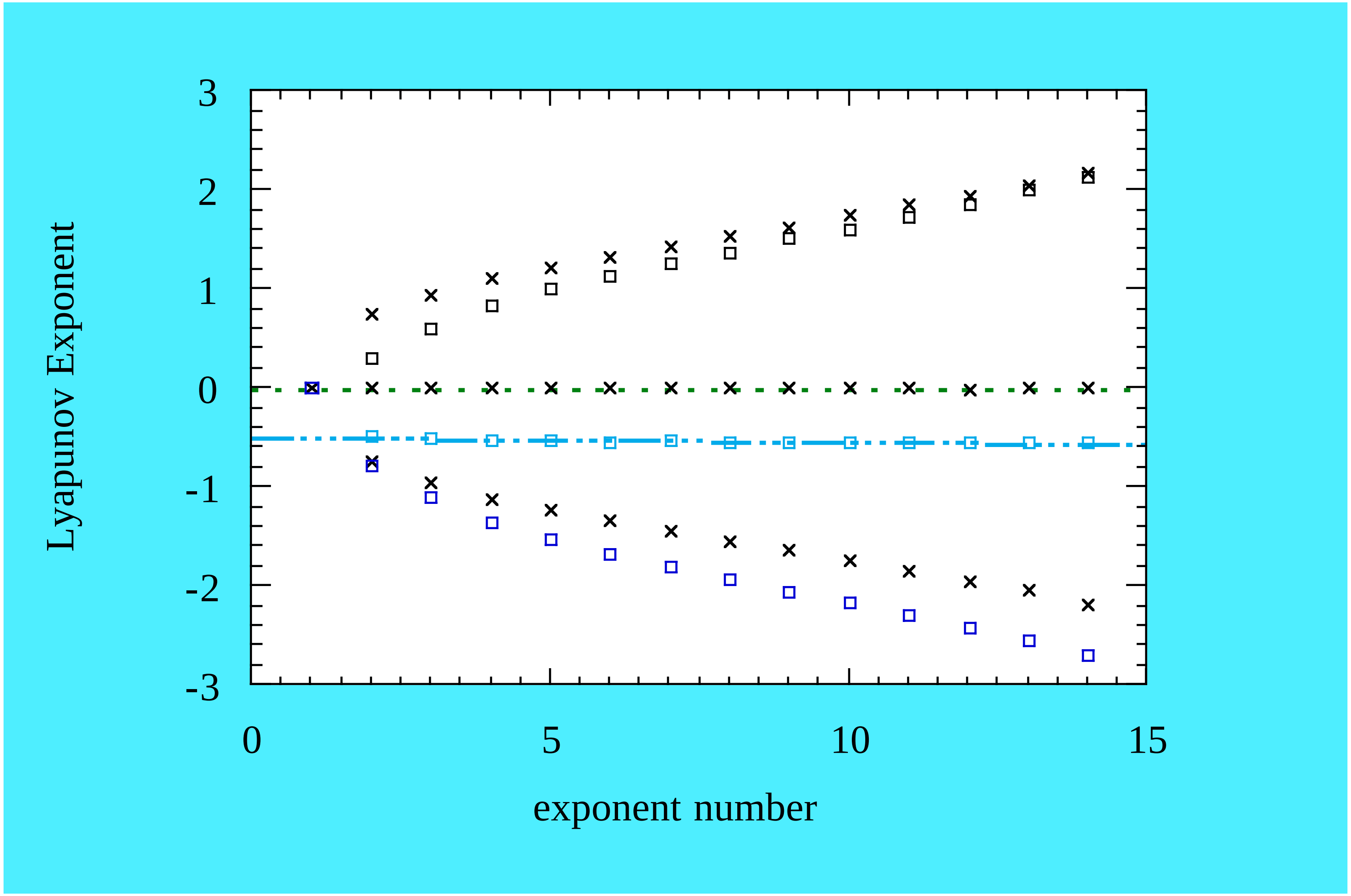
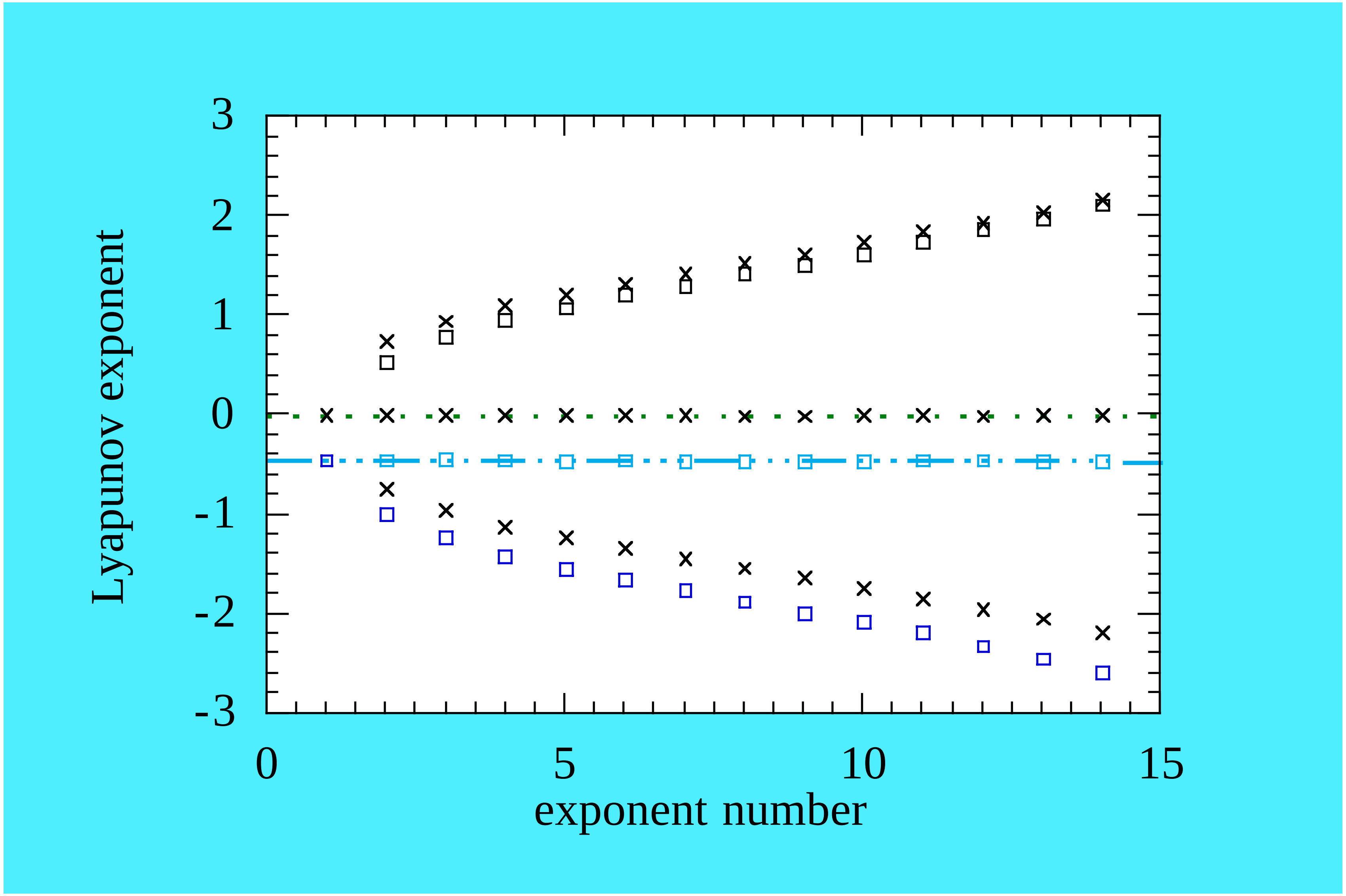


Lyapunov spectrum for colour conductivity of 8 WCA disks.

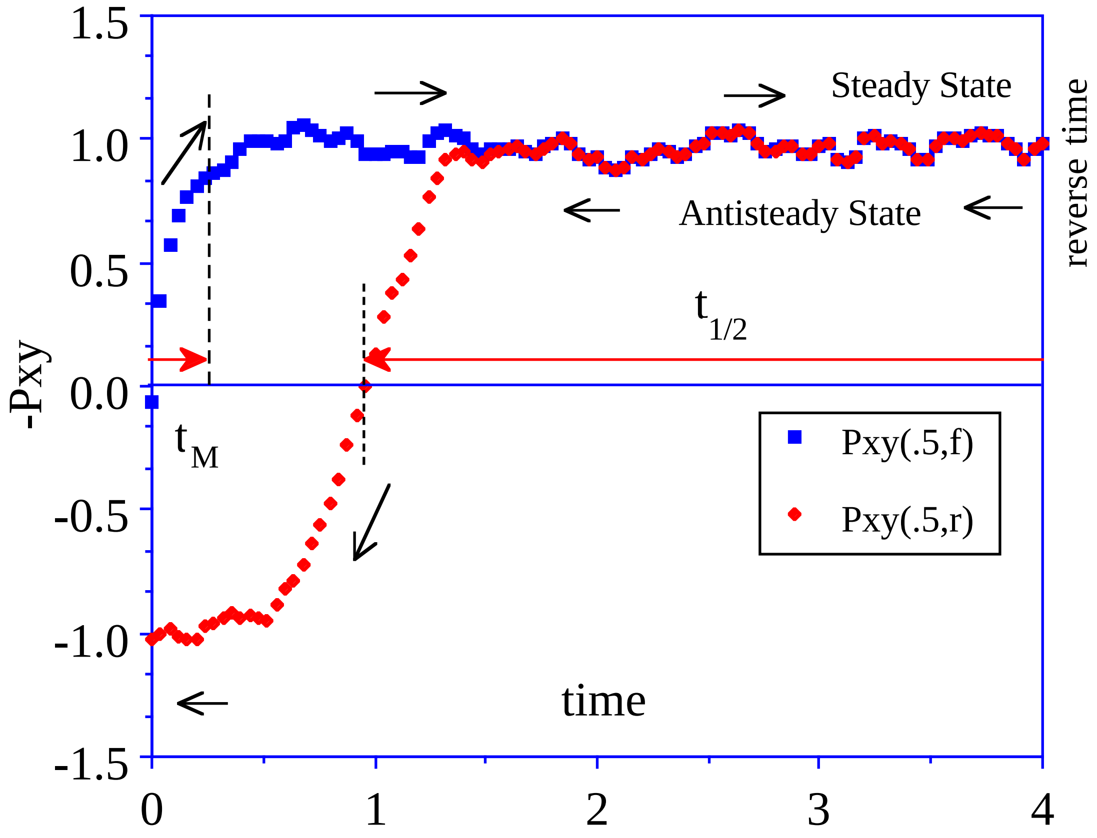


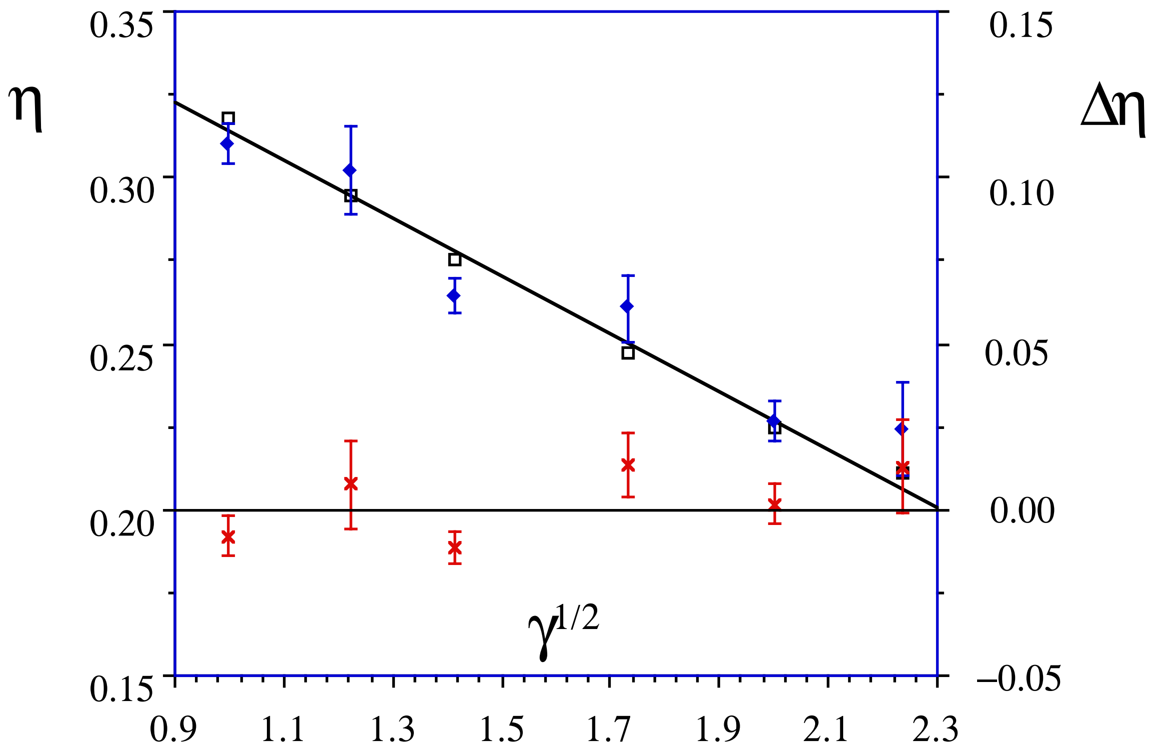
Lyapunov spectrum for shear flow of 8 WCA disks.

Using the Conjugate Pairing Rule, the self diffusion coefficient can be calculated from the maximal Lyapunov exponents in a NEMD Colour Conductivity simulation,

$$D = \frac{-3(kT)^2(\lambda_1 + \lambda_{6N})}{F_c^2} \qquad (43)$$

In order to calculate λ_{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
Steady State
Antisteady State
reverse time
$t_{1/2}$
t_M
time
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:

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

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

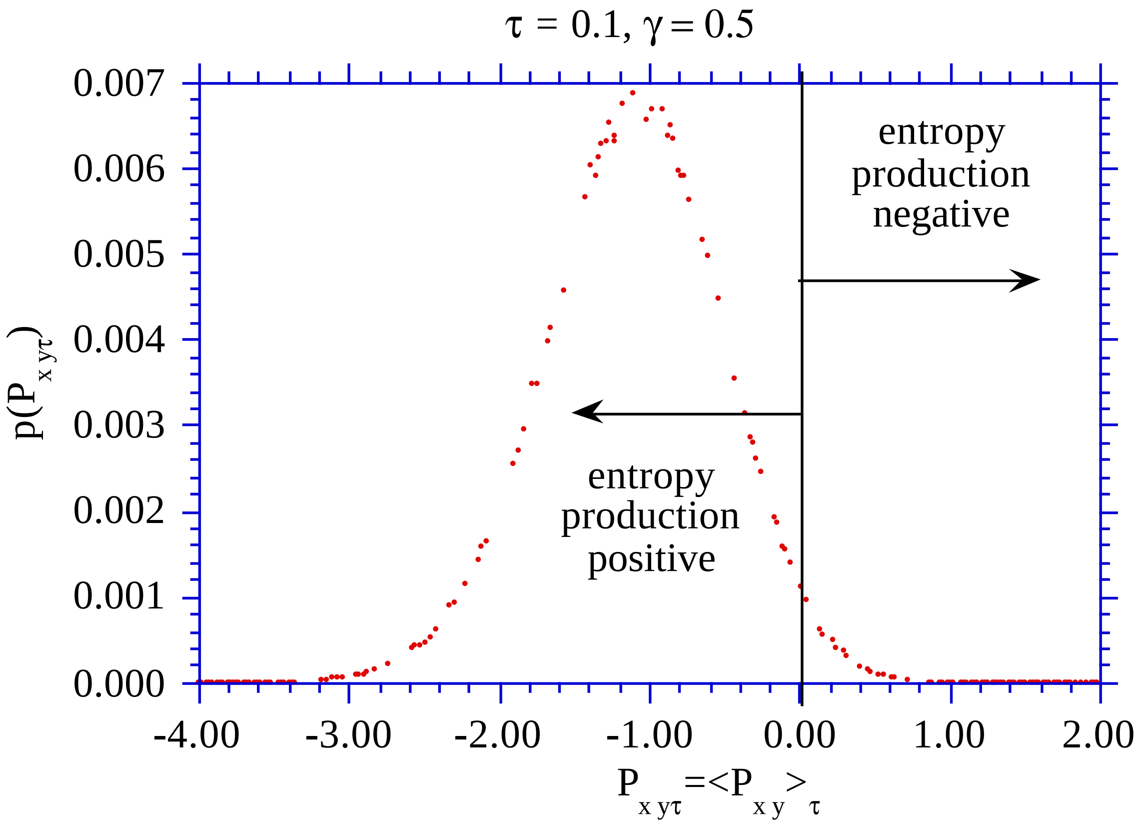
And the ratio of the limiting $(\tau\to\infty)$ probabilities that the system is on a segment i and its conjugate anti segment, i^*, is,

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

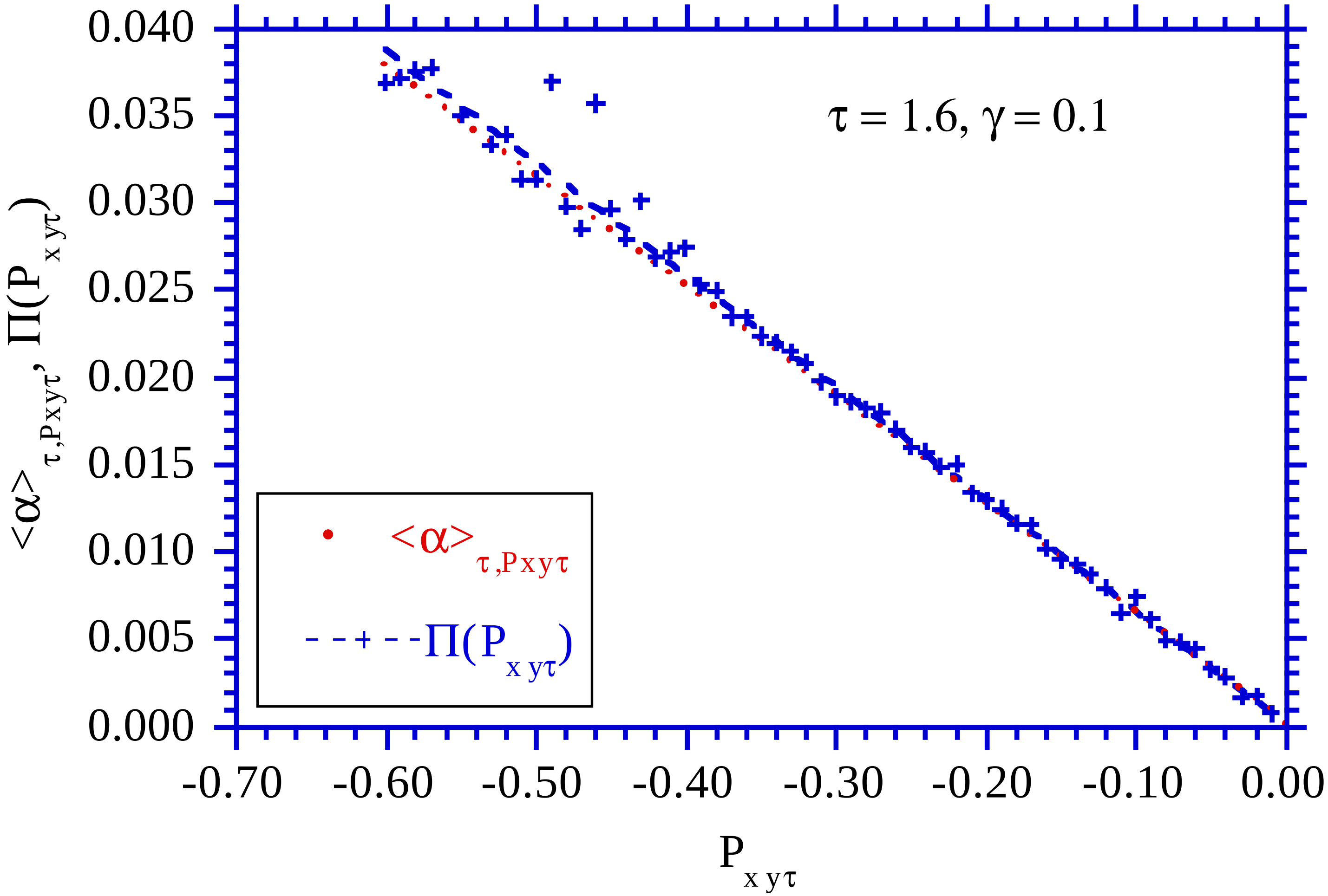
$$= \exp[\tau\sum_{n}\lambda_{ni}] = \exp[-3N <\alpha>_{\tau i}\ \tau] \qquad (45)$$

where we used that,

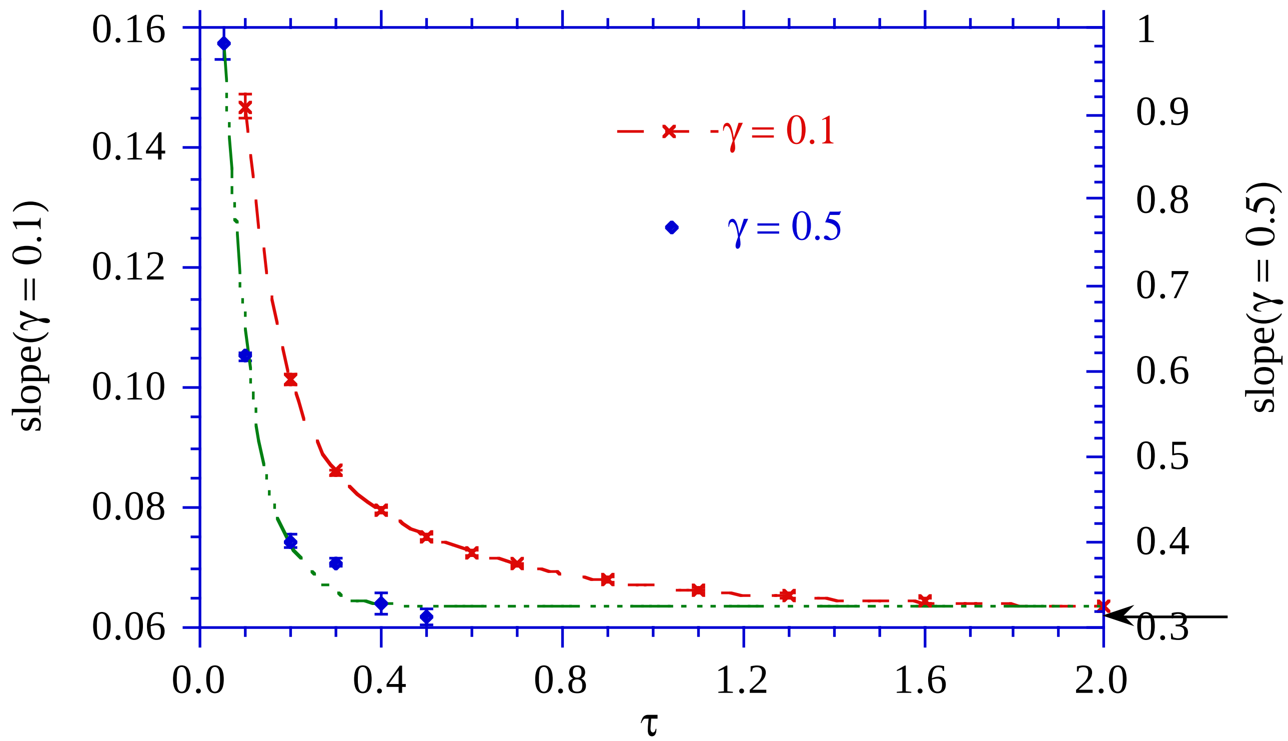
$$3N <\alpha>_{\tau i} = -\sum_{i=1}^{6N}\lambda_{ni} . \qquad (46)$$



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



We plot $\Pi = \ln[p(\langle P_{xy}\rangle_\tau) \,/\, p(\langle -P_{xy}\rangle_\tau)] \,/\, 2N\tau$ and $\langle\alpha\rangle_{\tau,Pxy}$, for τ=1.6 and γ = 0.1. These two functions are essentially linear in $\langle P_{xy}\rangle_\tau$ 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, $\partial\{\ln[p<P_{xy}>_{\tau} \ / \ p<-P_{xy}>_{\tau}]/2N\tau\}/\partial<P_{xy}>_{\tau}$, as a function of τ for γ=0.1, 0.5. The corresponding results for $<\alpha>_{\tau,Pxy}$, are not shown here since they are independent of the averaging time τ. 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 τ-independent, slope of $<\alpha>_{\tau,Pxy}$ as a function of $<P_{xy}>_{\tau}$, which is shown by the arrow.

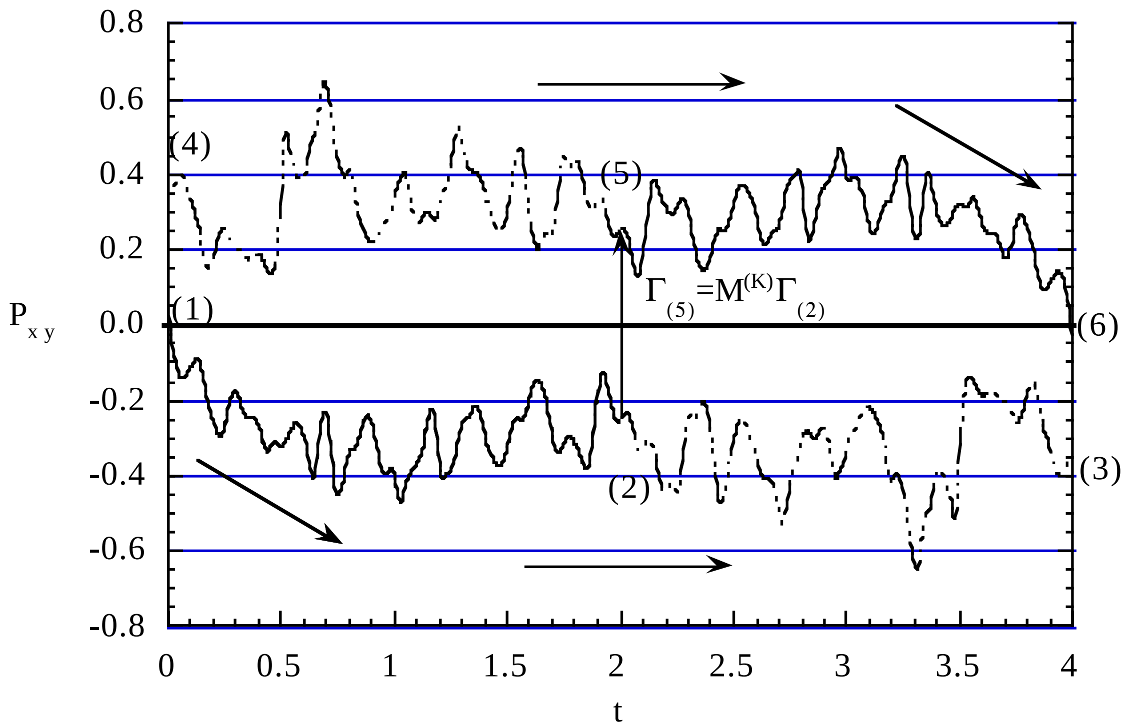
For transient states which evolve from equilibrium at t=0 towards the steady state we define:

$$<P_{xy}>_{\tau,(i)}, \equiv \frac{1}{\tau}\int_0^\tau P_{xy}(\boldsymbol{\Gamma}_{(i)}(s))ds, \tag{47}$$

For every such transient segment, we define the $i^{(K)}$ segment for which $< P_{xy} >_{\tau,(i^{(K)})} = - <P_{xy}>_{\tau,(i)}$. This is the Kawasaki mapped segment.

where, $M^K\Gamma = M^K(x,y,z,p_x,p_y,p_z,\gamma) = (x,-y,z,-p_x,p_y,-p_z,\gamma) \equiv \Gamma^{(K)}$. One can show,

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

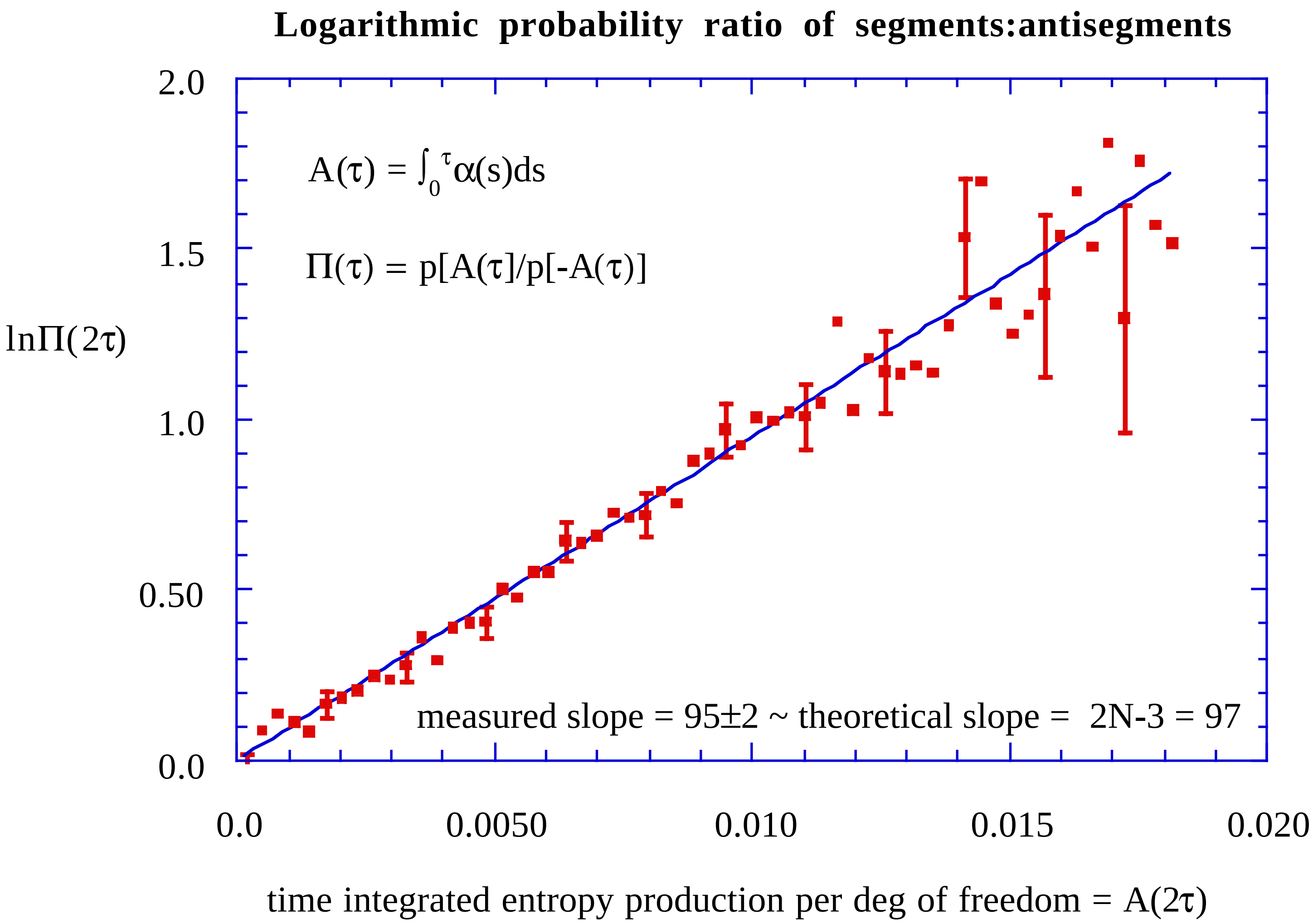


$$V_2 = V_1(\tau) = V_1(0)\exp[-\int_0^{\tau} 3N\alpha(s;\boldsymbol{\Gamma}_{(1)})ds] \tag{49}$$

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

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 Γ it must also be true for Γ(-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,

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

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

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

and therefore,

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

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

Using the Lagrangian form of the Kawasaki distribution function. Since $\Gamma_2=\Gamma_1(t)$, $\Gamma_5=\Gamma_4(t)$,

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

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

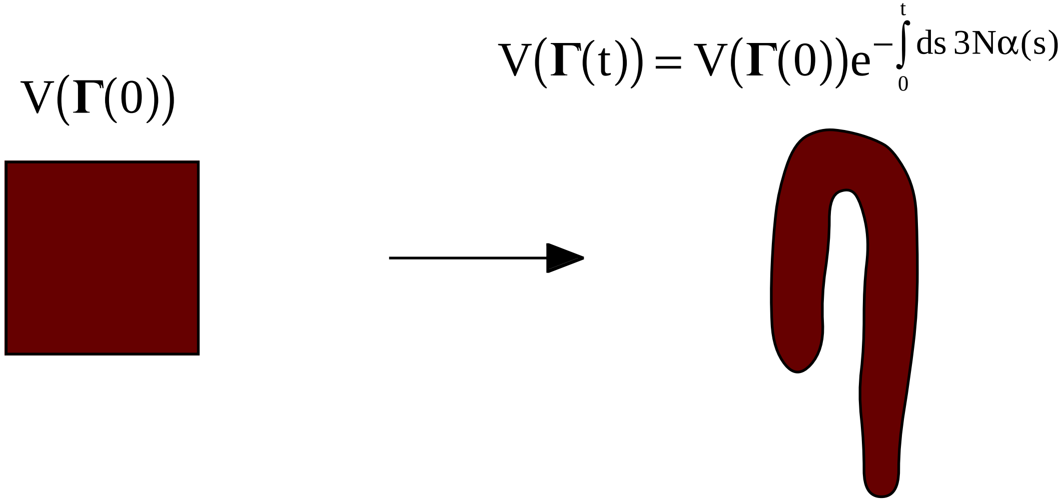
$$= \exp\left[-3N\langle\alpha\rangle_{1,3} 2t\right] \qquad (57)$$

Aside:

$$\frac{d\,\ln V(\boldsymbol{\Gamma}(t))}{dt} = -3N\alpha(t)$$

$$V(\boldsymbol{\Gamma}(t)) = V(\boldsymbol{\Gamma}(0))e^{-\int_0^t ds\, 3N\alpha(s)}$$

$$\Rightarrow f(\boldsymbol{\Gamma}(t),t) = f(\boldsymbol{\Gamma}(0),0)e^{\int_0^t ds\, 3N\alpha(s)}$$



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