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The Dissipation Theorem and Nonequilibrium Properties

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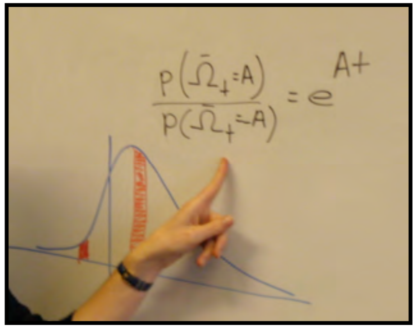
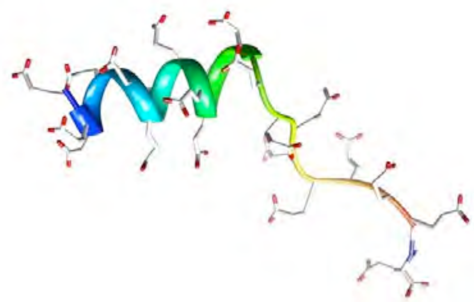
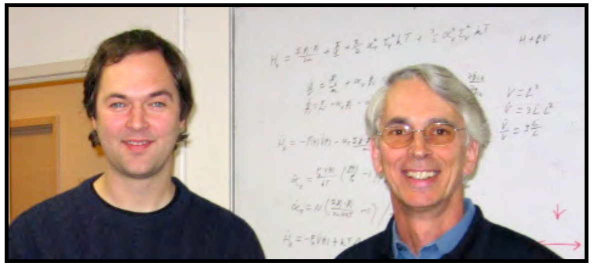




Collaborators



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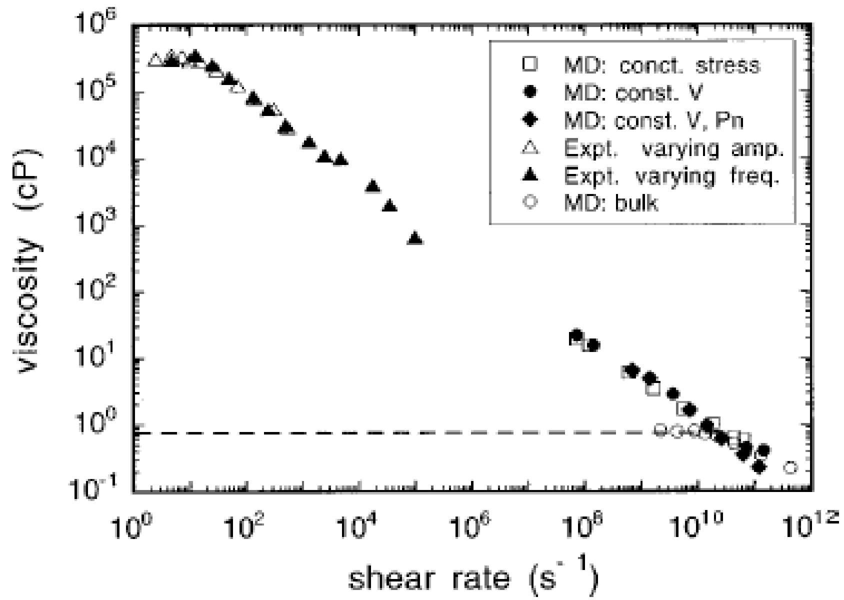
The Dissipation Theorem leads to the result:

$$\boxed{\langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle\, ds}$$

Phase Variable

Dissipation Function

Numerical Consequences



"MD study of the nanorheology of n-dodecane confined between planar surfaces"
~2.5 nm

$$\eta = \frac{-\langle P_{xy}(t)\rangle}{\gamma} = \frac{-\int P_{xy}(t) f(\Gamma,0)\, d\Gamma}{\gamma}$$

MD: Cui, McCabe, Cummings, Cochran, JCP, **118**, 8941 (2003)
Expt: Hu, Carson, Granick, PRL **66**, 2758 & Granick, Science, **253**, 1374 (1991)

Plan

Part A: The Dissipation Function

- Background
- Definition

Part B: Why is the Dissipation Function Useful?

- Example - Le Chatelier's principle

Part C: The Dissipation Theorem

- Derivation
- Theoretical implications
    - Steady state
    - Determination of equilibrium distribution
- Numerical implications

Part D: Summary

A. The Dissipation Function

- The time-integral of the dissipation function:
  - Logarithm of the probability of observing sets of trajectories and their time-reversed conjugate trajectories
  - Related to ‘relative entropy’ or difference in ‘surprise’ from information theory
- Defined in order to generalise the **Fluctuation Theorem**

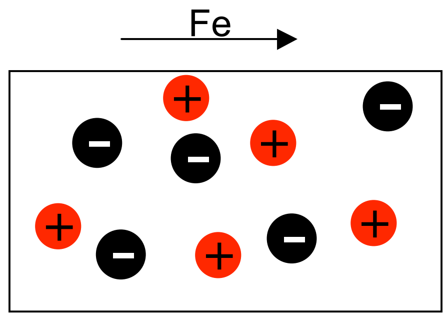
A. The Dissipation Function

The Fluctuation Theorem

$$\frac{p(J_t = A)}{p(J_t = -A)} = e^{-AF_e V\beta} \qquad J_t = \int_0^t ds\, J(s)$$

- Originally constant NVE
- Eqns of motion:

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \mathbf{C}_i \bullet \mathbf{F}_e$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i \bullet \mathbf{F}_e - \alpha \mathbf{p}_i$$

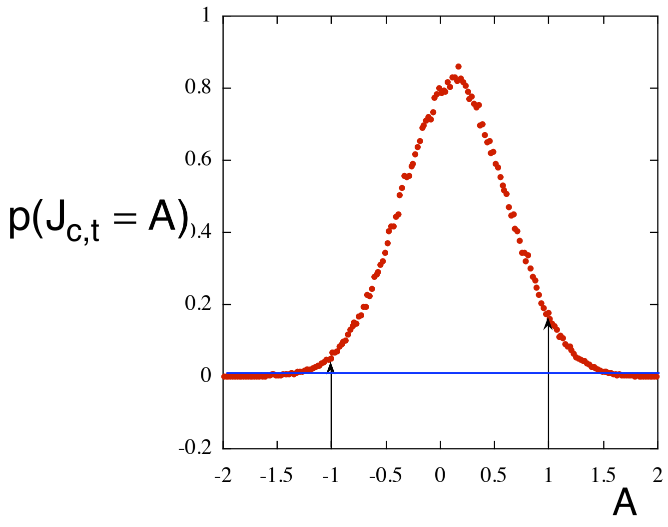


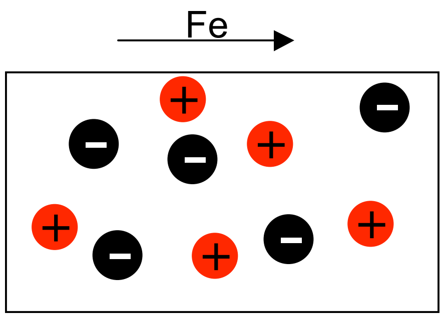
Isoenergetic constraint

A. The Dissipation Function

The Fluctuation Theorem

$$\frac{p(J_{c,t} = A)}{p(J_{c,t} = -A)} = e^{AF_e V\beta}$$





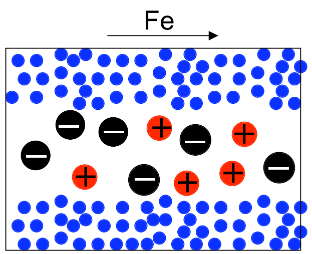
A. The Dissipation Function

The Fluctuation Theorem

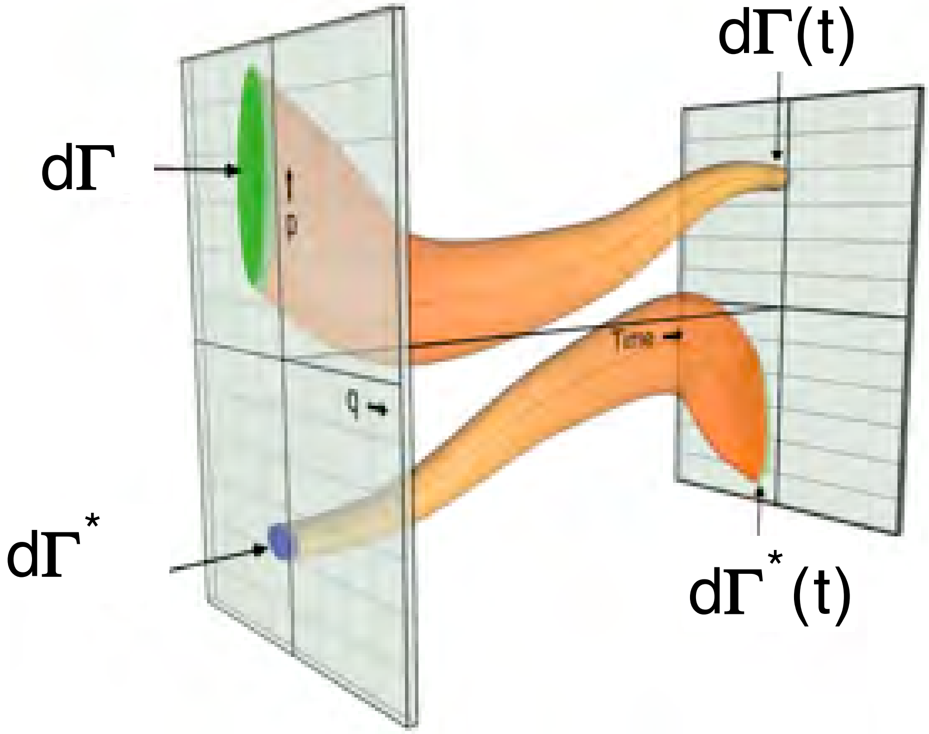
- Generalise
  - Time reversible, deterministic dynamics
  - Every trajectory will have a conjugate related by a time-reversible symmetry
  - The trajectory and its conjugate will have time-averaged dissipative fluxes that are equal in magnitude and opposite in sign
  - Ratio of observing sets of conjugate trajectories

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \mathbf{C}_i \bullet \mathbf{F}_e$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i \bullet \mathbf{F}_e - S_i \alpha \mathbf{p}_i$$



A. The Dissipation Function



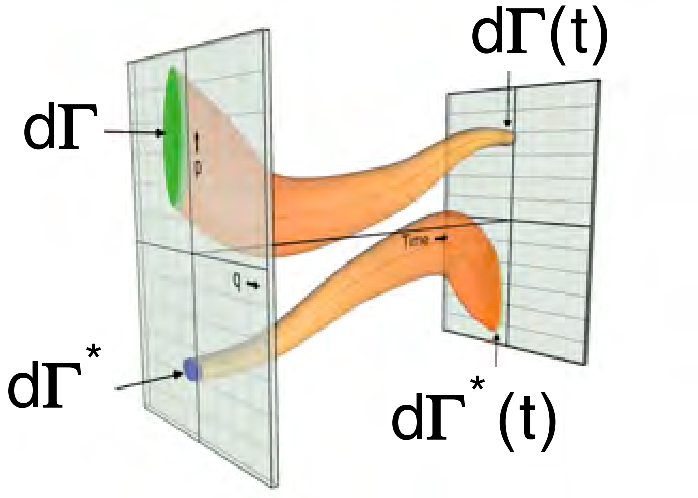
If the dynamics is reversible $\Gamma = iS^t\Gamma^*$.

$$\left|\frac{d\Gamma}{d\Gamma(t)}\right| = \exp\left(-\int_0^t \Lambda(s)\,ds\right) = e^{-\Lambda_t(\Gamma)} = \left|\frac{d\Gamma}{d\Gamma^*}\right|$$

$$\Lambda = \frac{\partial}{\partial\Gamma}\bullet\dot{\Gamma} \qquad \Lambda_t = \int_0^t \Lambda(s)\,ds$$

A. The Dissipation Function

Now consider the relative probability of observing the phase volumes $d\Gamma$ and $d\Gamma^*$:



$f(\Gamma,0)$ $f(\Gamma,t)$

$$\frac{p(d\Gamma)}{p(d\Gamma^*)} = \frac{f(\Gamma,0)\,d\Gamma}{f(\Gamma^*,0)\,d\Gamma^*}$$

$$= \frac{f(\Gamma,0)}{f(\Gamma(t),0)} e^{-\Lambda_t(\Gamma)}$$

$$\equiv e^{\Omega_t(\Gamma)}$$

*ergodic consistency

$$\boxed{\Omega_t(\Gamma) = \ln \frac{f(\Gamma,0)}{f(\Gamma(t),0)} - \Lambda_t}$$

$$\Omega_t(\Gamma) = -J_t V F_e \beta$$

A. The Dissipation Function

Fluctuation Theorem for the Dissipation Function

The **fluctuation theorem** for any dissipation function, Ω, is:

$$\frac{p(\Omega_t = A)}{p(\Omega_t = -A)} = e^{A}$$

$$\Omega_t = \int_0^t ds\, \Omega(s)$$

Using the FT, it is simply to show the **Second Law Inequality**:

$$\langle \Omega_t \rangle \geq 0$$

Evans & Searles, Ad. Phys. **51**, 1529-1585 (2002)
Sevick, Prabhakar, Williams & Searles, Ann. Rev. Phys. Chem. **59**, 603-633 (2008)

Part B

Why is the Dissipation Function Useful?

Why is the Dissipation Function Useful?

- For nonequilibrium dynamics the dissipation function takes on a form resembling the rate of extensive entropy production ($-JVF_e/(kT)$) and can be shown to be equal to it at small fields

$$\Omega = \frac{\Sigma}{k_B} + O(F_e^2)$$

- It satisfies a Fluctuation Theorem - in small systems it gives a probability of observing positive and negative values

- Its time-averaged value is always positive in a nonequilibrium system (Second Law Inequality)

- It is the central argument in the **Dissipation Theorem**

B. Why is the DF interesting?

Example: Le Chatelier's Principle

If a chemical system at equilibrium experiences a change in concentration, **temperature**, volume, or total pressure, then the equilibrium shifts to partially counter-act the imposed change.

$$\text{Folded Protein} \rightleftharpoons \text{Unfolded Protein} \qquad q = \Delta H > 0$$

Increase in temperature favours the forward reaction - shifts the equilibrium to the right

$$\text{Folded Protein} \rightleftharpoons \textbf{Unfolded Protein}$$

B. Why is the DF interesting?

The Dissipation Function for Temperature Change

Defined as:

$$\Omega_t(\Gamma) = \ln \frac{f(\Gamma,0)}{f(\Gamma(t),0)} - \Lambda_t$$

Need to know

- the initial distribution
  - Nosé-Hoover extended canonical distribution
- dynamics which allows a temperature change
  - Nosé-Hoover thermostatted dynamics
  - temperature change must be a time-symmetric protocol - step function

B. Why is the DF interesting?

Dissipation Function for Temperature Change

Substitute for f and Λ and rearrange:

$$\Omega_t(\Gamma) = (\beta_1 - \beta_2)\left(H_0(\Gamma(t)) - H_0(\Gamma(0))\right)$$

$$\boxed{\left\langle (\beta_1 - \beta_2)\left(H_0(\Gamma(t)) - H_0(\Gamma(0))\right)\right\rangle \geq 0}$$

$$\beta_1 > \beta_2 \qquad T_2 > T_1$$

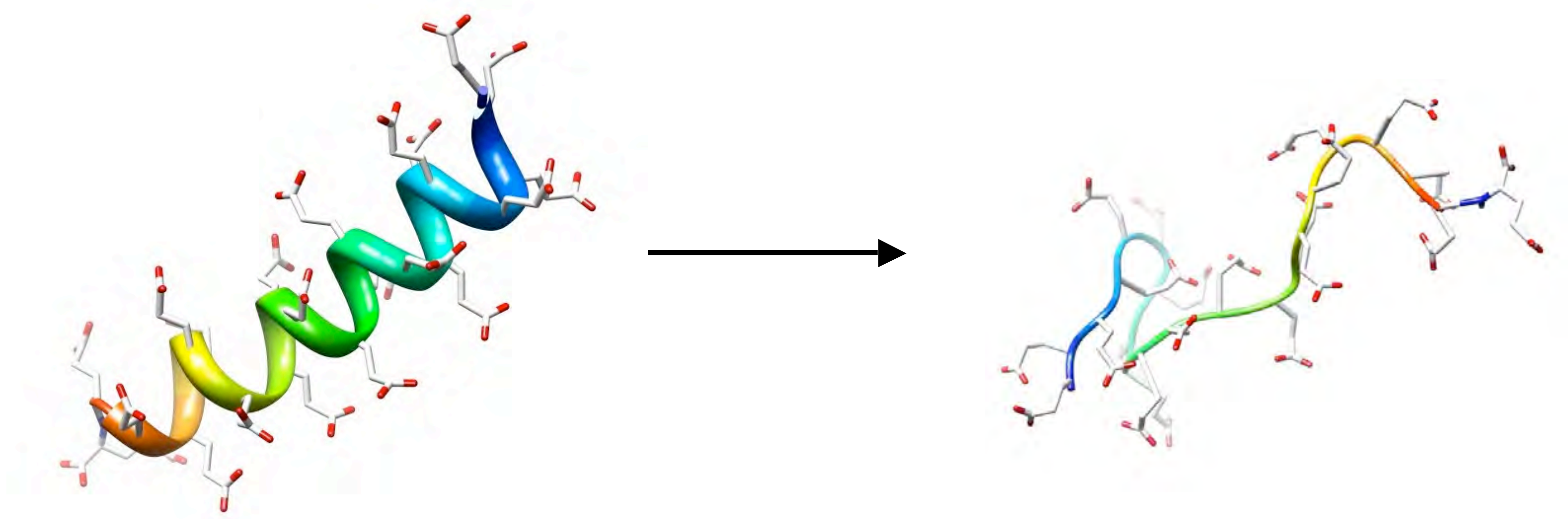
$$\left\langle H_0(\Gamma(t)) - H_0(\Gamma(0))\right\rangle = \Delta H \geq 0$$

B. Why is the DF interesting?

Dissipation Function for Temperature Change

But also satisfy the Fluctuation Theorem

$$\boxed{\frac{p\left(\left(H_0(\Gamma(t))-H_0(\Gamma(0))\right)=A\right)}{p\left(\left(H_0(\Gamma(t))-H_0(\Gamma(0))\right)=-A\right)}=e^{(\beta_1-\beta_2)A}}$$



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- It is the central argument in the **Dissipation Theorem**

Part C

The Dissipation Theorem

$$\Omega_t(\Gamma) = \ln \frac{f(\Gamma,0)}{f(\Gamma(t),0)} - \Lambda_t$$

C. The Dissipation Theorem

Derivation

- The evolution of the phase space density in its streaming form is:

$$\frac{df(\Gamma,t)}{dt} = \left(\frac{\partial}{\partial t} + \dot{\Gamma}(\Gamma)\frac{\partial}{\partial \Gamma}\right) f(\Gamma,t) = -\Lambda(\Gamma) f(\Gamma,t)$$

- The solution to this is:

$$f(\Gamma(t),t) = e^{-\int_0^t \Lambda(\Gamma(s))\,ds} f(\Gamma,0) = e^{-\Lambda_t(\Gamma)} f(\Gamma,0)$$

C. The Dissipation Theorem

$$f(\Gamma(t),t) = e^{-\Lambda_t(\Gamma)} f(\Gamma,0)$$

Remember - the definition of the dissipation function is

$$\frac{f(\Gamma,0)}{f(\Gamma(t),0)} e^{-\Lambda_t(\Gamma)} \equiv e^{\Omega_t(\Gamma)}$$

So:

$$f(\Gamma(t),t) = e^{-\Lambda_t(\Gamma)} f(\Gamma,0) = e^{\Omega_t(\Gamma)} f(\Gamma(t),0)$$

True for any Γ, so transform $\Gamma(t) \rightarrow \Gamma(0)$

$$f(\Gamma(0),t) = e^{\Omega_t(\Gamma(-t))} f(\Gamma(0),0) = e^{\int_{-t}^{0} \Omega(\Gamma(s))ds} f(\Gamma(0),0)$$

C. The Dissipation Theorem

Response of phase variables

We can use the distribution function to evaluate

$$\langle B(t)\rangle = \int B(\Gamma)f(\Gamma,t)d\Gamma = \int B(\Gamma)e^{\int_{-t}^{0}\Omega(\Gamma(s))ds}f(\Gamma,0)d\Gamma$$

By differentiation and integration

$$\langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle ds$$

Note that the ensemble average is wrt to the initial distribution.

C. The Dissipation Theorem

Comparison with past work..

$$f(\Gamma(0),t) = e^{\int_{-t}^{0}\Omega(\Gamma(s))ds} f(\Gamma(0),0) \qquad \langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle ds$$

- Kawasaki - adiabatic (unthermostatted)
- Evans and Morriss - homogeneously thermostatted nonequilibrium dynamics (Gaussian isokinetic)
- This is more general

Evans, Searles, Williams, JCP, **128** 014504(2008); 249901 (2008)

C. The Dissipation Theorem

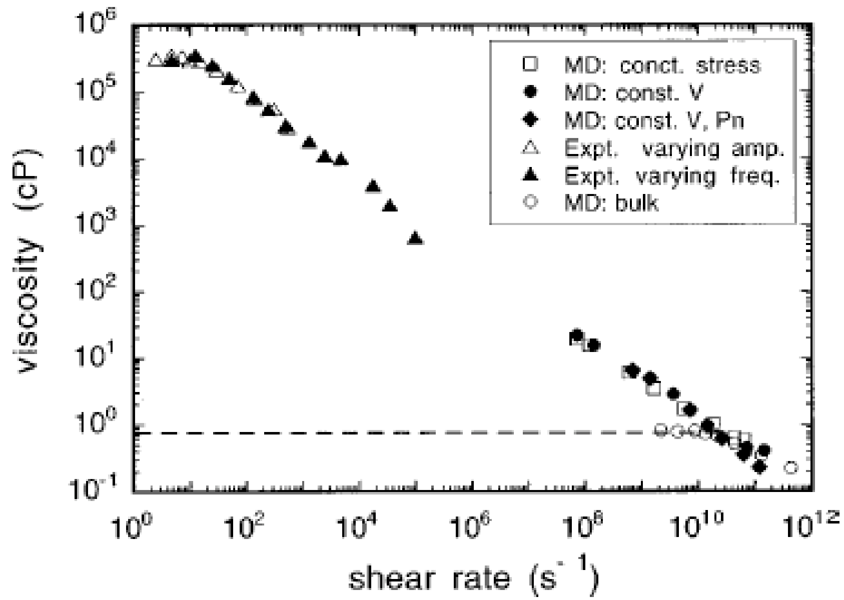
Theoretical Consequences

- Nonlinear response for arbitrary dynamics, (inc. boundary thermostatting, part of the system subject to field etc.)

- Application to systems that are relaxing towards equilibrium (so dynamics is just the equilibrium dynamics)

C. The Dissipation Theorem

Numerical Consequences



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C. The Dissipation Theorem

Numerical Consequences

$$\langle B(t)\rangle = \int B(t) f(\Gamma,0)\, d\Gamma$$

$$\langle B(t)\rangle - \langle B(t)\rangle_{eq} = \int B(t;F_e) f(\Gamma,0)\, d\Gamma - \int B(t;0) f(\Gamma,0)\, d\Gamma$$

Odd B only!

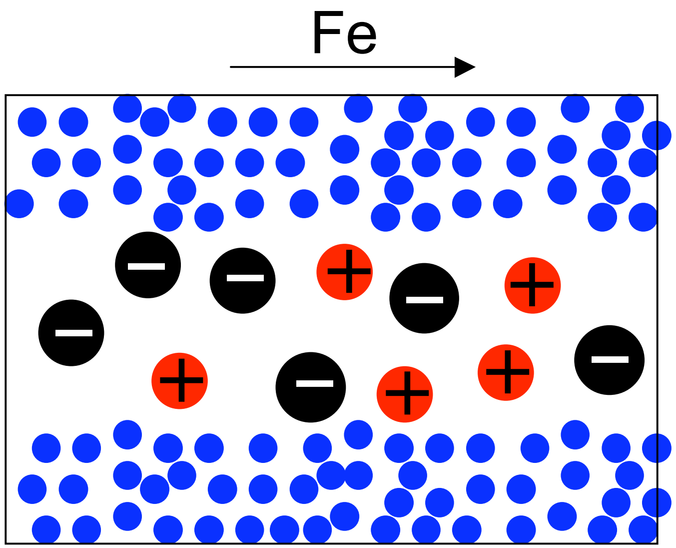
$$\langle B(t)\rangle = \int B(\Gamma) f(\Gamma,t) d\Gamma = \int B(\Gamma) e^{\int_{-t}^{0} \Omega(\Gamma(s))ds} f(\Gamma,0) d\Gamma$$

$$\langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle\, ds$$

C. The Dissipation Theorem

Numerical Consequences

- Colour diffusion between thermostatted walls



Fluid particles:

$$\dot{q}_i = \mathbf{p}_i / m$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + c_i \mathbf{F}_e$$

Wall particles:

$$\dot{q}_i = \mathbf{p}_i / m$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{F}_{wi} - \alpha \mathbf{p}_i$$

$$\alpha = \frac{\sum_{i=1}^{N_{wall}} \mathbf{F}_i \bullet \mathbf{p}_i}{\sum_{i=1}^{N_{wall}} \mathbf{p}_i \bullet \mathbf{p}_i}$$

$$\Omega = \sum_{i=N_{wall}+1}^{N_{part}} c_i p_{xi} F_e / k_B T_{wall}$$

C. The Dissipation Theorem

Numerical Consequences

Considered various properties and fields -
colour current and fluid pressure

$$\langle B(t)\rangle = \int B(t) f(\Gamma,0)\, d\Gamma - \langle B(t)\rangle_{eq}$$

Expect best at
high fields

$$\langle B(t)\rangle = \int B(\Gamma) f(\Gamma,t) d\Gamma = \int B(\Gamma) e^{\int_{-t}^{0} \Omega(\Gamma(s))ds} f(\Gamma,0) d\Gamma$$

Expect best at
low fields

$$\langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle ds$$

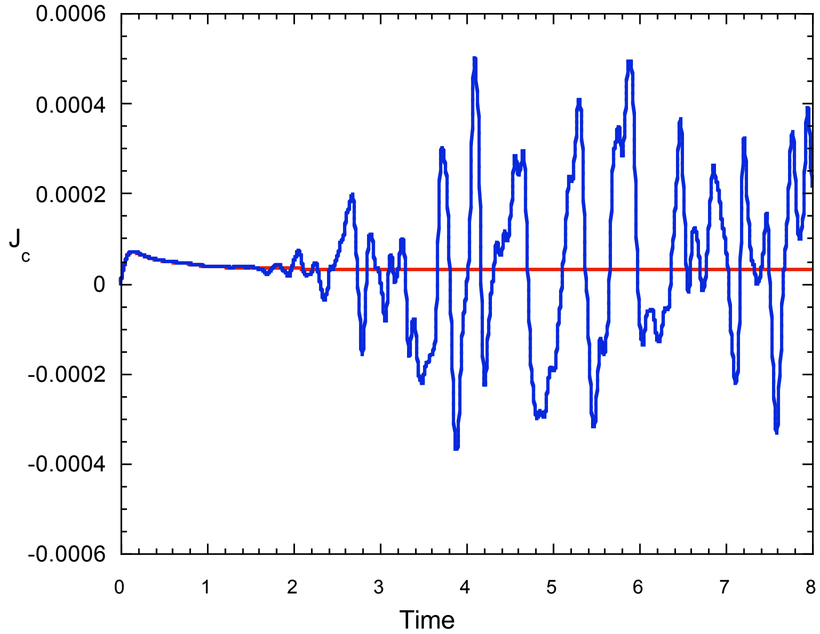
C. The Dissipation Theorem

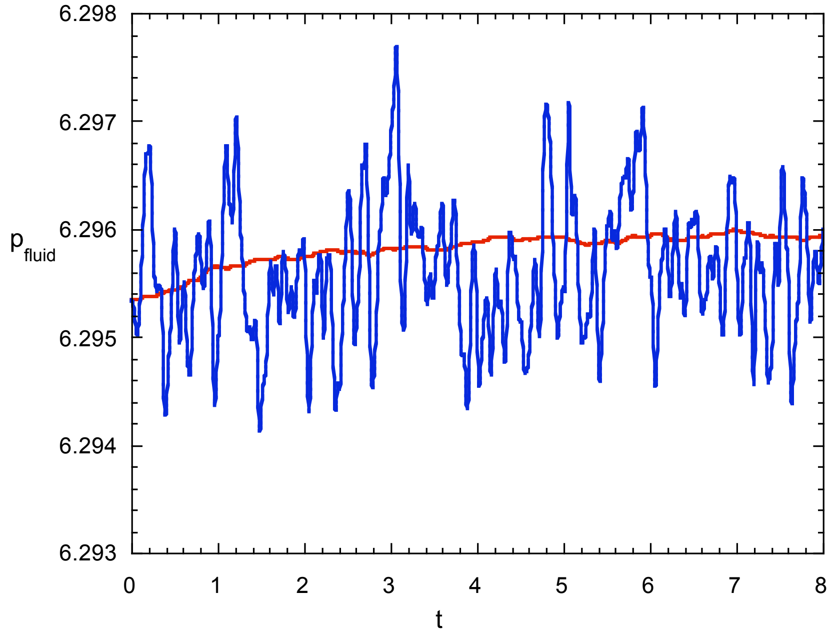
Numerical Consequences

F_e = 0.001; n=0.8; T_{wall}=1.0

$$\langle B(t)\rangle = \int B(t) f(\Gamma,0)\, d\Gamma$$

$$\langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle\, ds$$





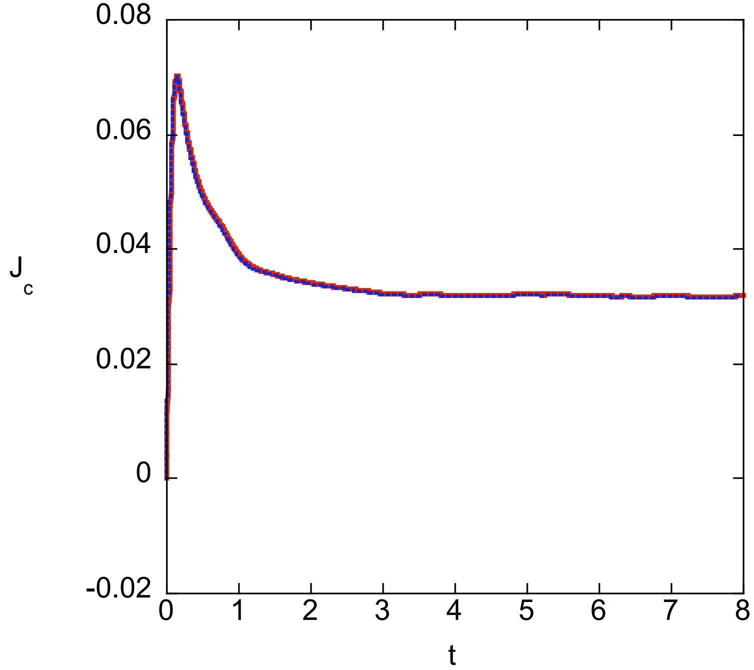
C. The Dissipation Theorem

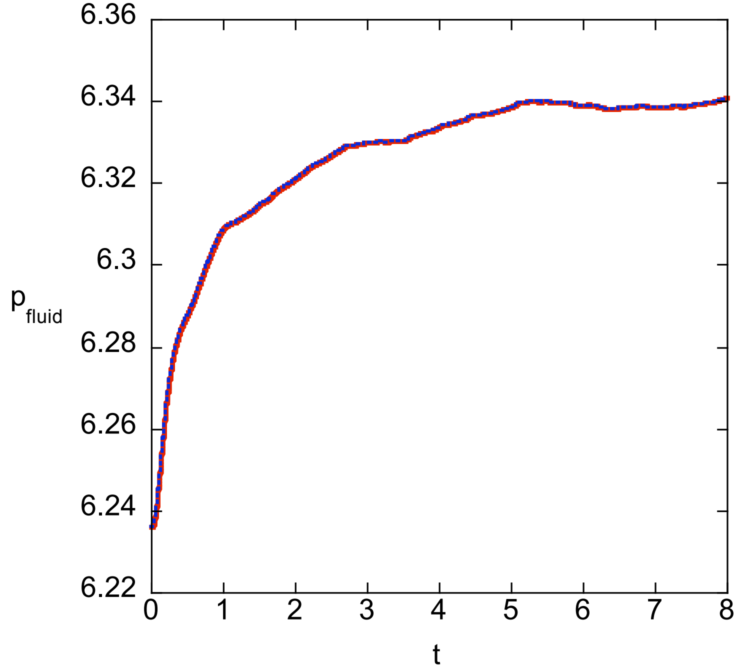
Numerical Consequences

$F_e = 1.0$; $n=0.8$; $T_{wall}=1.0$

$$\langle B(t)\rangle = \int B(t) f(\Gamma,0)\, d\Gamma$$

$$\langle B(t)\rangle = \langle B(0)\rangle + \int_0^t \langle B(s)\Omega(0)\rangle\, ds$$

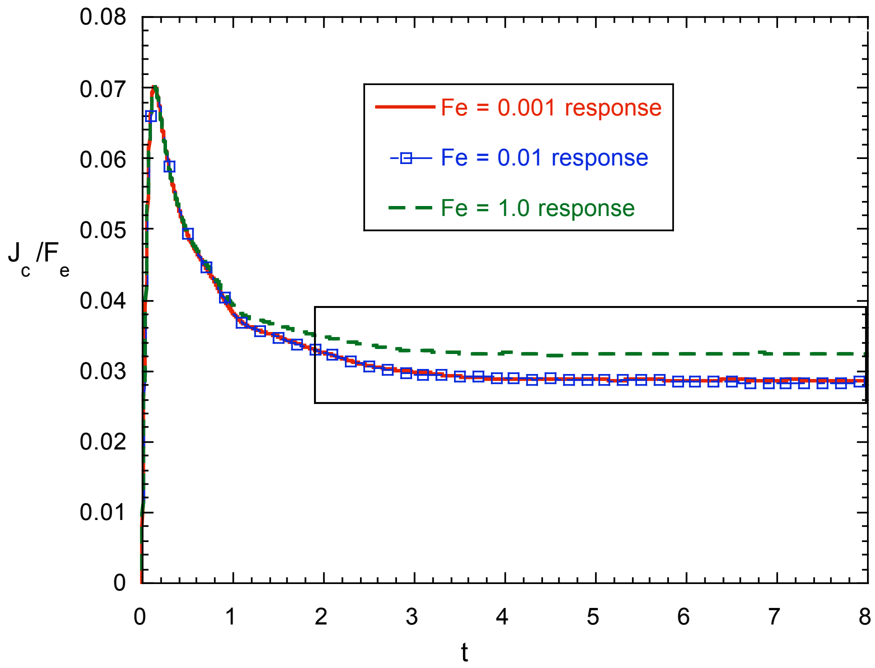


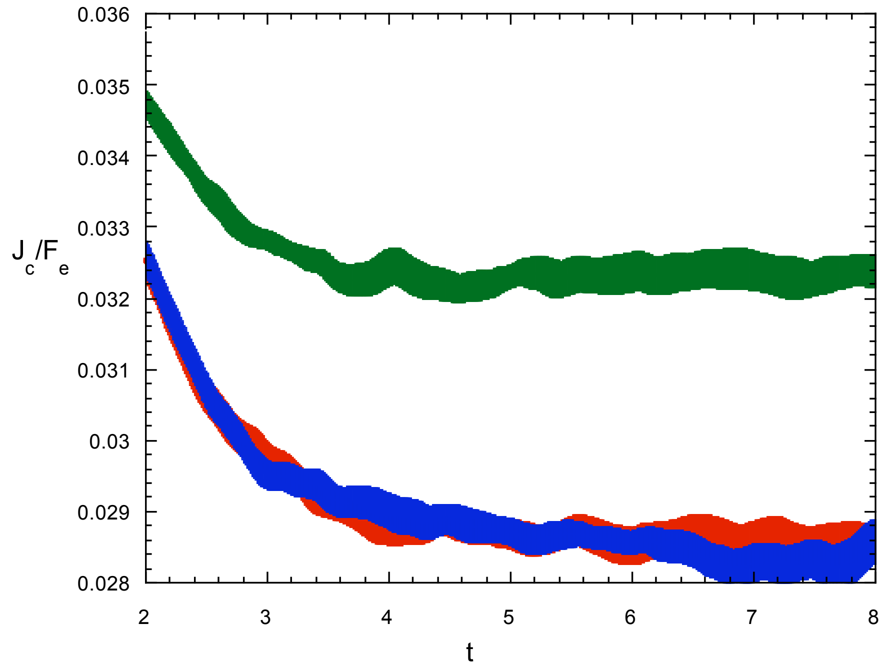


C. The Dissipation Theorem

Numerical Consequences

The Fe=0.001 and Fe=0.01 conductivities match (error bars similar size and smaller than the blue squares)





Part D

Summary and Future Work

Conclusions and Future …

- The dissipation function is of central importance in nonequilibrium statistical mechanics - appears in the **fluctuation theorem**, **second law inequality** and the **dissipation theorem**
- The dissipation theorem gives a relation for the nonlinear response of phase functions
- The dissipation theorem shows how a distribution function changes due to application/change/removal of a field
- The dissipation theorem provides a **practical route** to properties of inhomogeneously thermostatted systems (e.g. wall thermostatted or remotely thermostatted) at small fields

- Like to use this approach to study more practical problems
- Relationship between formation of a steady state and correlations - explore more widely
- Other numerical approaches to obtaining accurate results more efficiently

Acknowledgements

- Australian Research Council for their support through a Discovery Grant
- Collaborators
- DUBS, GU and ANUSF for computing time and support