Non-equilibrium thermodynamics

Background to NEMD simulations

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Multicomponent fluids

Balance equations

- An extra equation is required – mass fraction balance for each component
- Extra terms are included to account for body forces (e.g. gravity)
- New flux – diffusive flux of component k

$$\mathbf{J}_k = \rho_k \left(\mathbf{v}_k - \mathbf{v} \right)$$

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \mathbf{P} + \sum_k \rho_k \mathbf{F}_k^e$$

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q - \mathbf{P}^T : \nabla \mathbf{v} + \sum_k \mathbf{J}_k \cdot \mathbf{F}_k^e$$

$$\rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k$$

Multicomponent fluids

Gibbs equation

- An extra term involving the chemical potential
- Rate of change of the entropy includes extra terms

$$T\frac{ds}{dt} = \frac{du}{dt} - \frac{p}{\rho^2}\frac{d\rho}{dt} - \sum_{k=1}^{n} \mu_k \frac{dc_k}{dt}$$

$$\rho\frac{ds}{dt} = -\frac{1}{T}\left(\nabla\cdot\mathbf{J}_q + \mathbf{P}^T : \nabla\mathbf{v} - \sum_k \mathbf{J}_k\cdot\mathbf{F}_k^e\right) + \frac{p}{T}\nabla\cdot\mathbf{v} + \frac{1}{T}\sum_{k=1}^{n}\mu_k\nabla\cdot\mathbf{J}_k$$

Multicomponent fluids

Entropy derivative

- After substituting for the heat flux and the pressure tensor, we find

Divergence of entropy flux

$$\rho\frac{ds}{dt} = -\nabla\cdot\left[\frac{1}{T}\left(\mathbf{J}_q - \sum_{k=1}^{n}\mu_k\mathbf{J}_k\right)\right] - \frac{1}{T^2}\mathbf{J}_q\cdot\nabla T - \frac{1}{T}\boldsymbol{\Pi}^T : \nabla\mathbf{v}$$

$$- \frac{1}{T}\sum_{k=1}^{n}\mathbf{J}_k\cdot\left(T\nabla\left(\frac{\mu_k}{T}\right) - \mathbf{F}_k^e\right)$$

Extra term in entropy production

- The entropy flux has changed and there is an extra term in the entropy production due to diffusive transport

Multicomponent fluids

Constitutive equations

- The linear transport equations are now

Flux due to concentration gradient

Flux due to temperature gradient – thermal diffusion, Soret effect

$$\mathbf{J}_1 = -\rho D \nabla c_1 - \rho c_1 c_2 D' \nabla T$$

$$\mathbf{J'}_q = -\lambda \nabla T - \rho_1 \frac{\partial \mu_1}{\partial c_1} T D'' \nabla c_1$$

Heat flow due to temperature gradient

Heat flow due to concentration gradient – Dufour effect

Constitutive equations

- The linear transport equations now show coupling – concentration gradient and temperature gradient are both vectorial
- Note the primed heat flux vector (allows concentration gradient instead of chemical potential gradient as thermodynamic force)

Spin angular momentum transport

Balance equations – single component

- Molecules with a significant moment of inertia – rod like, liquid crystals, colloidal etc.
- The balance equations now include total angular momentum transport

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}^e$$

$$\rho \frac{d\mathbf{M}}{dt} = -\nabla \cdot \mathbf{Q}_M + \rho \mathbf{G}^e_M$$

Spin angular momentum

- Total angular momentum can be split into two parts – orbital and spin

$$\mathbf{M} = \mathbf{L} + \mathbf{S}$$

- This leads to an equation for the spin angular momentum

$$\rho \frac{d\mathbf{S}}{dt} = -\nabla \cdot \mathbf{Q} - 2\mathbf{P}^a + \rho \mathbf{\Gamma}^e$$

Spin angular momentum transport

Balance equations – spin angular momentum

- The spin angular momentum balance equation now has two source terms
- One due to applied torques
- One due to conversion of orbital angular momentum to spin angular momentum

Source terms

$$\rho \frac{d\mathbf{S}}{dt} = -\nabla \cdot \mathbf{Q} - 2\mathbf{P}^a + \rho \mathbf{\Gamma}^e$$

Spin diffusion

Spin relaxation

- Linear momentum converts to spin angular momentum via the orbital angular momentum
- Note: antisymmetric part of the pressure tensor is important!

Spin angular momentum transport

Entropy production

- Extra terms corresponding to spin relaxation and diffusion

Thermodynamic force for spin relaxation

$$\sigma = -\frac{1}{T}\left[\frac{1}{T}\mathbf{J}_q \cdot \nabla T + \Pi \nabla \cdot \mathbf{v} + \mathbf{P}^{ts} : (\nabla \mathbf{v})^{ts} + \mathbf{P}^{a} \cdot (\nabla \times \mathbf{v} - 2\boldsymbol{\omega})\right.$$
$$\left. + Q \nabla \cdot \boldsymbol{\omega} + \mathbf{Q}^{ts} : (\nabla \boldsymbol{\omega})^{ts} + \mathbf{Q}^{a} \cdot (\nabla \times \boldsymbol{\omega})\right]$$

Electropumping in nanofluidics

Extended Navier-Stokes equations

applied body force

$$\rho \frac{\partial v_x}{\partial t} = (\eta_0 + \eta_r) \frac{\partial^2 v_x}{\partial y^2} + 2\eta_r \frac{\partial \Omega_z}{\partial y} + \rho F^e$$

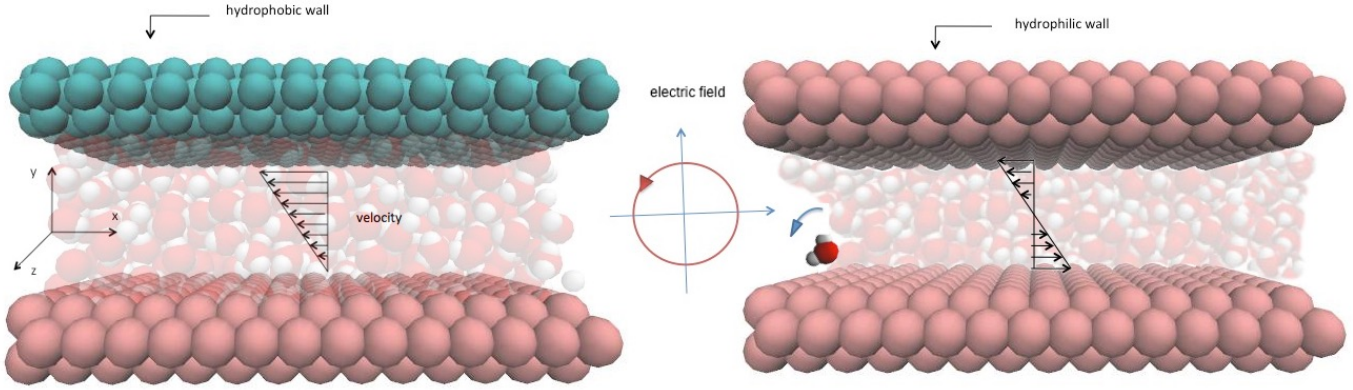
$$\rho \Theta \frac{\partial \Omega_z}{\partial t} = (\zeta_0 + \zeta_r) \frac{\partial^2 \Omega_z}{\partial y^2} - 2\eta_r \left(\frac{\partial v_x}{\partial y} + 2\Omega_z \right) + \rho \Gamma_z^e$$

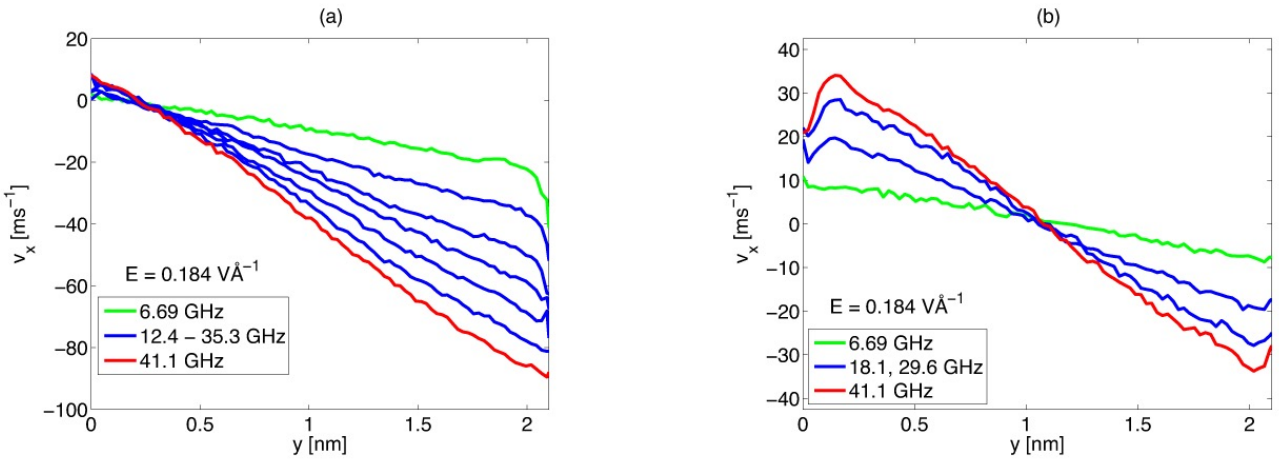
applied torque

Includes spin angular velocity for extended molecules

Translational and angular velocities are coupled!

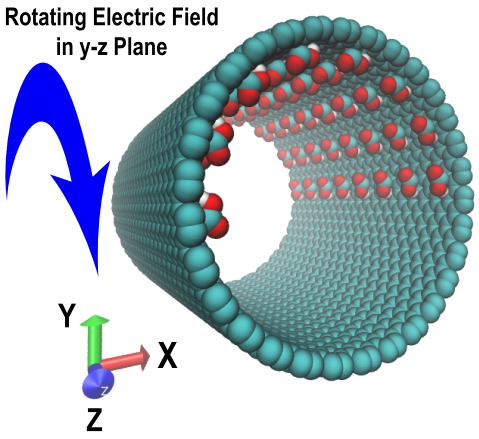
Planar geometry – SPCE water

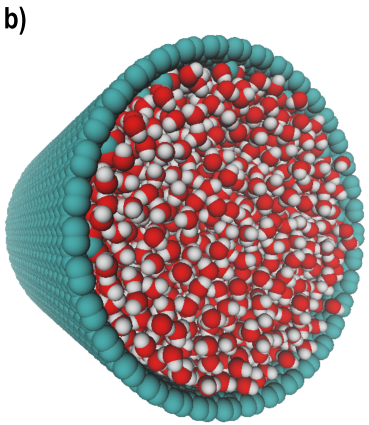




S. De Luca, B. D. Todd, J. S. Hansen and P. J. Daivis, *J. Chem. Phys.*, 2013, **138**, 154712.

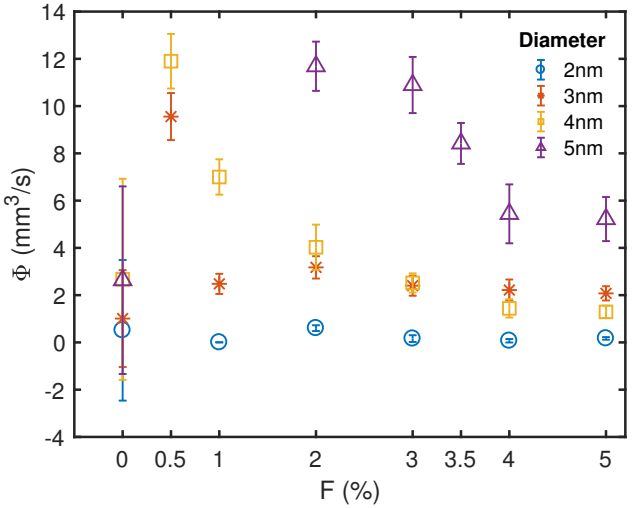
Carbon nanotube – SPCE water





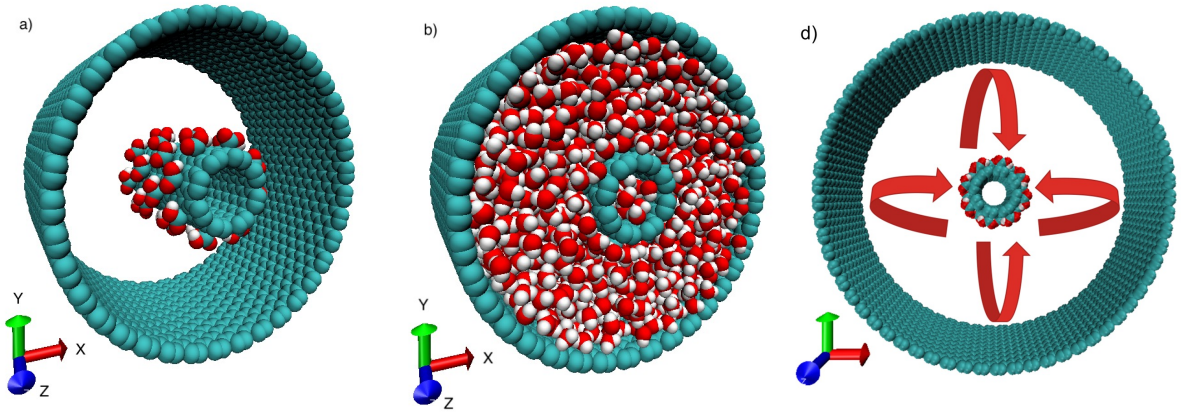
Functionalize with COOH to create hydrophobic surface.

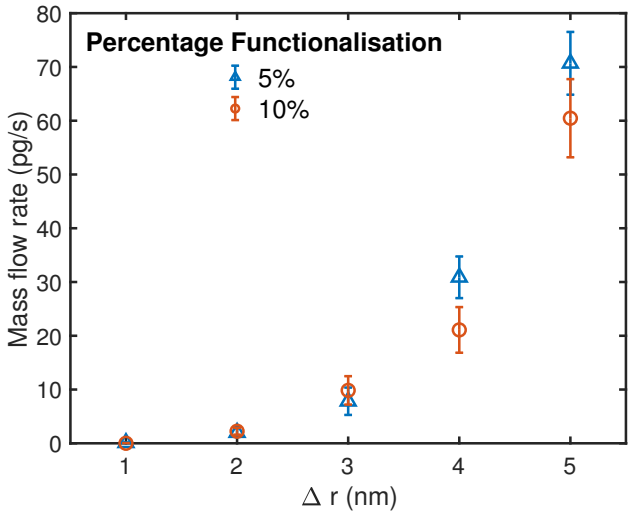
Hope that experimentalists can do it!



D. Ostler, S. K. Kannam, P. J. Daivis, F. Frascoli and B. D. Todd, *J. Phys. Chem. C*, 2017, **121**, 28158–28165.

Carbon nanotube – concentric geometry





- Rotating radial electric field.
- Flow rate decreases with increasing functionalization due to crowding.
- Compromise between stick b.c. and crowding to optimize flow rate.
- Pumping efficiency is better than Poiseuille (pressure driven flow).

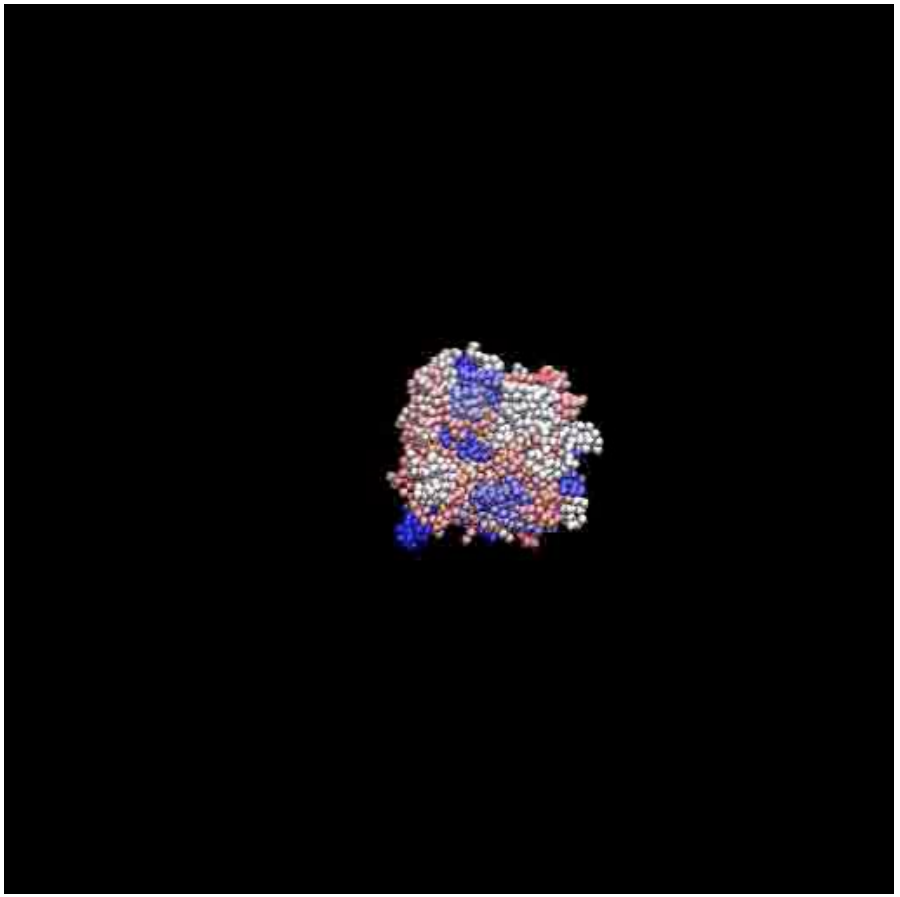
D. Ostler, S. K. Kannam, F. Frascoli, P. J. Daivis and B. D. Todd, *Langmuir*, 2019, **35**, 14742–14749.

Anisotropic heat flow in strongly sheared fluids

Motivation

- Heat flow in materials that become highly anisotropic due to strong shear (e.g. polymer melts)
- Nanofluidic flows - nonlinear coupling, nonlocal response
- We assume:

$$\mathbf{J}_q = \mathbf{J}_q\left(\nabla T, \nabla \mathbf{v}, \nabla\nabla \mathbf{v}\right)$$



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$$\mathbf{J}_q = \mathbf{J}_q\left(\nabla T, \nabla \mathbf{v}, \nabla\nabla \mathbf{v}\right)$$

Constitutive equation

Expand the flux in powers of the thermodynamic forces

- first order in ∇T

- linear/bilinear in $\nabla \mathbf{v}$ and $\nabla\nabla \mathbf{v}$

- up to 6th rank isotropic property tensors

Planar velocity field: $\nabla \mathbf{v} = \mathbf{ji}\dot{\gamma}(y)$

With this velocity field, we find

$$\mathbf{J}_q = -\boldsymbol{\lambda}_{eff}\nabla T + \zeta\frac{\partial\dot{\gamma}}{\partial y}\mathbf{i} + 2\xi\dot{\gamma}\frac{\partial\dot{\gamma}}{\partial y}\mathbf{j}$$

Daivis and Coelho, PRE **61**, 6003 (2000)

Anisotropic heat flow in strongly sheared fluids

Heat flux

$$\mathbf{J}_q = -\boldsymbol{\lambda}_{eff}\nabla T + \zeta\frac{\partial\dot{\gamma}}{\partial y}\mathbf{i} + 2\xi\dot{\gamma}\frac{\partial\dot{\gamma}}{\partial y}\mathbf{j}$$

Heat flow in flow direction driven by strain rate curvature

Transverse heat flow driven by coupling between strain rate and its curvature

with

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

Simple planar shear

- Almost perfect linear velocity profile
- Curvature is zero

Anisotropic heat flow in strongly sheared fluids

Computation of the heat flux – diffusive flux of internal energy

Kinetic part

Configurational part

$$\mathbf{J}_q(\mathbf{r},t) = \sum_i^N u_i \mathbf{c}_i \delta(\mathbf{r}-\mathbf{r}_i) - \frac{1}{2}\sum_i^N \sum_{j\neq i}^N \mathbf{r}_{ij}\mathbf{F}_{ij} \cdot \left[\mathbf{v}_i - \mathbf{v}(\mathbf{r})\right] \int_0^1 \delta(\mathbf{r}-\mathbf{r}_i - \lambda \mathbf{r}_{ij}) d\lambda$$

Internal energy of particle i

thermal velocity of particle I

Integrate over a small volume element to compute the volume averaged heat flux

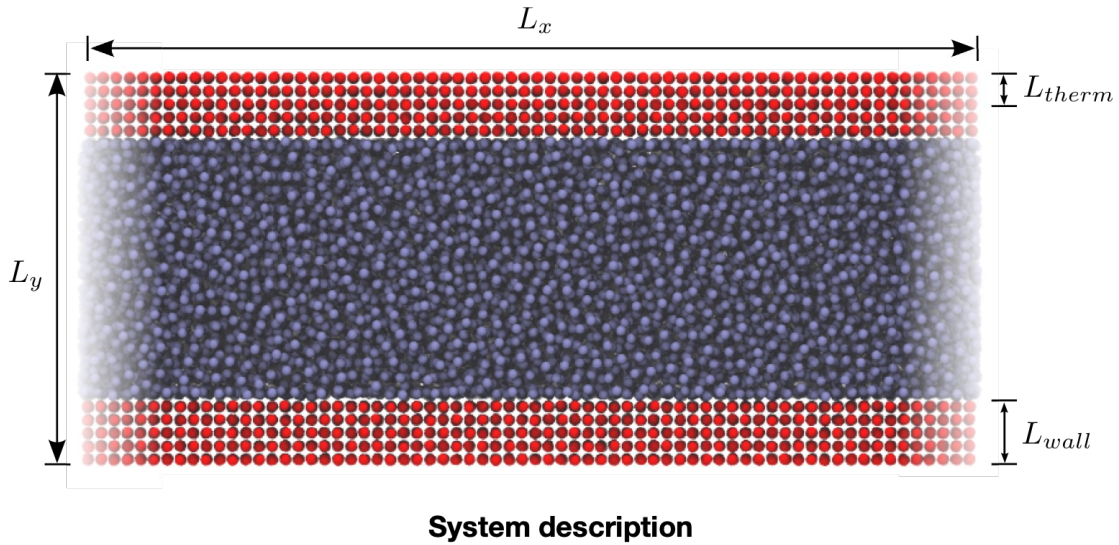
OR

Integrate over a small area element to compute the surface averaged heat flux

Anisotropic heat flow in strongly sheared fluids

Molecular dynamics simulations

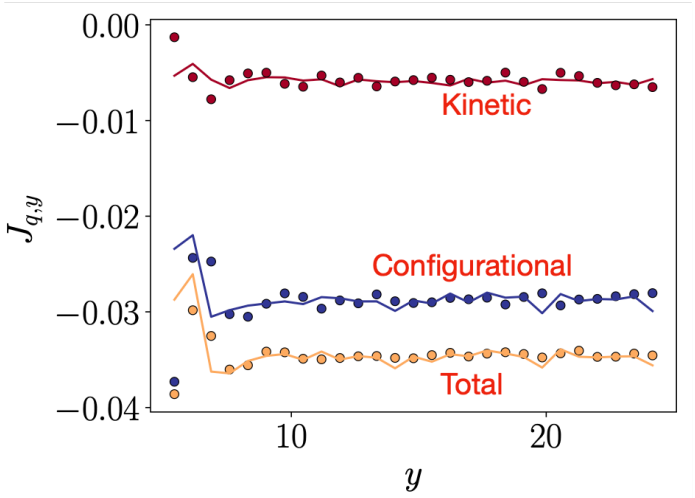
- heat flow between two walls with different T (e.g. 0.8 – 1.2) – no flow
- determine zero shear thermal conductivity
- Simple purely repulsive (WCA) atomic LJ fluid at liquid density
- Atomistic, thermostatted walls



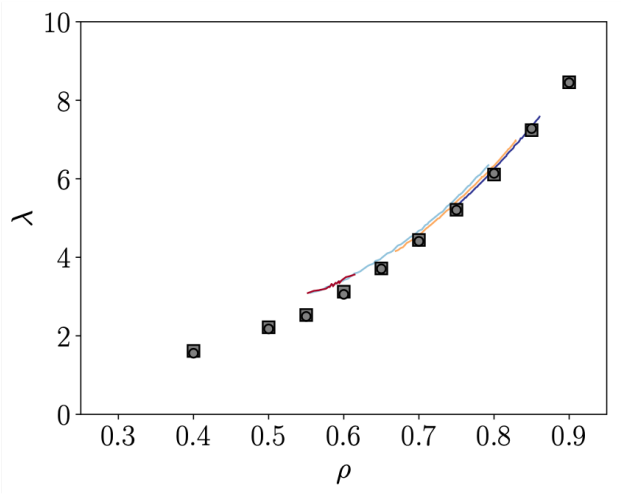
System description

Anisotropic heat flow in strongly sheared fluids

Results



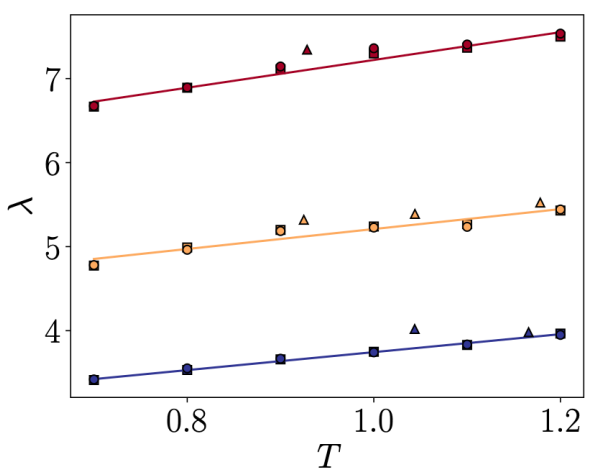
Lines - VA volume averaged
Points - MoP surface averaged
Density = 0.6



Thermal conductivity - comparison with liquid argon, T = 110 - 140 K
WCA cut-off.

Anisotropic heat flow in strongly sheared fluids

Results – T dependence

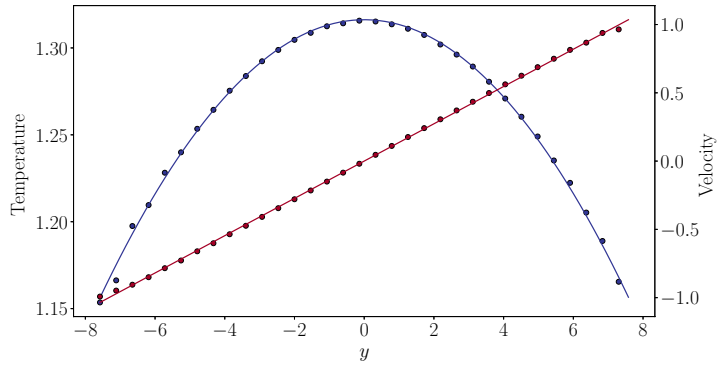


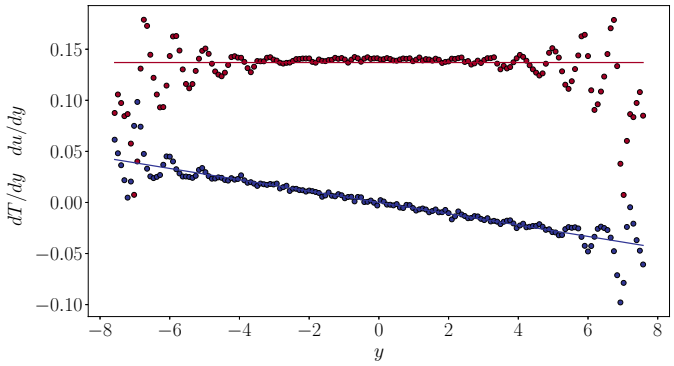
Squares - VA
Circles - MoP
Triangles - exp
Density = 0.65, 0.75, 0.85

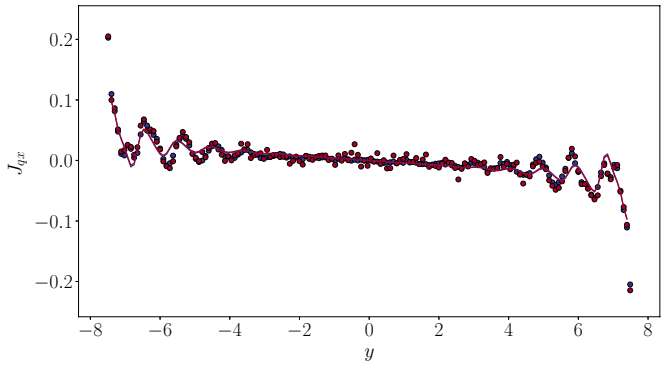
Thermal conductivity - comparison with liquid argon, T = 110 - 140 K
WCA cut-off.

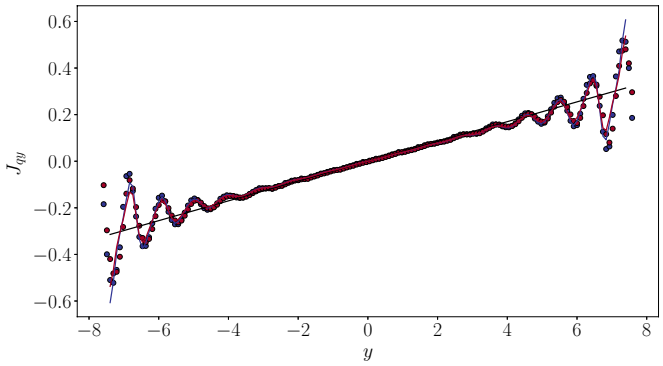
Anisotropic heat flow in strongly sheared fluids

Results – planar shear (moving walls)





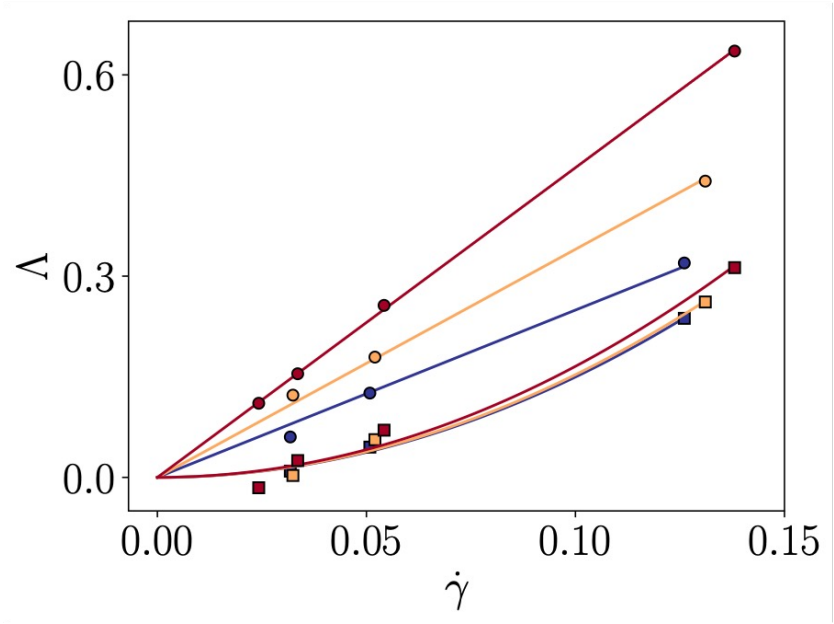




Small but measurable heat flux opposite to the flow direction

Anisotropic heat flow in strongly sheared fluids

Results – dependence on shear rate



$\Lambda_1 = \lambda_1 \dot{\gamma}$ circles

$\Lambda_2 = 3\lambda_2 \dot{\gamma}^2$ squares

Smith, Daivis and Todd, J.Chem.Phys. 150, 064103 (2019)

References

1. S.R. de Groot and P. Mazur, Non-equilibrium Thermodynamics Dover, N.Y. 1984. (Reprinting of the 1962 edition) - in my opinion, still the best introduction to classical irreversible thermodynamics.
2. W. Yourgrau, A. van der Merwe and G. Raw, Treatise on Irreversible and Statistical Thermophysics, Dover, N.Y. 1982. (Reprinting of the 1966 edition) – excellent addition to the above, with more discussion and physical reasoning.
3. D. Kondepudi and I. Prigogine, Modern thermodynamics: from heat engines to dissipative structures, Wiley, Hoboken, 2015. Introduction suitable for undergraduates – Prigogine won a Nobel prize for his work on n.e. thermodynamics, and this book is full of insight.

References

4. J.D. Jou, J. Casas-Vazquez and G. Lebon, Extended Irreversible Thermodynamics, Springer Berlin Heidelberg, 2001. An example of an approach to possible extensions of the classical theory that includes Non-Newtonian fluids and non-classical heat flow. Still somewhat controversial, but very fully worked through, providing many opportunities for tests of their ideas. Excellent bibliographies to guide further research.
5. B.D. Todd and P.J. Daivis, Nonequilibrium Molecular Dynamics: Theory , Algorithms and Applications, Cambridge University Press, N.Y. 2017. Discusses applications of n.e. thermodynamics in the context of n.e. molecular dynamics simulations, plus topics not discussed in the classical texts, like the statistical mechanical expressions for temperature, pressure tensor and heat flux vector.