Institute Henri Poincaré

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Nonlinear response theory and the fluctuation theorem.

Lecture I:

Chaos, Lyapunov Exponents and Transport Coefficients

By

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Abstract

We very briefly describe the historical development of nonequilibrium statistical mechanics and computer simulation. We describe how algorithms were developed and how they were proved to be correct. We also describe the impact that the mathematical study of chaos has had on nonequilibrium statistical mechanics. We briefly describe new mathematical relationships between transport processes, the Second Law of Thermodynamics and chaotic measures.

Equations of motion

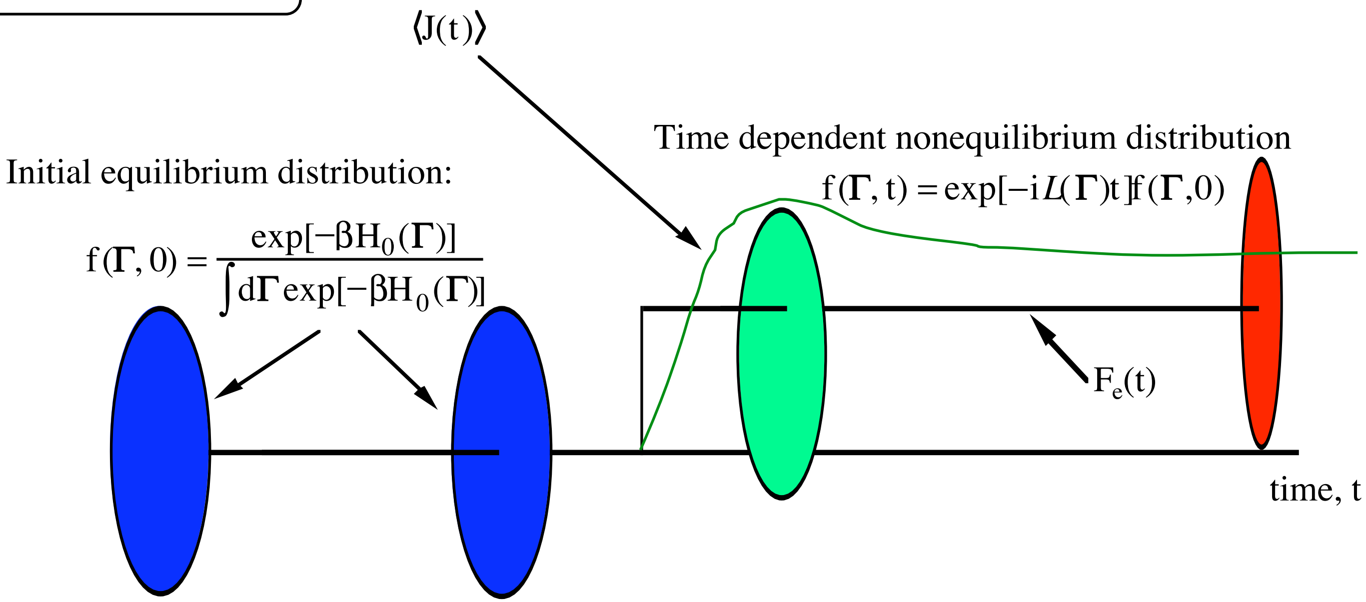
$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m} + C_i\mathbf{F}_e$$

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i + D_i\mathbf{F}_e - \alpha\mathbf{p}_i$$

Heat Q, is removed by the thermostat to ensure the possibility of a nonequilibrium steady state. J is called the dissipative flux. The momenta appearing in the equations of motion are peculiar.

α is chosen to keep the peculiar kinetic energy, K, constant:

Gaussian Thermostat
$$\frac{dQ}{dt} = -2K\alpha = -\mathbf{J}\bullet\mathbf{F}_e$$



Initial equilibrium distribution:

$$f(\mathbf{\Gamma},0) = \frac{\exp[-\beta H_0(\mathbf{\Gamma})]}{\int d\mathbf{\Gamma}\exp[-\beta H_0(\mathbf{\Gamma})]}$$

Time dependent nonequilibrium distribution

$$f(\mathbf{\Gamma},t) = \exp[-iL(\mathbf{\Gamma})t]f(\mathbf{\Gamma},0)$$

Liouville Equation for N-particle distribution function

The Liouville equation is analogous to the mass continuity equation in fluid mechanics. The “mass” is the number of ensemble members. This quanitity is conserved (like mass). The mass density can change in time either at a fixed position in phase space:

$$\frac{\partial f(\boldsymbol{\Gamma},t)}{\partial t} = -\frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet [\dot{\boldsymbol{\Gamma}} f(\boldsymbol{\Gamma},t)] \equiv -iLf(\boldsymbol{\Gamma},t)$$

or for thermostatted systems, as a function of time, along a streamline in phase space:

$$\frac{df}{dt} = [\frac{\partial}{\partial t} + \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial}{\partial \boldsymbol{\Gamma}}]f = -f\Lambda$$

Λ is called the *phase space compression factor*, and

$$\mathrm{iL} = \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial}{\partial \boldsymbol{\Gamma}} ..., \quad iL = \frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet \dot{\boldsymbol{\Gamma}} ..., \quad iL - \mathrm{iL} = \frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet \dot{\boldsymbol{\Gamma}} \equiv \Lambda(\boldsymbol{\Gamma})$$

Equation of motion of phase function

$$\frac{dA(\boldsymbol{\Gamma})}{dt} = \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial A(\boldsymbol{\Gamma})}{\partial \boldsymbol{\Gamma}} \equiv \mathrm{iL}A(\boldsymbol{\Gamma})$$

Thermostats

Deterministic, time reversible, homogeneous thermostats were simultaneously but independently proposed by Hoover and Evans in 1982. Later they realised that the equations of motion could be derived from Gauss' Principle of Least Constraint (Evans, Hoover, Failor, Moran & Ladd (1983)).

The form of the equations of motion is

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

α can be chosen such that the energy is constant or such that the kinetic energy is constant. In the latter case the equilibrium, field free distribution function can be proved to be the isokinetic distribution, $f(\boldsymbol{\Gamma}) \sim \delta(\sum p_i^2 / 2m - 3Nk_BT/2)\exp[-\Phi(q)/k_BT]$.

In 1984 Nosé showed that if α is determined as the time dependent solution of the equation

$$\frac{d\alpha}{dt} = \left[\left(\sum p_i^2 / 2m\right) / \left(3Nk_BT/2\right) - 1\right] / \tau^2$$

then $\forall \tau$, in an ergodic system the equilibrium distribution is canonical $f(\boldsymbol{\Gamma}) \sim \exp[-H_0(\boldsymbol{\Gamma})/k_BT]$..

Thermostatted Response theory

Assume system is canonical at t=0.

$$f(\boldsymbol{\Gamma},0)=\frac{\exp[-\beta H_0(\boldsymbol{\Gamma})]}{\int d\boldsymbol{\Gamma}\,\exp[-\beta H_0(\boldsymbol{\Gamma})]}$$

$$f(\boldsymbol{\Gamma},t)=\exp[-(iL+\Lambda)t]f(\boldsymbol{\Gamma},0)$$

Using a *Dyson decomposition* (and some operator algebra) gives,

$$f(\boldsymbol{\Gamma},t)=\exp[-\int_0^t ds\ \Lambda(s)]\exp[-\beta H_0(-t)]$$

For the equations of motion,

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

From equations of motion,

$$\frac{dH_0}{dt} = \frac{dH_0}{dt}^{ad} + \frac{dH_0}{dt}^{therm}$$

$$= -\mathbf{J}(\mathbf{\Gamma}) \cdot \mathbf{F}_e - 2K\alpha$$

$$= 0, \quad \dot{H}_0 = 0$$

$$= \dot{\Phi}, \quad \dot{K} = 0.$$

but

$$\Lambda = 3N\alpha + O(1).$$

This leads in the isokinetic case, to the so-called *Kawasaki* expression for the nonequilibrium distribution function, (Evans & Morriss (1984)).

$$f(\mathbf{\Gamma}, t) = \exp[-\beta \int_0^t ds\, \mathbf{J}(-s) \bullet \mathbf{F}_e] f(\mathbf{\Gamma}, 0)$$

We can use this to compute averages,

$$< B(t) >= \int d\boldsymbol{\Gamma}\ f(\boldsymbol{\Gamma},t)B(\boldsymbol{\Gamma})$$

$$= \int d\boldsymbol{\Gamma}\ B(\boldsymbol{\Gamma})\exp[-\beta\int_0^t ds\ \mathbf{J}(-s)\bullet\mathbf{F}_e]f(\boldsymbol{\Gamma},0)$$

Since

$$d < B(t) > /dt = -\beta\int d\boldsymbol{\Gamma}\ B(\boldsymbol{\Gamma})\mathbf{J}(-t)\bullet\mathbf{F}_e f(\boldsymbol{\Gamma},t)$$

$$= -\beta\int d\boldsymbol{\Gamma}\ B(t)\mathbf{J}(0)\bullet\mathbf{F}_e f(\boldsymbol{\Gamma},0)$$

We can write averages in terms of the *Transient Time Correlation Function*, (Evans & Morriss, (1984)).

$$< B(t) >= -\beta\mathbf{F}_e \bullet \int_0^t ds < \mathbf{J}(0)B(s) >$$

In the weak field limit we can linearise both Kawasaki and TTCF giving, the *Linear Response Green-Kubo formula*

$$\lim_{F_e\to 0} < B(t) >= -\beta\mathbf{F}_e\bullet\int_0^t ds < \mathbf{J}(0)B(s) >_{eq}$$

NB All dynamics is thermostatted and <…> has the external field applied.

Further observations concerning thermostats

- If $\mathbf{J}(\mathbf{\Gamma}), B(\mathbf{\Gamma}) = O(1)$, then $< \mathbf{J}(0)B(t_{\text{Newton}}) >_{eq} = O(1/N)$ and,

$$< \mathbf{J}(0)B(t_{\text{Newton}}) >_{eq} - < \mathbf{J}(0)B(t_{\text{thermo}}) >_{eq} = O\left(1/N^2\right)$$

- For the infinite family of μ-thermostats,

$$\dot{p}_{i\beta} = F_{i\beta} - \alpha \mathrm{Sgn}(p_{i\beta}) | p |_{i\beta}^{\mu}, \quad \beta = x, y, z$$

Only μ=1 generates an equilibrium state.

Green-Kubo Relations for linear thermal (Navier Stokes) Transport Coefficients

1 Self Diffusion coefficient

$$D = \frac{1}{3}\int_0^\infty ds < \mathbf{v}_i(0) \bullet \mathbf{v}_i(s) >_{eq}$$

2 Thermal Conductivity

$$\lambda = \frac{V}{3k_B T^2}\int_0^\infty ds < \mathbf{J}_Q(0) \bullet \mathbf{J}_Q(s) >_{eq}$$

3 Shear Viscosity

$$\eta = \frac{V}{k_B T}\int_0^\infty ds < P_{xy}(0) P_{xy}(s) >_{eq}$$

4 Bulk Viscosity

$$\eta_V = \frac{1}{V k_B T}\int_0^\infty ds < [p(0)V(0) - < pV >][p(s)V(s) - < pV >] >_{eq}$$

NEMD Algorithms for Navier-Stokes transport coefficients.

Dolls Tensor algorithm for flow, $H = H_0 + \sum \mathbf{q}_i \mathbf{p}_i : (\nabla \mathbf{u}(t))^T$

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{q}_i \bullet \nabla \mathbf{u}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \nabla \mathbf{u} \bullet \mathbf{p}_i - \alpha \mathbf{p}_i$$

(Hoover, Evans, Hickman, Ladd, Ashurst, Moran (1980)).

Evans Heat Flow algorithm

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

$$\begin{aligned}\dot{\mathbf{p}}_i &= \mathbf{F}_i - (E_i - \bar{E})\mathbf{F} \\ &\quad - \frac{1}{2}\sum_{j=1}^{N} \mathbf{F}_{ij}\mathbf{q}_{ij} \bullet \mathbf{F} + \frac{1}{2N}\sum_{j,k=1}^{N} \mathbf{F}_{jk}\mathbf{q}_{jk} \bullet \mathbf{F} - \alpha \mathbf{p}_i\end{aligned}$$

where (Evans, (1982)).

$$\bar{E} = \{\sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j}^{N} \Phi_{ij}\} / N$$

Colour Conductivity algorithm for self diffusion

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{i}c_i F_c - \alpha(\mathbf{p}_i - \mathbf{i}c_i J_x / \rho)$$

where

$$J_x = \frac{1}{V}\sum_{i=1}^{N} c_i \dot{x}_i \quad \text{and} \sum_{i=1}^{N}(\mathbf{p}_i - \mathbf{i}c_i J_x / \rho)^2 / m = 3Nk_B T$$

(Evans and Morriss (1983)).

Sllod algorithm for shear viscosity is exact for adiabatic planar shear flow

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{q}_i \bullet \nabla \mathbf{u}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \bullet \nabla \mathbf{u} - \alpha \mathbf{p}_i$$

, which is equivalent to: $\ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t) y_i$

(Evans and Morriss (1984)).

The shear flow algorithms must be accompanied by appropriate periodic boundary conditions - (Lees, Edwards (1972)).

For each algorithm, the Navier-Stokes transport coefficient, L, is evaluated as

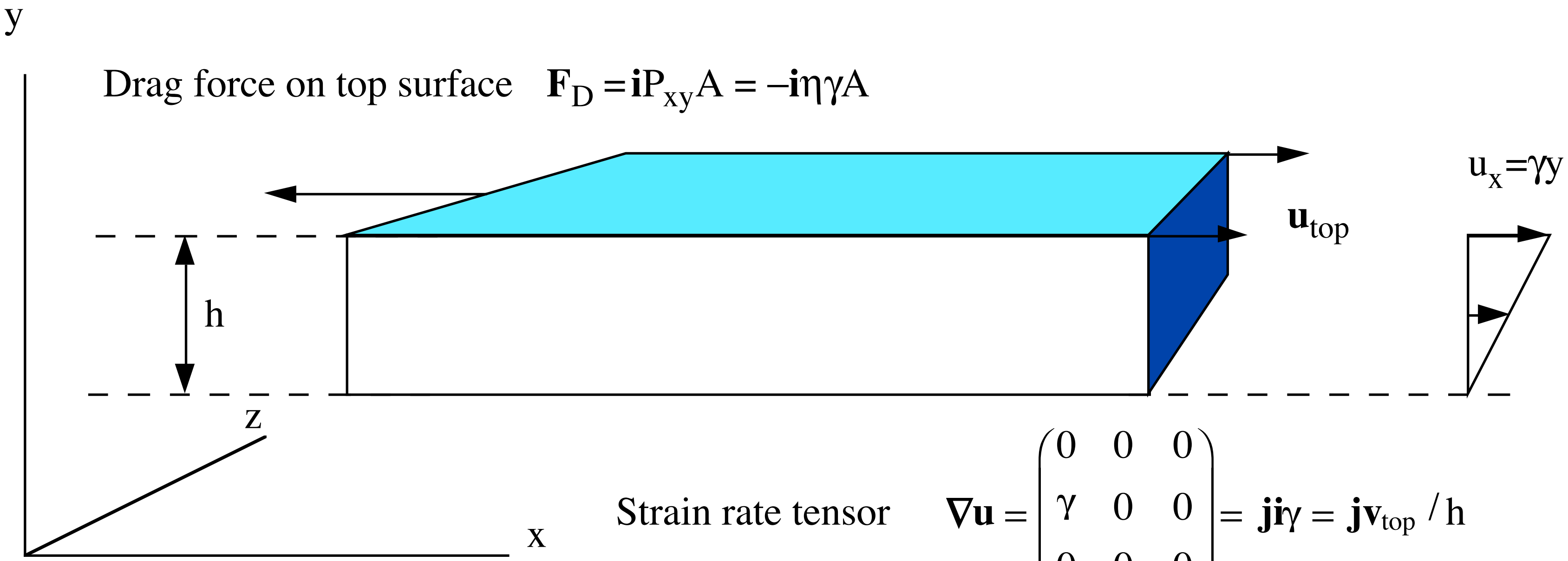
$$L(0) = \lim_{F\to 0} \lim_{t\to\infty} \frac{1}{F_e t} \int_0^t ds\ J(s)$$

Note: NEMD algorithms and Green Kubo relations are also known for thermal and mutual diffusion (Soret and Dufour effects) in nonideal binary mixtures, and for the 12 or so viscosity coefficients of nematic liquid crystals.

Advantages of NEMD over Green-Kubo:

- Nonlinear transport can be studied. GK is solely for linear transport.
- Can study structural changes induced in systems by the nonequilium fluxes and forces.
- Is usually more efficient than GK.

Newton's Constitutive Relation for Shear Flow

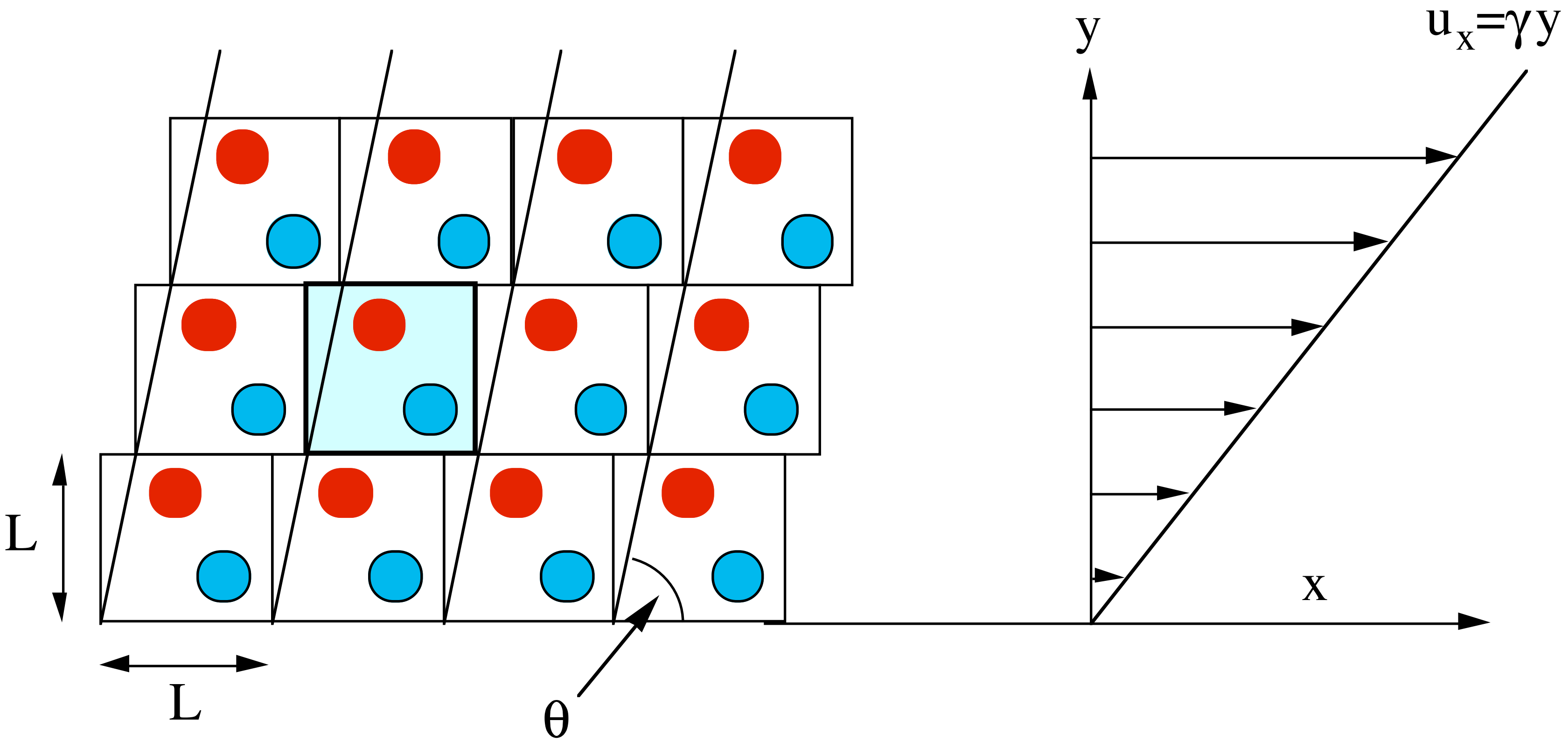


Drag force on top surface $\mathbf{F}_D = \mathbf{i}P_{xy}A = -\mathbf{i}\eta\gamma A$

Strain rate tensor $\nabla\mathbf{u} = \begin{pmatrix} 0 & 0 & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \mathbf{ji}\gamma = \mathbf{j}\mathbf{v}_{top}/h$

Viscous heating, $\dfrac{dQ}{dt} = -\text{force } \mathbf{x} \text{ velocity} = P_{xy}A\gamma h = P_{xy}\gamma V$

Lees-Edwards periodic boundary conditions for shear flow

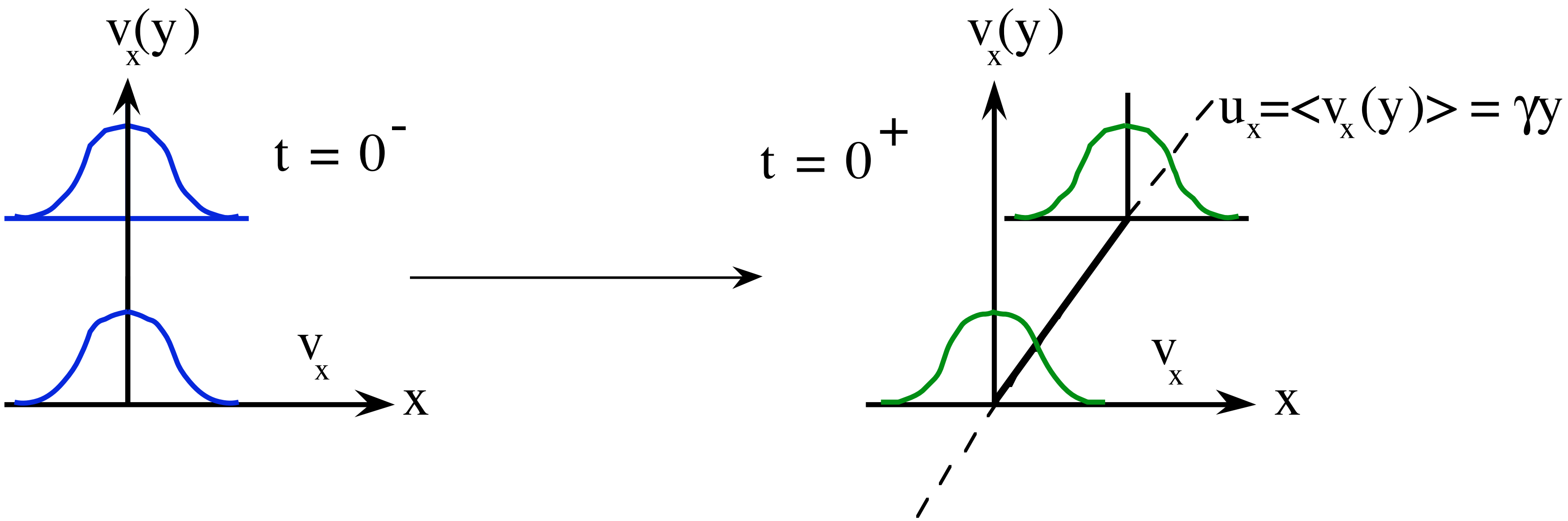


The Sllod equations of motion are equivalent to Newton’s equations for t > 0+, with a linear shift applied to the initial x-velocities of the particles.

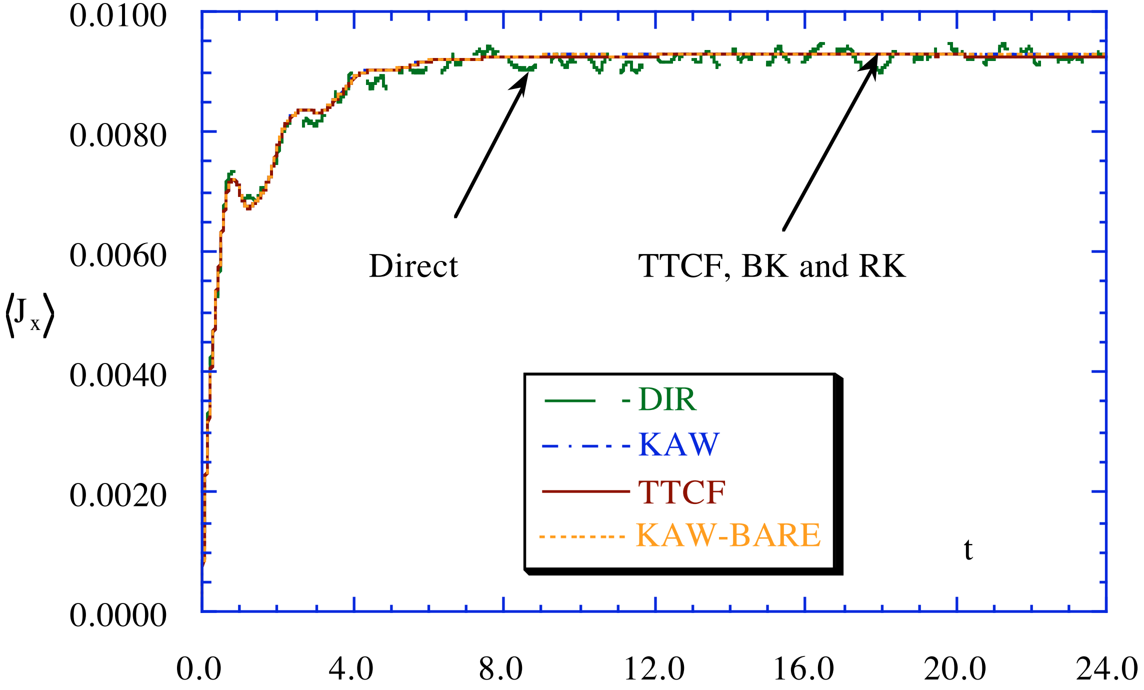
Sllod algorithm for shear viscosity

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_i\end{aligned}$$

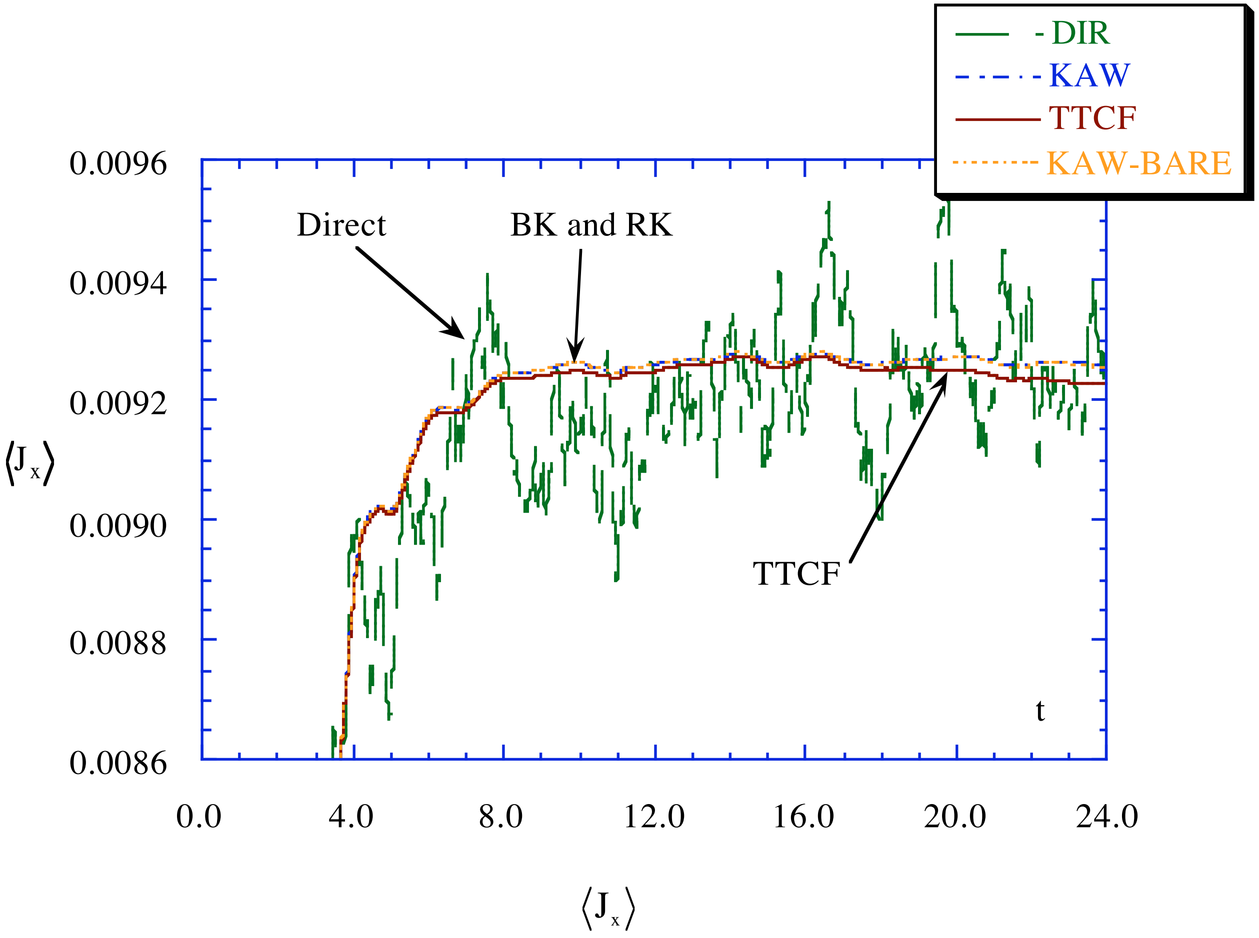
, which is equivalent to: $\ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t) y_i$



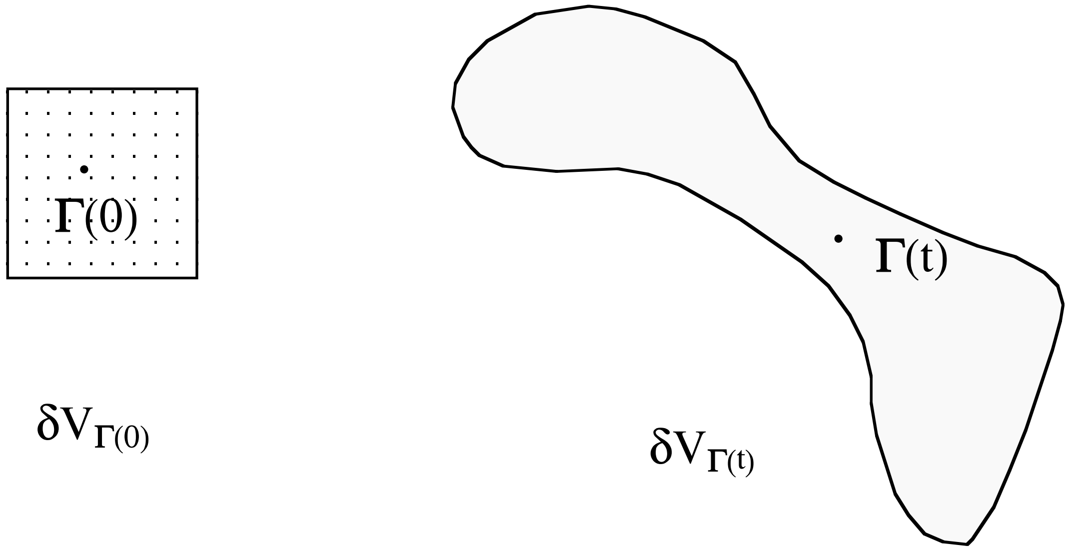
Therefore Sllod is exact arbitrarily far from equilibrium.



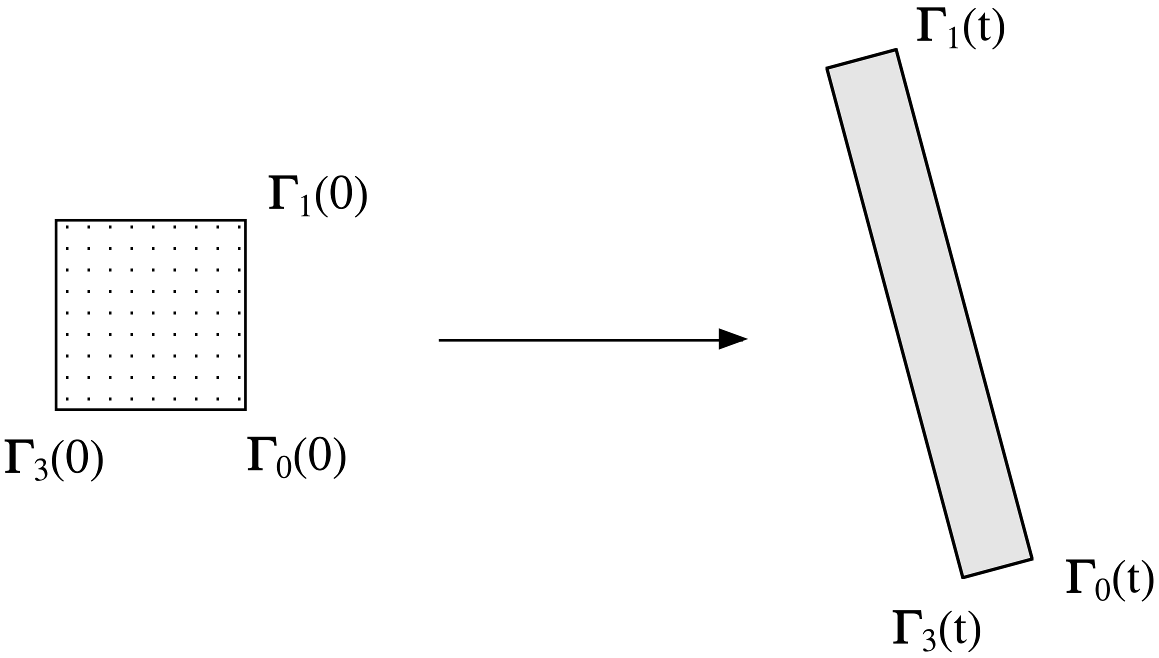
We compare the results of direct NEMD simulation against Kawasaki and TTCF for 2-particle colour conductivity.


- DIR
KAW
TTCF
KAW-BARE
Direct
BK and RK
TTCF
0.0096
0.0094
0.0092
0.0090
0.0088
0.0086
⟨J_x⟩
t
0.0
4.0
8.0
12.0
16.0
20.0
24.0
⟨J_x⟩

Instability of Phase Space Trajectories



The deformation of a small initial phase space volume element, $\delta V_{\Gamma(0)}$ around $\Gamma(0)$ to an evolved volume element $\delta V_{\Gamma(t)}$. Both volume elements contain the same number of ensemble members.



The mother and first daughter trajectories $\Gamma_0(t), \Gamma_1(t)$ evolve according to the natural dynamics of the system. The first daughter is infinitesmally close to mother$|\Gamma_0(t) - \Gamma_1(t)| \to 0$. The largest lyapunov exponent λ_1 is defined,

$$\lim_{t\to\infty} |\Gamma_1(t) - \Gamma_0(t)| = |\Gamma_1(0) - \Gamma_0(0)| e^{\lambda_1 t}$$

If we now choose a second infinitesmally nearby daughter trajectory, $\Gamma_2(t)$, such that,

$$\left(\boldsymbol{\Gamma}_1(t)-\boldsymbol{\Gamma}_0(t)\right)\bullet\left(\boldsymbol{\Gamma}_2(t)-\boldsymbol{\Gamma}_0(t)\right)=0,\ \forall t\,,$$

then the second largest Lyapunov exponent is defined as,

$$\lim_{t\to\infty} |\boldsymbol{\Gamma}_2(t)-\boldsymbol{\Gamma}_0(t)|=|\boldsymbol{\Gamma}_2(0)-\boldsymbol{\Gamma}_0(0)|\,e^{\lambda_2 t}.$$

There are 6N Lyapunov exponents $\{\lambda_1>\lambda_2>\lambda_3>\lambda_4,....\}$. The 6N dimensional phase space volume evolves as,

$$\lim_{t\to\infty}\ \lim_{\delta V(\boldsymbol{\Gamma},0)\to 0} \delta V(\boldsymbol{\Gamma}(t),t)=\delta V(\boldsymbol{\Gamma},0)\exp[\sum_{i=1}^{6N}\lambda_i t]$$

The Liouville equation states that, (1/f)df/dt = 3Nα. We can see that the accessible volume of phase space, V~1/f, decreases to zero.

$$\lim_{t\to\infty}\overline{\int d\boldsymbol{\Gamma}\ f(\boldsymbol{\Gamma},t)\frac{d\ln[f(\boldsymbol{\Gamma},t)]}{dt}} = -\left\langle\frac{d\ \ln\delta V\left(\boldsymbol{\Gamma}(t)\right)}{dt}\right\rangle_{F_e} = -\sum_{i=1}^{6N}\lambda_i = 3N\langle\alpha\rangle_{F_e}$$

If $\dot{H}_0 = 0 = -P_{xy}\gamma V - \alpha \sum p_i^2 / m$ then for **isoenergetic** shear flow in a nonequilibrium steady state

:

$$\eta(\gamma) = \frac{-k_B T}{V\gamma^2} \sum_{i=1}^{6N} \lambda_i(\gamma)$$

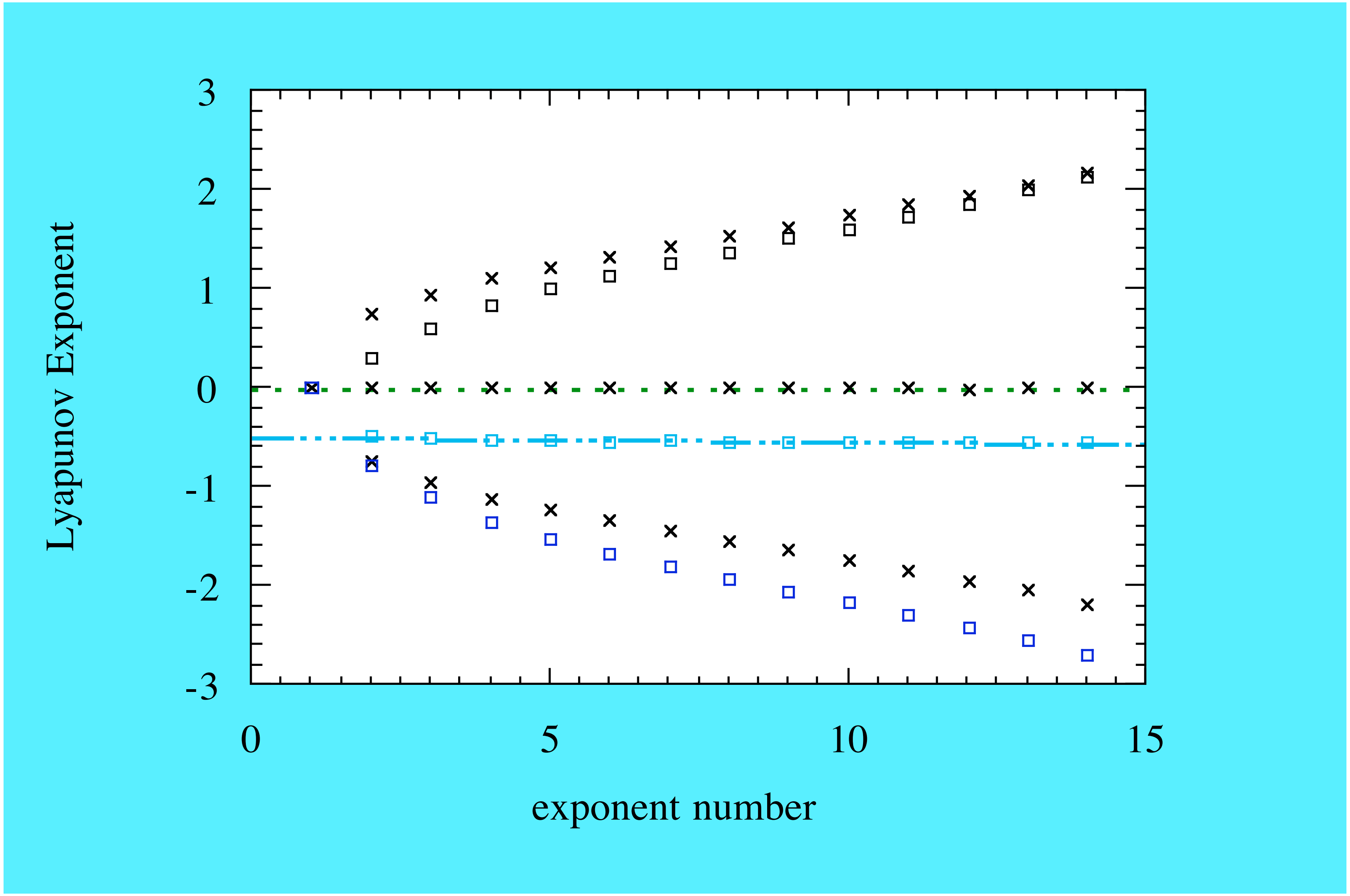
We this the *Lyapunov Sum Rule* for shear viscosity (Posch and Hoover (1988)).

Conjugate Pairing Rule

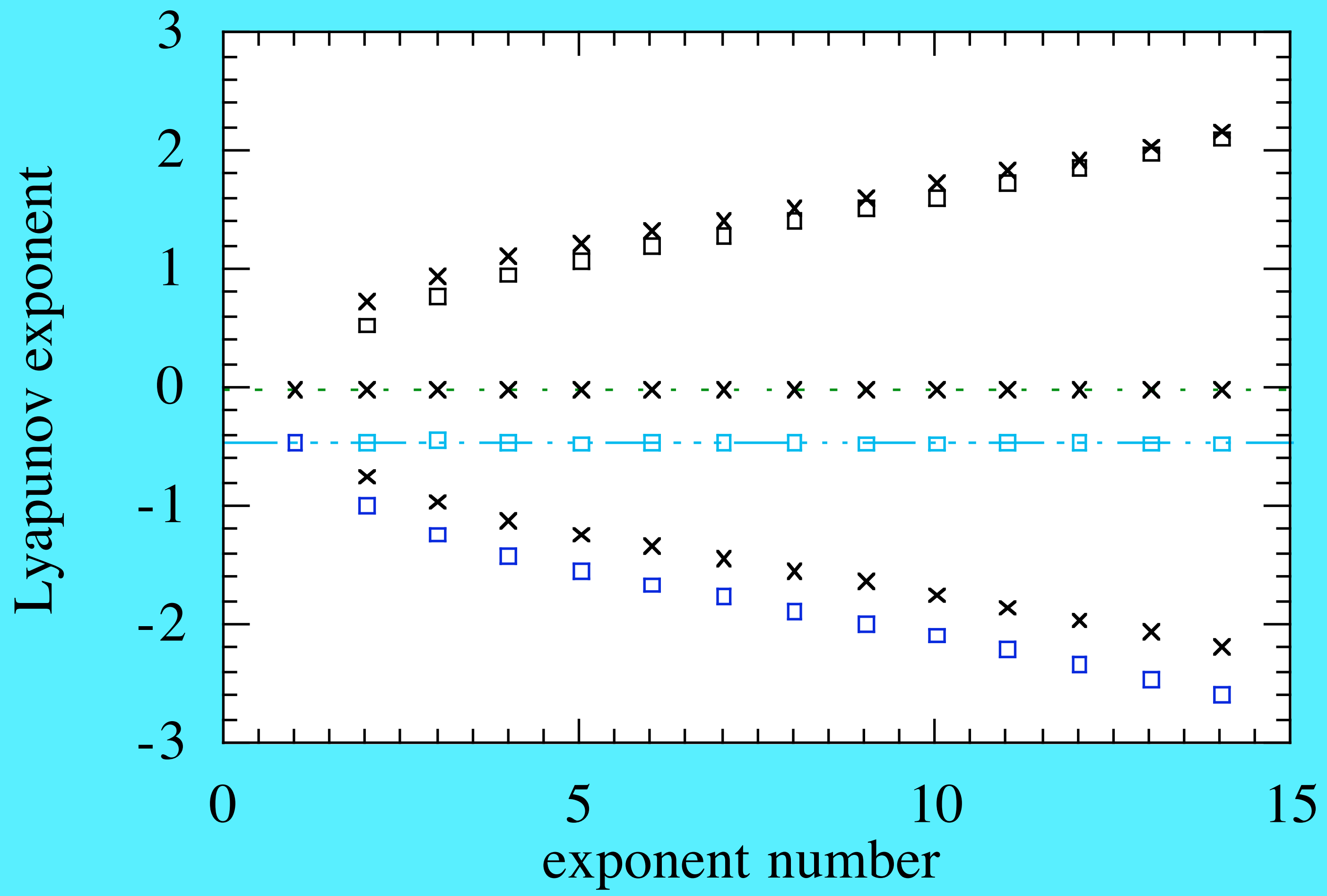
For Hamiltonian systems, **or more precisely** *symplectic* systems that are thermostatted by a homogeneous Gaussian thermostat, ergostat or Nose-Hoover thermostat, the Lyapunov exponents occur in conjugate pairs, λ_i, $\lambda_{i'}$.

$$\lambda_i + \lambda_{i'} = - < \alpha > = 2\bar{\lambda}$$

This relationship is referred to as the *Conjugate Pairing Rule,* (Evans Cohen and Morriss (1990)).



Lyapunov spectrum for colour conductivity.

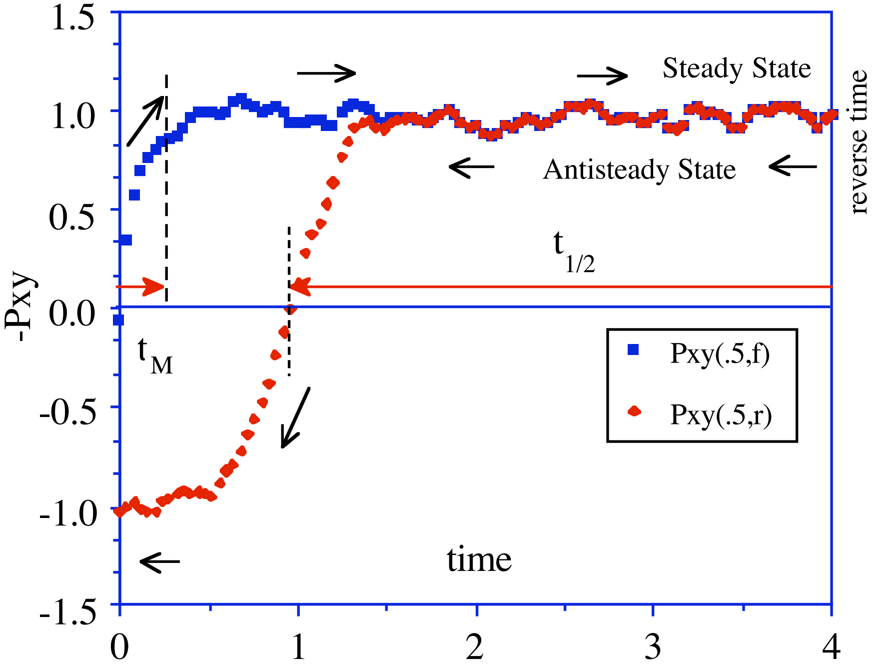


Lyapunov spectrum for thermostatted shear flow.

Using the Conjugate Pairing Rule the shear viscosity can be related to the maximal Lyapunov exponents,

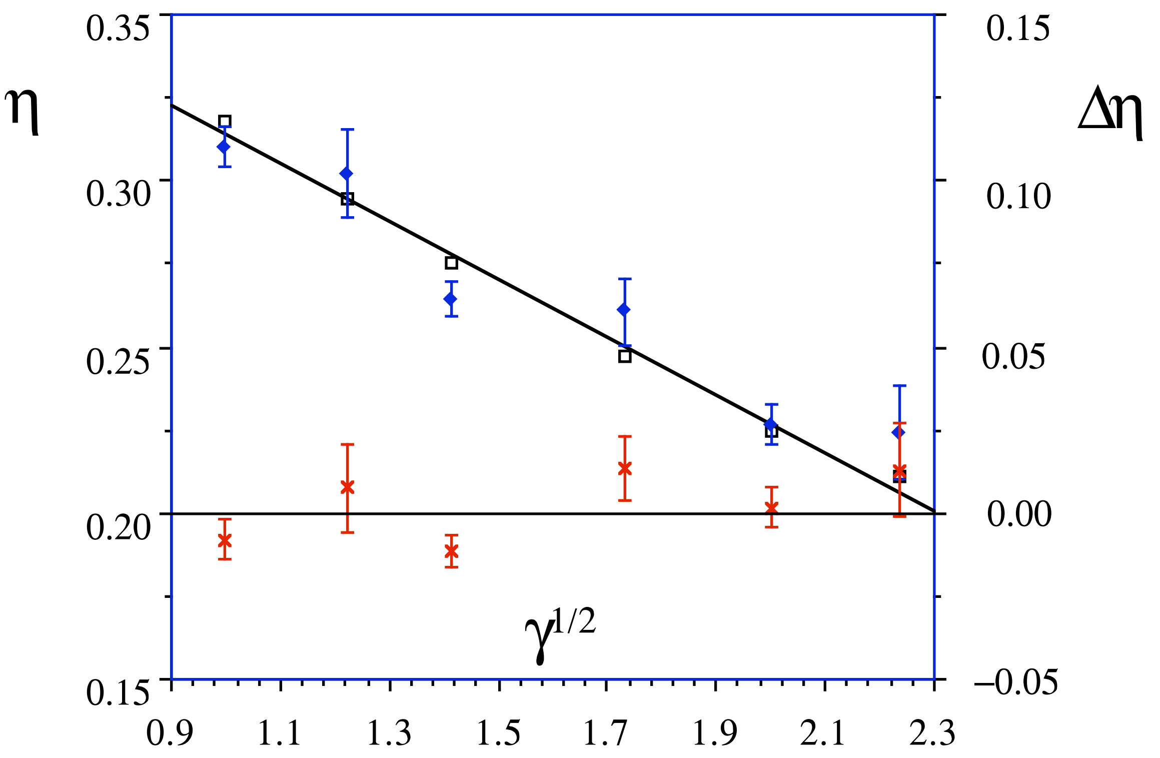
$$\eta(\gamma) = \frac{-3nk_B T}{\gamma^2}[\lambda_{max}(\gamma) + \lambda_{min}(\gamma)],$$

In order to calculate λ_{min}, normally an **extraordinarily** difficult task; we calculate the largest Lyapunov exponent for the time reversed *anti-steady state*:



$$\lambda_{min}(\text{steady state}) = -\lambda_{max}(\text{anti steady state})$$

Observation: Anti steady states are less stable than the usual steady state but that is NOT why entropy production is positive.



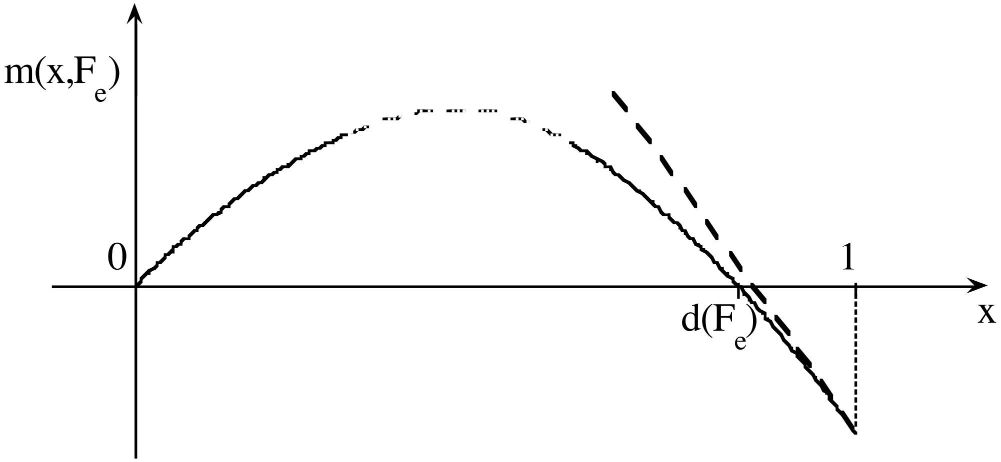
The figure above compares the shear viscosity computed directly using NEMD with the value obtained using the Conjugate Pairing Rule.

Transport Coefficients and the Kaplan-Yorke Dimension

The Kaplan-Yorke dimension of a nonequilibrium steady state is defined as,

$$D_{KY} = N_{KY} + \sum_{i=1}^{N_{KY}} \lambda_i \Big/ \left|\lambda_{N_{KY}+1}\right|$$

N_{KY} is the largest integer for which $\sum_{i=1}^{N_{KY}} \lambda_i > 0$



Then from this definition one can derive an exact formula for the linear transport coefficient (Evans, Cohen, Searles & Bonetto (2000)).

$$L(0) = \lim_{F_e \to 0} \frac{(2dN - f - D_{KY}(F_e))\lambda_{max}(F_e = 0)nk_B T}{NF_e^2}.$$

This equation has a status that is equivalent to that of a Green-Kubo relation for transport coefficients.

The corresponding expression for the Kaplan-Yorke dimension of the steady state attractor is,

$$D_{KY}(F_e) = 2dN - f - \frac{L(0)F_e^2 V}{\lambda_{max}(F_e = 0)k_B T} + O(F_e^4)$$

In practice the dimensional reduction in real non turbulent Navier-Stokes fluids is tiny $O(1/N_A)$!!

Summary: Exact formulae for transport coefficients

Constitutive Equation - definition:

$$J(F_e) \equiv -L(F_e)F_e$$

Green-Kubo relation:

$$\lim_{F_e \to 0} < \mathbf{J}(t) >= -\beta V \int_0^t ds < \mathbf{J}(0)\mathbf{J}(s) >_{eq} \bullet \mathbf{F}_e \equiv L(0)\mathbf{F}_e$$

Kaplan-Yorke relation:

$$L(0) = \lim_{F_e \to 0} \frac{(2dN - f - D_{KY}(F_e))\lambda_{max}(F_e = 0)nk_B T}{NF_e^2}$$

Transient Time Correlation Function:

$$< \mathbf{J}(t) >= -\beta V \int_0^t ds < \mathbf{J}(0)\mathbf{J}(s) > \bullet \mathbf{F}_e \equiv L(\mathbf{F}_e)\mathbf{F}_e$$

Kawasaki:

$$< \mathbf{J}(t) >= \left\langle \mathbf{J}(0) \exp[-\beta \int_0^t ds\, \mathbf{J}(-s) \bullet \mathbf{F}_e] \right\rangle \equiv L(\mathbf{F}_e)\mathbf{F}_e$$

Conjugate Pairing Rule:

$$L\left(F_e\right) = \frac{-3nk_B T}{F_e^2}[\lambda_{max}\left(F_e\right) + \lambda_{min}\left(F_e\right)],$$

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