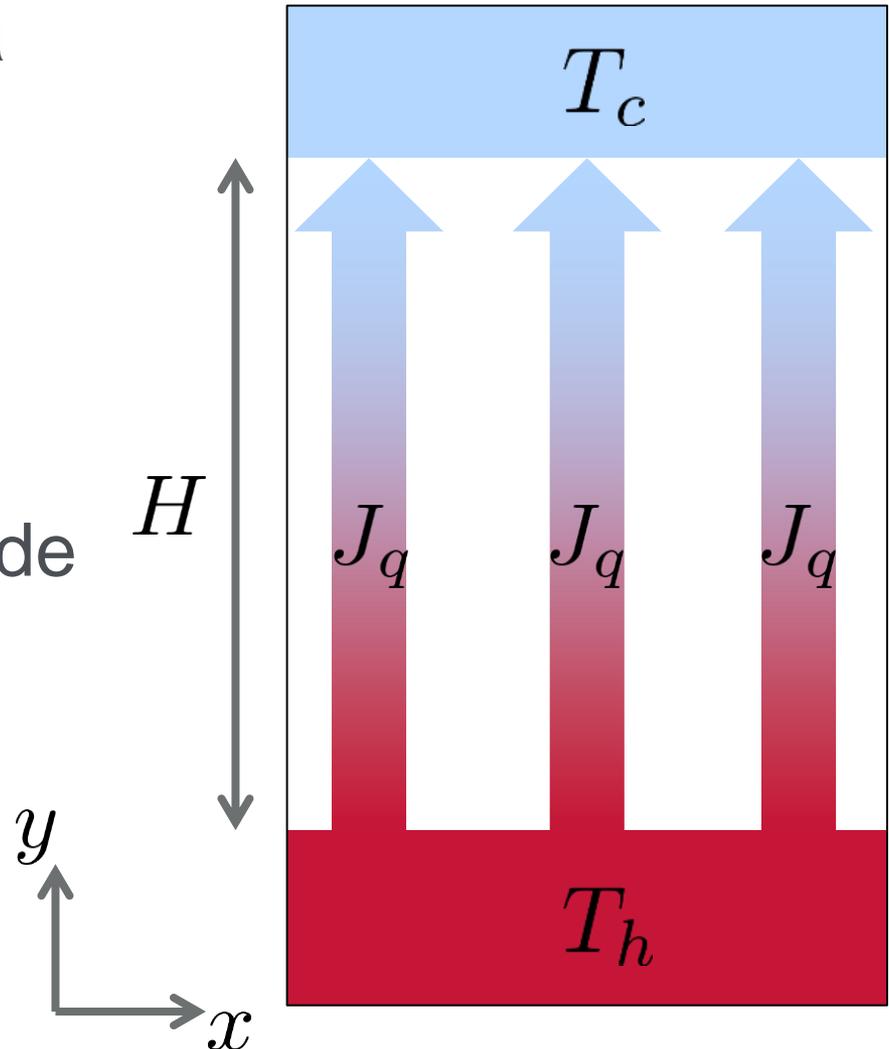
Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

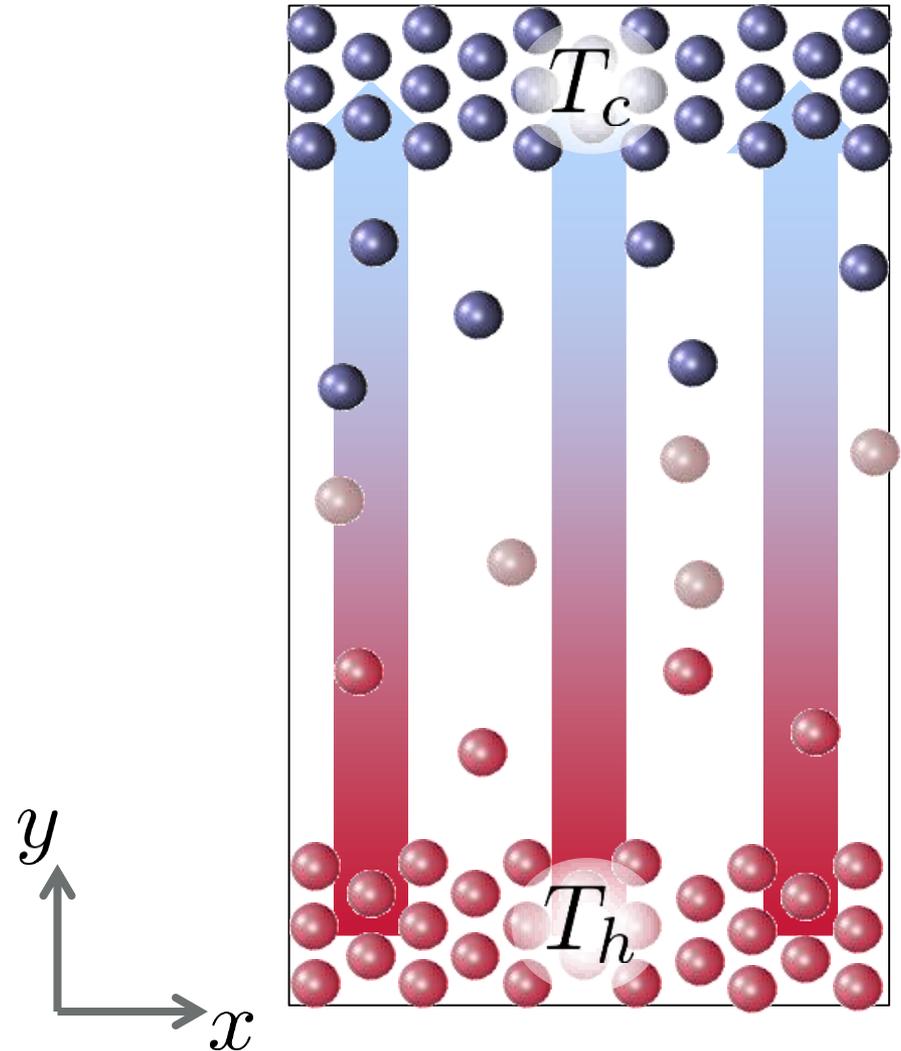
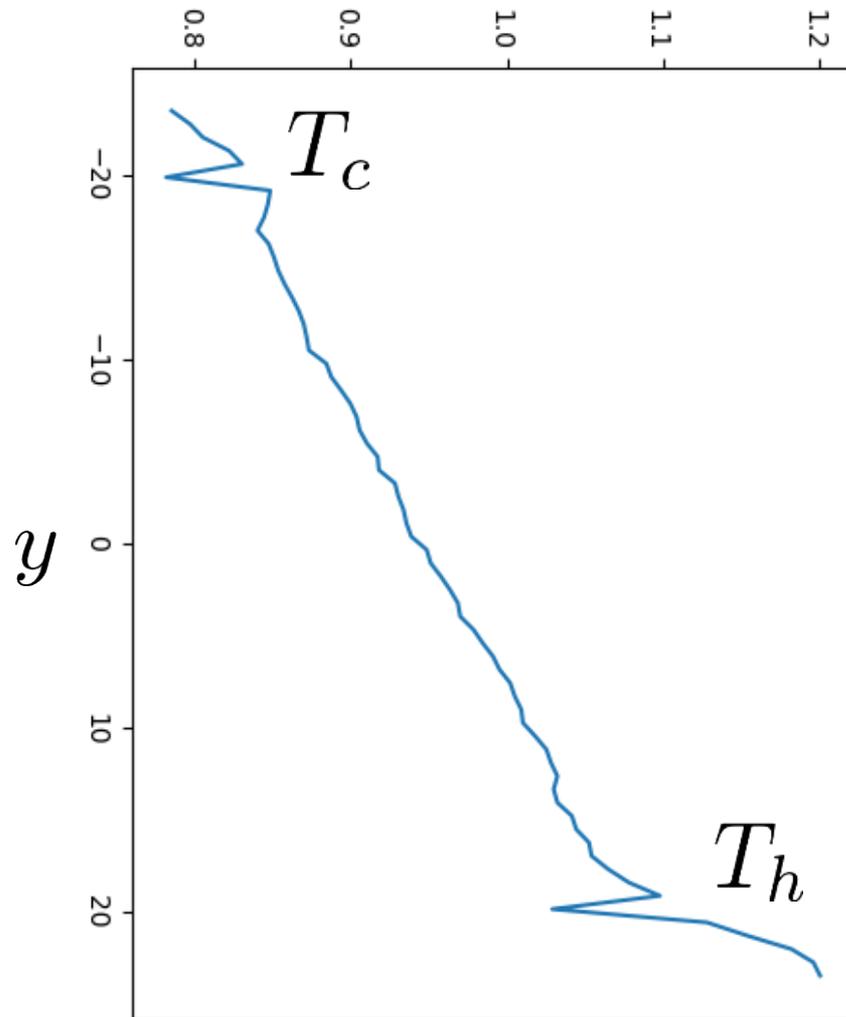
$$\frac{\partial T}{\partial y} \approx \frac{T_c - T_h}{H}$$

- Proportional to magnitude of temperature gradient

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



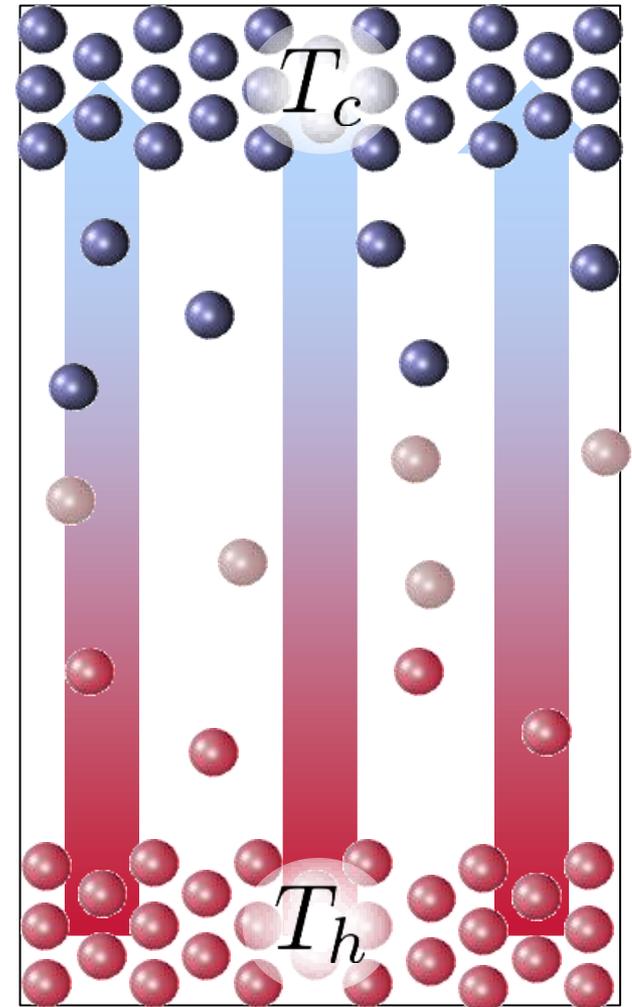
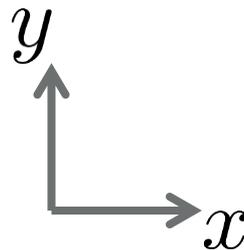
Fourier's law of Heat Conduction



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

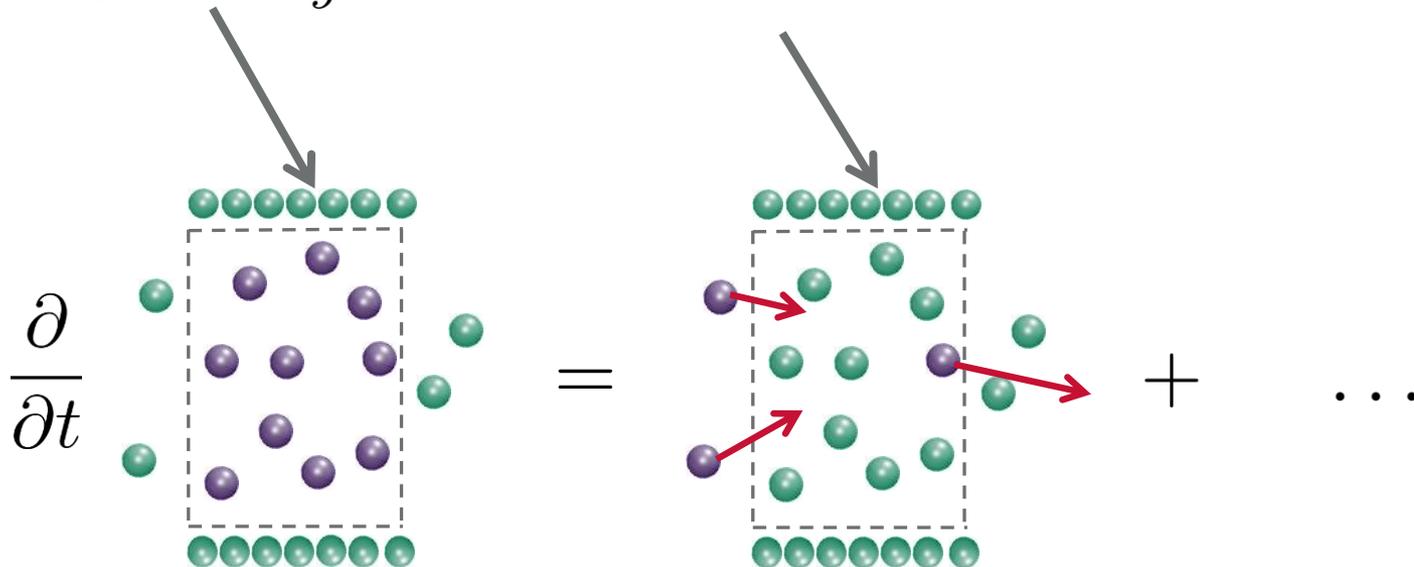
$$\lambda = -\frac{J_q}{\partial T / \partial y}$$



Measuring Heat Flux in MD

- Consider the energy equation

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

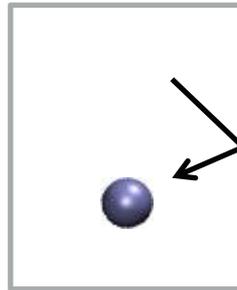


Pressure (Stress) in an MD Simulation

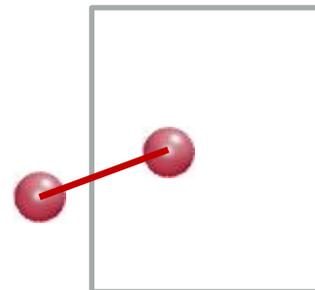
- Pressure definition in a dense molecular system
 - Kinetic part due to fluctuations
 - Configurational part due to liquid structure

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

*Kinetic
theory part
Momentum due
to average of
molecules
crossing a plane
and returning*



$$c_i = \dot{r}_i - u$$

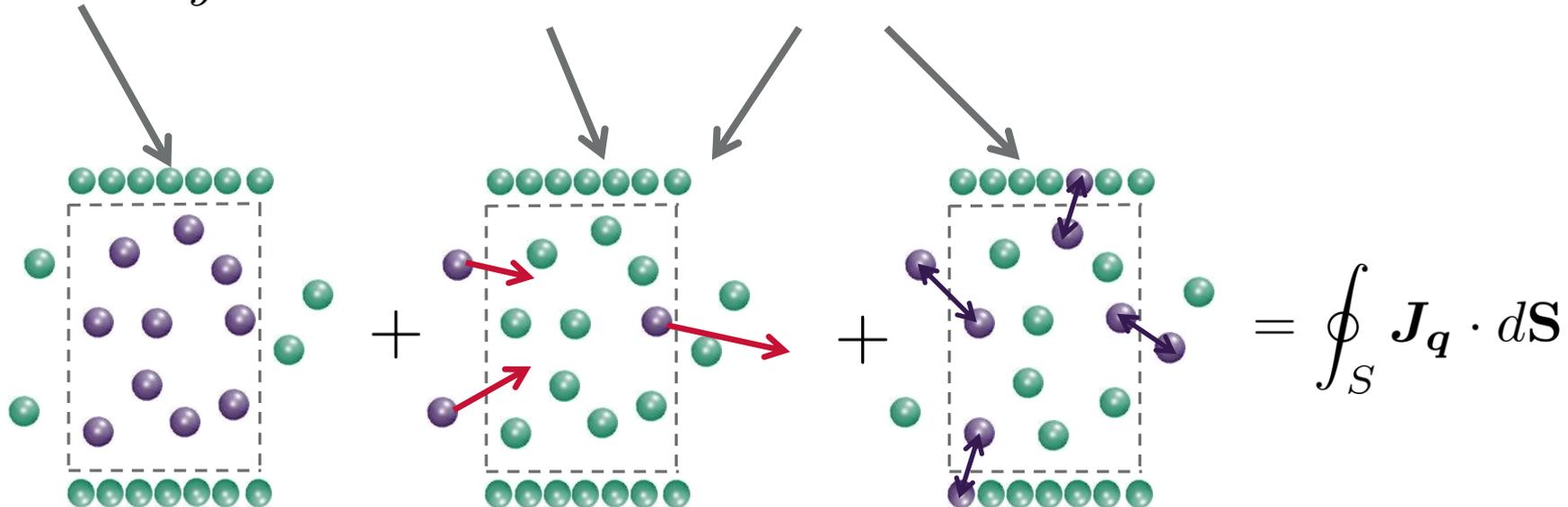


*Configurational
part
Inter-molecular
bonds act like the
stress in a
stretched spring*

Measuring Heat Flux in MD

- Consider the energy equation

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

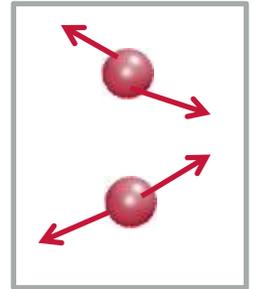


Volume Average Heat Flux

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

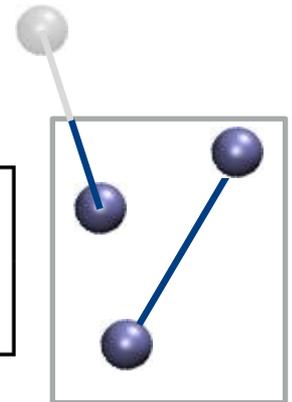
Kinetic

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



Configurational

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

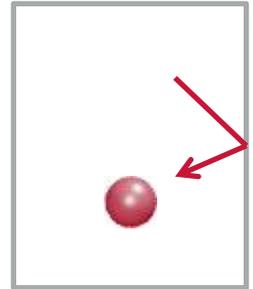


Surface (MOP) Heat Flux

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

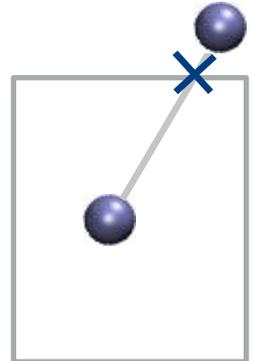
Kinetic

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



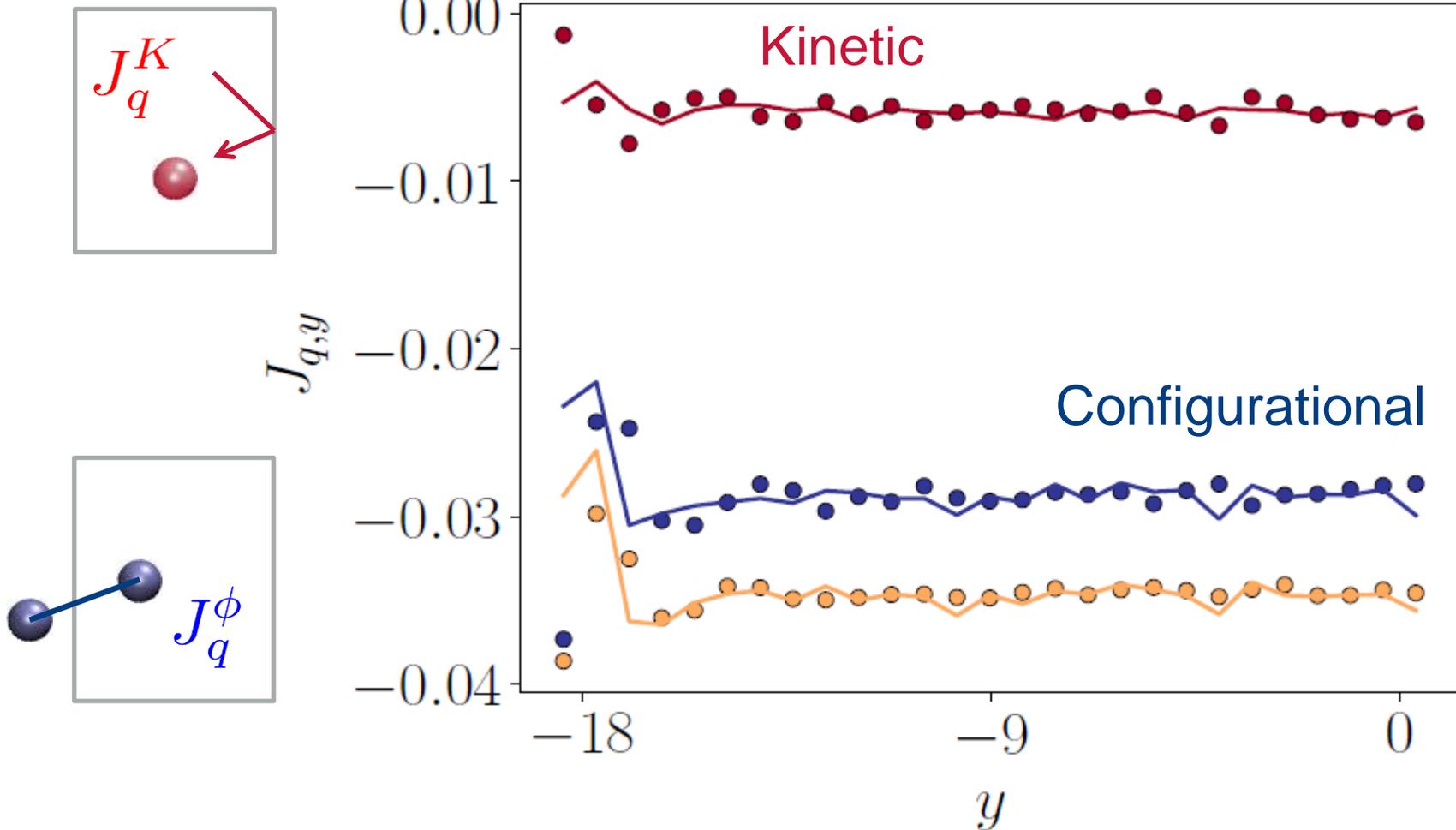
Configurational

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



Measuring Heat Flux in MD

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



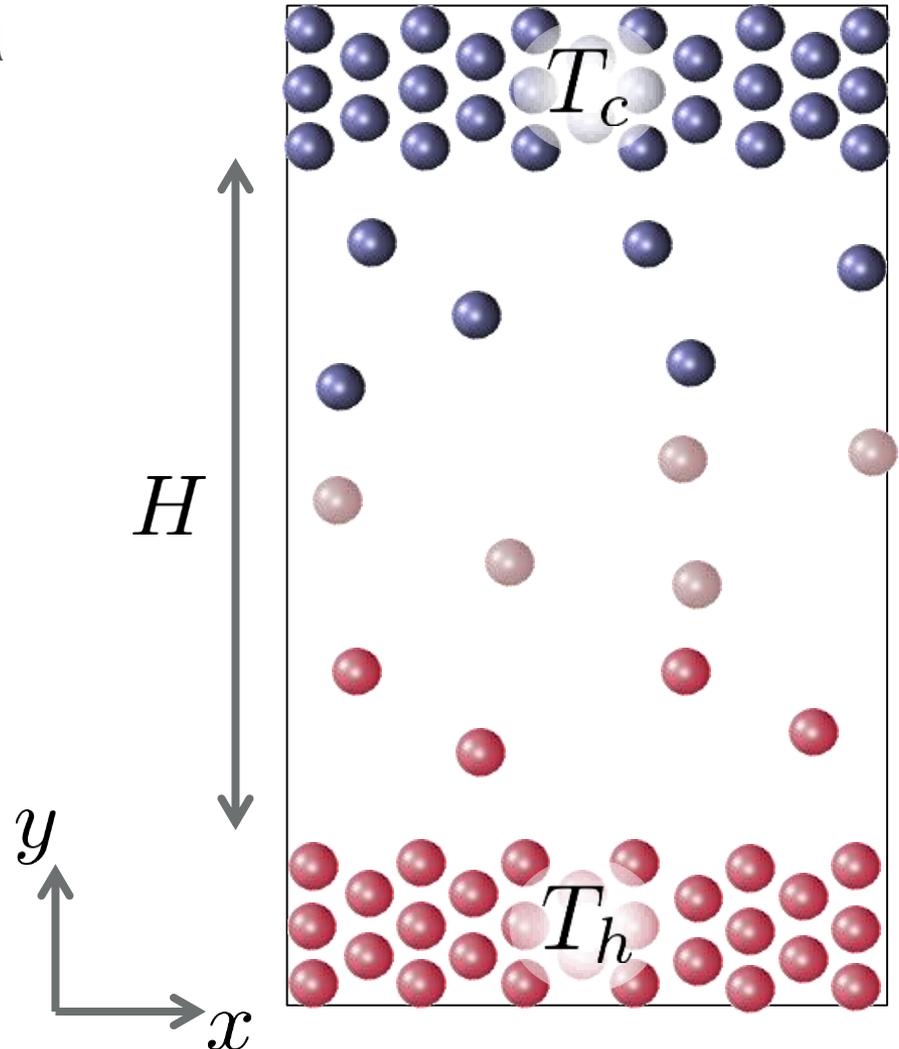
Fourier's law of Heat Conduction

- Heat flux J_q driven by a temperature difference

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

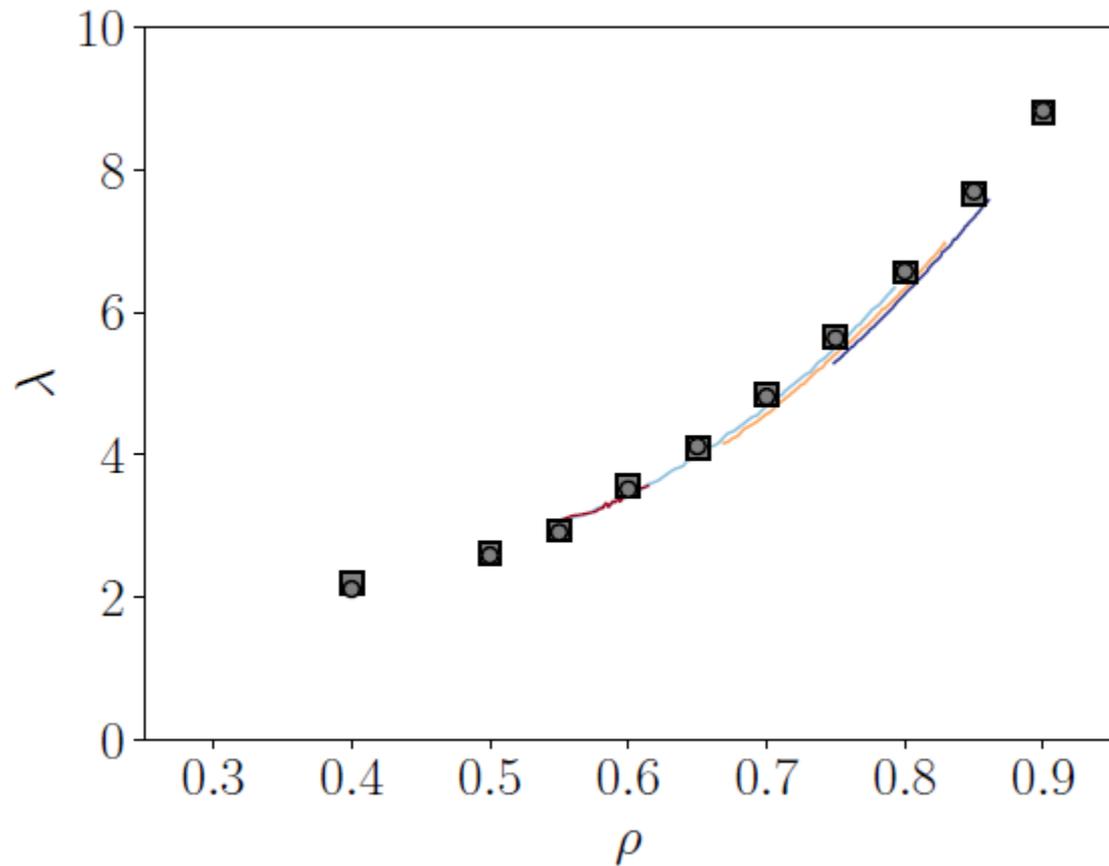
- Using heat flux and temperature gradient,

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



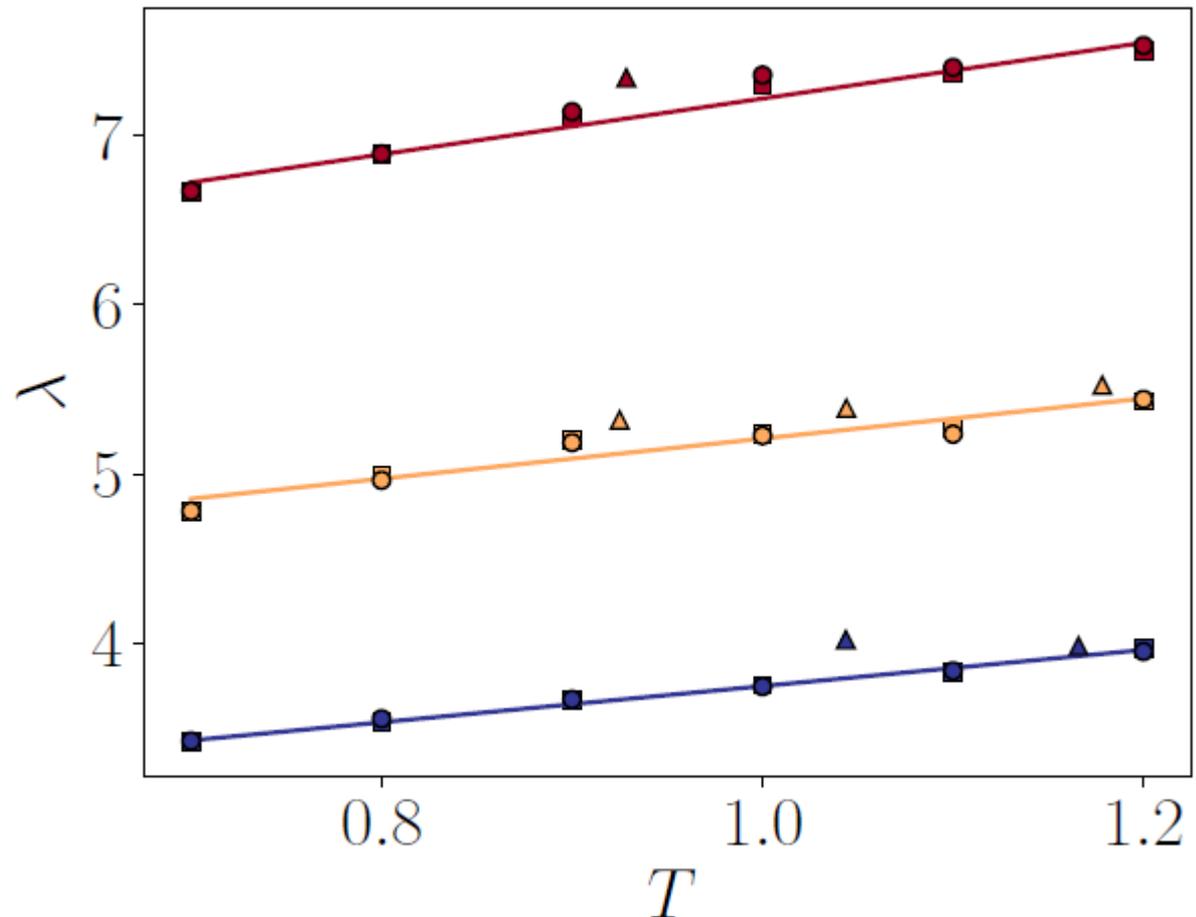
Fourier's law of Heat Conduction

- 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

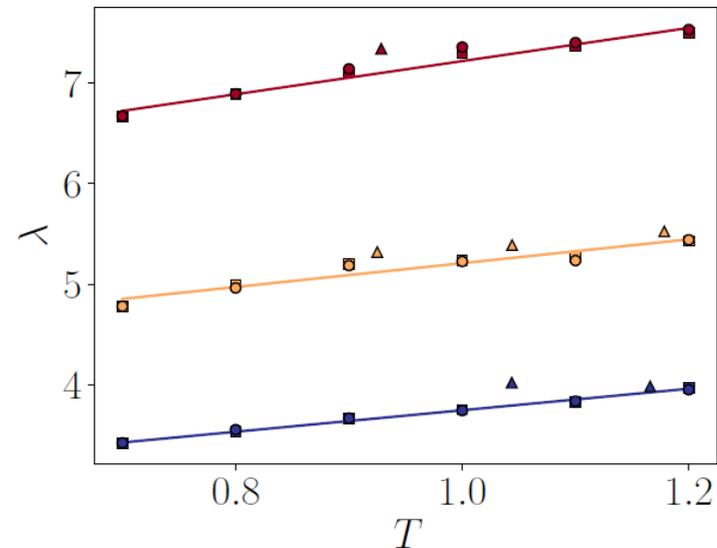
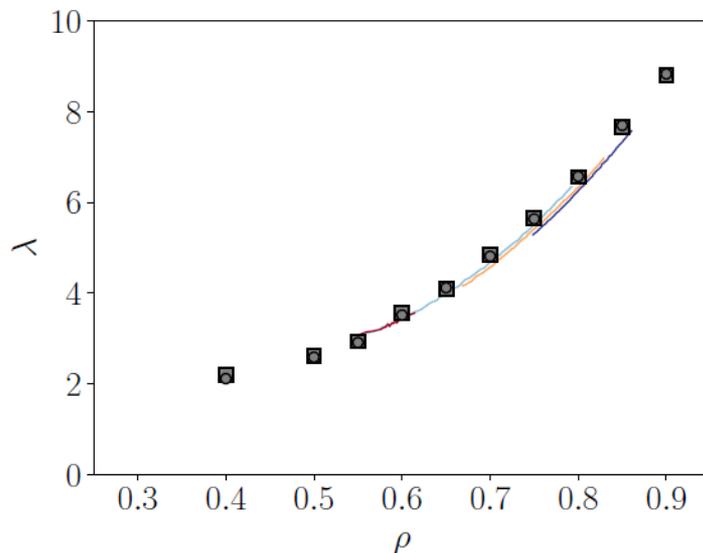


Fourier's law of Heat Conduction

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

$$\lambda(\rho, T) = 21.3\rho^2 - 14.2\rho + 3.92$$

$$+ (T - 1) [13\rho^2 - 17\rho + 6.63]$$





Section 3

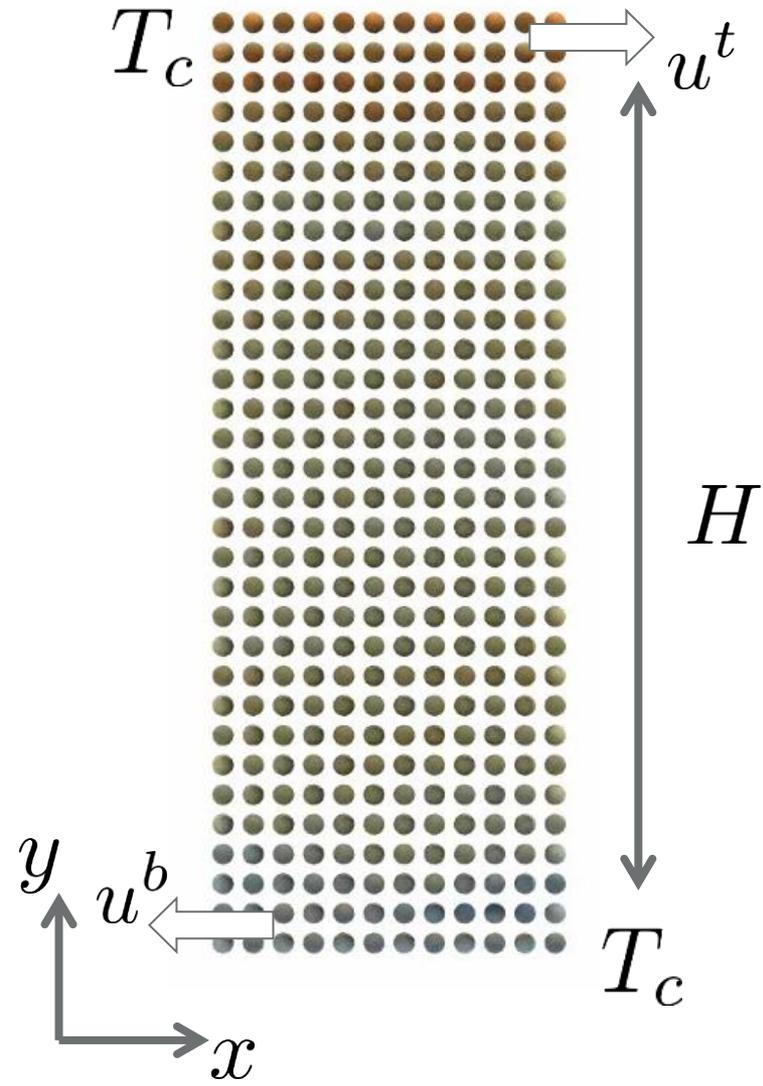
SHEAR-DRIVEN (COUETTE) FLOW

Couette Flow

- Shear flow driven by walls

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

- Walls are thermostatted

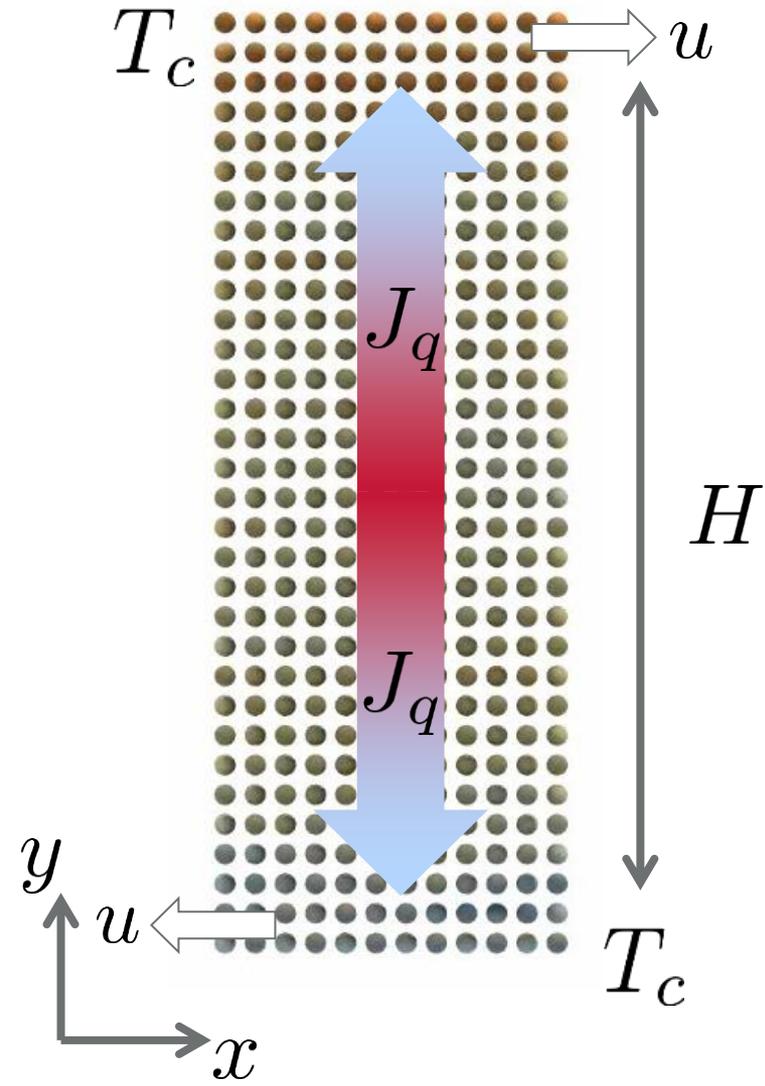


Couette Flow

- 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

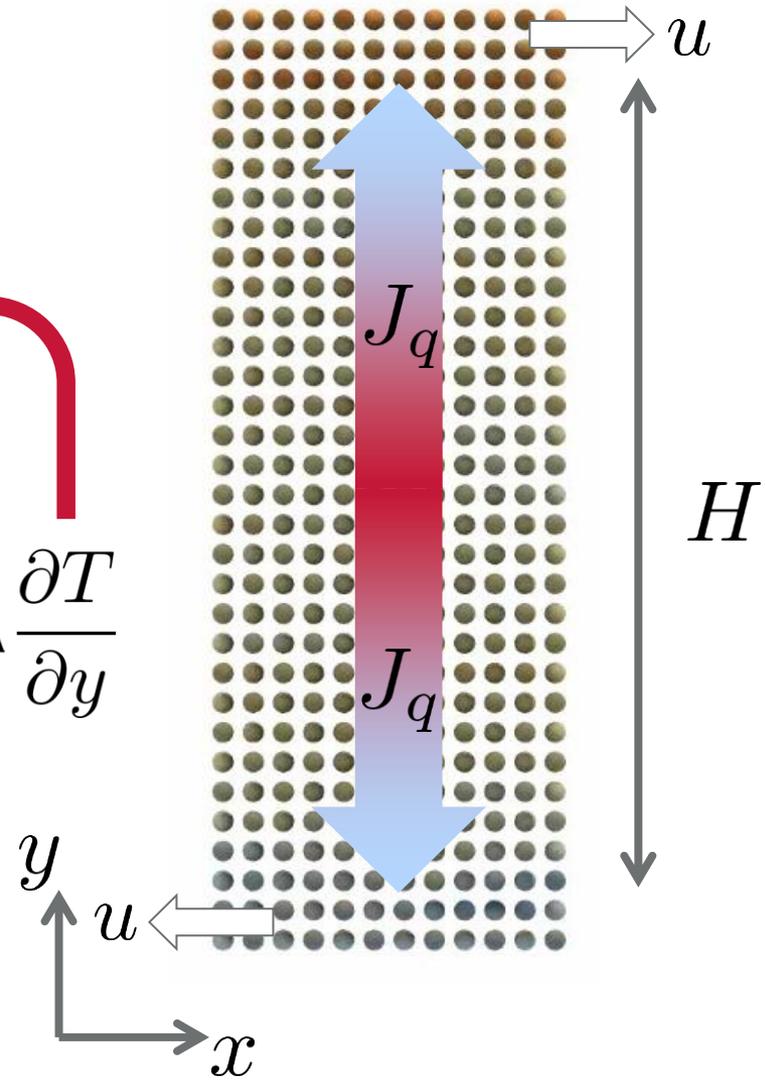


Couette Flow

- 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 $J_{q,y} = -\lambda \frac{\partial T}{\partial y}$



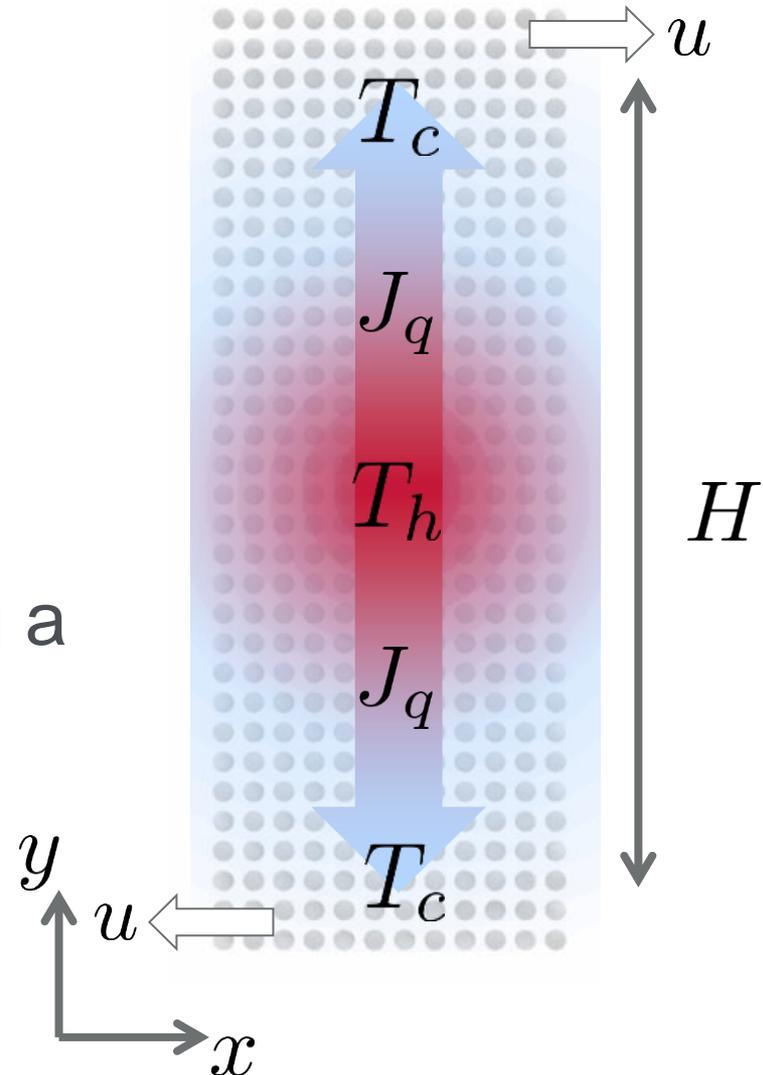
Couette Flow

- Shear flow generates heat

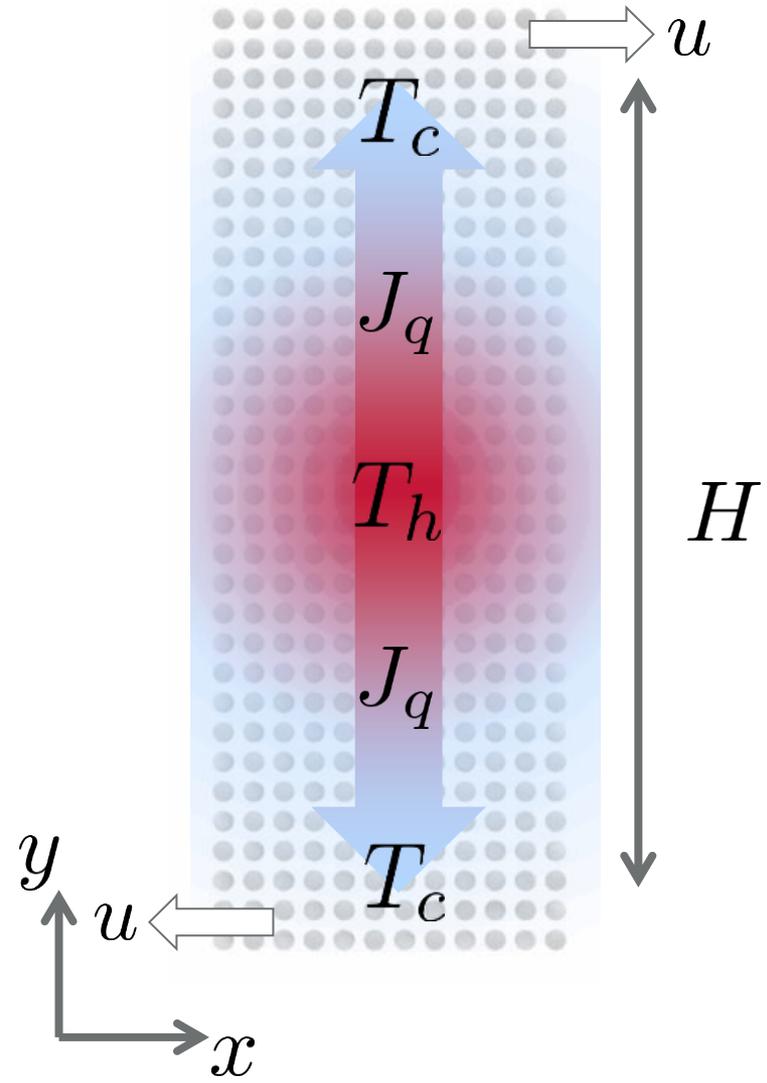
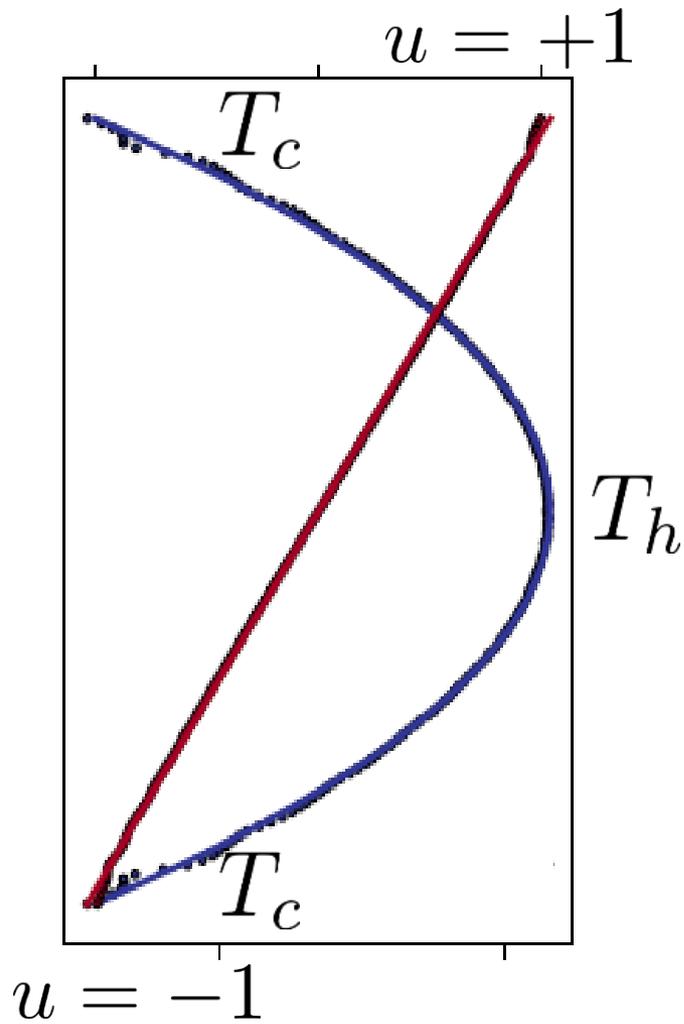
$$\underbrace{\Pi_{xy} \dot{\gamma}}_{\text{Stress Work}} = \underbrace{-\lambda \frac{\partial^2 T}{\partial y^2}}_{\text{Heat Flux}}$$

- 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

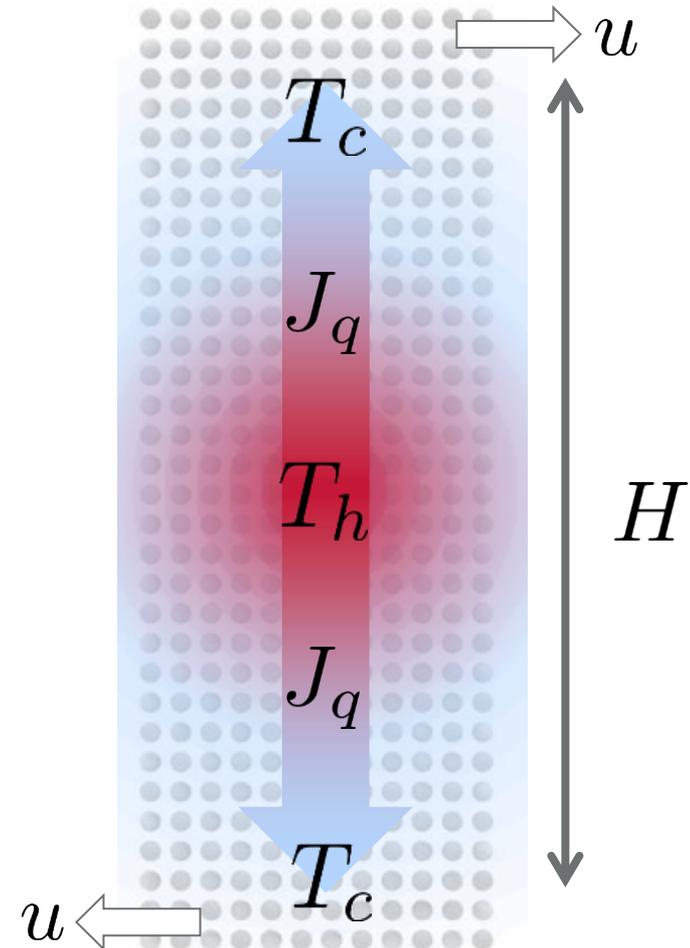
- Heat flux J_q driven by a temperature difference

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

- 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

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

λ

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

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

$$\mathbf{J}_q \approx -\lambda_{\text{eff}} \cdot \nabla T$$

Beyond Fourier's law of Heat Conduction

- Taylor expansion in gradients of T and u

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

λ

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

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

- 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

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

λ

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

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

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

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

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

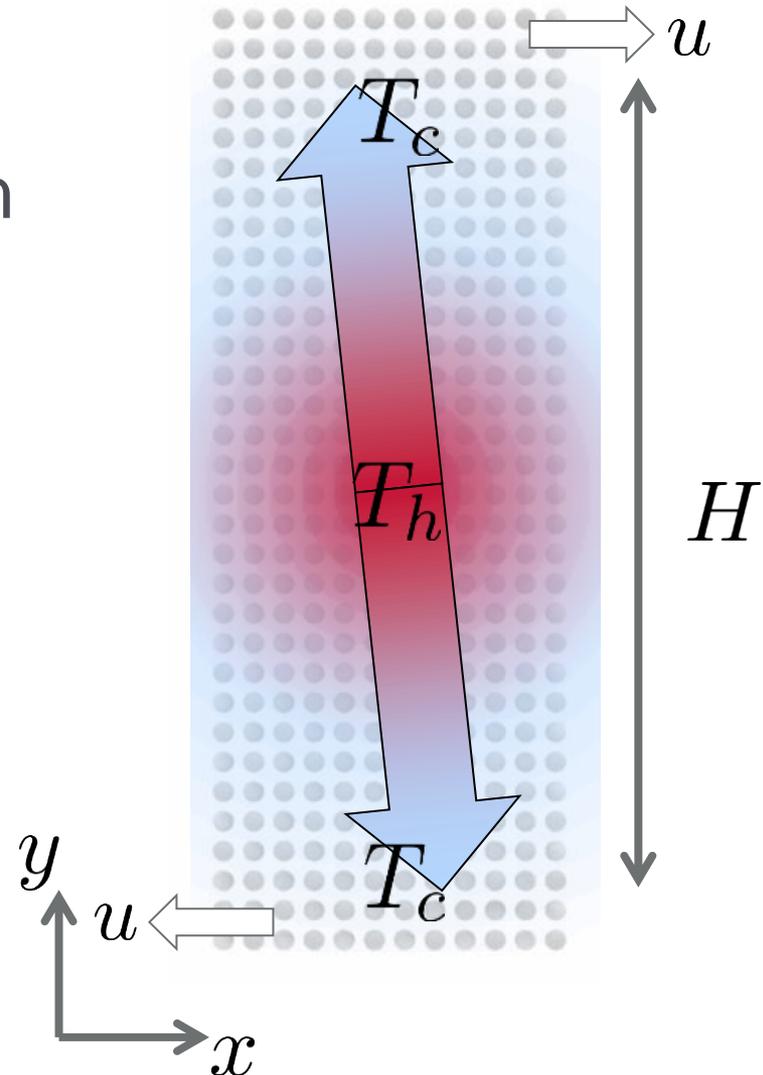
Beyond Fourier's law of Heat Conduction

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

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

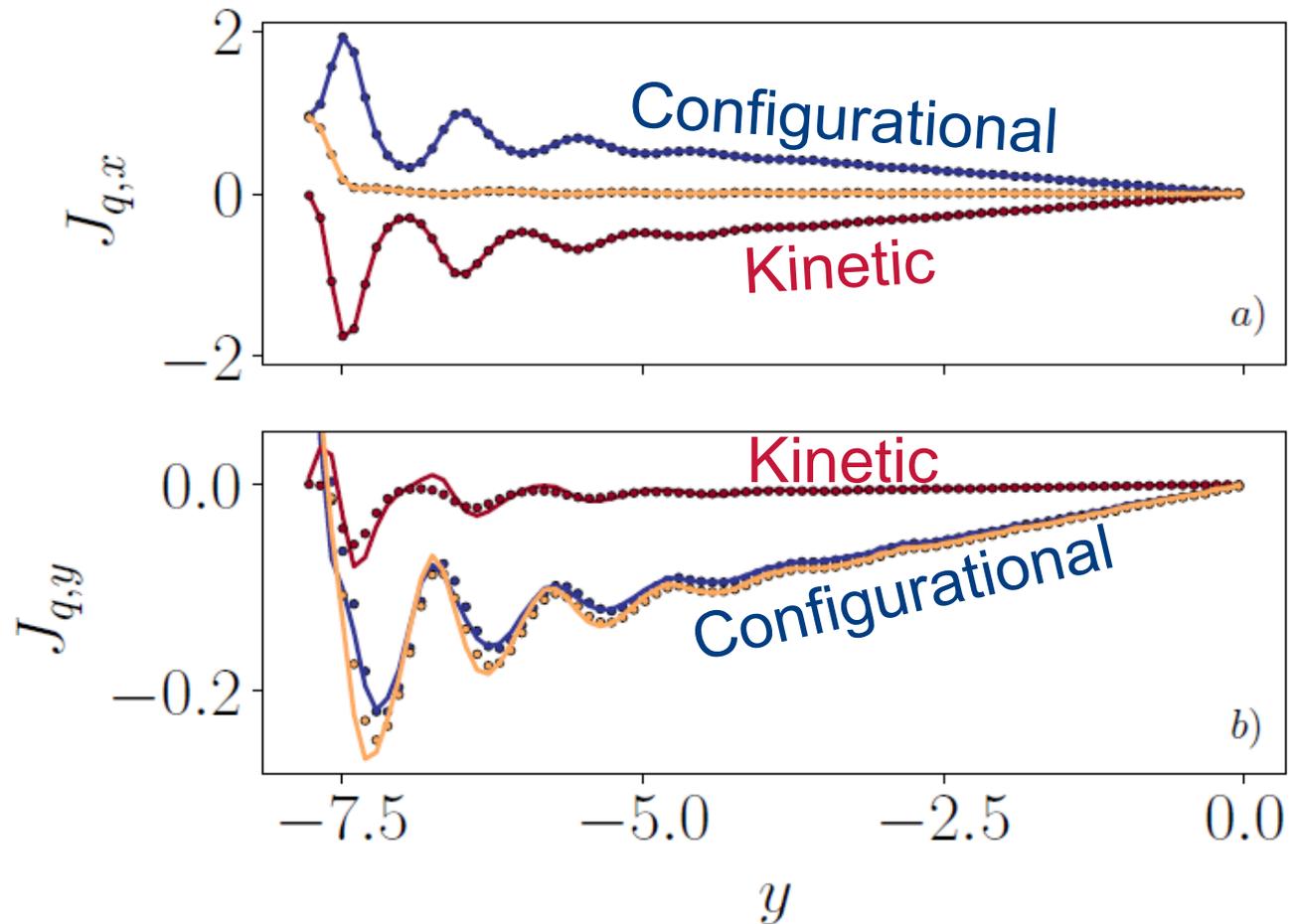
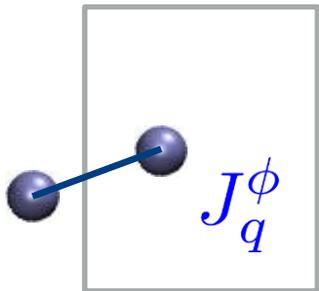
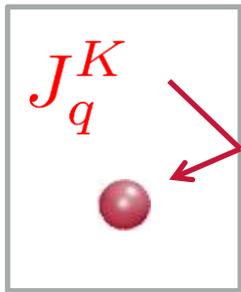
- An extra term in addition to Fourier's coefficient

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

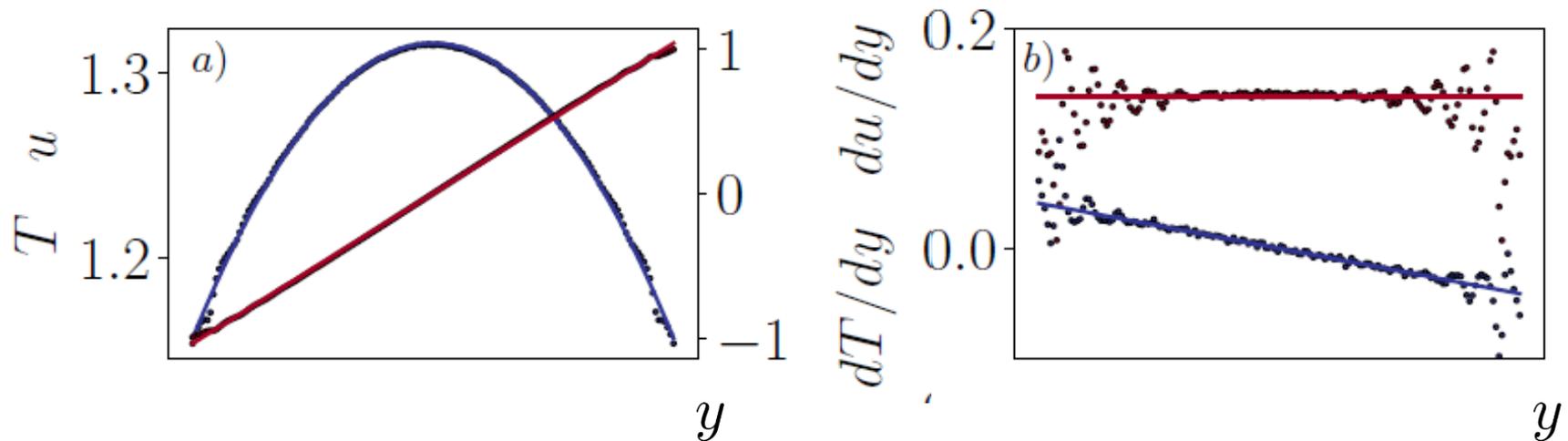


Heat Flux Components

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

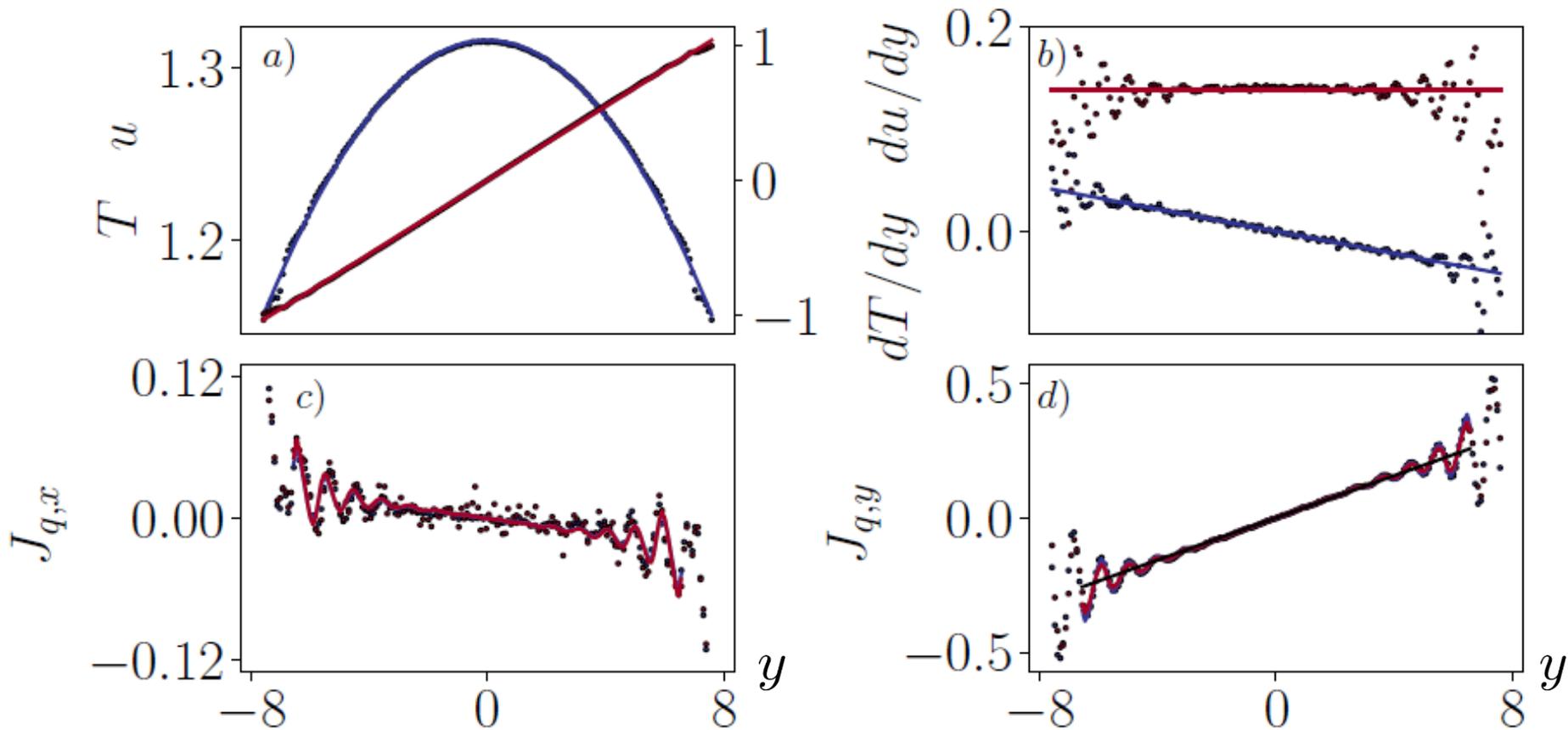


Fitting MD Channel to Get Coefficients



- 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



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

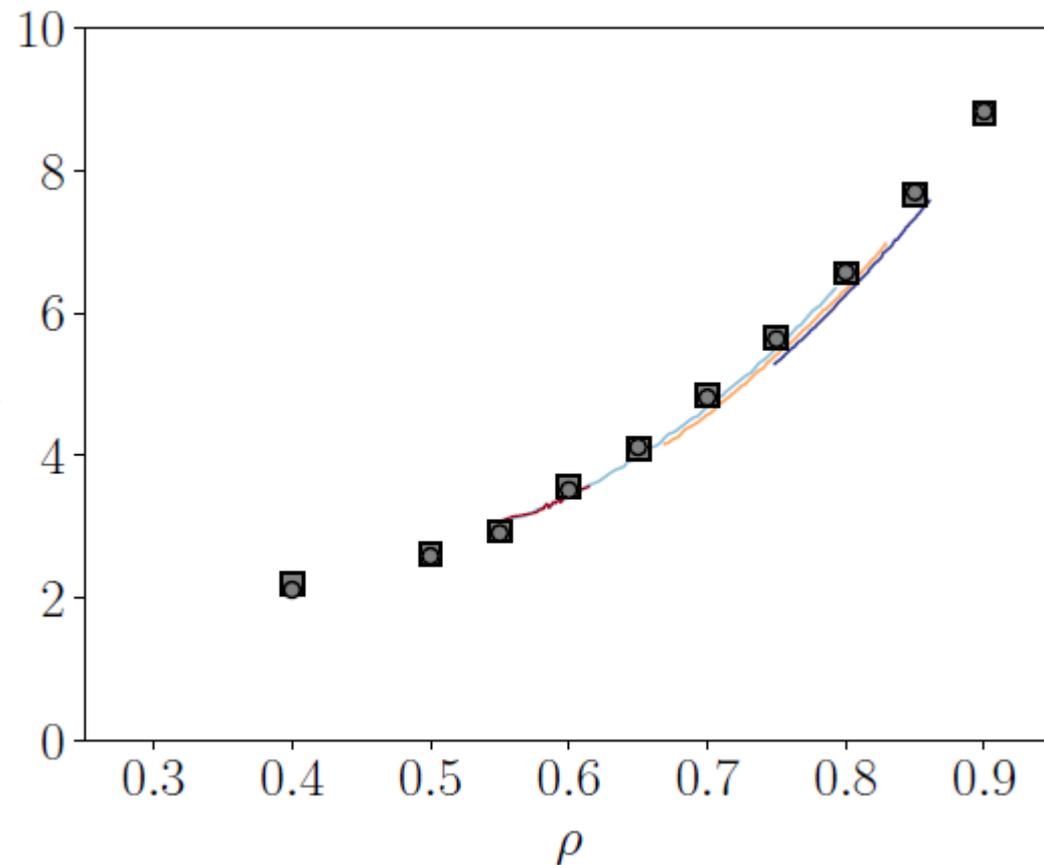
$$J_{q,y} = -\lambda \frac{\partial T}{\partial y} - 3\lambda_2 \dot{\gamma}^2 \frac{\partial T}{\partial y}$$

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

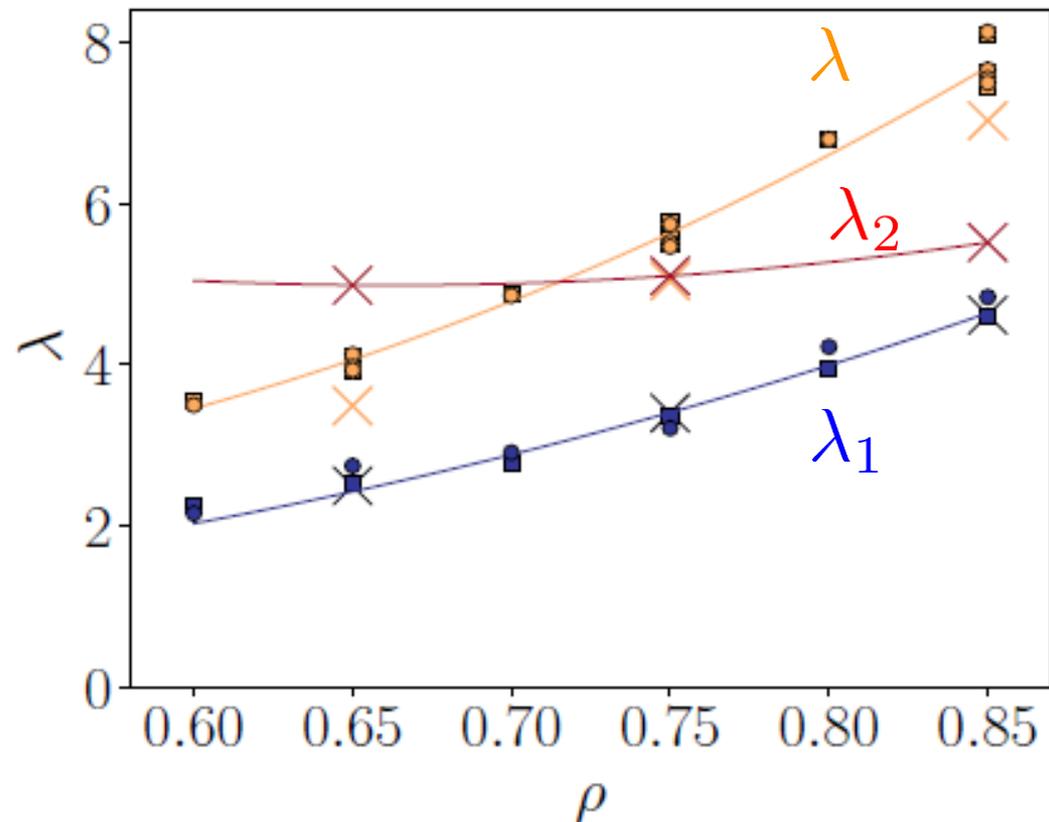
- Run over a range of different density channels

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

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

- Fourier's law shows good agreement with experimental results

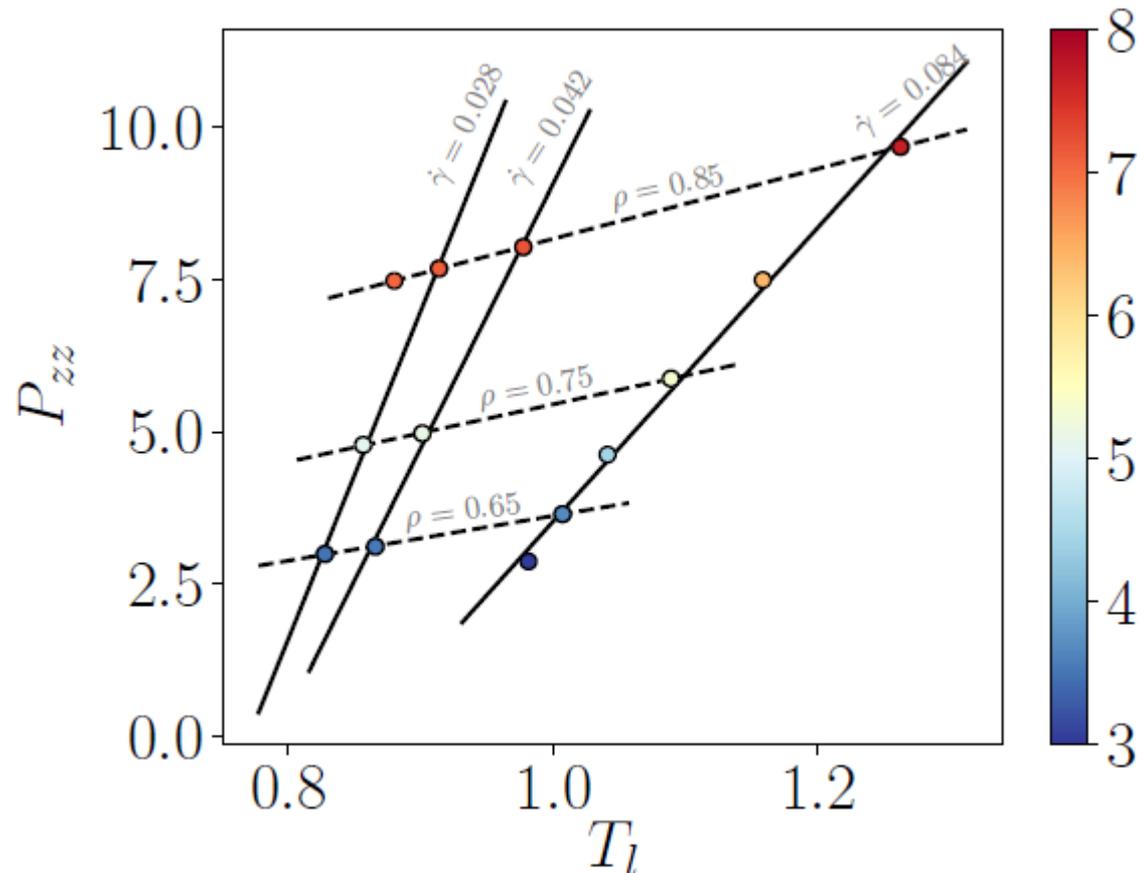
- Additional coefficients **experimentally testable**



Range of Strain Rates

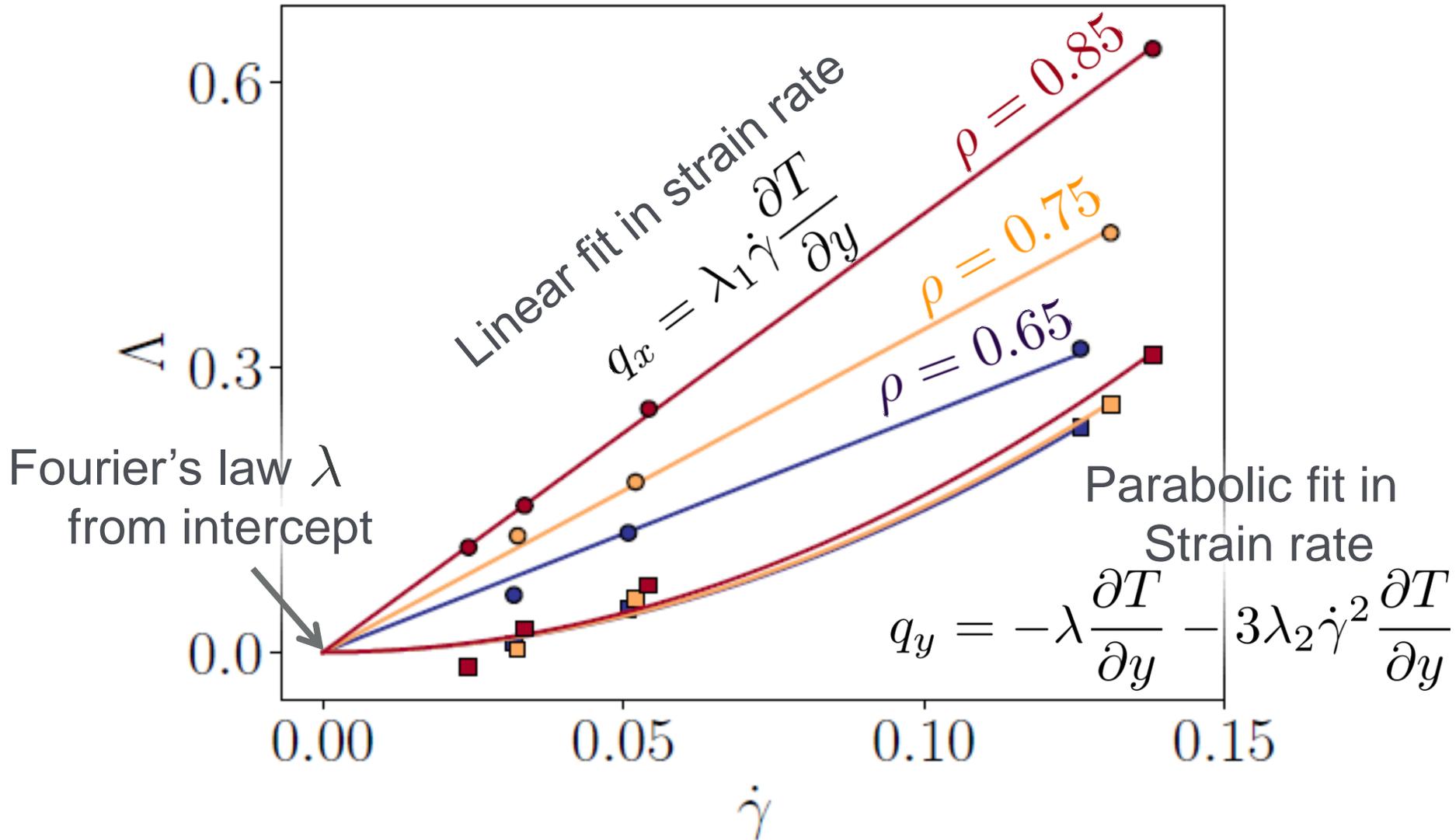
- Run over a range of systems with varying
 - Strain rate
 - Density
- Temperature varies depending on these values
- Use Fourier's law from part 2

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





Coefficients Vs. Strain Rate



Beyond Fourier's law of heat conduction

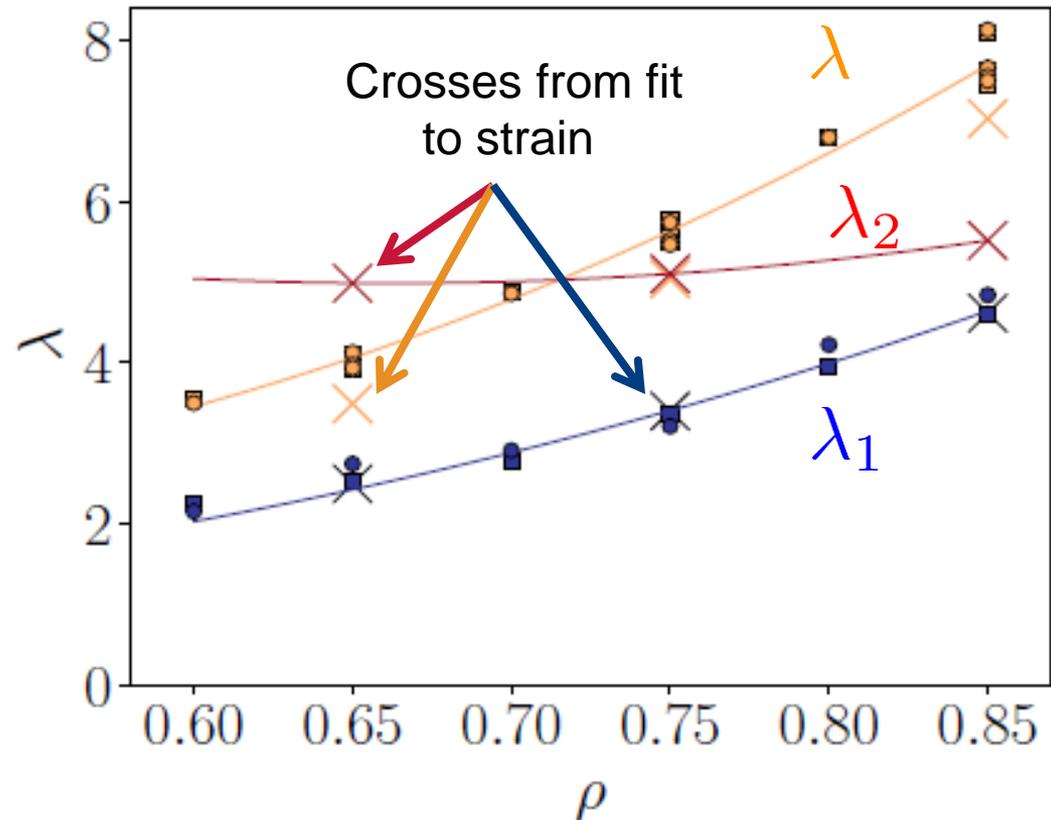
- Run over a range of different density channels

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

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

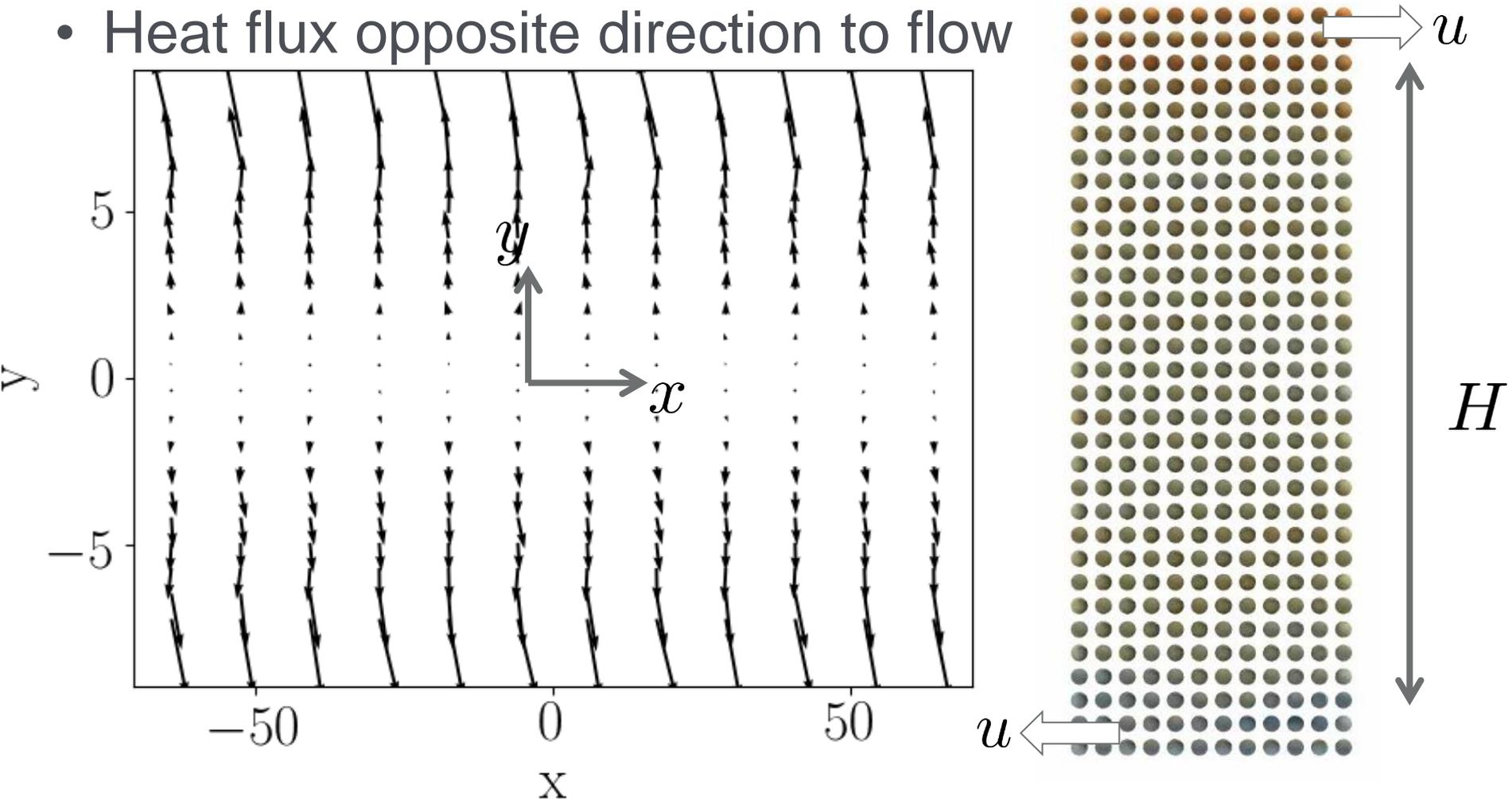
- Fourier's law shows good agreement with experimental results

- Additional coefficients **experimentally testable**



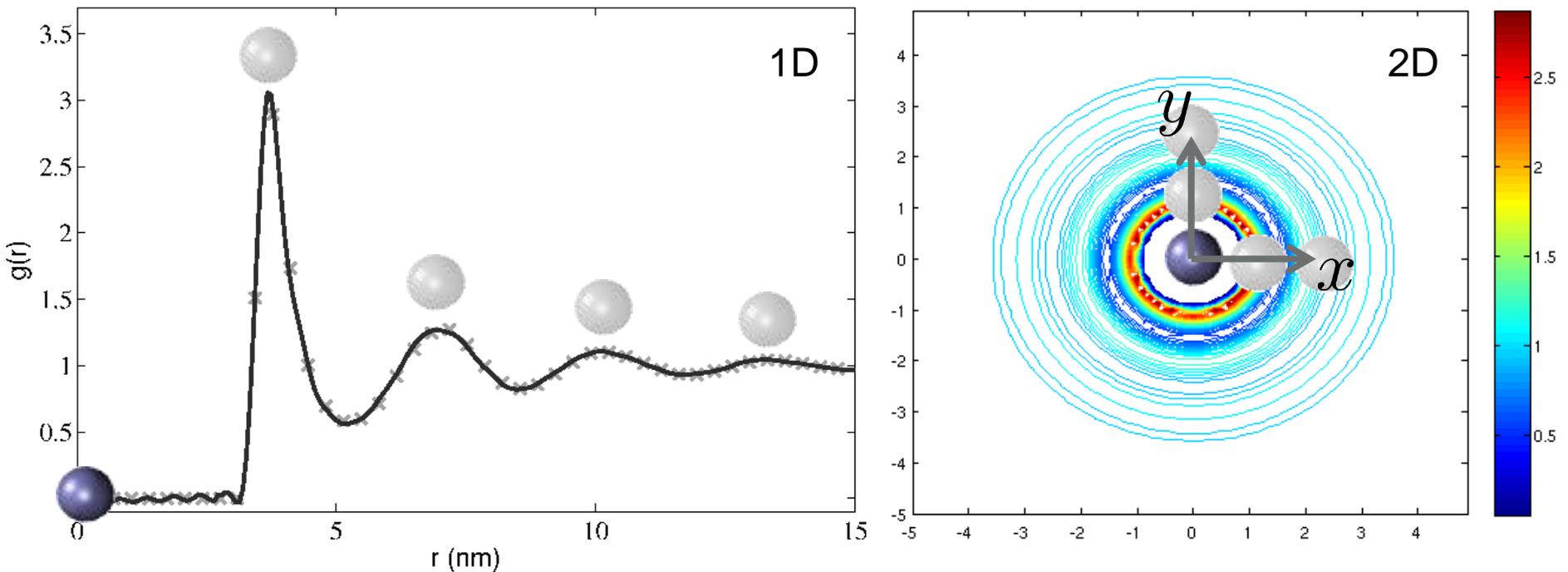
Vector Plot of Heat Flux

- Heat flux opposite direction to flow



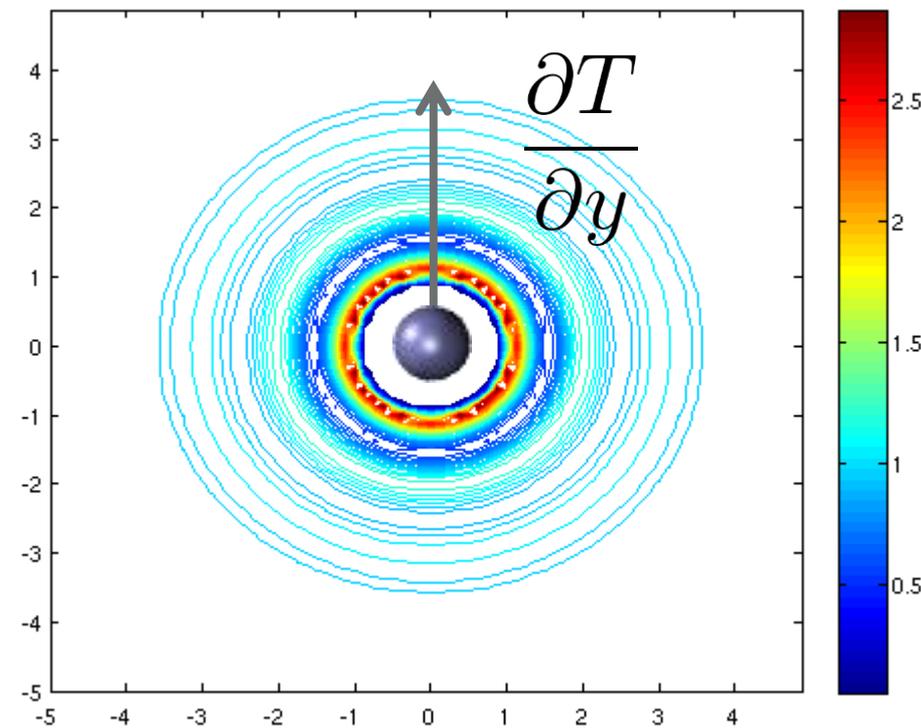
Proposed Mechanism

- Consider the Radial Distribution function

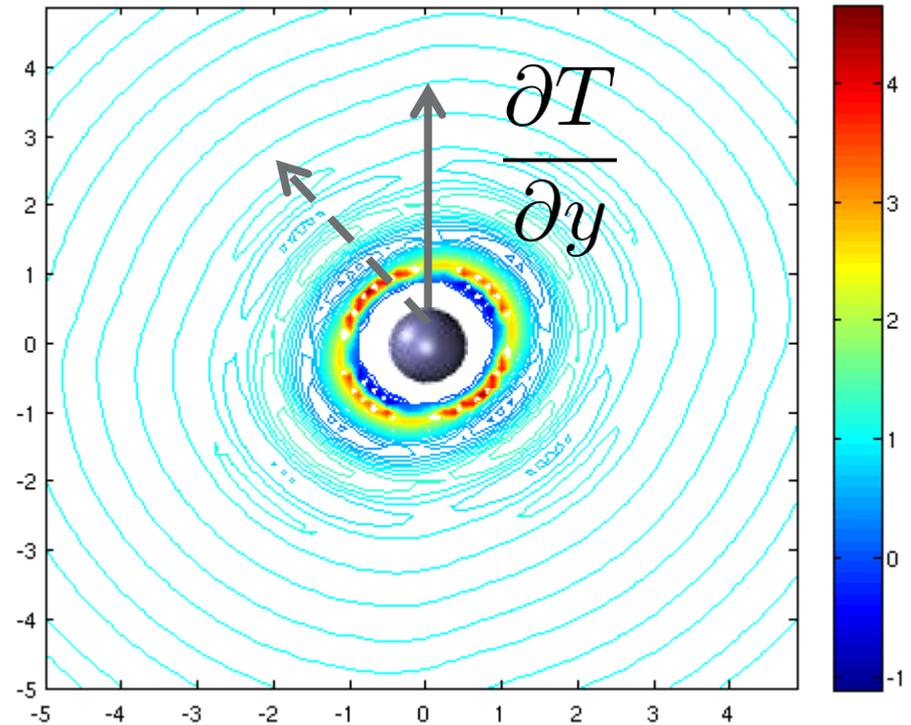


Proposed Mechanism

- 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

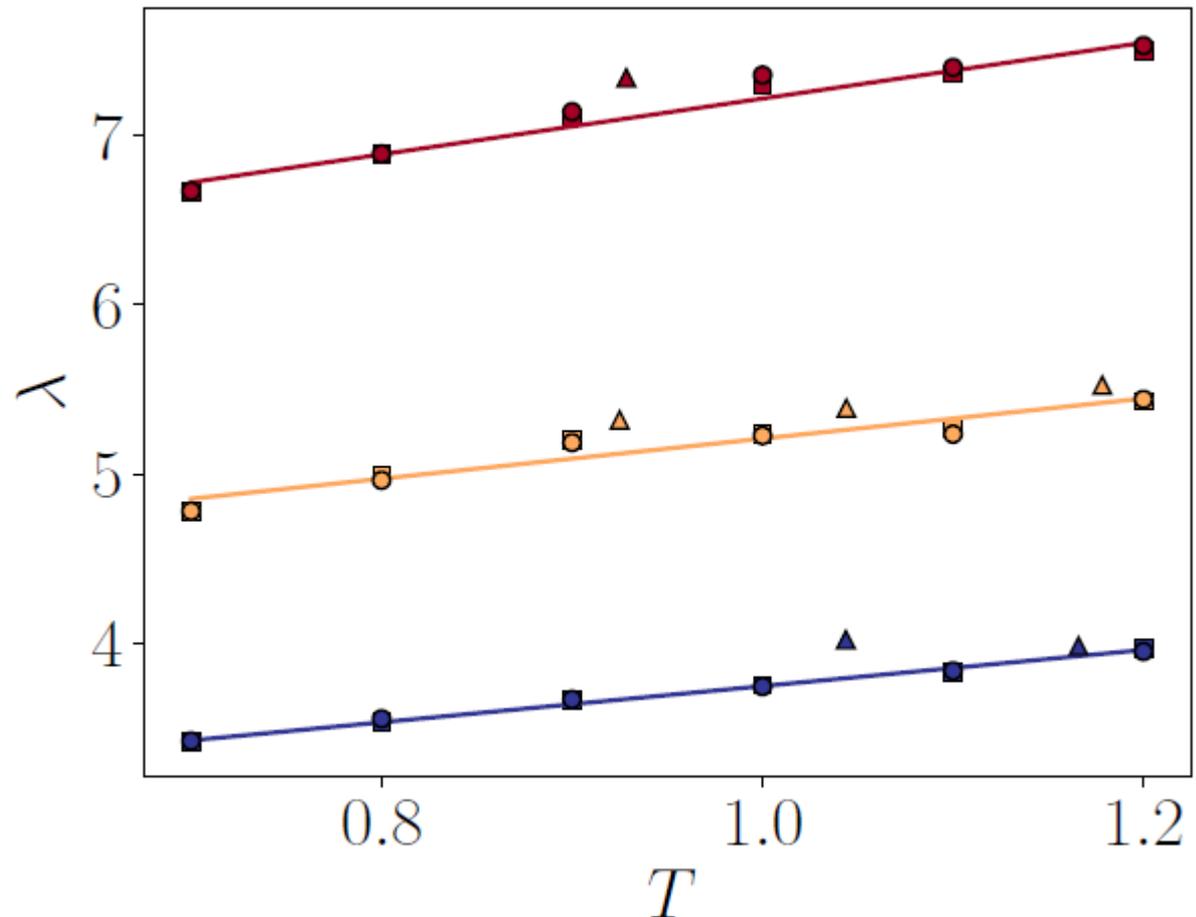
- Introduction
 - Heat Flux with Fourier's law and beyond
 - Molecular Dynamics
- Two Cases
 - Temperature-Driven Flow
 - Shear-Driven (Couette) Flow

Questions

- Any Questions?

Fourier's law of Heat Conduction

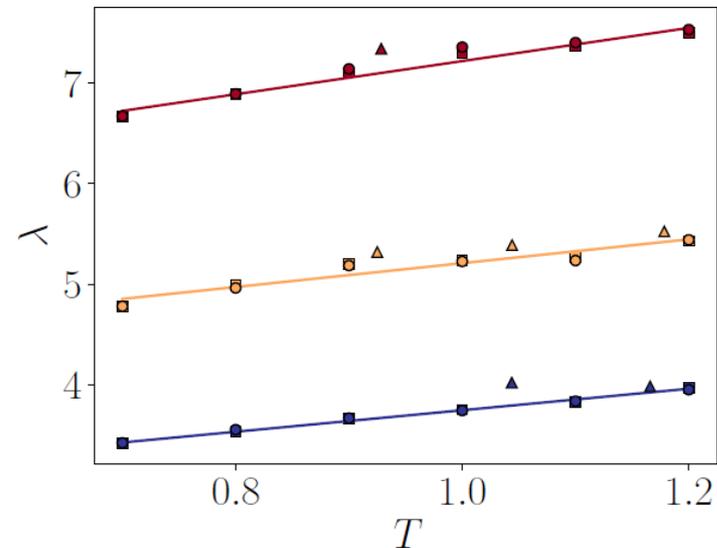
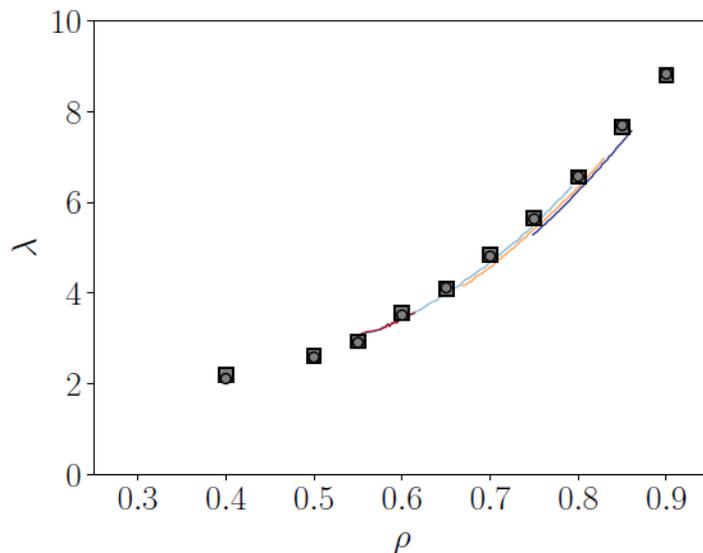
- Run over a range of different temperature channels
- Linear variation as a function of temperature



Fourier's law of Heat Conduction

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

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



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

Beyond Fourier's law of Heat Conduction

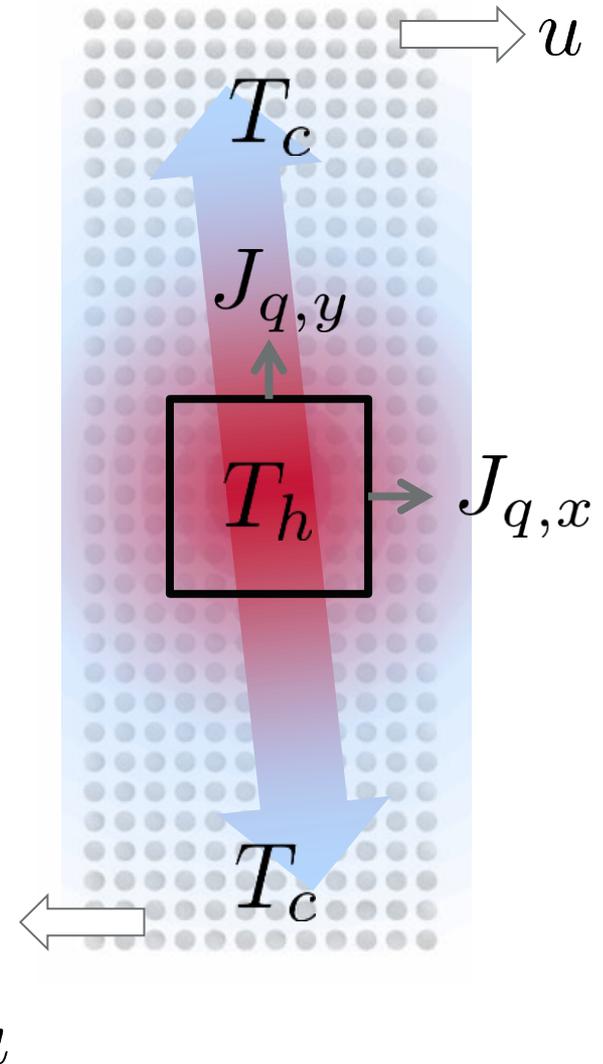
- We need to measure heat flux in
 - The parallel (x) direction
 - The wall-normal (y) direction
- Define a volume to measure the heat flux either

- Inside the volume

$$\int_V \mathbf{J}_q dV$$

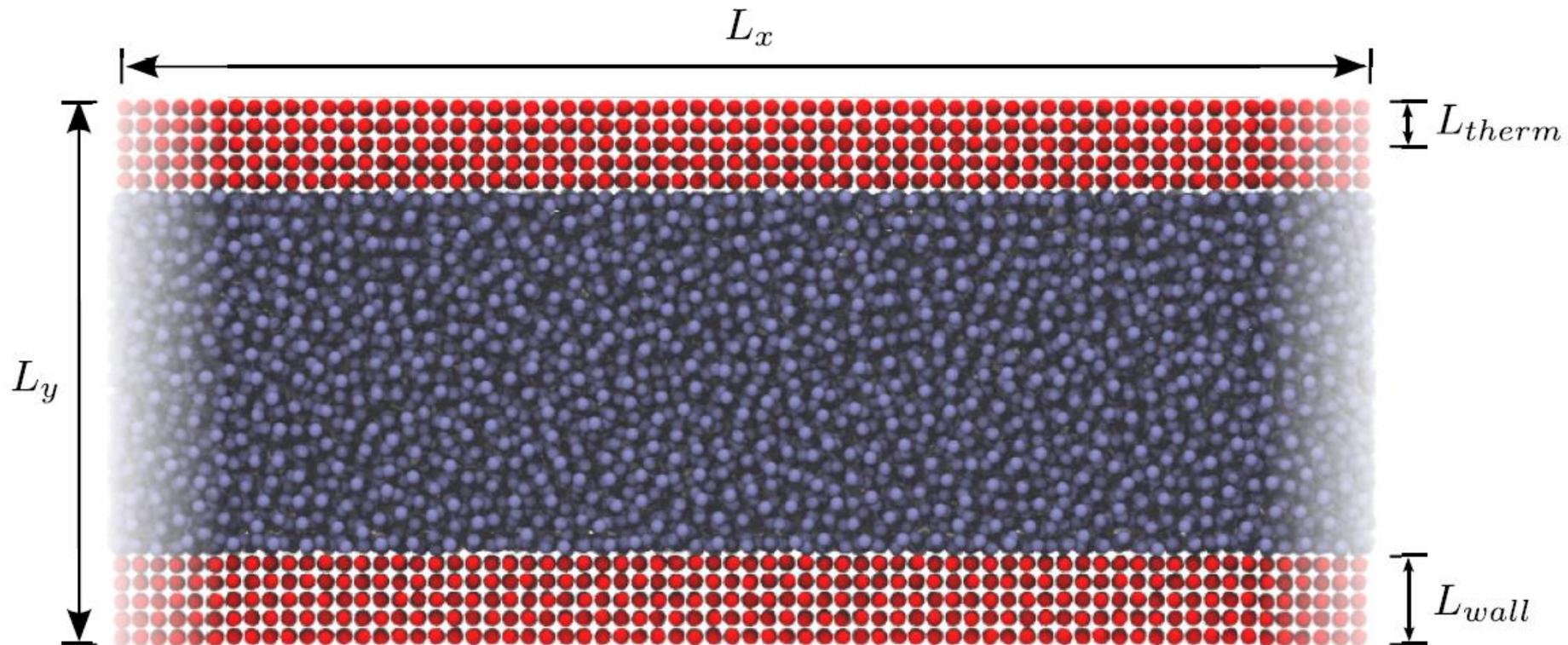
- Over the surfaces

$$\oint \mathbf{J}_q \cdot d\mathbf{S}$$



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)

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

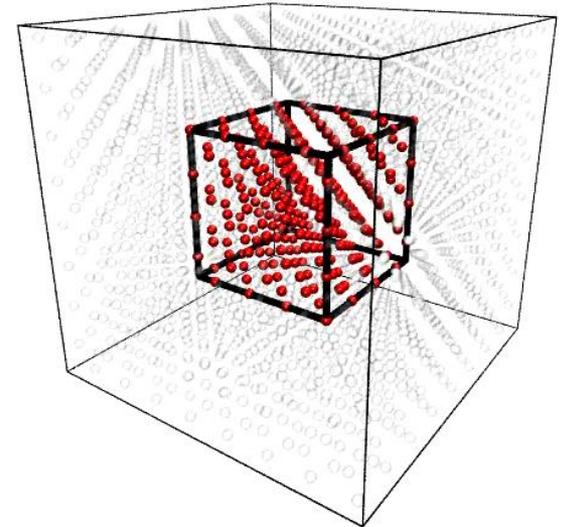
$$= [H(x^+ - x_i) - H(x^- - x_i)]$$

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

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

- 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)

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

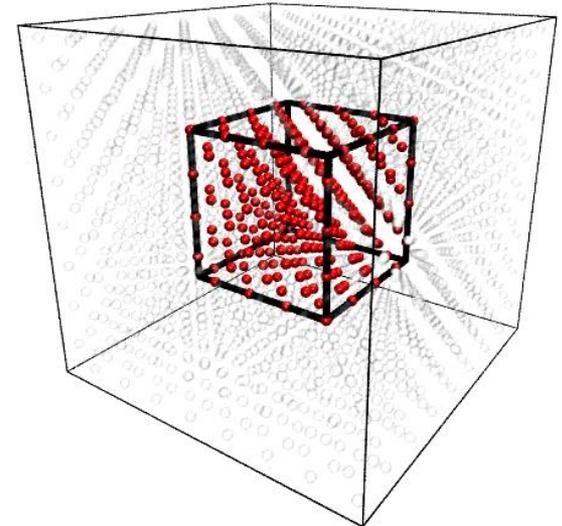
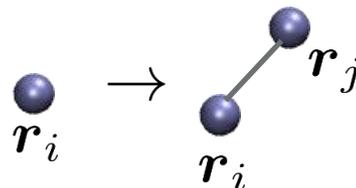
$$= [H(x^+ - x_i) - H(x^- - x_i)]$$

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

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

- Replace molecules with line of inter-molecular interaction

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



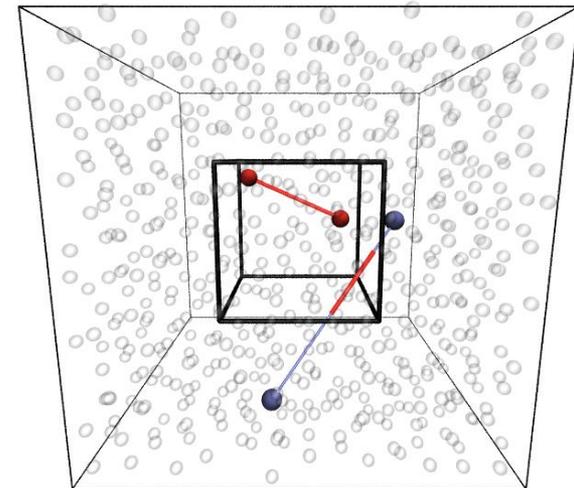
The Control Volume Functional

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

$$\begin{aligned} \vartheta_s \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij})dV = \\ [H(x^+ - x_i + sx_{ij}) - H(x^- - x_i + sx_{ij})] \\ \times [H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij})] \\ \times [H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij})] \end{aligned}$$

- Length of interaction inside the CV

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

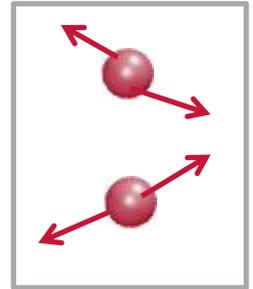


Volume Average Heat Flux

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

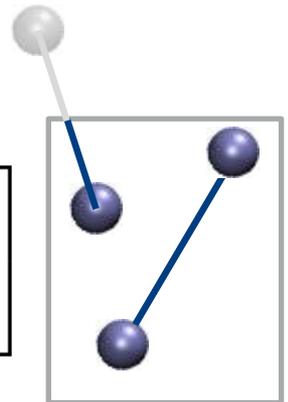
Kinetic

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



Configurational

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





Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

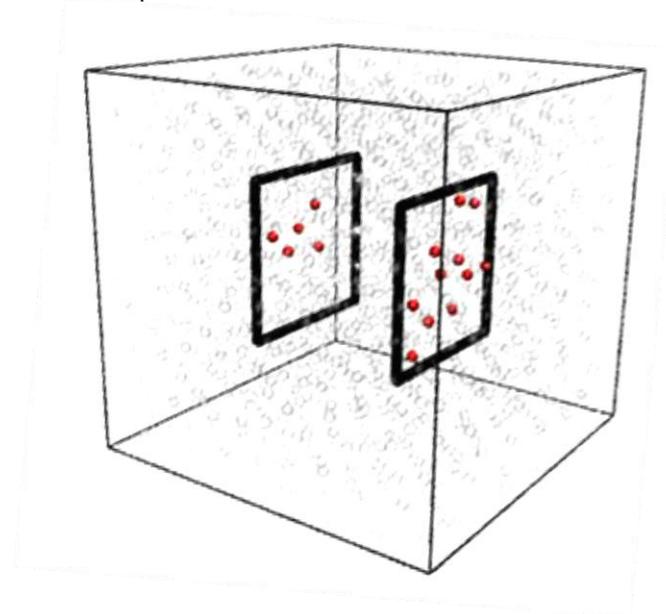
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = [\delta(x^+ - x_i) - \delta(x^- - x_i)] \\ \times [H(y^+ - y_i) - H(y^- - y_i)] \\ \times [H(z^+ - z_i) - H(z^- - z_i)]$$

- Vector form defines six surfaces

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

- Or in words

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





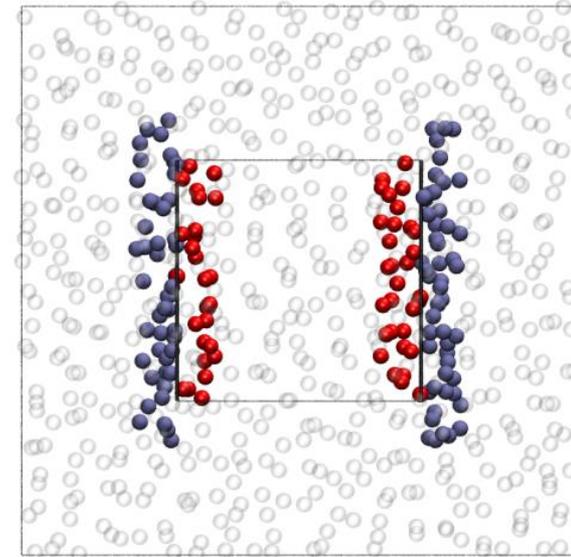
Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

$$\frac{\partial \vartheta_s}{\partial x} \equiv \left[\delta(x^+ - x_i + sx_{ij}) - \delta(x^- - x_i + sx_{ij}) \right]$$

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

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



- Surface fluxes over the top and bottom surface

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

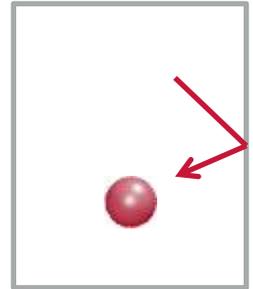
$$dS_{xij}^+ = \frac{1}{2} \underbrace{\left[\text{sgn}(x^+ - x_i) - \text{sgn}(x^+ - x_j) \right]}_{MOP} \boxed{S_{xij}}$$

Surface (MOP) Heat Flux

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

Kinetic

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



Configurational

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

