

# Finite size effects in simulations of molecular Joule-Thomson flow

David M. Rogers  
University of South Florida

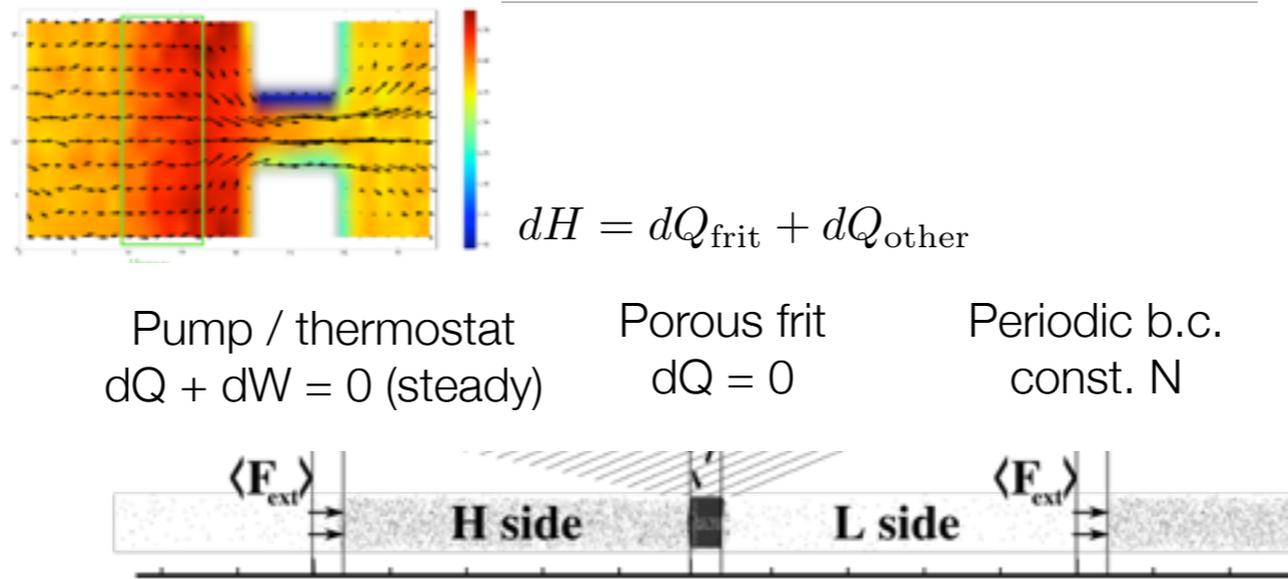
ACS 2018  
22 Mar., 2018

---



Conversion of energy or processing of water is always carried out with a nonequilibrium process. When everything is at equilibrium, we know how to use thermodynamics to calculate process costs and understand what changes take place on a molecular level. Out of equilibrium, there is always some dissipated work.

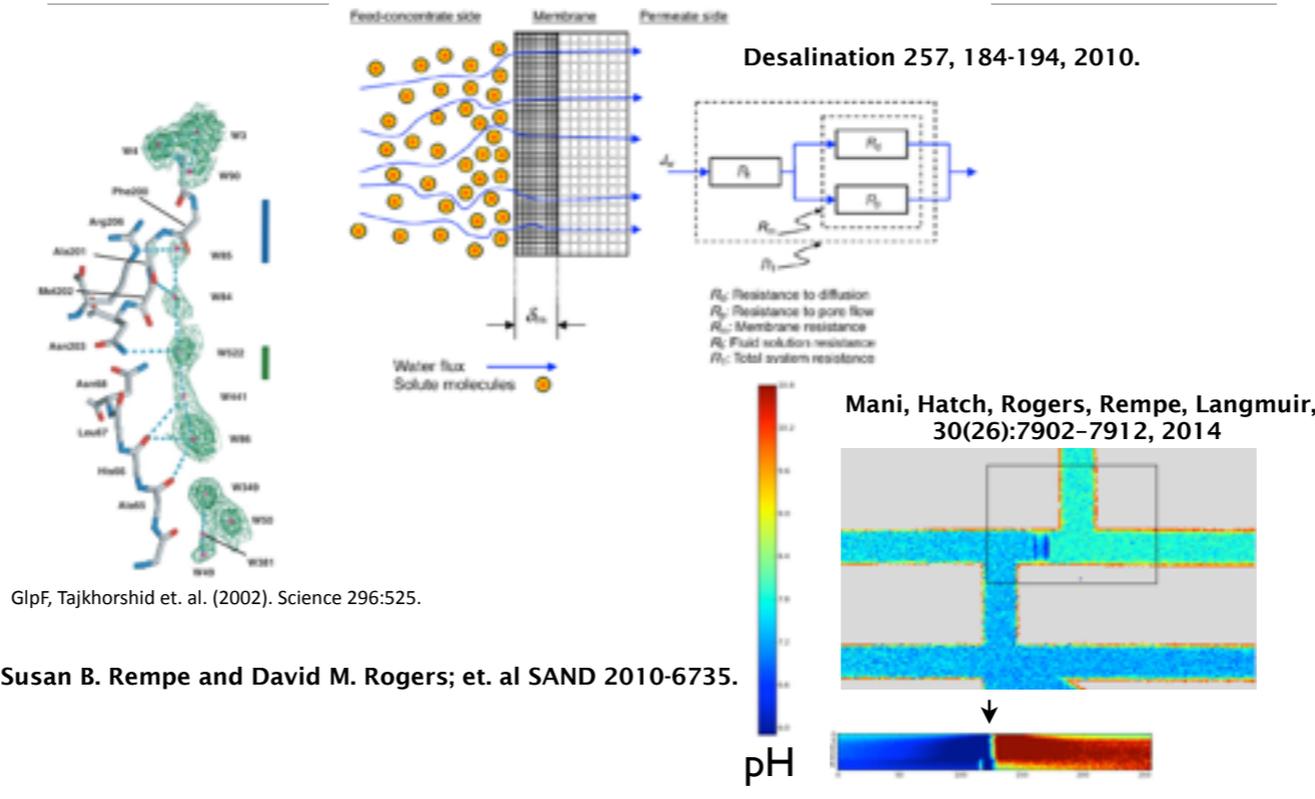
## Molecular Joule-Thomson Flow



Dayhoff & Rogers, Mol. Sim. 43: 467, 2017.

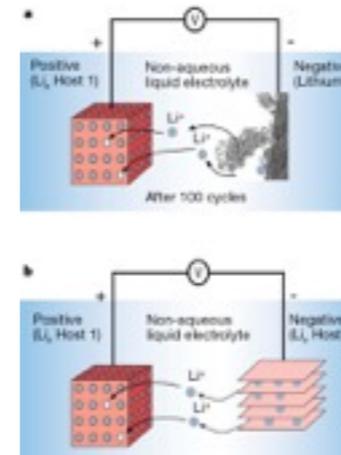
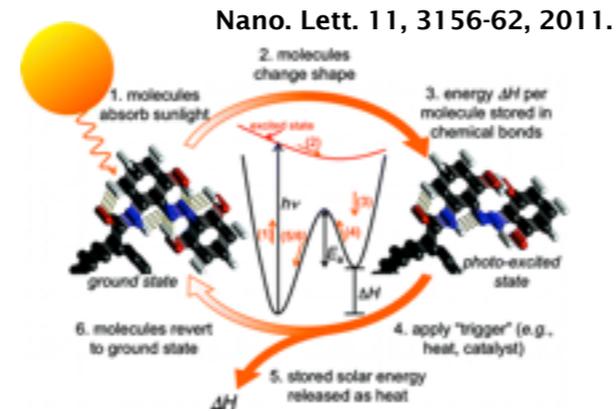
This talk covers the general method of simulating nonequilibrium steady-state operation for energy conversion devices. The focus will be on the prototype simulation here, of the Joule-Thomson effect in a nanochannel. Recall that your thermodynamics textbook says that - no matter how violent the expansion process at the pore is, the enthalpy of the gas on both sides must be equal because there is no heat transferred. We'll find that the story is not so simple at a molecular scale because interesting mesoscale phenomena appear.

# Nonequilibrium Materials Problems



Energy conversion devices always have two common elements -- an energy source that is out of equilibrium and a pathway for that energy to flow. Most of these employ transport across membranes that is driven by differences in concentration, voltage, pressure, or temperature. These are some other projects involving desalination and separation that I have been involved with over my career.

# Nonequilibrium Materials Problems



Nature 414, 359-367, 2001.

Simulating a nonequilibrium steady-state:

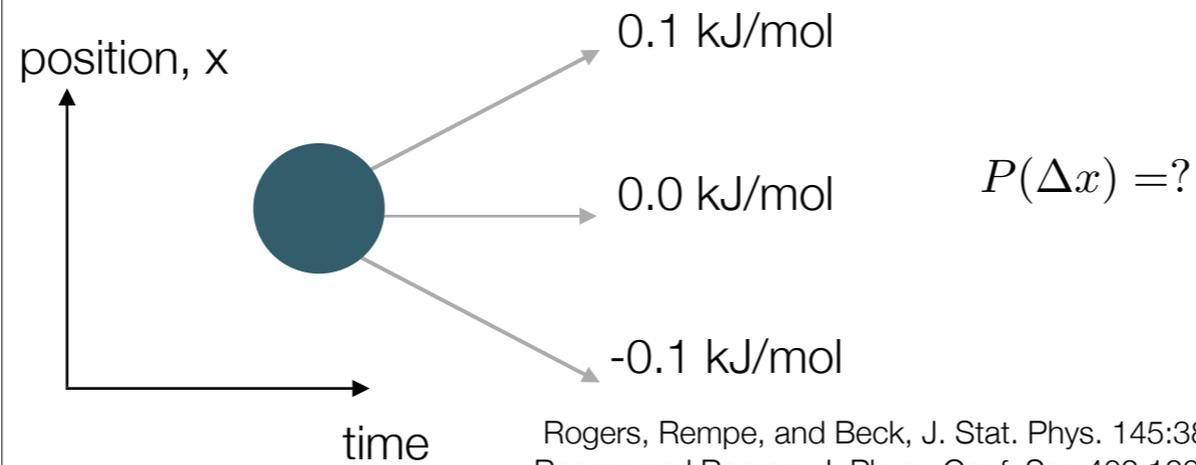
- External energy input?
- Dissipation?

Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).  
Rogers and Rempe, J. Phys., Conf. Ser. 402:12014 (2012).

Other energy conversion processes can take different forms, but still have the same elements. We can't just use equilibrium MD to simulate these systems - so how do we get details on their behavior? The key idea is to create a steady-state with both an external energy source and a sink (for dissipation).

## The Nonequilibrium Thermostat

- Usual ? : Given a diffusive system, find its properties.
- Alternative ? : *derive the transition distribution:*



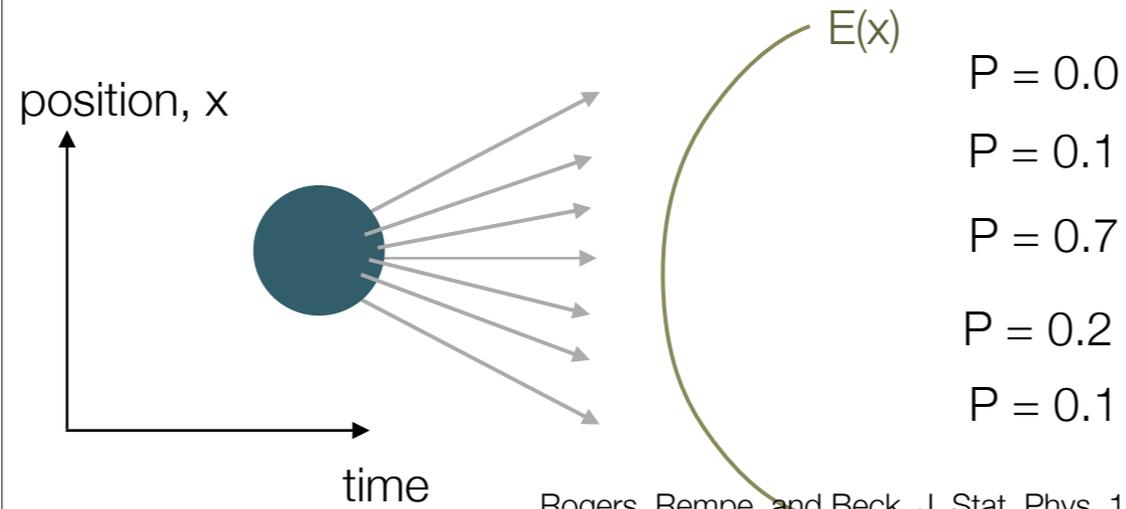
Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).  
Rogers and Rempe, J. Phys., Conf. Ser. 402:12014 (2012).

My work has shown that there is a very general way to do this. Rather than hunt around for a model that is close enough to what you want, start from scratch by asking "What transitions are possible?" and then "What are the probabilities for those transitions?"

## The Nonequilibrium Thermostat

- MaxEnt - constrain  $\Delta x^2$  and  $\Delta E$

$$P(\Delta x) \propto \exp \{ -\lambda_1 \Delta x^2 - \lambda_2 \Delta E \}$$



Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).  
Rogers and Rempe, J. Phys., Conf. Ser. 402:12014 (2012).

These types of questions are answered clearly by the maximum entropy method. For example, maximum entropy on movement,  $x - x'$ , with two constraints generates Brownian motion. The two constraints have Lagrange multipliers that turn out to be  $\beta/2$  and the inverse Gaussian width.

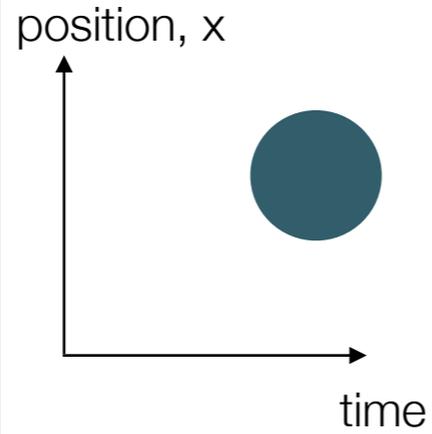
# The Nonequilibrium Thermostat

- MaxEnt result:

$$P(\Delta x) \propto \exp \{ -\lambda_1 \Delta x^2 - \lambda_2 \Delta E \}$$

Inverse Diffusion Constant

Inverse Temperature



Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).  
Rogers and Rempe, J. Phys., Conf. Ser. 402:12014 (2012).

It may seem a little like voodoo science (we're in New Orleans after all), but recall this is exactly the procedure we're used to in stat. mech. - where we just need a set of states and a temperature.

## Maximum *Transition Entropy*

---

- MaxEnt result:

$$P(\Delta x) \propto \exp \{ -\lambda_1 \Delta x^2 - \lambda_2 \Delta E \}$$

Inverse Diffusion Constant

Inverse Temperature

### **Key Conclusions:**

1. The environment is reduced to a random transition.
2. Temperature is a property of the environment *only*.
3. Value of T is determined by stationarity,

$$\langle \Delta E(\lambda_2) | x, t \rangle = 0$$

Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).  
Rogers and Rempe, J. Phys., Conf. Ser. 402:12014 (2012).

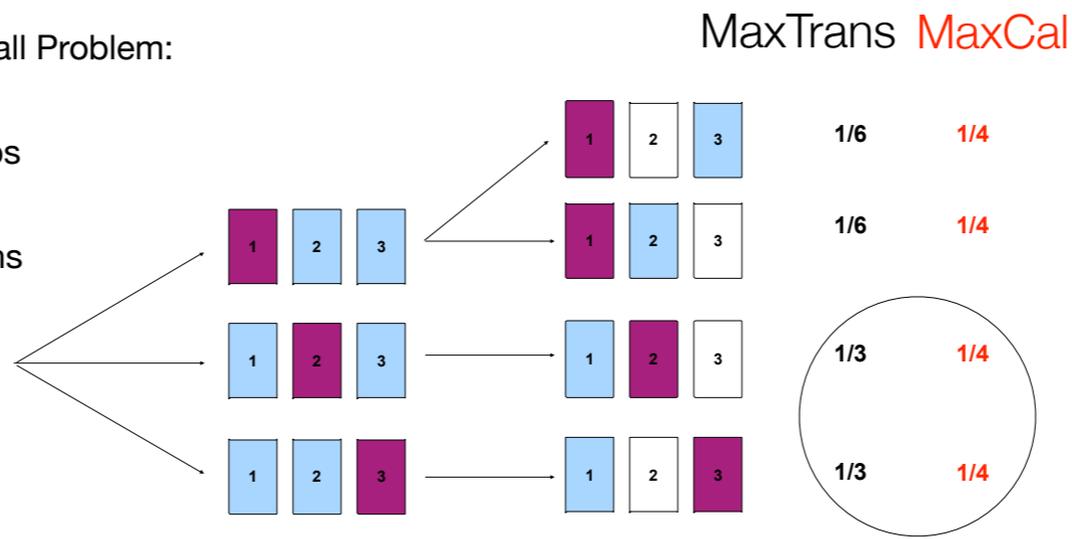
The models we get from this procedure usually turn out to be well-known. The Lagrange multipliers, however, are new. They are time-dependent parameterize that characterize the instantaneous state of the external environment. At every step, they have a thermodynamic conjugate relationship with the flow of energy, momentum, etc.

# MaxTrans vs. MaxCal

• Monty Hall Problem:

• 2 steps

• 4 paths



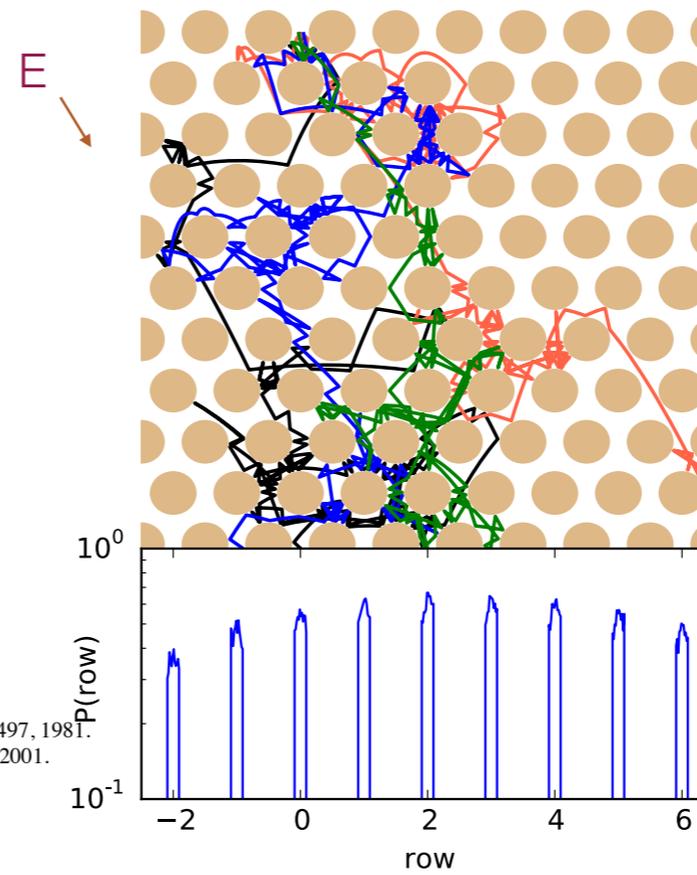
Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).  
 Rogers and Rempe, J. Phys., Conf. Ser. 402:12014 (2012).

I need to take a moment to differentiate MaxTrans from a related idea, Maximum Caliber. MaxCal was introduced by Jaynes as a probability distribution over trajectory space. The key difference is that MaxTrans is time-local. The distinction may not be important for time-independent processes, but for branching processes or time-dependent forces, MaxCal gives non-physical process probabilities.

## Really? Intermed. Test

- Model of electron motion through semiconductor
- Known to have diffusive properties
- Billiard models don't apply for free-streaming or large forces...

L. A. Bunimovich and Y. G. Sinai. *Commun. Math. Phys.*, 78:479–497, 1981.  
A. D. Chepelianskii and D. L. Shepelyansky. *PRL*, 87:034101, Jun 2001.  
N. Chernov. *Ann. Henri Poincaré*, 9(1):91–107, 2008.



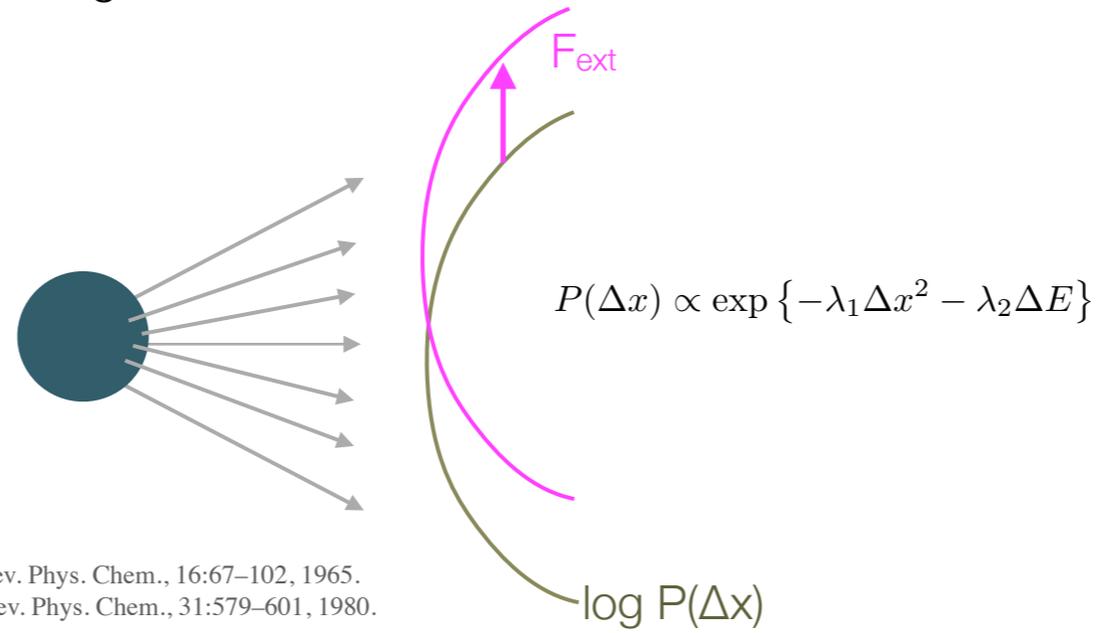
Maximum Entropy Closure for Nonequ. Stat. Mech. arXiv:1701.01466

A larger example to demonstrate this concept is the simulation of transport through a Galton board (Lorentz gas model). Few analytical results are available for the case with constant external force and small dissipation. However, the maximum entropy model with the constraints just mentioned predicts a Gaussian.

## Linearize it!

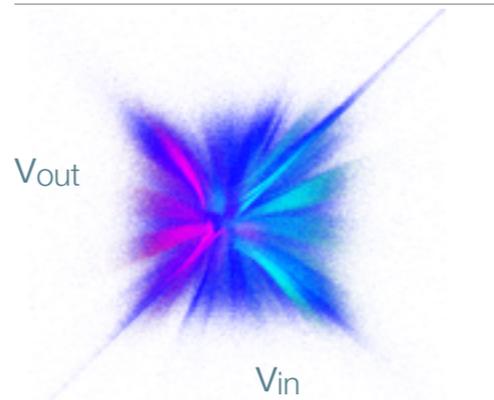
---

- The FDT with linear forces/flux relations is Gaussian process regression

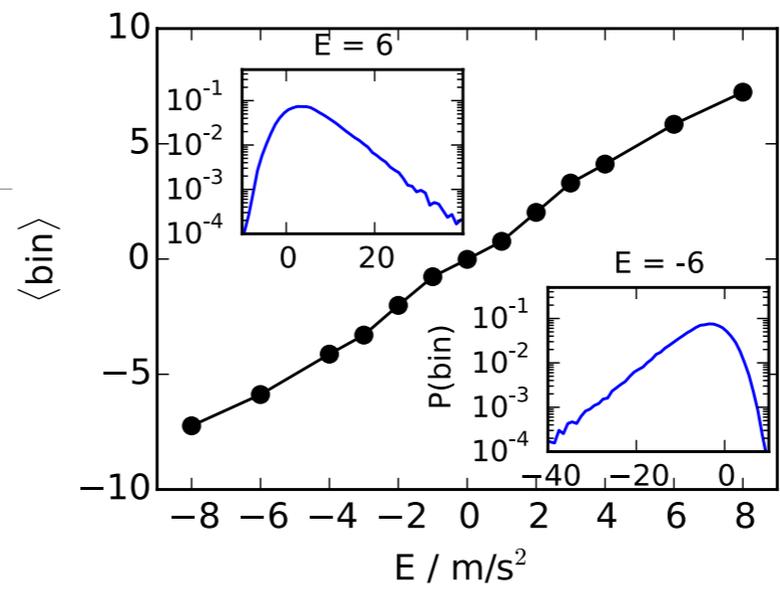


R. Zwanzig, Ann. Rev. Phys. Chem., 16:67–102, 1965.  
E. T. Jaynes, Ann. Rev. Phys. Chem., 31:579–601, 1980.

Linear is not good enough



- 10k trajectories, transient i.c.
- Flux statistics are not Gaussian under force.
- It's nonlinear even near the origin.



$n$  is conserved by symmetry...

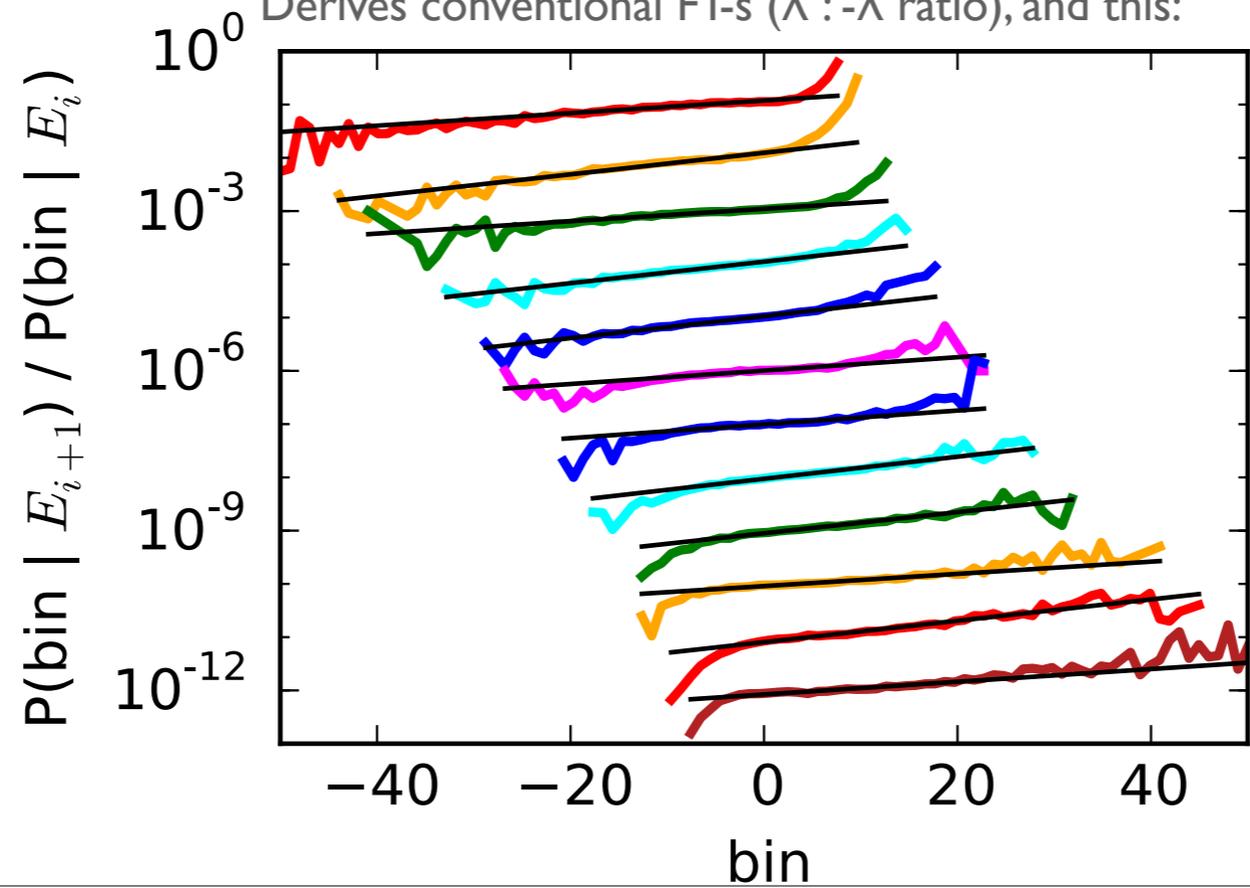
MaxEnt postulate:

$$P(\Delta n|\lambda) = P(\Delta n|0)e^{\lambda\Delta n}/Z(\lambda)$$

The actual distribution over ending columns (after falling 10 rows) is not quite Gaussian, but has long tails. A small tweak to the maximum entropy method-- to the maximum relative entropy -- captures this behavior.

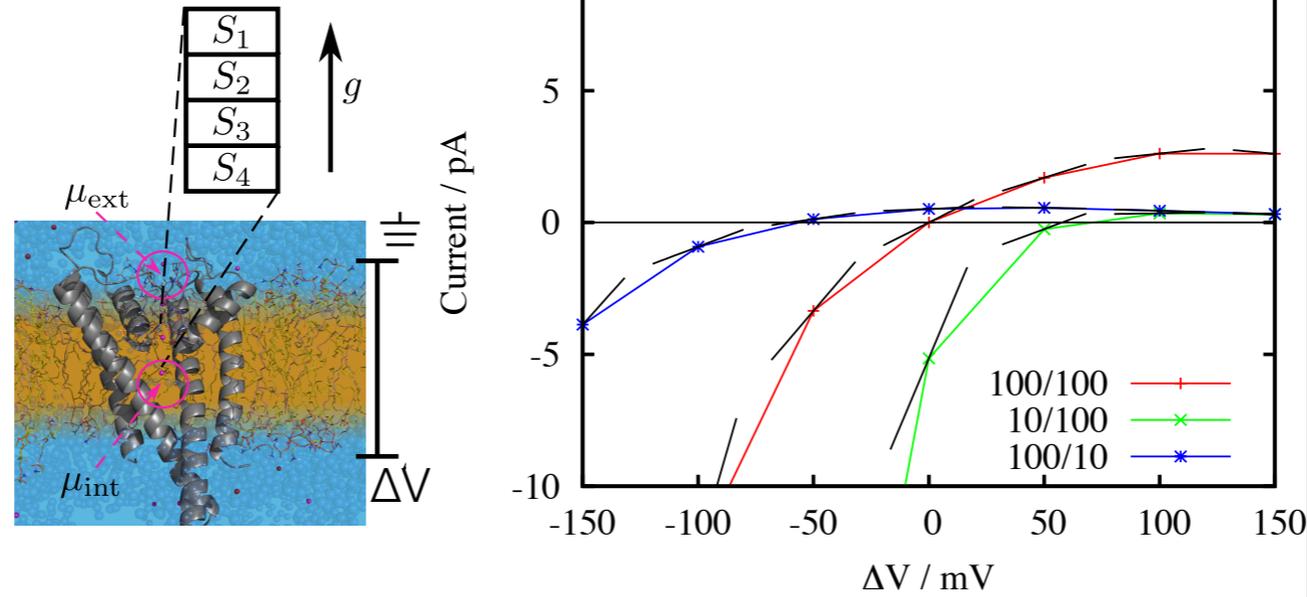
MaxTrans / Lg Deviation:  $\log P(J|\lambda) \simeq \lambda J - \log Z(\lambda)$

Derives conventional FT-s ( $\lambda : -\lambda$  ratio), and this:



What's more, the max-ent predictions hold up well here. I'm showing the ratio of two distributions at successively larger driving force. Just like the equilibrium density of states at two different temperatures, the nonequilibrium distributions show an exponential bias with increasing force.

# The FDT is just a second derivative



$$dQ = -I V$$

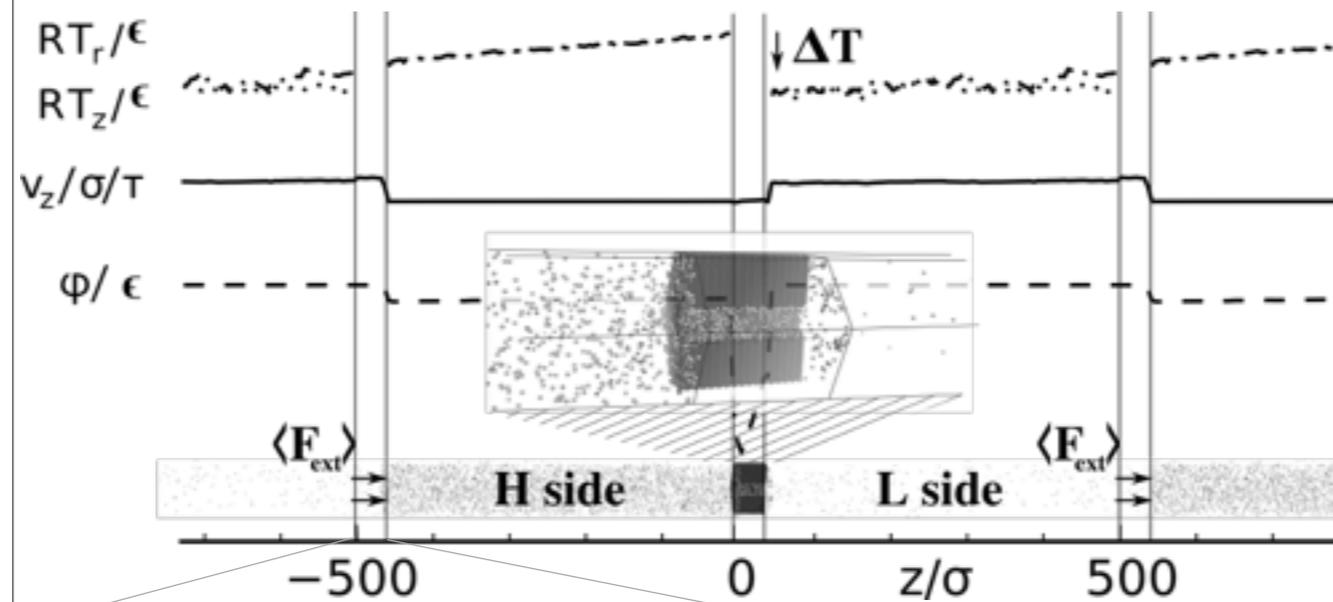
$$dW = I V + g \Delta\mu$$

First real demonstration of out-of-equilibrium FDT & Onsager reciprocity.

Rogers, Rempe, and Beck, J. Stat. Phys. 145:385 (2011).

Mathematically, this means the FDT -- connecting current fluctuations and driving forces, can be written just as for equilibrium as a second derivative of a partition function. Here, the partition function is over transition space. I'm showing a validation of this I did for a Markov ion channel model in 2011.

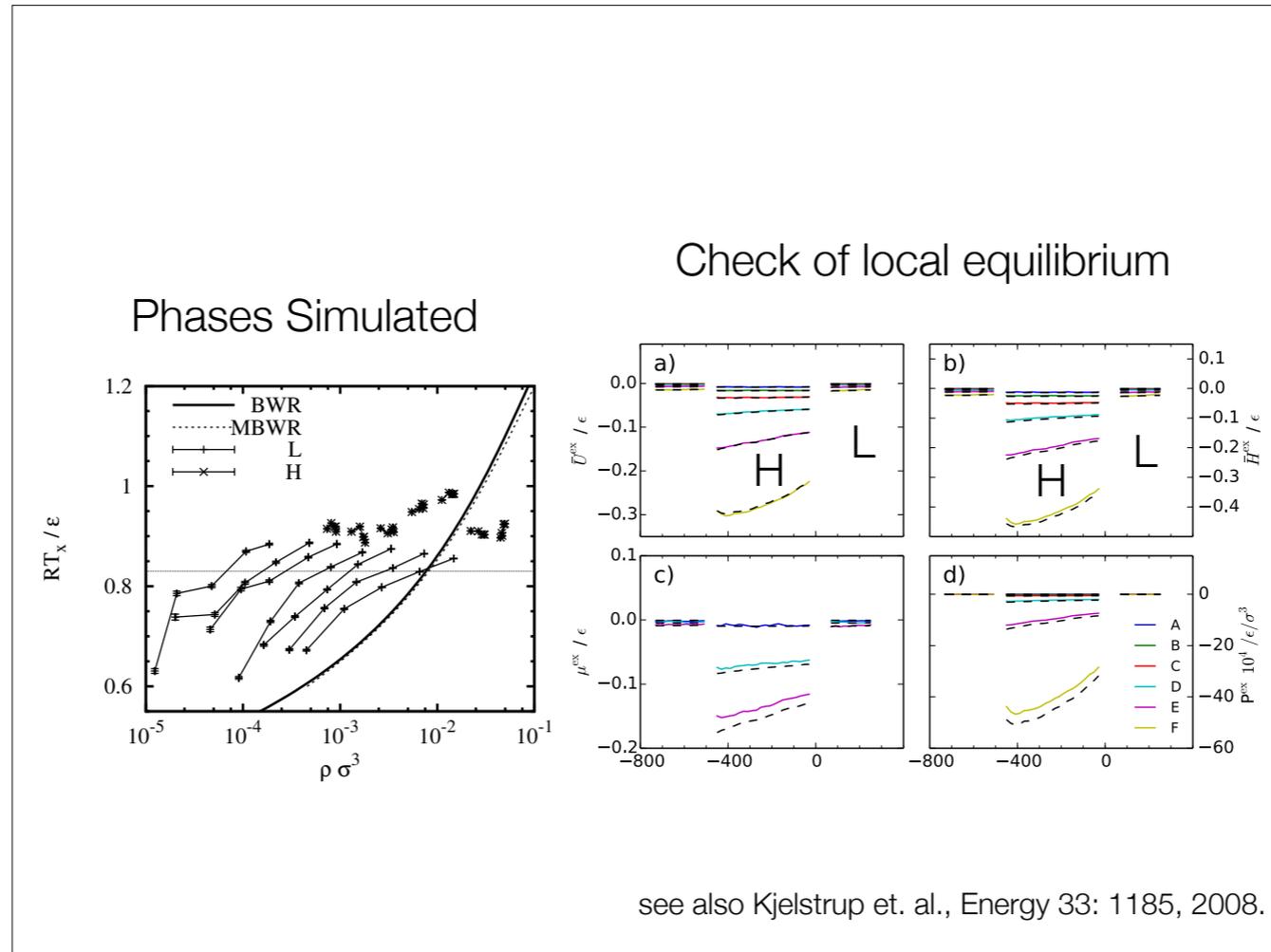
## JT Problem: Steady-State Results



same thermostat (but for gas) as:  
Zhu, Tajkhorshid and Schulten, Biophys. J. 86:50, 2004.

Dayhoff & Rogers, Mol. Sim. 43: 467, 2017.

Back to the JT flow problem, the thermostat regions obviously employ max-trans conditional on  $dE$  and  $dp$ . Without a pore, the steady-state is analytically equal to the Boltzmann distribution with nonzero average velocity. We'd like to understand the behavior at a macroscopic level, though. So we simulated the steady-state and checked the local average kinetic energy, density, chemical potential, pressure, etc.



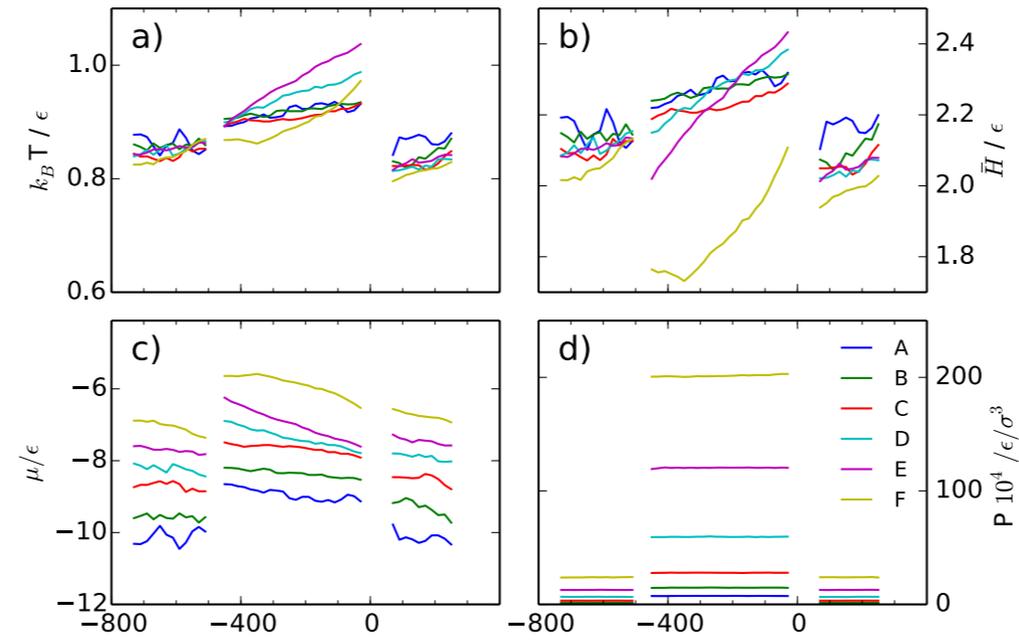
Most of the simulations involved low-temperature gas phases. These local properties are sometimes difficult to get statistics on (esp. inside the pore) but are well-defined in terms of hypothetical, spatially varying thermostats. We could do time-dependence, but again it's the sampling that's the issue - not the theory.

## Big question:

---

- Given input density, pressure and velocity, can we predict output density and pressure?
  - In other words, can we get state 'L' from state 'H'
- A1: Joule-Thomson reasoning says enthalpy is conserved, while velocity gives us the right density, and thus we have density and enthalpy — so yes.
- A2: Numerical...

JT Doesn't work - enthalpy is linear in distance?



Answer: heat flow in reverse

However, here we run into the first finite-size effect. JT doesn't work because there is heat flow against the flow direction that spoils the  $dQ = 0$  condition.

## Conserved quantities

---

- Density
  - Momentum (density derivative)
  - Energy (momentum derivative)
  - ...
- 
- MaxEnt closure at any level just requires a correlation function.

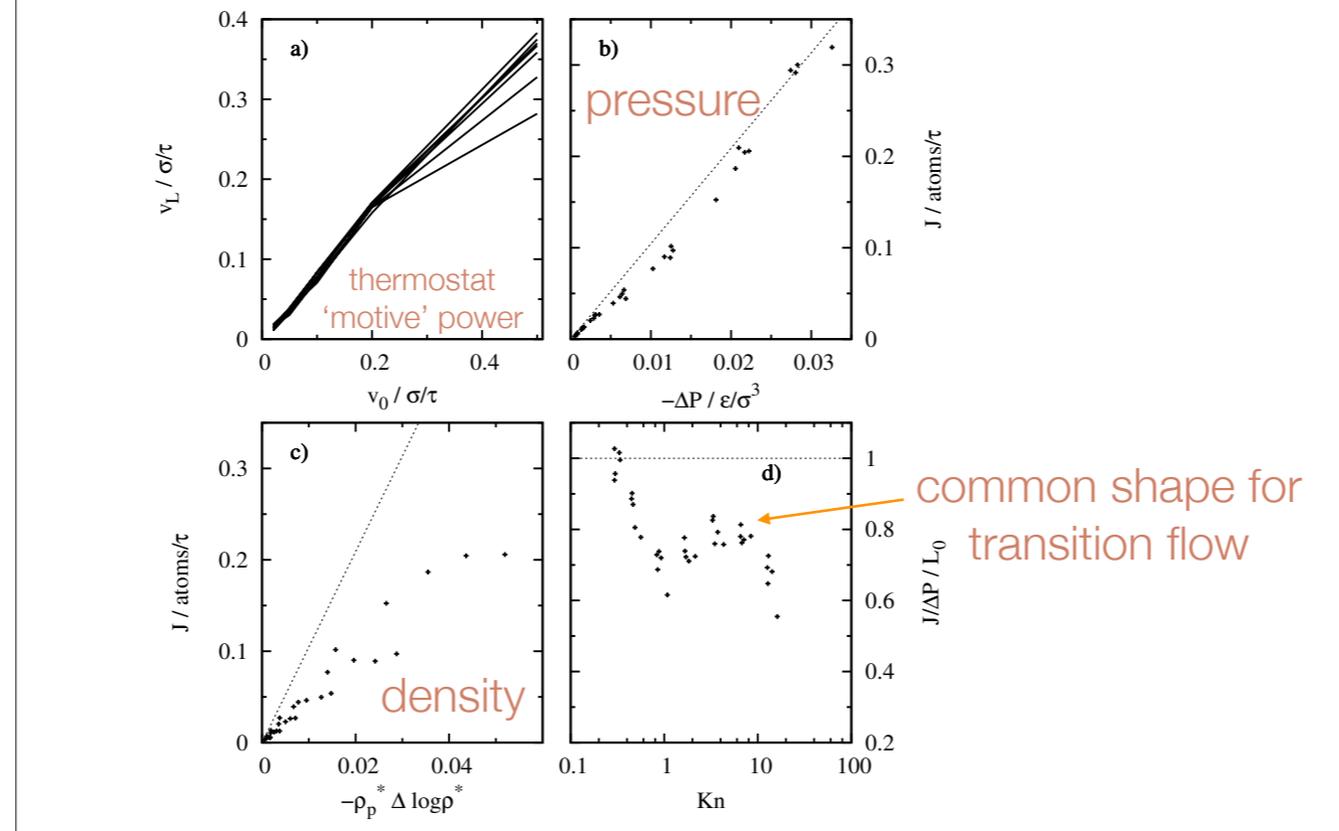
Hydrodynamic hierarchy justifies analyzing 'local' density, pressure and temperature

Mazenko, Nonequ. Stat Mech., 2006

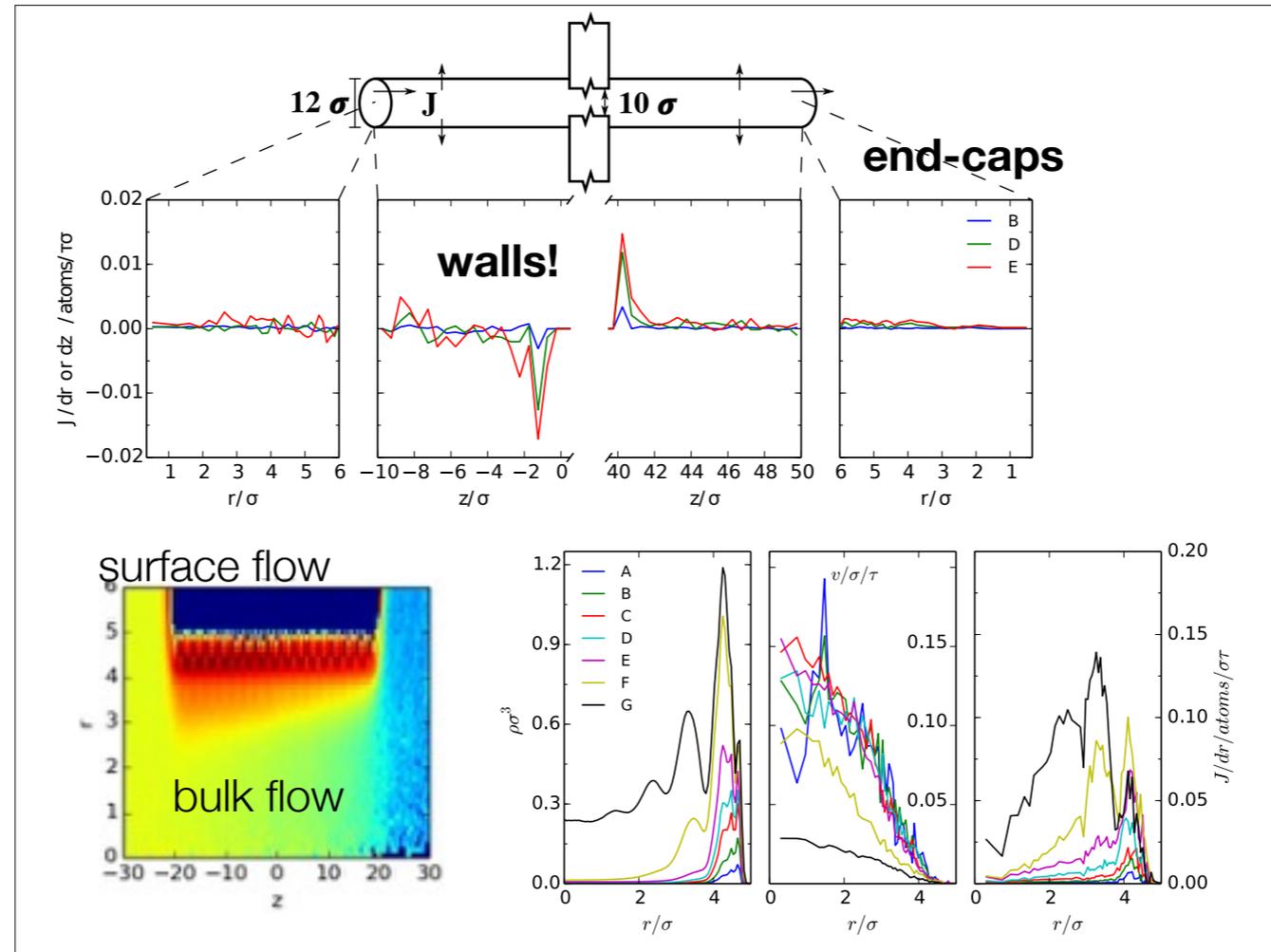
Mendl and Spohn, PRL 111, 2013.

Well, how do we use these mesoscale properties then? Note that stat. mech. physically works because it is based on conserved quantities. In nonequilibrium systems, there is still conservation of particle number, momentum, energy, etc. Even better, changes in particle number are completely predictable if we know the momentum everywhere. Changes in momentum are known when the energy density is known, and so-on.

Which closure is better - density or pressure?



The next obvious question is, "which closure is appropriate here." This question has been asked before, but our system is the "most hands-off" one studied to date -- removing the thermostat from the pore as much as possible.



Finally, there is a second interesting effect that forces us to pick up a real hydrodynamic model.

## Conclusions

---

- Transition distributions are more fundamental than equilibrium distributions - deriving equilibrium as stationary states.
- The Lagrange multipliers express *our information on* the environment.
  - Noise process is much simpler to model.
  - There is no “free energy” or “entropy” for a fully nonequilibrium system - only transition quantities.
- Work and heat acquire a dynamic definition as reversibly and irreversibly stored energy flows.
- Wavefunction collapse can be viewed as an inference process.

**Thanks To:**

