**Lecture Notes from the 4th Gordon Godfrey Workshop on,**

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# "NonEquilibrium Statistical Mechanics and Lyapunov Instability"

**by**

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## Liouville Equation for N-particle distribution function

$$\frac{\partial f(\boldsymbol{\Gamma},t)}{\partial t} = -\frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet [\dot{\boldsymbol{\Gamma}} f(\boldsymbol{\Gamma},t)] \equiv -iLf(\boldsymbol{\Gamma},t) \tag{1}$$

Equation of motion of phase function

$$\frac{dA(\boldsymbol{\Gamma})}{dt} = \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial A(\boldsymbol{\Gamma})}{\partial \boldsymbol{\Gamma}} \equiv i\mathrm{L}A(\boldsymbol{\Gamma}) \tag{2}$$

So,

$$i\mathrm{L} = \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial}{\partial \boldsymbol{\Gamma}} \ldots, \quad iL = \frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet \dot{\boldsymbol{\Gamma}} \ldots, \quad iL - i\mathrm{L} = \frac{\partial}{\partial \boldsymbol{\Gamma}} \bullet \dot{\boldsymbol{\Gamma}} \equiv \Lambda(\boldsymbol{\Gamma}) \tag{3}$$

and since,

$$\frac{df}{dt} = [\frac{\partial}{\partial t} + \dot{\boldsymbol{\Gamma}} \bullet \frac{\partial}{\partial \boldsymbol{\Gamma}}]f = -f\Lambda \tag{4}$$

$\Lambda$ is called the *phase space compression factor*. The formal solution of the equations of motion,

$$f(\boldsymbol{\Gamma},t) = \exp[-i\mathcal{L}t]f(\boldsymbol{\Gamma},0) = \sum_{n=0}^{\infty}\frac{(-i\mathcal{L}t)^n}{n!}f(\boldsymbol{\Gamma},0) \tag{5}$$

and

$$A(\boldsymbol{\Gamma}(t)) = \exp[+iLt]A(\boldsymbol{\Gamma}(0)) = \sum_{n=0}^{\infty}\frac{(iLt)^n}{n!}A(\boldsymbol{\Gamma}(0)) \tag{6}$$

## Response theory

$$f(\boldsymbol{\Gamma},0) = \frac{\exp[-\beta H_0(\boldsymbol{\Gamma})]}{\int d\boldsymbol{\Gamma}\exp[-\beta H_0(\boldsymbol{\Gamma})]} \tag{7}$$

$$f(\boldsymbol{\Gamma},t) = \exp[-(iL+\Lambda)t]f(\boldsymbol{\Gamma},0) \tag{8}$$

Now employ a *Dyson decomposition*

$$\exp[-(iL+\Lambda)t]$$

$$= \exp[-iLt] - \int_0^t ds\, \exp[-(iL+\Lambda)s]\Lambda\exp[-iL(t-s)] \tag{9}$$

Equations of motion

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

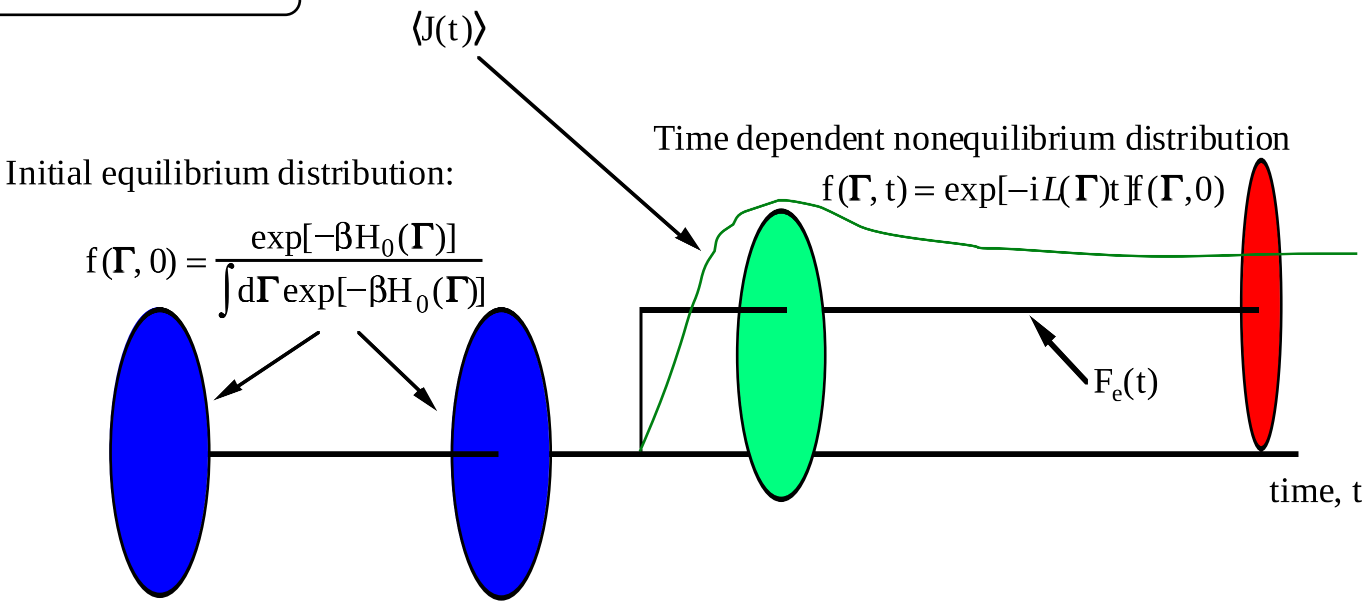
$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i + D_i \mathbf{F}_e - \alpha \mathbf{p}_i$$

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.

$\alpha$ is chosen to keep the peculiar kinetic energy, K, constant:

Gaussian Thermostat

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



Substitute recursively,

$$
\begin{aligned}
&\exp[-(iL+\Lambda)t] \\
&= \exp[-iLt] \\
&-\int_0^t ds_1 \exp[-iLs_1]\Lambda \exp[-iL(t-s_1)] \\
&+\int_0^t ds_1 \int_0^{s_1} ds_2 \exp[-iLs_2]\Lambda \exp[-iL(s_1-s_2)]\Lambda \exp[-iL(t-s_1)] \\
&-.....
\end{aligned}
\tag{10}
$$

$$
\begin{aligned}
&\exp[-(iL+\Lambda)t] \\
&= \exp[-iLt] \\
&-\int_0^t ds_1 \Lambda(s_1)\exp[-iLt] \\
&+\int_0^t ds_1 \int_0^{s_1} ds_2 \Lambda(s_2)\Lambda(s_1)\exp[-iLt] \\
&-..... \\
&= \exp[-\int_0^t ds\, \Lambda(s)]\exp[-iLt]
\end{aligned}
\tag{11}
$$

Substituting into the equation for the distribution function gives,

$$f(\boldsymbol{\Gamma},t) = \exp[-\int_0^t ds\ \Lambda(s)]\exp[-\beta H_0(-t)] \tag{12}$$

For isokinetic equations of motion,

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + C_i\mathbf{F}_e \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + D_i\mathbf{F}_e - \alpha\mathbf{p}_i \end{aligned} \tag{13}$$

From equations of motion,

$$\begin{aligned} \frac{dH_0}{dt} &= \frac{dH_0}{dt}^{ad} + \frac{dH_0}{dt}^{therm} \\ &= -\mathbf{J}(\boldsymbol{\Gamma}).\mathbf{F}_e - 2K\alpha \end{aligned} \tag{14}$$

and

$$\Lambda = 3N\alpha + O(1) \tag{15}$$

This leads to the so-called *Kawasaki* expression for the nonequilibrium distribution function,

$$f(\boldsymbol{\Gamma},t) = \exp[-\beta\int_0^t ds\ \mathbf{J}(-s)\bullet\mathbf{F}_e]f(\boldsymbol{\Gamma},0) \tag{16}$$

We can use this to compute averages,

$$\begin{aligned} < B(t) > &= \int d\boldsymbol{\Gamma}\ f(\boldsymbol{\Gamma},t)B(\boldsymbol{\Gamma}) \\ &= \int d\boldsymbol{\Gamma}\ B(\boldsymbol{\Gamma})\exp[-\beta\int_0^t ds\ \mathbf{J}(-s)\bullet\mathbf{F}_e]f(\boldsymbol{\Gamma},0) \end{aligned} \tag{17}$$

$$\begin{aligned} d < B(t) > / dt &= -\beta\int d\boldsymbol{\Gamma}\ B(\boldsymbol{\Gamma})\mathbf{J}(-t)\bullet\mathbf{F}_e f(\boldsymbol{\Gamma},t) \\ &= -\beta\int d\boldsymbol{\Gamma}\ B(t)\mathbf{J}(0)\bullet\mathbf{F}_e f(\boldsymbol{\Gamma},0) \end{aligned} \tag{18}$$

Yielding the *Transient Time Correlation Function* expression for an average,

$$< B(t) > = -\beta\mathbf{F}_e \bullet \int_0^t ds < \mathbf{J}(0)B(s) > \tag{19}$$

In the small field limit we can linearise both Kawasaki and TTCF giving, the *Linear Response formula*

$$\lim_{F_e \to 0} < B(t) > = -\beta \mathbf{F}_e \bullet \int_0^t ds < \mathbf{J}(0) B(s) >_{eq} \qquad (20)$$

## Green-Kubo Relations for linear thermal Transport Coefficients

1 Self Diffusion coefficient

$$D = \frac{1}{3}\int_0^{\infty} ds < \mathbf{v}_i(0) \bullet \mathbf{v}_i(t) >_{eq} \tag{21}$$

2 Thermal Conductivity

$$\lambda = \frac{V}{3k_B T^2}\int_0^{\infty} ds < \mathbf{J}_Q(0) \bullet \mathbf{J}_Q(t) >_{eq} \tag{22}$$

3 Shear Viscosity

$$\eta = \frac{V}{k_B T}\int_0^{\infty} ds < P_{xy}(0) P_{xy}(t) >_{eq} \tag{23}$$

4 Bulk Viscosity

$$\eta_V = \frac{1}{V k_B T}\int_0^{\infty} ds < [p(0)V(0) - < pV >][p(t)V(t) - < pV >] >_{eq} \tag{24}$$

# NEMD Algorithms for Navier-Stokes transport coefficients.

*Sllod* algorithm for shear viscosity

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_i, \text{ which is equivalent to: } \ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t) y_i \qquad (25)$$

*Sllod* algorithm for viscous flow

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \bullet \nabla\mathbf{u} - \alpha \mathbf{p}_i \qquad (26)$$

*Colour Conductivity* algorithm for self diffusion

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{i} c_i F_c - \alpha(\mathbf{p}_i - \mathbf{i} c_i J_x / \rho) \qquad (27)$$

where

$$J_x = \frac{1}{V}\sum_{i=1}^{N} c_i \dot{x}_i \quad \text{and} \quad \sum_{i=1}^{N} (\mathbf{p}_i - \mathbf{i} c_i J_x / \rho)^2 / m = 3Nk_B T \tag{28}$$

*Evans Heat flow algorithm*

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - (E_i - \overline{E})\mathbf{F} \\ &\quad - \frac{1}{2}\sum_{j=1}^{N} \mathbf{F}_{ij}\mathbf{q}_{ij} \bullet \mathbf{F} + \frac{1}{2N}\sum_{j,k=1}^{N} \mathbf{F}_{jk}\mathbf{q}_{jk} \bullet \mathbf{F} - \alpha \mathbf{p}_i \end{aligned} \tag{29}$$

where

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

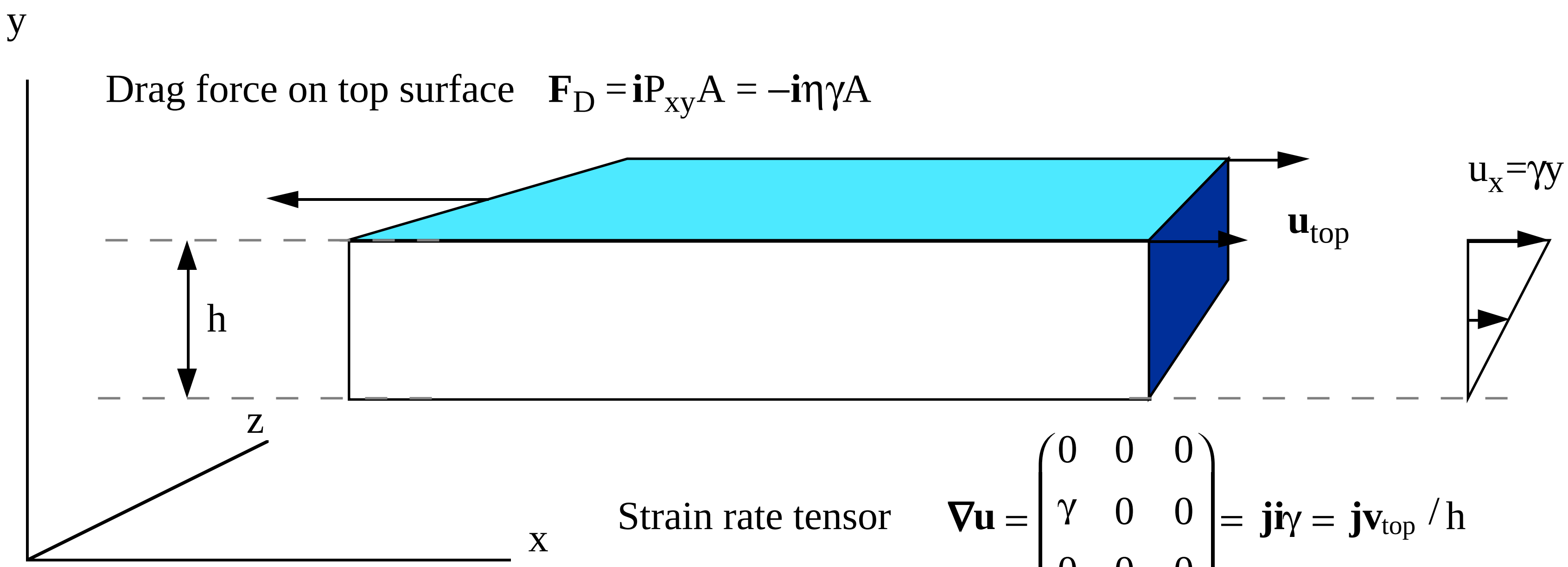
For each algorithm the Navier-Stokes transport coefficient, L, is evaluated as

$$L \approx \lim_{F \to 0} \lim_{t \to \infty} \frac{1}{t} \frac{\int_0^t ds J(s)}{F} \tag{30}$$

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.

## Newton's Constitutive Relation for Shear Flow

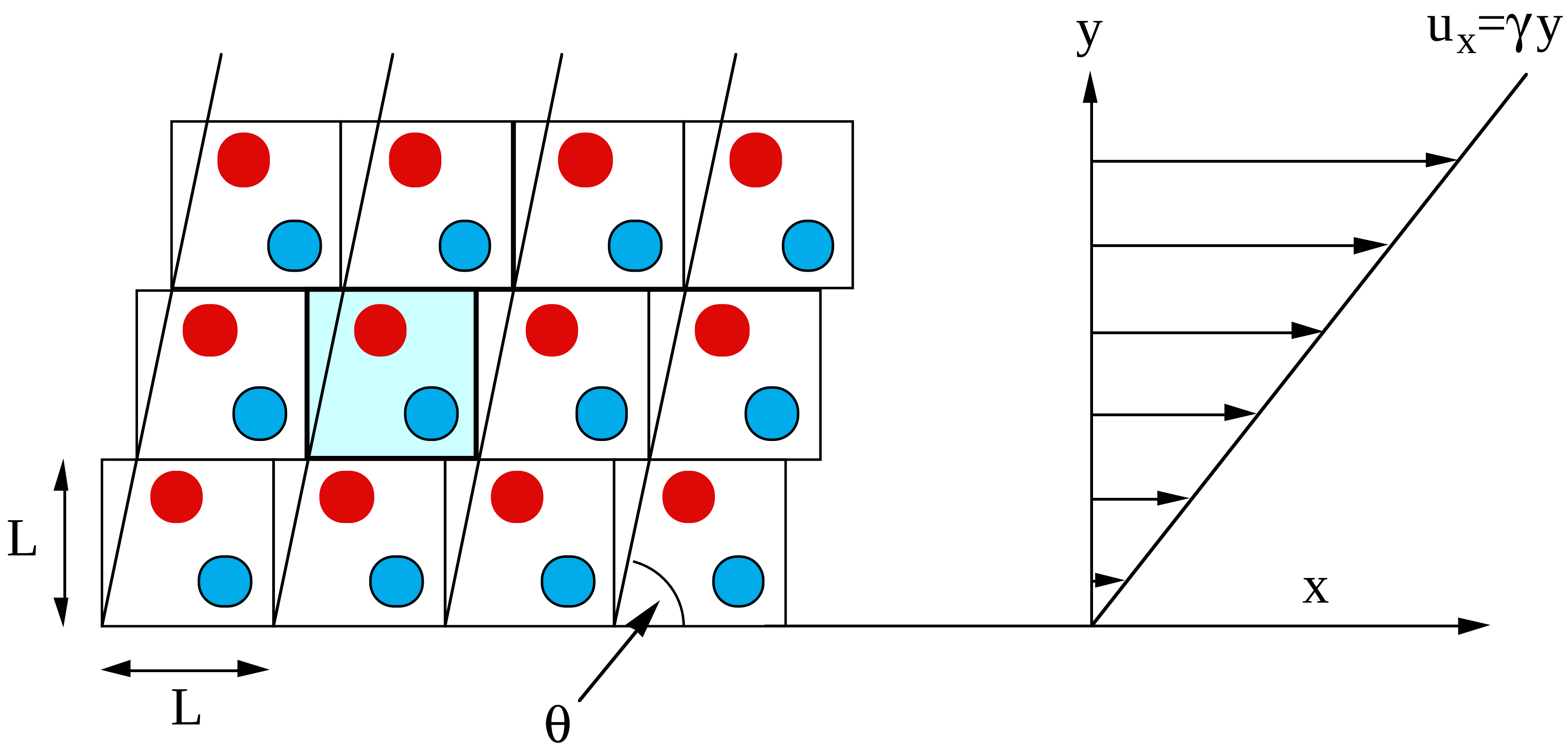
Drag force on top surface $\mathbf{F}_D = \mathbf{i}P_{xy}A = -\mathbf{i}\eta\gamma A$




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

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

Lees-Edwards periodic boundary conditions for shear flow.

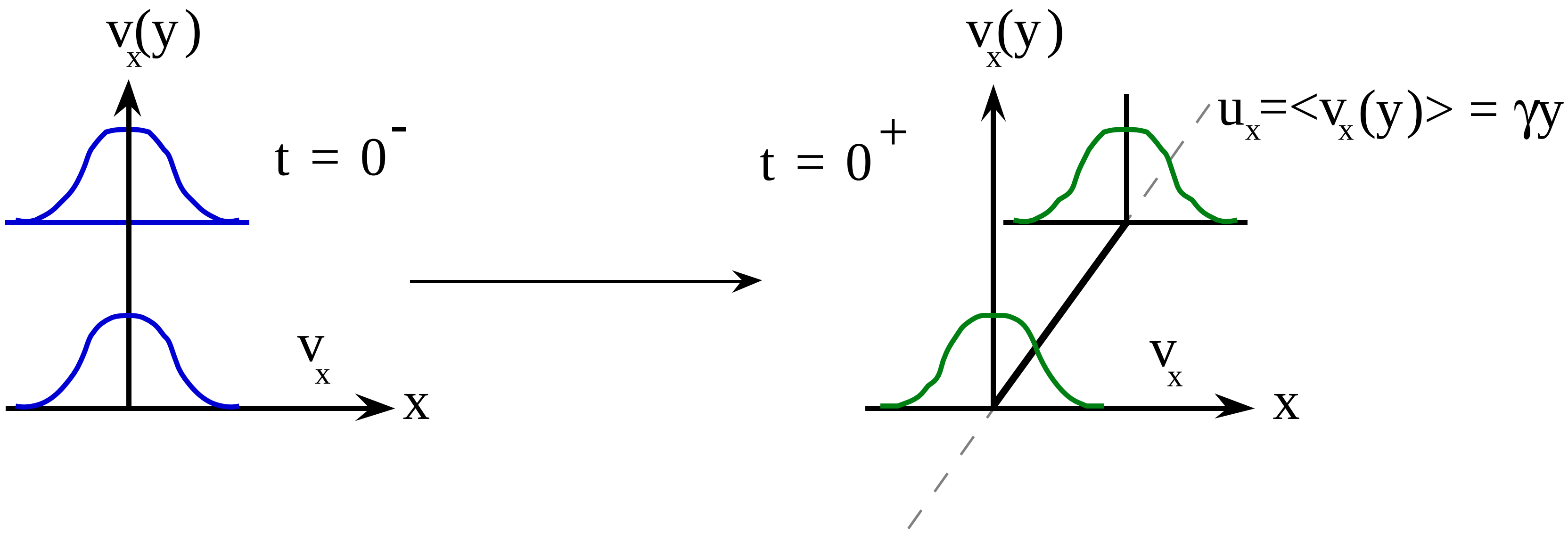


The Sllod equations of motion (25) are equivalent to Newtons equations for $t>0^+$, with a linear shift applied to the initial x-velocities of the particles.

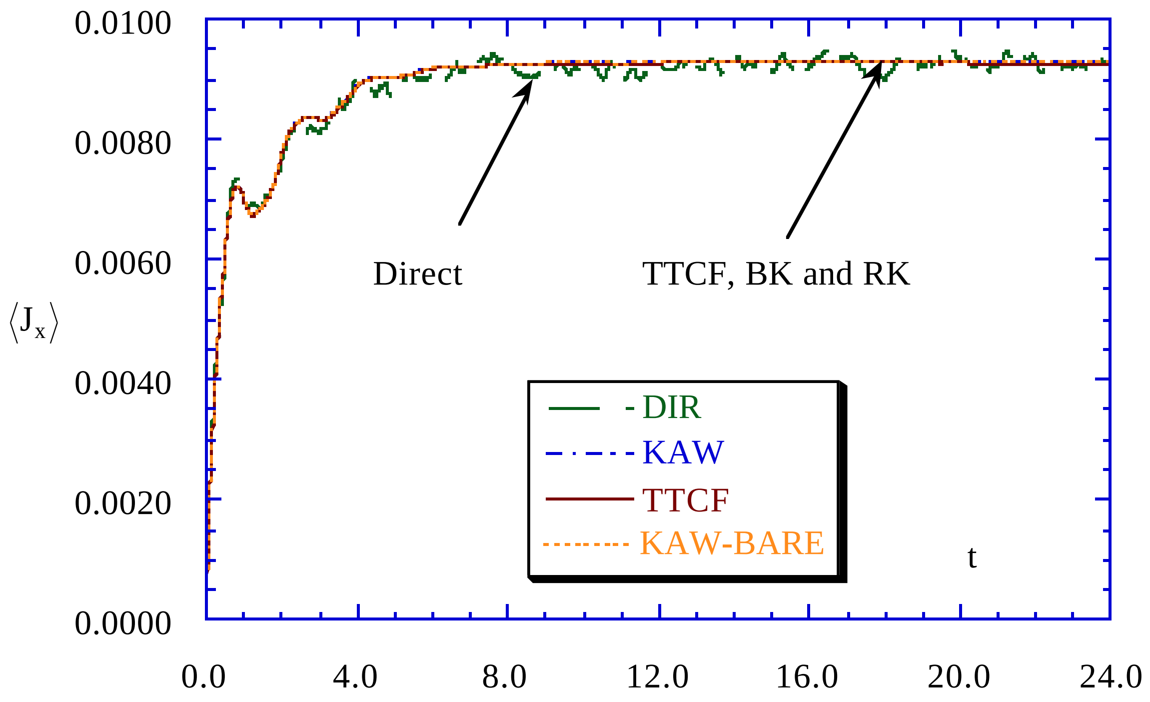
*Sllod* algorithm for shear viscosity

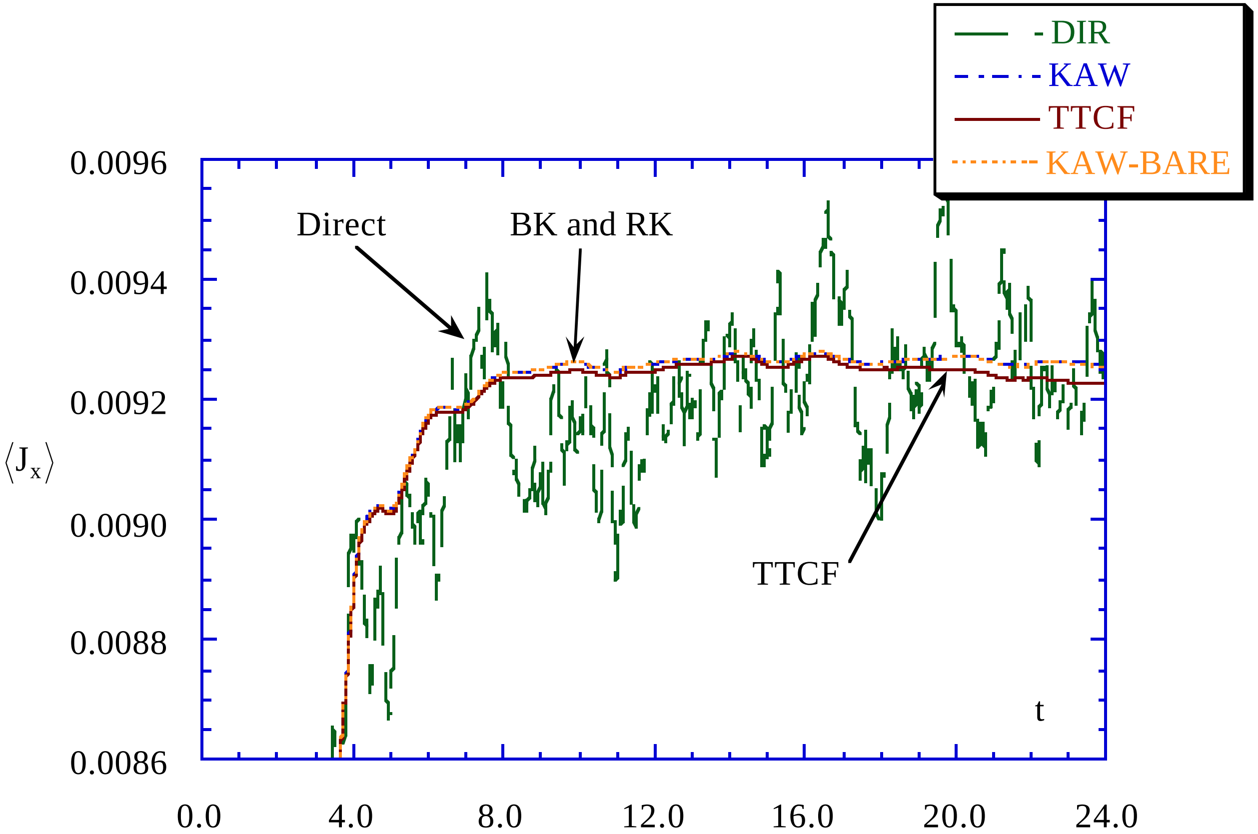
$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_i, \text{ which is equivalent to: } \ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m} + \mathbf{i}\gamma\delta(t) y_i \qquad (25)$$



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





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

## Instability of Phase Space Trajectories

The equations of motion for the infinitesimal tangent vectors are,

$$\frac{d}{dt}\delta\mathbf{\Gamma}_i(t) \equiv \mathbf{T}(\mathbf{\Gamma}) \bullet \delta\mathbf{\Gamma}_i(t) = \frac{\partial\dot{\mathbf{\Gamma}}(\mathbf{\Gamma}(t))}{\partial\mathbf{\Gamma}} \bullet \delta\mathbf{\Gamma}_i(t), \qquad (i = 1,..,6N). \tag{31}$$

In the infinitesimal limit, $\delta\mathbf{\Gamma}_i(0)\to\mathbf{0}$, the formal solution of this equation can be written as,

$$\delta\mathbf{\Gamma}_i(t) \equiv \exp_L[\int_0^t ds\mathbf{T}(\mathbf{\Gamma}(s))] \bullet \delta\mathbf{\Gamma}_i(0) \equiv \mathbf{L}(t) \bullet \delta\mathbf{\Gamma}_i(0), \tag{32}$$

The *Lyapunov exponents* are also the logarithms of the eigenvalues of the symmetric matrix, $\mathbf{\Lambda}$,

$$\mathbf{\Lambda} = \lim(t\to\infty)\mathbf{\Lambda}(t) = \lim(t\to\infty)\left[\mathbf{L}^T(t)\cdot\mathbf{L}(t)\right]^{1/2t} \tag{33}$$

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

$$\int d\mathbf{\Gamma}\frac{df(\mathbf{\Gamma},t)}{dt} = -\left\langle\frac{d\ln W(\mathbf{\Gamma}(t))}{dt}\right\rangle_{F_e} = -\sum_{i=1}^{6N}\lambda_i = -3N\langle\alpha\rangle_{F_e} \tag{34}$$

Using that $dH_0/dt \equiv 0$ and $\langle P_{xy} \rangle_\gamma = -\eta(\gamma)\gamma$, one has :

$$\eta(\gamma) = \frac{-k_B T}{V\gamma^2} \sum_{i=1}^{6N} \lambda_i(\gamma) \qquad (35)$$

We this the *Lyapunov Sum Rule* for shear viscosity.

We define **J**, **K**, as,

$$\mathbf{J} \equiv \begin{pmatrix} \mathbf{0}, \mathbf{I} \\ -\mathbf{I}, \mathbf{0} \end{pmatrix}; \qquad \mathbf{K} \equiv \begin{pmatrix} -\mathbf{I}, \mathbf{0} \\ \mathbf{0}, \mathbf{I} \end{pmatrix}, \qquad (36)$$

where **I** is the 3N x 3N identity matrix and **0** is the 3Nx3N null matrix. For Hamiltonian systems, **T**, satisfies the *infinitesimally symplectic* condition[17],

$$\mathbf{T}^T \bullet \mathbf{J} = -\mathbf{J} \bullet \mathbf{T} \qquad (37)$$

It is known that this condition is satisfied if the matrix **T**, can be written in the form,

$$\mathbf{T} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{X} & -\mathbf{A}^T \end{pmatrix} \qquad (38)$$

where the matrices **B** and **C** are symmetric. It is easy to show that if **T**, is real and satisfies the infinitesimally symplectic condition, (17), then **L**, satisfies the *globally* *symplectic* condition,

$$\mathbf{L}^{T}\mathbf{J}\mathbf{L} = \mathbf{J} \tag{39}$$

The proof relies on the fact that, $\exp_R\int_0^t -\mathbf{T}(s)ds \cdot \exp_L\int_0^t \mathbf{T}(s)ds = \exp_L\int_0^t \mathbf{T}(s)ds \cdot \exp_R\int_0^t -\mathbf{T}(s)ds = \mathbf{I}$, the identity operator. It is also easy to show that if $\mathbf{T}$ is infinitesimally symplectic then $\mathbf{L}^{T}\cdot\mathbf{L}$ is also globally symplectic.

If $\mathbf{T}$ is infinitesimally symplectic with eigenvalue $\lambda$, then $-\lambda$ is also an eigenvalue. Furthermore if $\mathbf{L}$ (or $\mathbf{L}^{T}\cdot\mathbf{L}$) is globally symplectic and has an eigenvalue $\lambda$, then $1/\lambda$, is also an eigenvalue of $\mathbf{L}$ (or $\mathbf{L}^{T}\cdot\mathbf{L}$).

Since the Lyapunov exponents are the logarithms of the eigenvalues of the Hermitian matrix, $\mathbf{\Lambda}$, the Lyapunov exponents occur in conjugate pairs, $\lambda_i$, $\lambda_{i'}(= -\lambda_i)$.

## Thermostatted Hamiltonian systems.

Define

$$\mathbf{T} \equiv \mathbf{T}' - \alpha\mathbf{I}/2 \equiv \mathbf{T}^{ad} - \alpha\mathbf{K}/2 - \alpha\mathbf{I}/2 \qquad (40)$$

$\mathbf{T}' \equiv \mathbf{T}^{ad} - \alpha\mathbf{K}/2$ is infinitesmally symplectic.

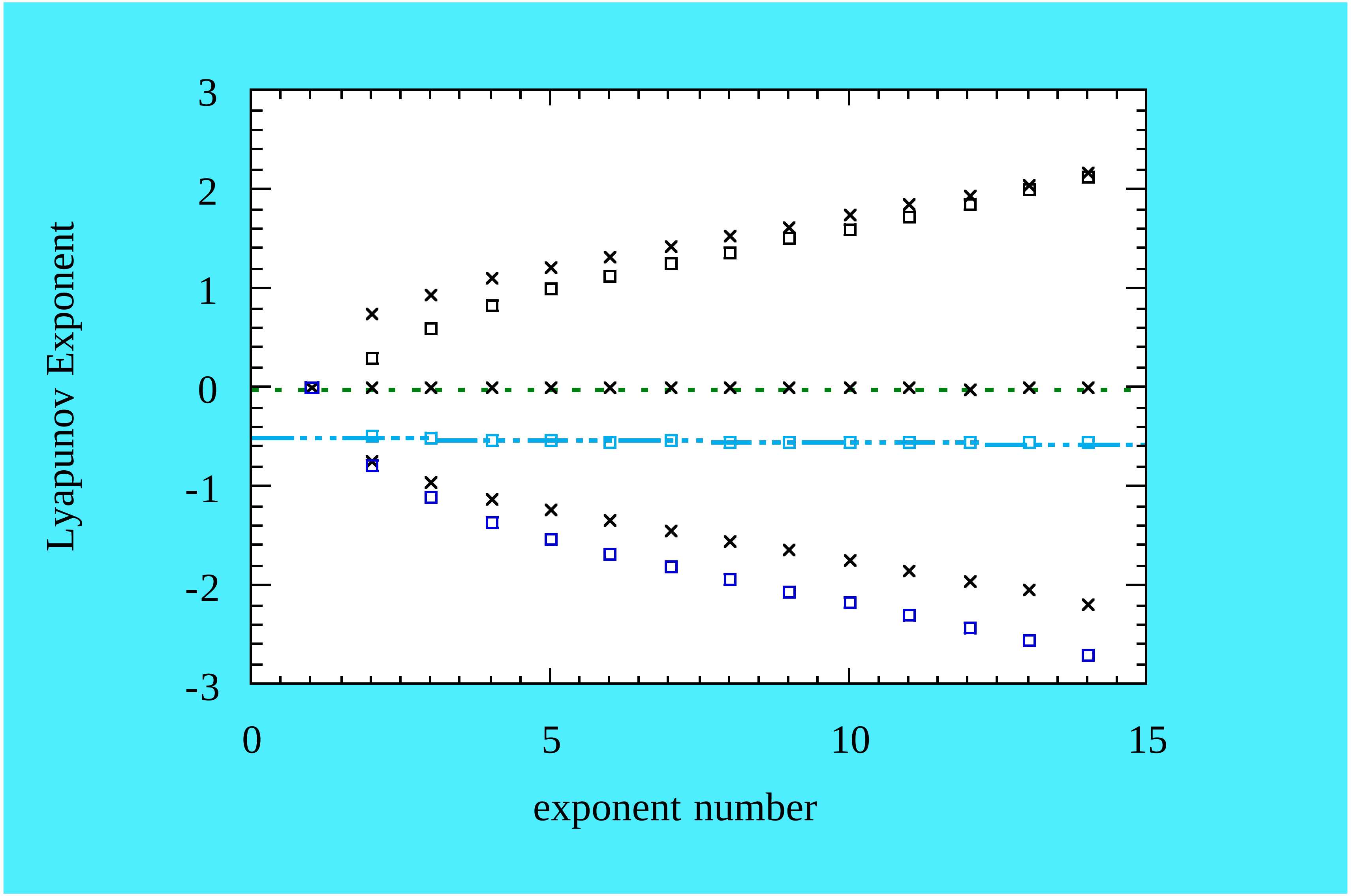
$$\mathbf{\Lambda}(t;\alpha) = \left[\exp_R[\int_0^t ds\,\mathbf{T}'^T(s) - \frac{\alpha(s)}{2}\mathbf{I}] \bullet \exp_L[\int_0^t ds\,\mathbf{T}'(s) - \frac{\alpha(s)}{2}\mathbf{I}]\right]^{1/2t}$$

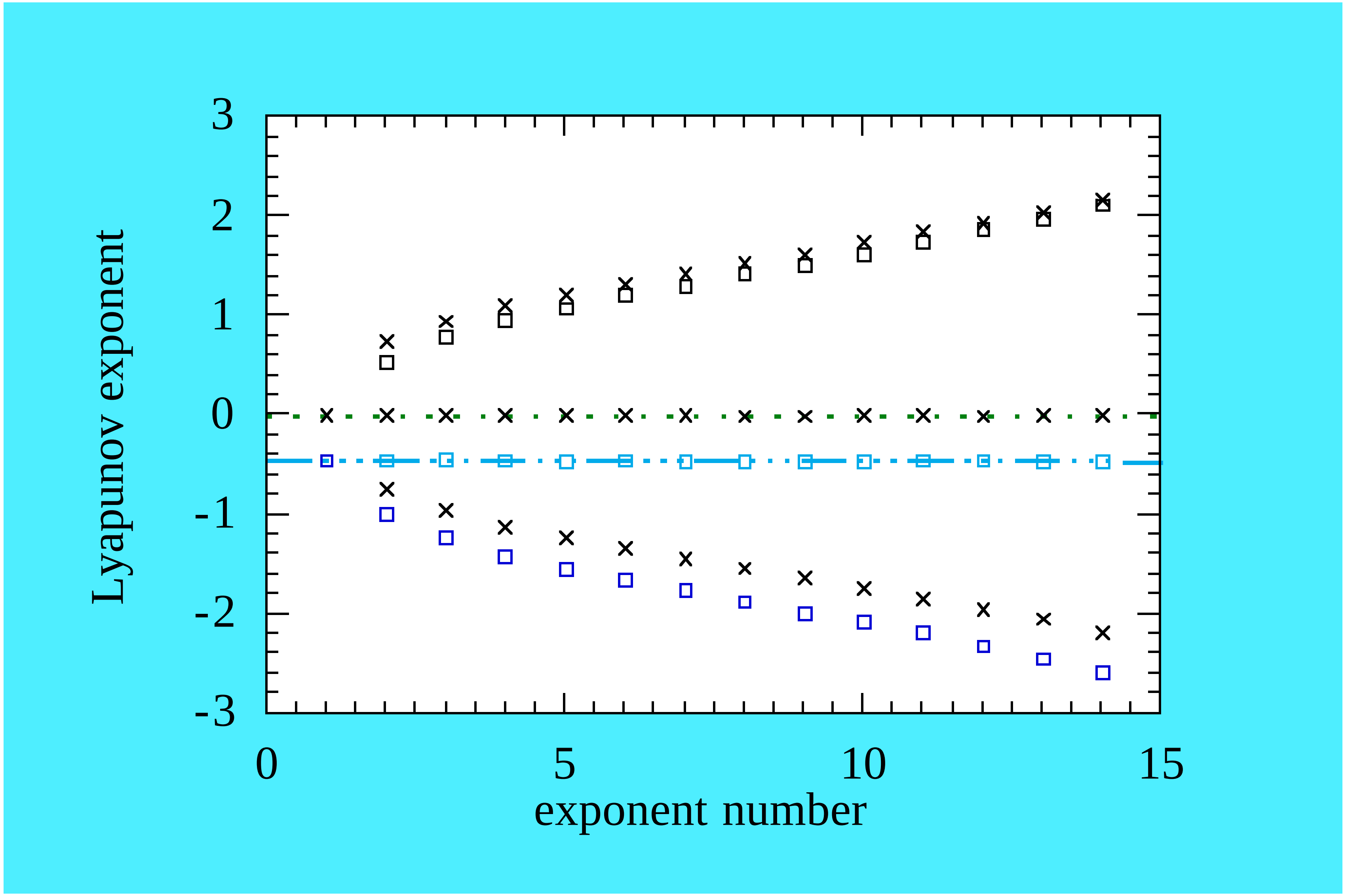
$$= \mathbf{\Lambda}'(t)\exp[-\int_0^t ds\,\alpha(s)\mathbf{I}]^{1/2t}$$

$$= \mathbf{\Lambda}'(t)\exp[-\frac{<\alpha>}{2}]\mathbf{I} \qquad (41)$$

This implies, that conjugate pairs of Lyapunov exponents $\lambda_i$, $\lambda_{i'}$, for Gaussian thermostatted Hamiltonian systems obey the *Conjugate Pairing Rule,*

$$\lambda_i + \lambda_{i'} = -<\alpha> = 2\bar{\lambda} \qquad (42)$$

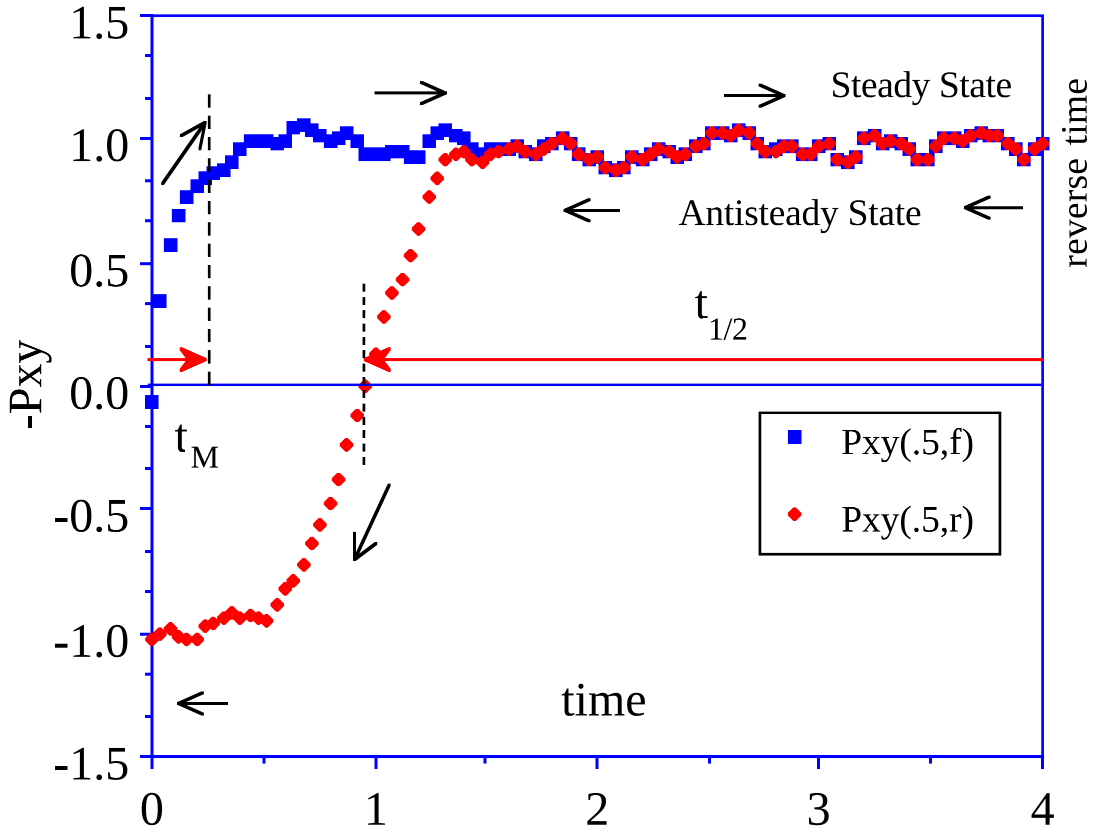

3
2
1
0
-1
-2
-3
0
5
10
15
Lyapunov Exponent
exponent number


3
2
1
0
-1
-2
-3
0
5
10
15
Lyapunov exponent
exponent number

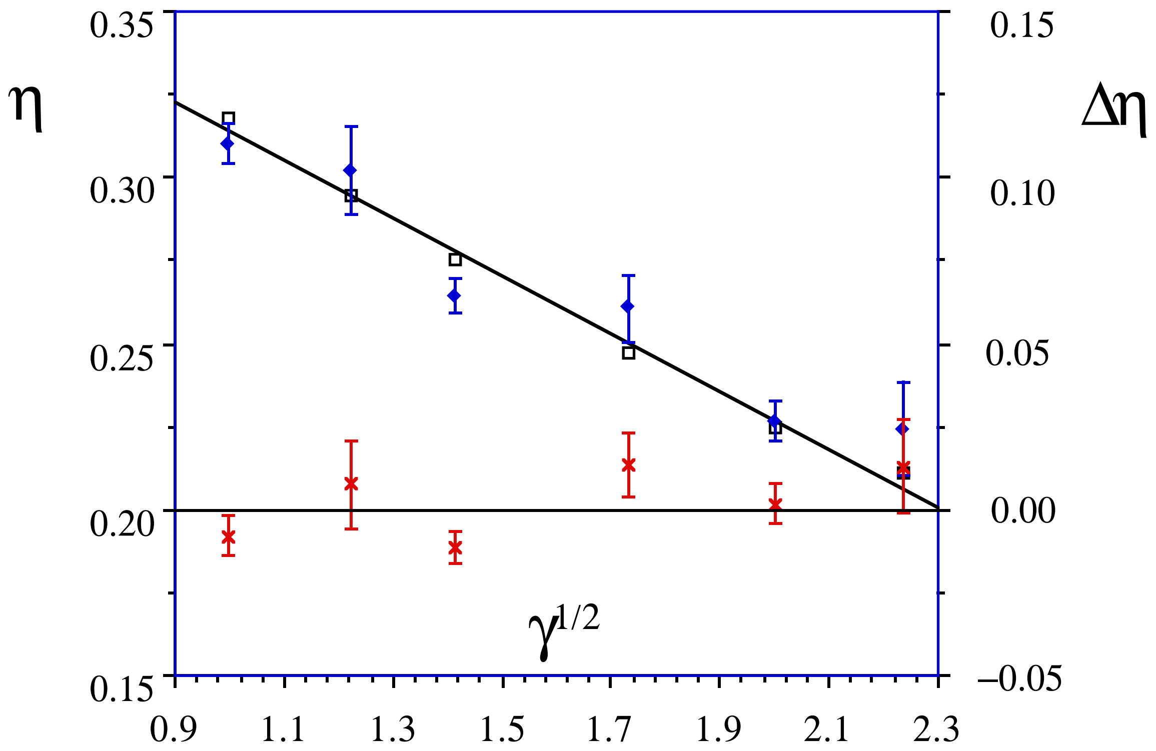
Using the Conjugate Pairing Rule,

$$\eta(\gamma) = \frac{-3nk_BT}{\gamma^2}[\lambda_{max}(\gamma) + \lambda_{min}(\gamma)], \tag{43}$$

In order to calculate $\lambda_{min}$, normally an **extraordinarily** difficult task, we calculate the largest Lyapunov exponent for the time reversed *anti-steady state*.



1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-Pxy
0
1
2
3
4
time
Steady State
Antisteady State
reverse time
t1/2
tM
Pxy(.5,f)
Pxy(.5,r)




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

## Second Law violations in Nonequilibrium Steady States

For reversible deterministic N-particle thermostatted systems, we examine the question of why it is so difficult to find time reversed trajectories, that will at long times, under the application of an external dissipative field, lead to Second Law violating nonequilibrium steady states.

In a nonequilibrium steady state:

$$\mu_i = \frac{\exp[-\sum_{n|\lambda_{ni}>0} \lambda_{ni}\tau]}{\sum_j \exp[-\sum_{m|\lambda_{mj}>0} \lambda_{mj}\tau]} \qquad (44)$$

where $\{\lambda_{ni};n=1,..6N\}$ is the set of local Lyapunov exponents, for segment, i.

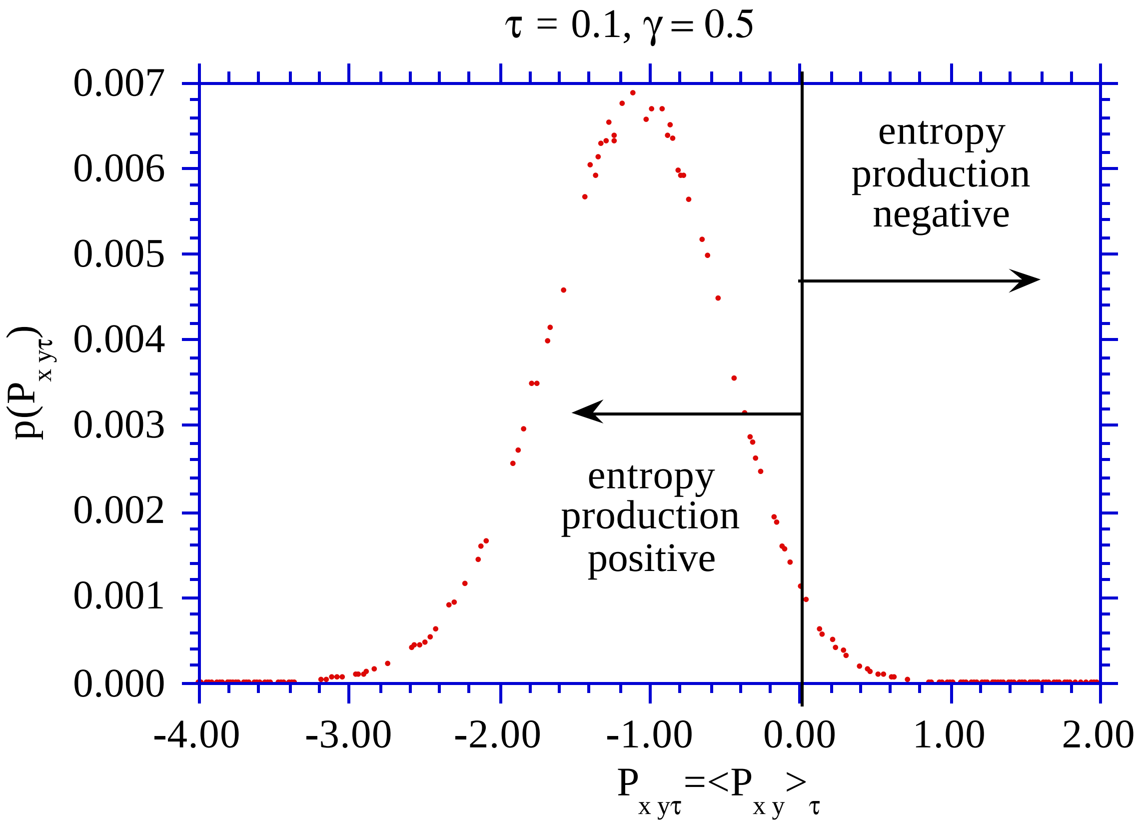
And the ratio of the limiting $(\tau\rightarrow\infty)$ probabilities that the system is on a segment i and its conjugate anti segment, i*, is,

$$\frac{\mu_{i^*}}{\mu_i} = \frac{\exp[-\sum_{n|\lambda_{ni^*}>0} \lambda_{ni^*}\tau]}{\exp[-\sum_{m|\lambda_{mi}>0} \lambda_{mi}\tau]} = \frac{\exp[\sum_{n|\lambda_{ni}>0} \lambda_{ni}\tau]}{\exp[-\sum_{m|\lambda_{mi}<0} \lambda_{mi}\tau]}$$

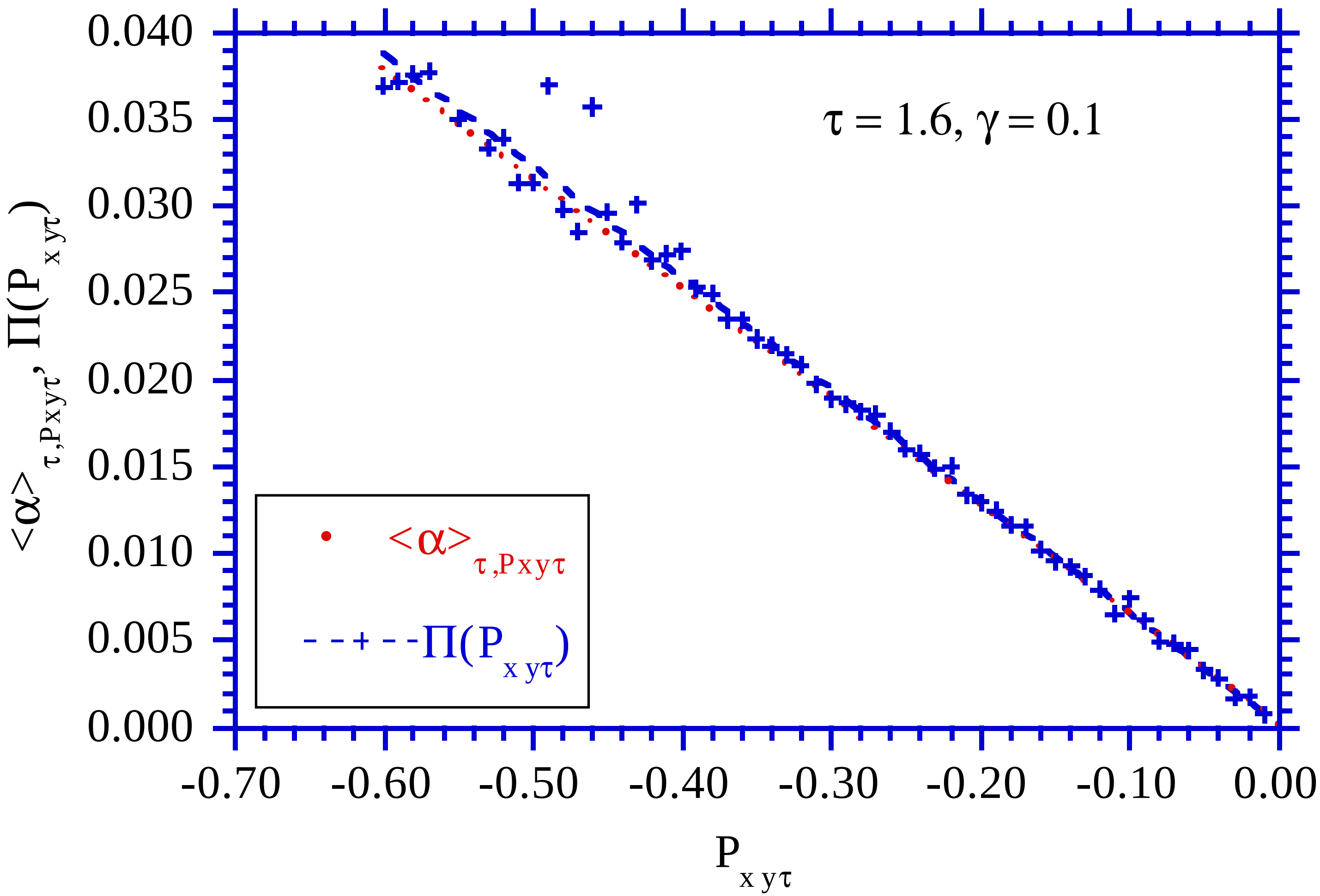
$$= \exp[\tau\sum_{n} \lambda_{ni}] = \exp[-3N < \alpha >_{\tau i} \tau] \tag{45}$$

where we used that,

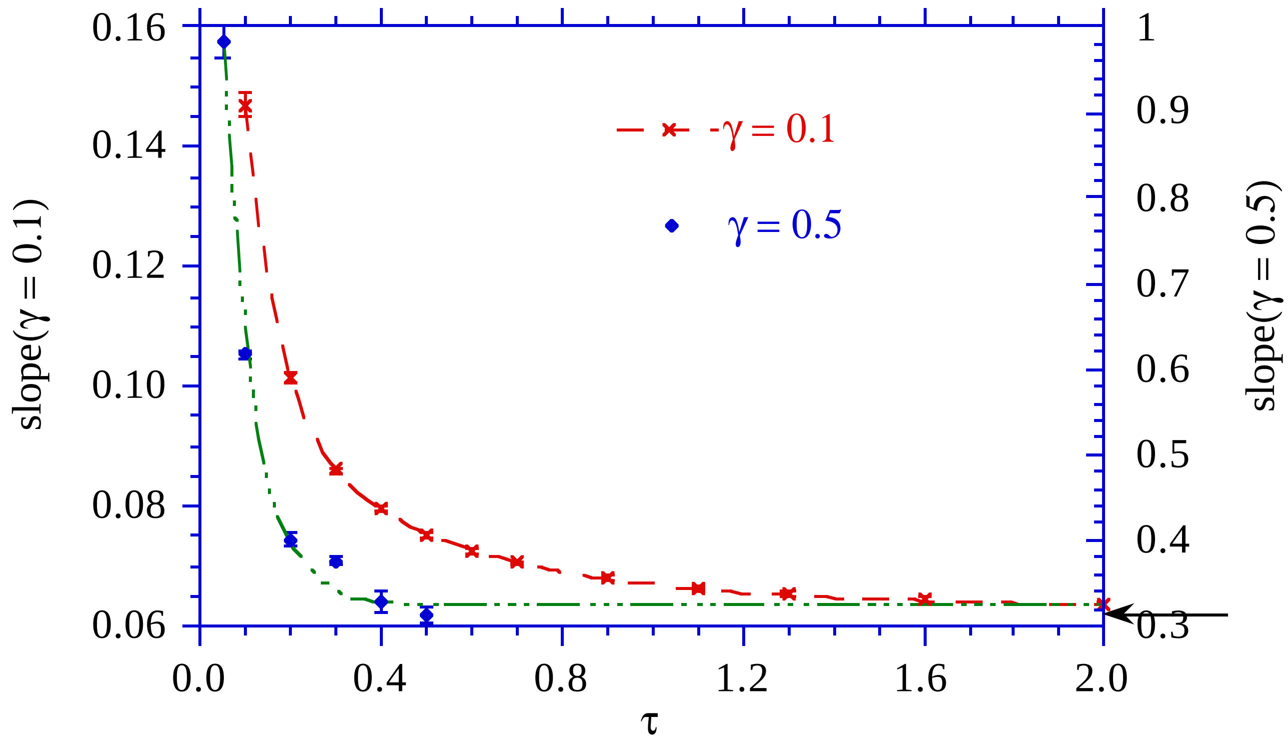
$$3N < \alpha >_{\tau i} = -\sum_{i=1}^{6N} \lambda_{ni} \quad . \tag{46}$$




We show the probability distribution of $<P_{xy}>_\tau$ . The distribution is approximately Gaussian. As can be seen the right hand tail of the distribution where $<P_{xy}>_\tau > 0$ consists of K-states which for a time, τ, defy the Second Law of thermodynamics.




We plot $\Pi = \ln[p(<P_{xy}>_\tau) / p(<-P_{xy}>_\tau)] / 2N\tau$ and $<\alpha>_{\tau,Pxy}$, for $\tau=1.6$ and $\gamma = 0.1$. These two functions are essentially linear in $<P_{xy}>_\tau$ with slopes that are very nearly identical. The straight line shows a weighted least squares fit to $\Pi(<P_{xy}>_\tau)$.



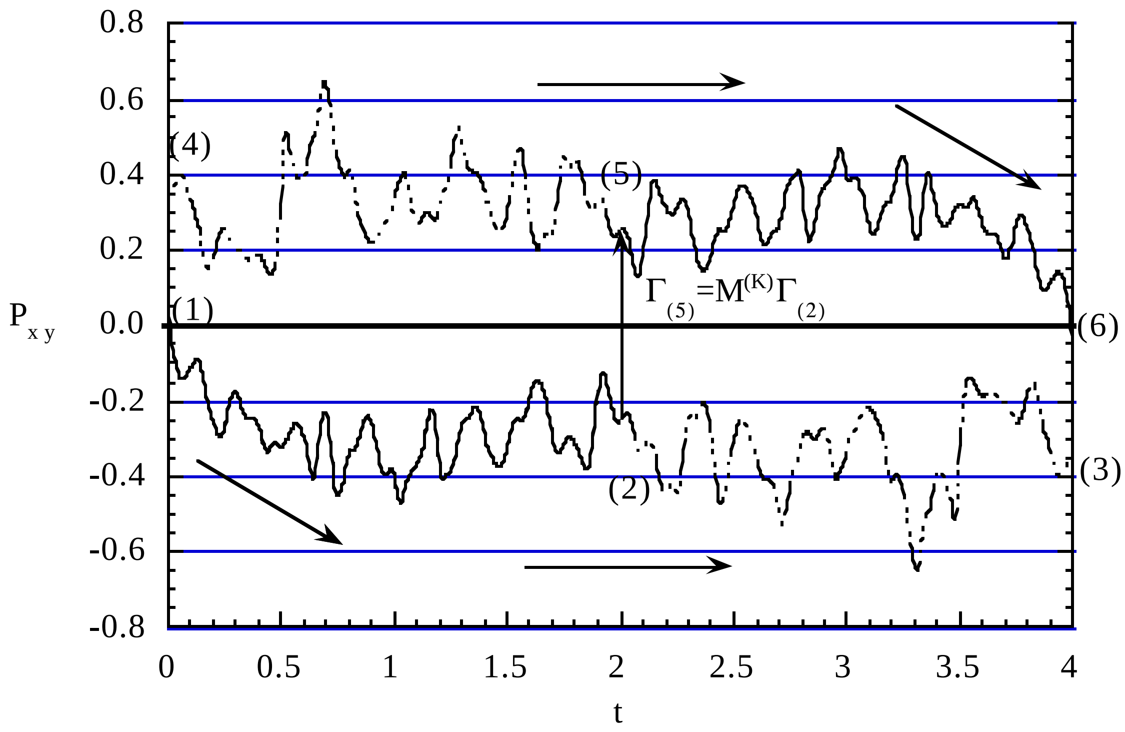

We graph the slope, $\partial\{\ln[p\langle P_{xy}\rangle_\tau \,/\, p\langle -P_{xy}\rangle_\tau]/2N\tau\}/\partial\langle P_{xy}\rangle_\tau$, as a function of $\tau$ for $\gamma$=0.1, 0.5. The corresponding results for $\langle\alpha\rangle_{\tau,Pxy}$, are not shown here since they are independent of the averaging time $\tau$. In determining the slopes a weighted least squares fit of the data was used. We see that as $\tau\to\infty$, the slope approaches the $\tau$-independent, slope of $\langle\alpha\rangle_{\tau,Pxy}$ as a function of $\langle P_{xy}\rangle_\tau$, which is shown by the arrow.

For transient states which evolve from equilibrium at t=0 towards the steady state we define:

$$\langle P_{xy}\rangle_{\tau,(i)}, \equiv \frac{1}{\tau}\int_0^{\tau} P_{xy}(\boldsymbol{\Gamma}_{(i)}(s))ds, \qquad (47)$$

For every such transient segment, we define the $i^{(K)}$ segment for which $\langle P_{xy}\rangle_{\tau,(i^{(K)})} = -\langle P_{xy}\rangle_{\tau,(i)}$. This is the Kawasaki mapped segment.
where, $M^K\boldsymbol{\Gamma} = M^K(x,y,z,p_x,p_y,p_z,\gamma) = (x,-y,z,-p_x,p_y,-p_z,\gamma) \equiv \boldsymbol{\Gamma}^{(K)}$. One can show,

$$P_{xy}(-t,\boldsymbol{\Gamma},\gamma) = \exp[-iL(\boldsymbol{\Gamma},\gamma)t]P_{xy}(\boldsymbol{\Gamma}) = -P_{xy}(t,\boldsymbol{\Gamma}^{(K)},\gamma) \qquad (48)$$

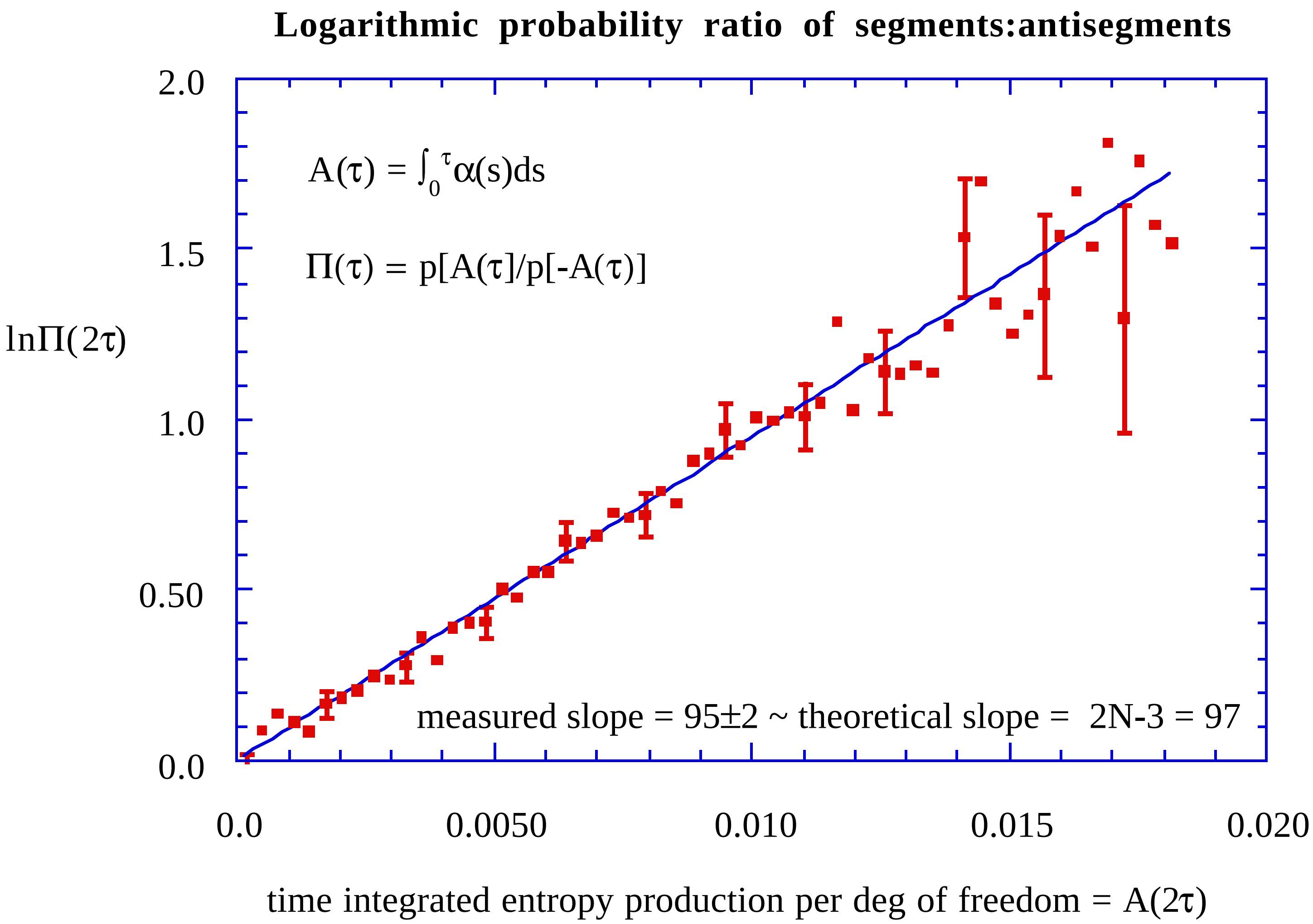



$$V_2 = V_1(\tau) = V_1(0)\exp[-\int_0^{\tau} 3N\alpha(s;\mathbf{\Gamma}_{(1)})ds] \tag{49}$$

$$V_3 = V_1(2\tau) = V_1(0)\exp[-\int_0^{2\tau} 3N\alpha(s;\mathbf{\Gamma}_{(1)})ds]. \tag{50}$$

So the ratio of observing transient segments and their conjugates is:

$$\mu_{1*}/\mu_1 = V_4/V_1(0) = V_1(2\tau)/V_1(0) = \exp[\int_0^{2\tau} -3N\alpha(s;\mathbf{\Gamma}_{(1)})ds], \quad \forall\tau. \quad (51)$$



## Lagrangian form of the Kawasaki Distribution

Clearly one can write,

$$\exp(iL(\mathbf{\Gamma})t)f(\mathbf{\Gamma},0) = f(\mathbf{\Gamma},-t) \qquad (52)$$

However, since this equation is true for all $\mathbf{\Gamma}$ it must also be true for $\mathbf{\Gamma}$(-t), so that,

$$\exp(iL(\mathbf{\Gamma}(-t))t)f(\mathbf{\Gamma}(-t),0) = f(\mathbf{\Gamma}(-t),-t) \qquad (53)$$

Using a Dyson decomposition of the distribution function propagator, one can show that,

$$\exp(iL(\mathbf{\Gamma})t) = \exp[-\int_0^t 3N\alpha(\mathbf{\Gamma}(s))ds]\exp[iL(\mathbf{\Gamma})t] \qquad (54)$$

Substituting equation (54) into (53) gives,

$$f(\boldsymbol{\Gamma}(-t),-t) = \exp[-\int_0^t 3N\alpha(\boldsymbol{\Gamma}(s-t))ds]\exp[iL(\boldsymbol{\Gamma}(-t))t]f(\boldsymbol{\Gamma}(-t),0)$$

$$= \exp[-\int_0^t 3N\alpha(\boldsymbol{\Gamma}(s-t))ds]f(\boldsymbol{\Gamma}(0),0)$$

$$= \exp[\int_0^{-t} 3N\alpha(\boldsymbol{\Gamma}(s))ds]f(\boldsymbol{\Gamma}(0),0) \tag{55}$$

and therefore,

$$f(\boldsymbol{\Gamma}(t),t) = \exp[\int_0^t 3N\alpha(\boldsymbol{\Gamma}(s))ds]f(\boldsymbol{\Gamma}(0),0) \tag{56}$$

We call this equation the Lagrangian form of the Kawasaki distribution.

Using the Lagrangian form of the Kawasaki distribution function. Since $\mathbf{\Gamma}_2 = \mathbf{\Gamma}_1(t)$, $\mathbf{\Gamma}_5 = \mathbf{\Gamma}_4(t)$,

$$\frac{\mu_{i^*}}{\mu_i} = \frac{f(\mathbf{\Gamma}_1(0),0)}{f(\mathbf{\Gamma}_4(0),0)}$$

$$= \frac{1}{\exp\left[3N\int_0^{2t} ds\, \alpha(\mathbf{\Gamma}_1(s))\right]}$$

$$= \exp\left[-3N\langle\alpha\rangle_{1,3} 2t\right] \tag{57}$$

# REFERENCES

***Nonlinear Response Theory:*** D. J. Evans and G. P. Morriss, *Statistical Mechanics of NonEquilibrium Liquids* (Academic Press, London, 1990).

***Proof of Conjugate Pairing Rule:*** D. J. Evans, E. G. D. Cohen and G. P. Morriss, Phys. Rev., A**42** (1990) 5990.

***Numerical Tests of Conjugate Pairing Rule:*** S. Sarman, D.J. Evans, and G. P. Morriss, Phys. Rev., A**45** (1992) 2233.

***Green Kubo Relation for Lyapunov exponents:*** D.J. Evans, Phys. Rev. Letts., **69** (1992) 395.

***Probability of Second Law violations in Nonequilibrium Steady States***: D.J. Evans, E.G.D. Cohen and G.P. Morriss, Phys. Rev. Letts., **71** (1993) 2401; *ibid* **71** (1993) 3616.

***Equilibrium Microstates which Generate Second Law violating Steady States:*** D.J. Evans and Debra J. Searles, Phys. Rev. E, **50** (1994) 1645.