Fluctuating Hydrodynamics of Flow through Porous Membranes

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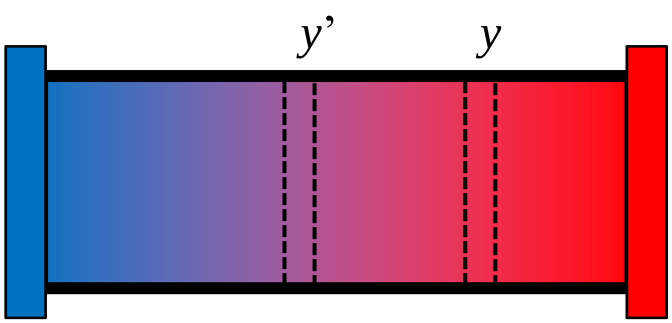
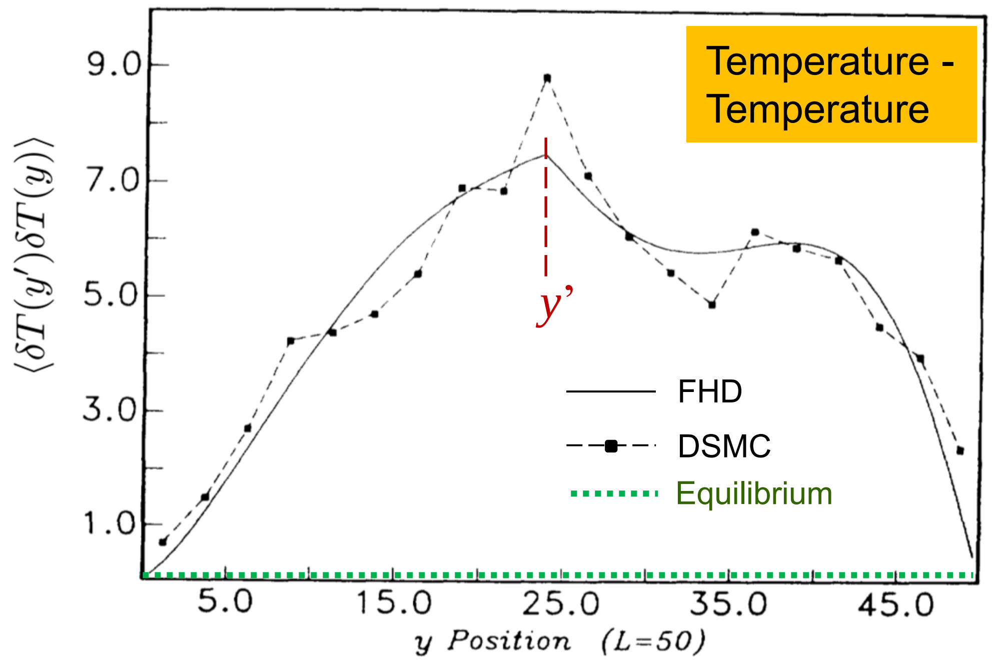
Non-equilibrium Fluctuations

Hydrodynamic fluctuations are long-ranged in a fluid held at a non-equilibrium steady state.

$$\langle \delta\rho(y')\delta v(y) \rangle \propto \nabla T$$

$$\langle \delta T(y')\delta T(y) \rangle \propto (\nabla T)^2$$





M. Malek Mansour, ALG, G. Lie and E. Clementi, *Phys. Rev. Lett.* **58** 874 (1987).

Fluctuating Hydrodynamics (FHD)

Landau and Lifshitz introduced stochastic flux terms into the equations of hydrodynamics to model spontaneous fluctuations in fluids.

$$\frac{\partial}{\partial t}(\rho) = -\nabla \cdot (\rho \mathbf{u}),$$

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) = -\nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) - \nabla P - \nabla \cdot \left[\mathbf{\Pi} + \widetilde{\mathbf{\Pi}}\right],$$

$$\frac{\partial}{\partial t}(\rho E) = -\nabla \cdot (\rho \mathbf{u} E + P \mathbf{u}) - \nabla \cdot \left[\mathbf{Q} + \widetilde{\mathbf{Q}}\right] - \nabla \cdot \left(\left[\mathbf{\Pi} + \widetilde{\mathbf{\Pi}}\right] \cdot \mathbf{u}\right).$$

[Stress tensor]

[Heat flux]

L. D. Landau E. M. Lifshitz, *Fluid Mechanics*, 1st Ed., Pergamon (1959).
J. M. Ortiz de Zarate and J. V. Sengers, *Hydrodynamic Fluctuations in Fluids and Fluid Mixtures*, Elsevier (2006).

Dissipative Fluxes in FHD

The deterministic stress tensor and heat flux take their standard linear forms (Stokes and Fourier laws),

$$\Pi_{ij} = -\eta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) + \delta_{ij}\left(\frac{2}{3}\eta\nabla\cdot\mathbf{u}\right), \qquad \text{and} \qquad \mathbf{Q} = -\kappa\nabla T$$

Stochastic stress tensor and heat flux are independent noises, white in space and time, with zero mean and variances,

$$\langle\widetilde{\Pi}_{ij}(\mathbf{r},t)\widetilde{\Pi}_{kl}(\mathbf{r}',t')\rangle = 2k_B\eta T\left[(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) - \tfrac{1}{3}\delta_{ij}\delta_{kl}\right]\delta(t-t')\delta(\mathbf{r}-\mathbf{r}'),$$

$$\langle\widetilde{Q}_i(\mathbf{r},t)\widetilde{Q}_j(\mathbf{r}',t')\rangle = 2k_B\kappa T^2\delta_{ij}\delta(t-t')\delta(\mathbf{r}-\mathbf{r}').$$

Finite Volume SPDE solver

Write the FHD equations as: $\frac{\partial}{\partial t}\mathbf{U} = -\nabla \cdot \mathbf{F} - \nabla \cdot \mathbf{D} - \nabla \cdot \tilde{\mathbf{S}}$

Time integration: $\frac{\partial}{\partial t}\mathbf{U} = \frac{\partial}{\partial t}(\ \rho,\ \rho\mathbf{u},\ \rho E\ )$

- Three-stage Runge-Kutta

Hyperbolic: $\mathbf{F} = (\ \rho\mathbf{u},\ \rho\mathbf{u}\mathbf{u} + P\mathbf{I},\ \rho\mathbf{u}E + \mathbf{u}P\ )$

- Four point centered

Parabolic: $\mathbf{D} = (\ 0,\ \mathbf{\Pi},\ \mathbf{Q} + \mathbf{u} \cdot \mathbf{\Pi}\ )$

- Two point centered

Stochastic: $\tilde{\mathbf{S}} = (\ 0,\ \tilde{\mathbf{\Pi}},\ \tilde{\mathbf{Q}} + \mathbf{u} \cdot \tilde{\mathbf{\Pi}}\ )$

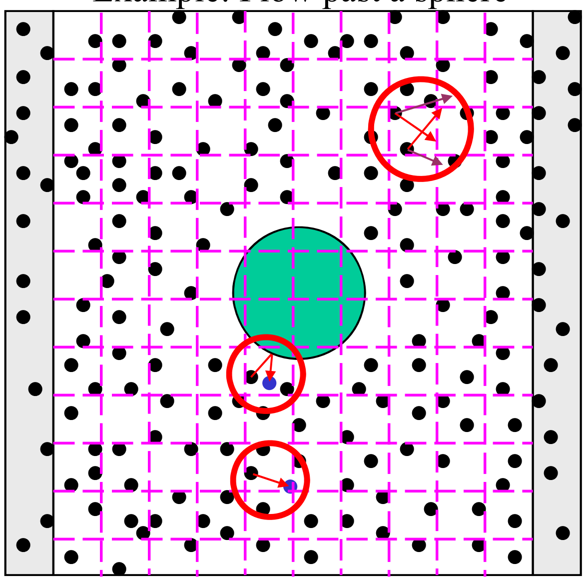
- Weighted 2 point centered

J.B. Bell, ALG, and S. Williams, *Physical Review E* **76** 016708 (2007).
A. Donev, E. Vanden-Eijnden, ALG, and J.B. Bell, *Comm. Applied Math. Comp. Sci.* **5** 149–197 (2010).

Direct Simulation Monte Carlo (DSMC)

- Initialize system with particles
- Loop over time steps
  - Create particles at open boundaries
  - Move *all* the particles
  - Process any interactions of particle & boundaries
  - Sort particles into cells
  - Sample statistical values
  - Select and execute random collisions

Example: Flow past a sphere

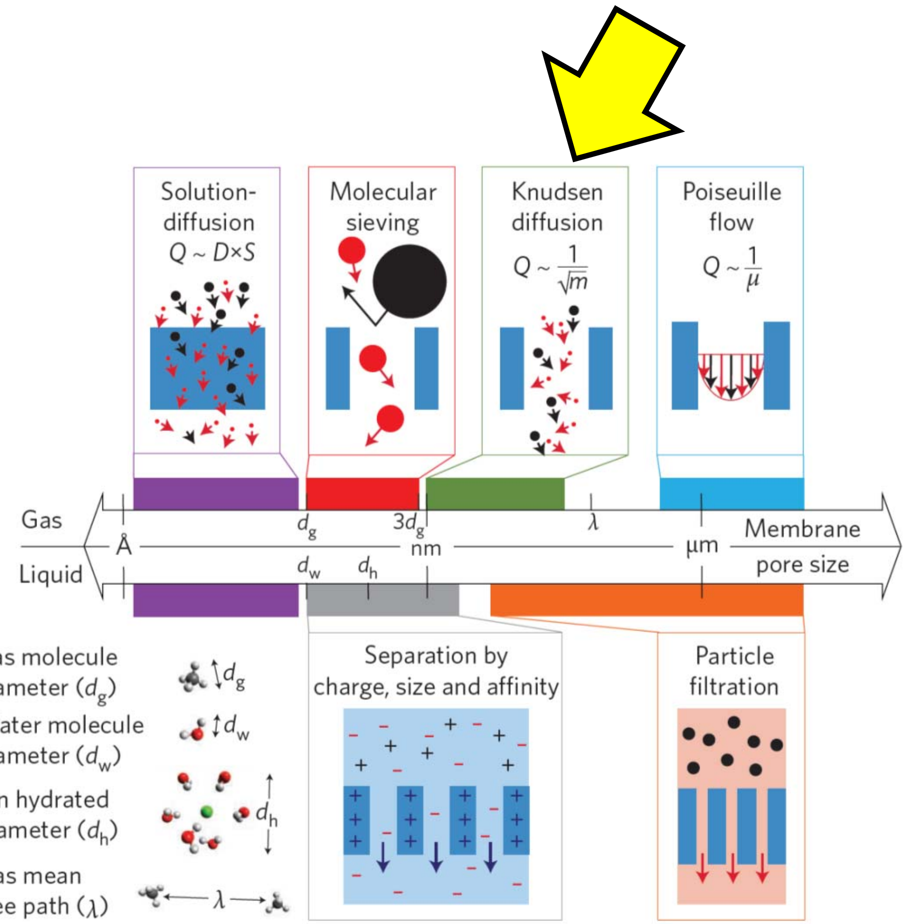


G.A. Bird, *Molecular Gas Dynamics and Direct Simulation of Gas Flows*, Clarendon, Oxford (1994)
F. Alexander and ALG, *Computers in Physics*, **11** 588 (1997)

Porous Membranes

Effusion (Knudsen diffusion) is gas transport through a membrane with pore sizes roughly between the mean free path and the molecule diameter.

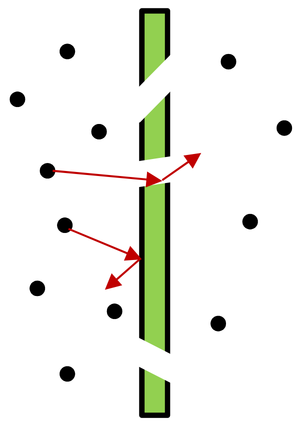
For standard conditions this range in pore size is between 100 nm to 2 nm.

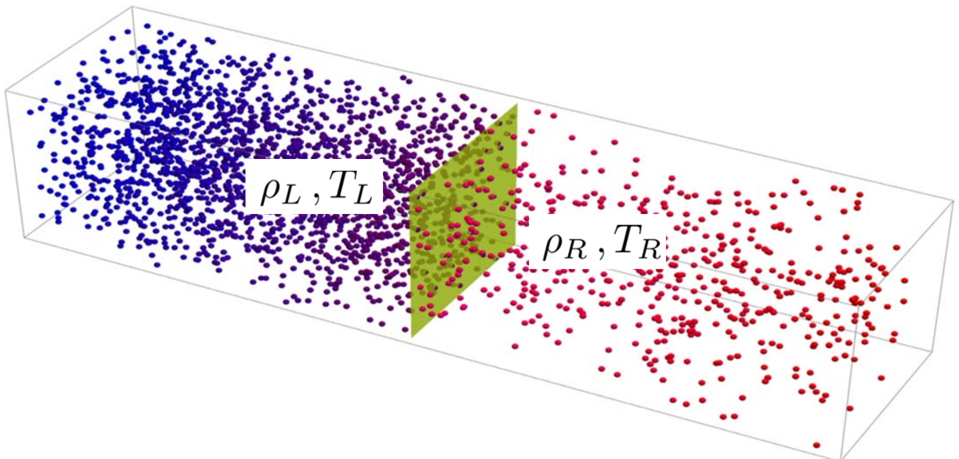


L. Wang, et al., *Nature Nanotechnology* **12** 509–522 (2017)

Transport by Effusion

Molecules reaching the interface cross it with probability *f*.





The mean fluxes of mass and energy are,

$$\langle J_M \rangle = \frac{f A\, k_B^{1/2}}{\sqrt{2\pi m}} \left(\rho_L T_L^{1/2} - \rho_R T_R^{1/2} \right), \qquad \langle J_{\mathcal{E}} \rangle = \frac{2 f A\, k_B^{3/2}}{m\sqrt{2\pi m}} \left(\rho_L T_L^{3/2} - \rho_R T_R^{3/2} \right).$$

Langevin Model for Effusion Membrane

In FHD we model the mass and energy crossing the membrane with the Langevin equations,

$$\frac{d}{dt}M = \langle J_M \rangle + \widetilde{J}_M, \qquad \frac{d}{dt}\mathcal{E} = \langle J_\mathcal{E} \rangle + \widetilde{J}_\mathcal{E},$$

where the white noises have variances and covariances,

$$\langle \widetilde{J}_M(t)\widetilde{J}_M(t')\rangle = \frac{mfA\,k_B^{1/2}}{\sqrt{2\pi m}}\left(\rho_R T_R^{1/2} + \rho_L T_L^{1/2}\right)\delta(t-t')$$

$$\langle \widetilde{J}_\mathcal{E}(t)\widetilde{J}_\mathcal{E}(t')\rangle = \frac{6fA\,k_B^{5/2}}{m\sqrt{2\pi m}}\left(\rho_R T_R^{5/2} + \rho_L T_L^{5/2}\right)\delta(t-t'),$$

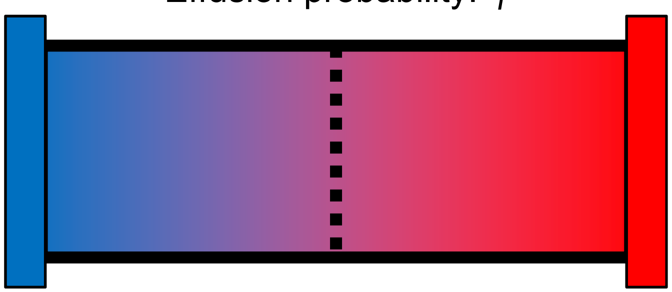
$$\langle \widetilde{J}_\mathcal{E}(t)\widetilde{J}_M(t')\rangle = \frac{2fA\,k_B^{3/2}}{\sqrt{2\pi m}}\left(\rho_R T_R^{3/2} + \rho_L T_L^{3/2}\right)\delta(t-t').$$

Note: Mass and energy noises are correlated

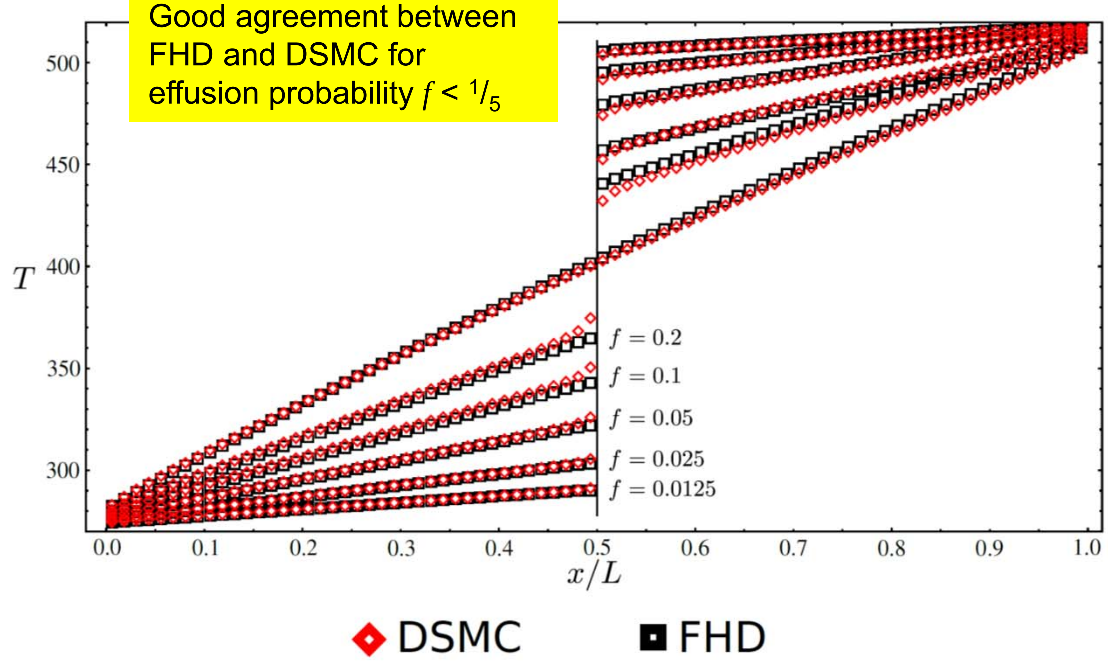
Temperature Profiles

Simulated a dilute gas with a temperature gradient in a system bisected by a porous effusion membrane.

Porous Membrane
Effusion probability: f



Good agreement between FHD and DSMC for effusion probability $f < {}^{1}/_{5}$

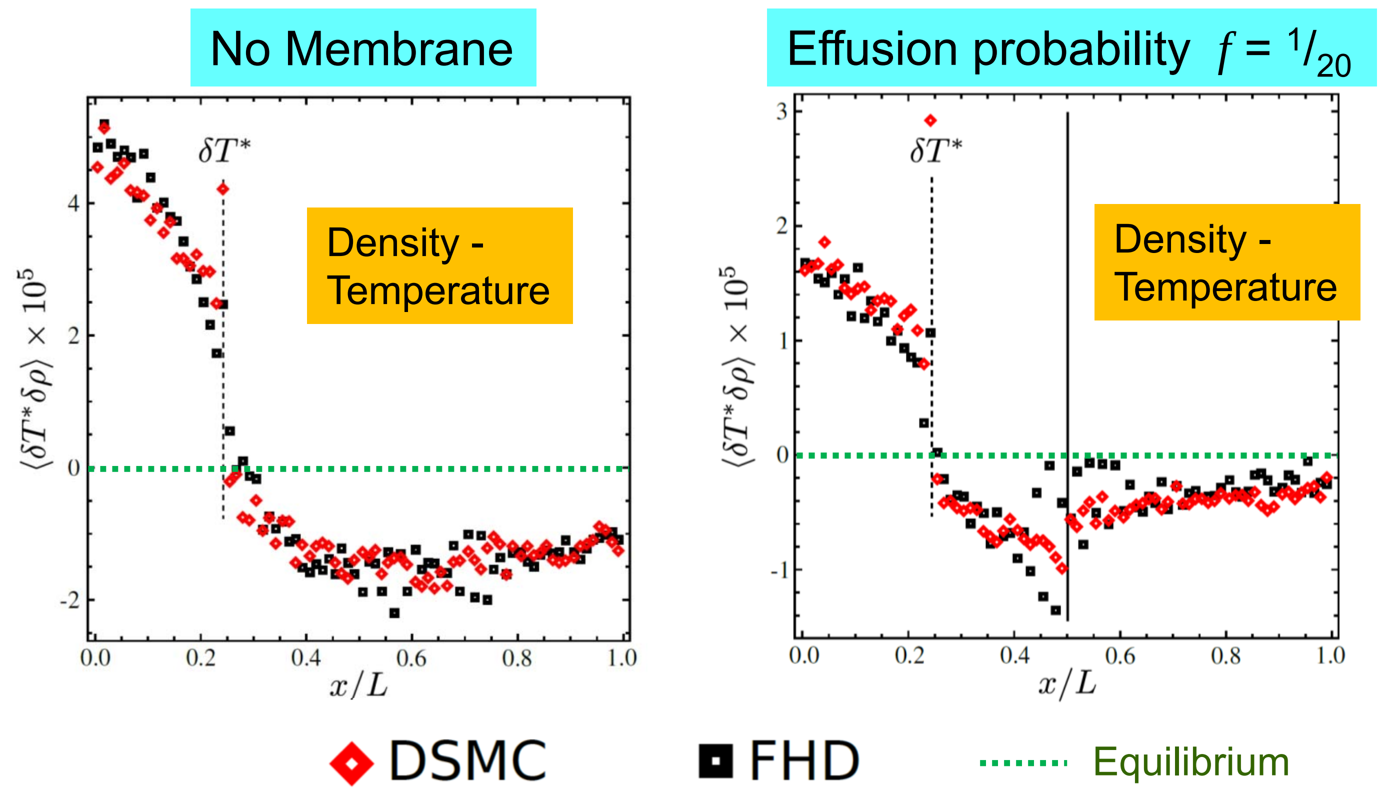


D. Ladiges, A. Nonaka, J.B. Bell, and ALG, *Physics of Fluids* **31**, 052002 (2019)

Correlations of Fluctuations

Temperature gradient is reduced by ~3 and so is density-temperature correlation

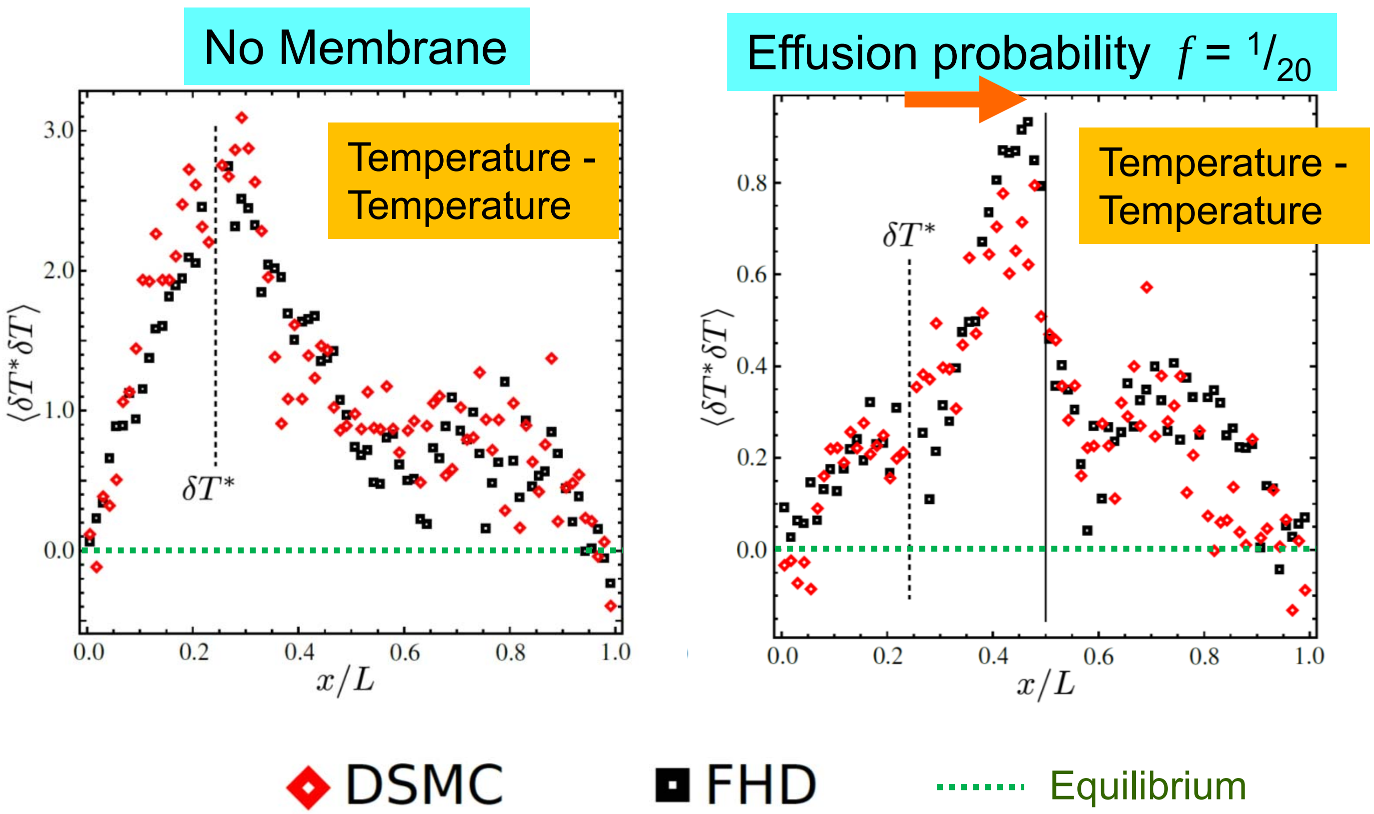
Correlation persists across the membrane



Correlations of Fluctuations

Temperature-temperature correlation is reduced but persists across the membrane

Correlation peak is significantly shifted towards the membrane



Master Equation Interface Model

Also tested a Master equation formulation using the Gillespie (SSA) algorithm in FHD.

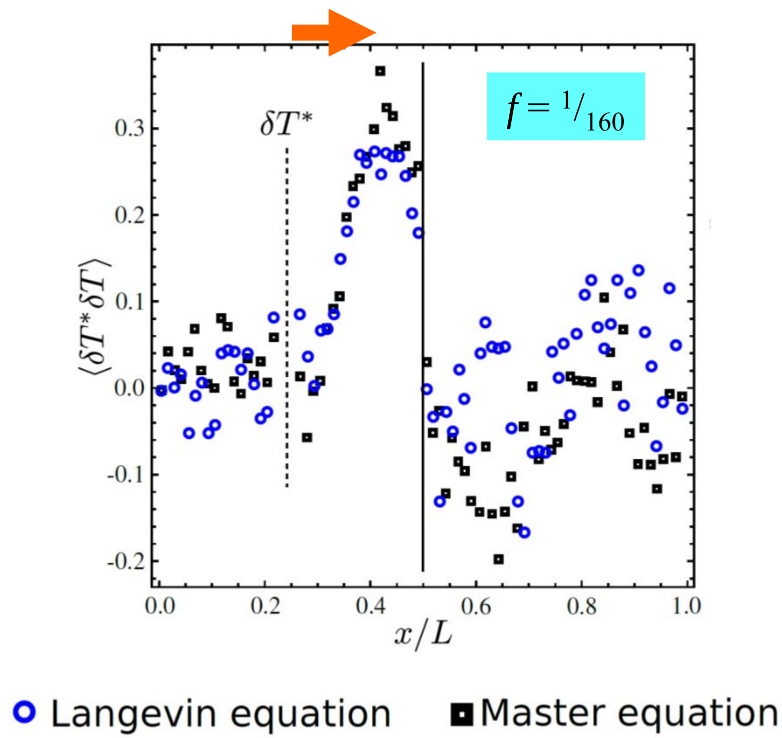
$$\tau_{\mathrm{e}} = \frac{m}{\rho f A}\sqrt{\frac{2\pi m}{k_B T}}$$

Mean waiting time for crossings

$$P_\epsilon(\epsilon) = \frac{\epsilon}{k_B^2 T^2}\, e^{-\epsilon/(k_B T)}$$

Distribution of molecule energies

The Langevin and Master equation models produced equivalent results.



Stochastic Heat Equation

To investigate the shift in the peak we consider the linearized stochastic heat equation,

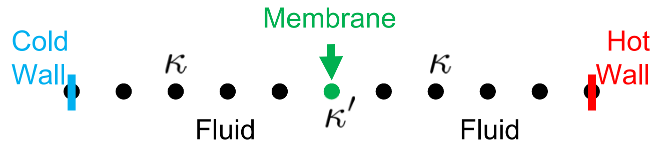
$$\rho c_v \frac{\partial}{\partial t}\delta T(y,t) = \frac{\partial}{\partial y}\kappa(y)\frac{\partial}{\partial y}\delta T - \frac{\partial}{\partial y}\widetilde{Q}$$

with

$$\langle \widetilde{Q}(y,t)\widetilde{Q}(y',t')\rangle = 2k_B\,\kappa(y)T_0(y)^2\;\delta(t-t')\delta(y-y').$$

Discretizing in space, $\mathbf{U} = [\delta T_1, \ldots, \delta T_N]$

$$\frac{\partial}{\partial t}\mathbf{U} = -\mathbf{A}\mathbf{U} + \mathbf{B}\boldsymbol{\xi}$$



For this Ornstein-Uhlenbeck process we find the covariance $\sigma_{i,j} = \langle \delta T_i \delta T_j \rangle$ by solving

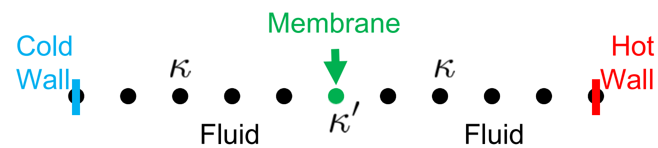
$$\mathbf{A}\boldsymbol{\sigma} + \boldsymbol{\sigma}\mathbf{A}^{\mathrm{T}} = \mathbf{B}\mathbf{B}^{\mathrm{T}}$$

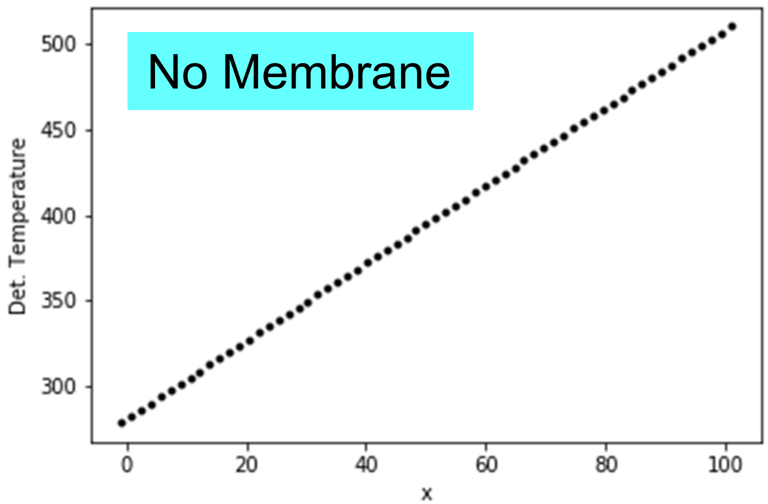
using linear algebra (e.g., by numerical relaxation)

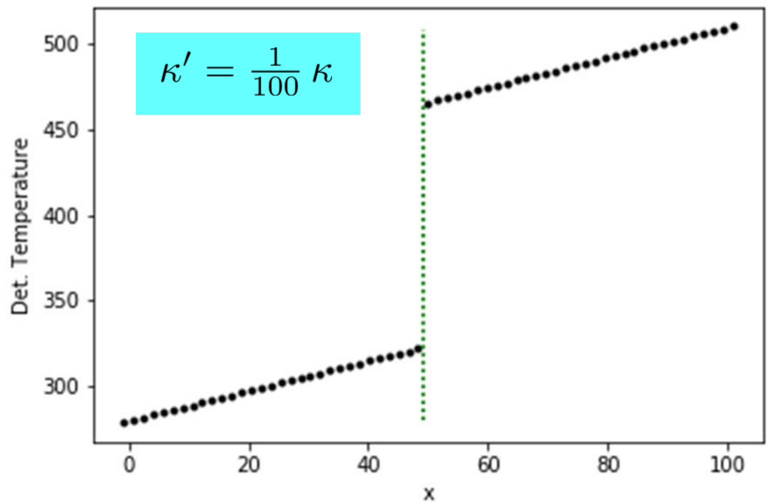
D. Ladiges, J.B. Bell, and ALG, in preparation (2019)

Temperature Profile

Deterministic temperature profiles are qualitatively similar to FHD and DSMC results

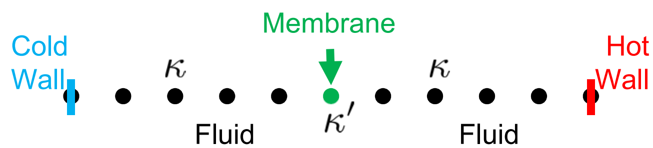


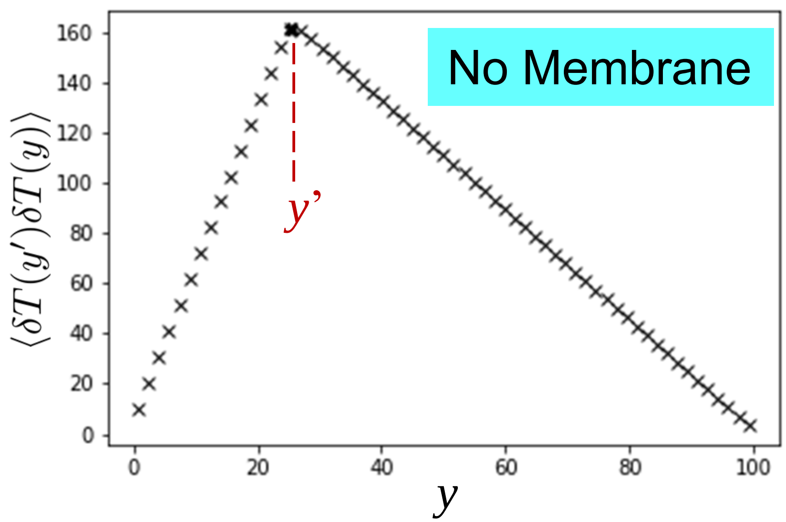


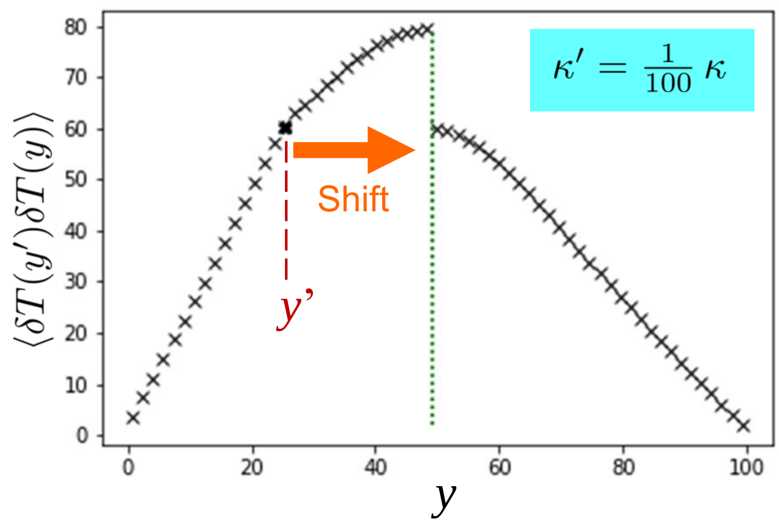


Correlations of Fluctuations

Temperature-temperature correlation is qualitatively similar to the FHD and DSMC result.







Summary & Future Work

Summary:

- Long range correlations persist through an effusive interface.
- Reduced magnitude largely due to change in ∇T.
- Distortion predicted by the stochastic heat equation.
- FHD can simulate gas transpiration; faster than DSMC.

Future work:

- Shear gradient; Concentration gradient
- Correlations parallel to the membrane
- Molecular sieving
- Ion transport in electrolytes
- Active transport (transport & chemistry)

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Thank you Aleks Donev for organizing this session