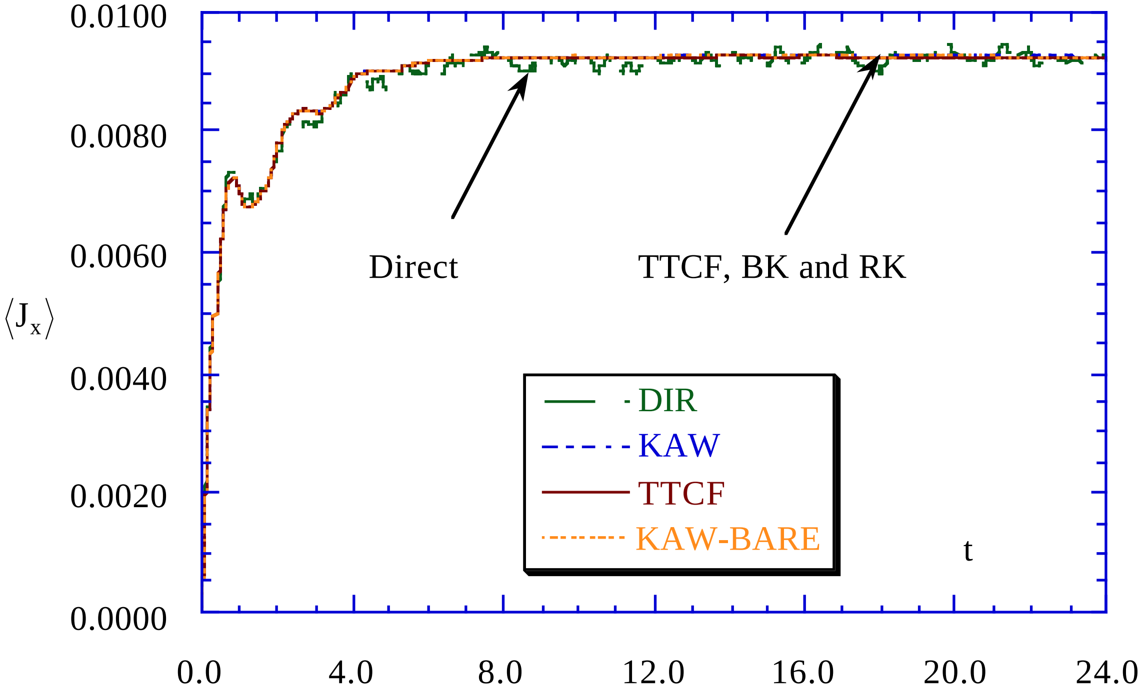
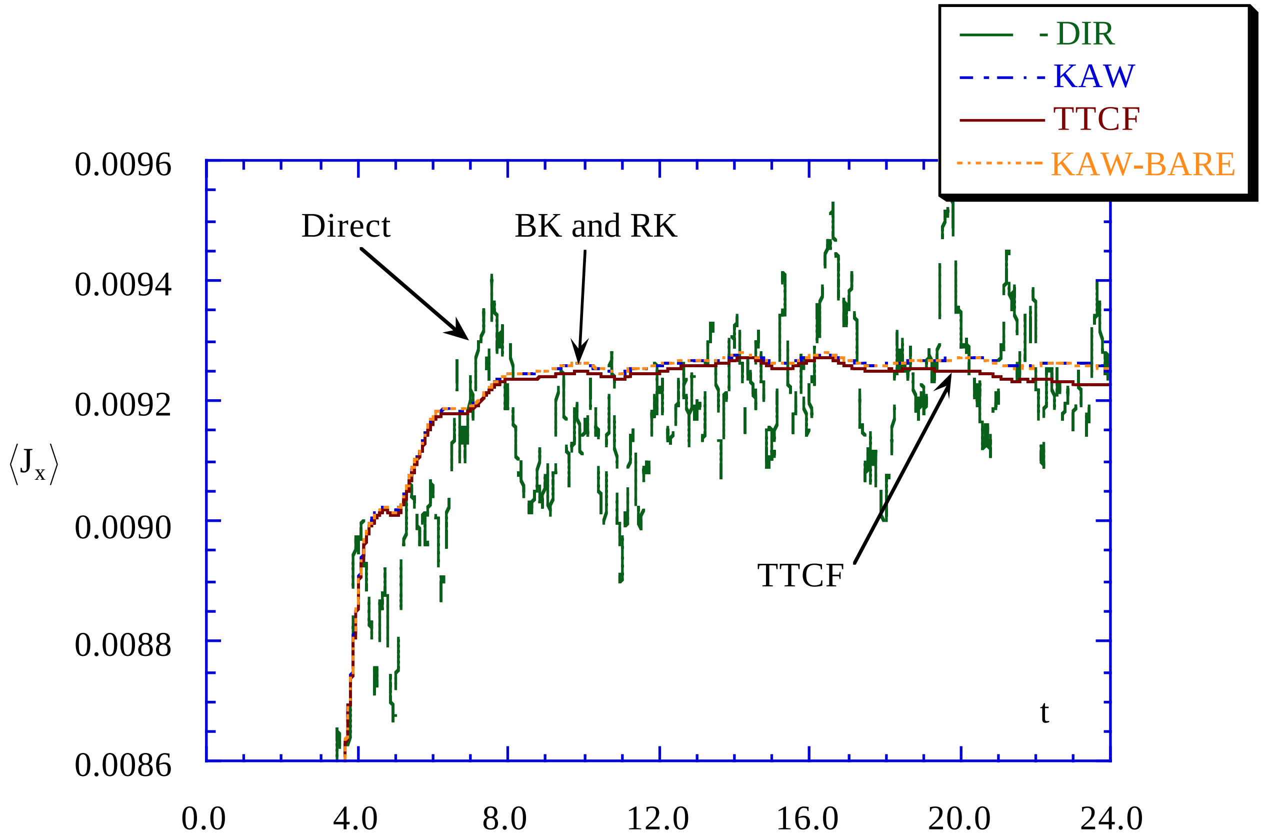
# Tests of Nonlinear Resonse Theory

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
Direct
BK and RK
TTCF
$\langle J_x \rangle$
t
0.0
4.0
8.0
12.0
16.0
20.0
24.0

## Entropy

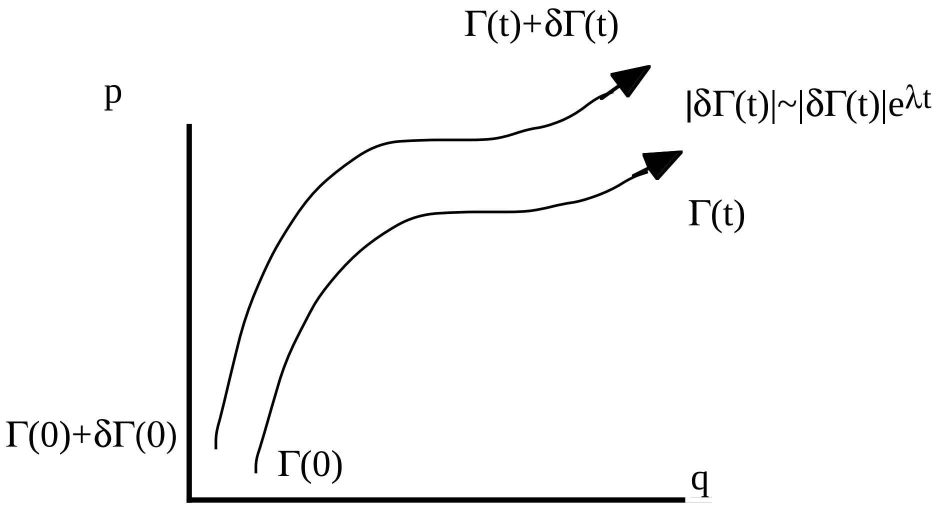
$$S(t) \equiv -k_B \int d\mathbf{\Gamma}\, f(\mathbf{\Gamma},t) \ln f(\mathbf{\Gamma},t)$$

$$\begin{aligned}\dot{S}(t) &= -k_B \int d\mathbf{\Gamma}\, [1 + \ln f(\mathbf{\Gamma},t)] \partial f(\mathbf{\Gamma},t)/\partial t \\ &= -k_B \int d\mathbf{\Gamma}\, \dot{\mathbf{\Gamma}} \bullet \partial f(\mathbf{\Gamma},t)/\partial \mathbf{\Gamma} \\ &= +k_B \int d\mathbf{\Gamma}\, f(\mathbf{\Gamma},t) \partial \dot{\mathbf{\Gamma}} \bullet / \partial \mathbf{\Gamma} \\ &= -3Nk_B \langle \alpha(t) \rangle\end{aligned}$$

In the steady state where averages of phase functions are by definition, time independent, the entropy diverges (at a constant rate) towards -∞!

In the absence of a thermostat the entropy of *any* Hamiltonian system is a constant of the motion (Gibbs, 1902)!

## Instability of Phase Space Trajectories




The equations of motion for the infinitesimal tangent vectors are,

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

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

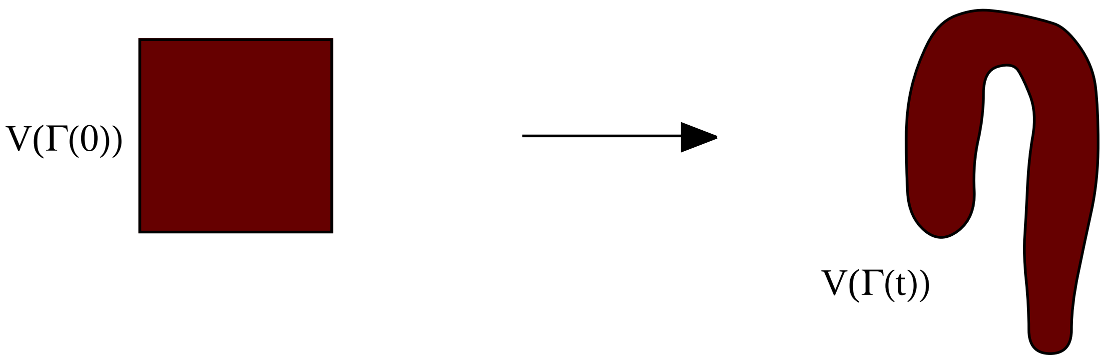
$$\delta\boldsymbol{\Gamma}_i(t) \equiv \exp_L[\int_0^t ds\,\mathbf{T}(\boldsymbol{\Gamma}(s))]\bullet\delta\boldsymbol{\Gamma}_i(0) \equiv \mathbf{L}(t)\bullet\delta\boldsymbol{\Gamma}_i(0), \tag{32}$$

The *Lyapunov exponents* are also the logarithms of the eigenvalues of the symmetric matrix, Λ,

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

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

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




In the steady state,

$$\left\langle \dot{H}_0 \right\rangle = 0 = -\left\langle P_{xy} \right\rangle \gamma V - 2K\langle\alpha\rangle$$
$$\Rightarrow \eta(\gamma)\gamma^2 V = 3Nk_B T\langle\alpha\rangle$$
$$\Rightarrow \sum_{i=1}^{6N} \lambda_i = -3N\langle\alpha\rangle = -\eta(\gamma)\gamma^2 V \big/ k_B T$$

so,

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

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

## Symplectic Matrices

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

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

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,

$$\mathbf{T}^{T}\bullet\mathbf{J} = -\mathbf{J}\bullet\mathbf{T} \tag{37}$$

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

$$\mathbf{T} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & -\mathbf{A}^{T} \end{pmatrix} \tag{38}$$

where the matrices **B** and **C** are symmetric. **L**, satisfies the *globally symplectic* condition if,

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

Identities:

If $\mathbf{L}$ is g-symplectic: $\mathbf{L}^{T}\bullet\mathbf{J}\bullet\mathbf{L} \equiv \mathbf{J}$

Using the fact that $\mathbf{J}\bullet\mathbf{J} = -\mathbf{1}$,

$$\mathbf{L}^{T}\bullet\mathbf{J}\bullet\mathbf{L} = \mathbf{J} \;\Rightarrow\; \mathbf{L}^{T}\bullet\mathbf{J}\bullet\mathbf{L}\bullet\mathbf{J} = -\mathbf{1} \Rightarrow\; \mathbf{L}^{T}\bullet\mathbf{J}\bullet\mathbf{L}\bullet\mathbf{J}\bullet\mathbf{L}^{T} = -\mathbf{L}^{T}$$

$$\Rightarrow \mathbf{L}^{T\text{-}1}\bullet\; \mathbf{L}^{T}\bullet\mathbf{J}\bullet\mathbf{L}\bullet\mathbf{J}\bullet\mathbf{L}^{T} = -\mathbf{L}^{T\text{-}1}\bullet\mathbf{L}^{T} \Rightarrow \mathbf{J}\bullet\mathbf{L}\bullet\mathbf{J}\bullet\mathbf{L}^{T} = -\mathbf{1}$$

$$\Rightarrow \mathbf{L}\bullet\mathbf{J}\bullet\mathbf{L}^{T} = \mathbf{J}$$

If, $\mathbf{\Lambda} \equiv \mathbf{L}^{T} \bullet \mathbf{L}$ then $\mathbf{\Lambda}$ is g – symplectic

$\mathbf{\Lambda}^{T} \bullet \mathbf{J} \bullet \mathbf{\Lambda} = \mathbf{J} \;\; = \mathbf{\Lambda} \bullet \mathbf{J} \bullet \mathbf{\Lambda}$

Pf :

$(\mathbf{L}^{T} \bullet \mathbf{L})^{T} \bullet \mathbf{J} \bullet \mathbf{L}^{T} \bullet \mathbf{L} = \mathbf{L}^{T} \bullet \mathbf{L} \bullet \mathbf{J} \bullet \mathbf{L}^{T} \bullet \mathbf{L}$

$= \mathbf{L}^{T} \bullet \mathbf{J} \bullet \mathbf{L}$

$= \mathbf{J}$

If $\mathbf{L}$ is g-symplectic and

$\mathbf{L}(t) \equiv e_{L}^{\int_0^t \mathbf{T}(s)ds}$

then $\mathbf{T}$ is i-symplectic.

Differentiate wrt t,

$\mathbf{L}^{T} \bullet \mathbf{T}^{T}(t) \bullet \mathbf{J} \bullet \mathbf{L} + \mathbf{L}^{T} \bullet \mathbf{J} \bullet \mathbf{T}(t) \bullet \mathbf{L} = 0$

$\therefore \mathbf{T}^{T} \bullet \mathbf{J} = -\mathbf{J} \bullet \mathbf{T}$

Conversely if $\mathbf{T}$ is i-symplectic then $\mathbf{L}$ is g-symplectic.

$\mathbf{T}^{T}(t) \bullet \mathbf{J} = -\mathbf{J} \bullet \mathbf{T}(t), \quad \forall t \ldots$ §

then at t = 0

$\mathbf{L}^{T}(0) \bullet \mathbf{J} \bullet \mathbf{L}(0) = \mathbf{J}$ (Because $\mathbf{L}(0) = \mathbf{1}$)… #

Differentiate wrt t :

$$\frac{d}{dt}\mathbf{L}^{T}(t)\bullet\mathbf{J}\bullet\mathbf{L}(t)=\mathbf{L}^{T}(t)\bullet(\mathbf{T}^{T}(t)\bullet\mathbf{J}+\mathbf{J}\bullet\mathbf{T}(t))\bullet\mathbf{L}(t)$$

If we use § we see that

$$\frac{d}{dt}\mathbf{L}^{T}(t)\bullet\mathbf{J}\bullet\mathbf{L}(t)=0,\quad \forall t$$

Combining this with #, we see that

$$\therefore \mathbf{L}^{T}(t)\bullet\mathbf{J}\bullet\mathbf{L}(t)=\mathbf{J},\quad \forall t.$$

$\mathbf{L}$ is g-symplectic iff $\mathbf{T}$ is i – symplectic

## i-form of the Symplectic Eigenvalue theorem

If $\mathbf{T}^{T}\bullet\mathbf{J}=-\mathbf{J}\bullet\mathbf{T}$

$$\mathbf{T} \bullet \mathbf{u}_i = \nu_i \mathbf{u}_i$$

$$\mathbf{J} \bullet \mathbf{T} \bullet \mathbf{u}_i = \nu_i \mathbf{J} \bullet \mathbf{u}_i$$

$$\mathbf{T}^T \bullet \mathbf{J} \bullet \mathbf{u}_i = -\nu_i \mathbf{J} \bullet \mathbf{u}_i$$

and therefore if $\nu_i$ is an eigenvalue of the i-symplectic matrix **T**, so too is $-\nu_i^*$.

## g-form of the Symplectic Eigenvalue theorem

If, **L** is g-symplectic and

$$\mathbf{L} \bullet \mathbf{x} = \lambda \mathbf{x}$$

$$(\mathbf{J} \bullet \mathbf{x})^T \bullet \mathbf{L} = \mathbf{x}^T \bullet \mathbf{J}^T \bullet \mathbf{L}$$

But from the g-symp condition,

$$\mathbf{L}^T \bullet \mathbf{J}^T \bullet \mathbf{L} \equiv \mathbf{J}^T \Rightarrow \mathbf{J}^T \bullet \mathbf{L} = \mathbf{L}^{T-1} \bullet \mathbf{J}^T$$

So,

$$(\mathbf{J} \bullet \mathbf{x})^T \bullet \mathbf{L} = \mathbf{x}^T \bullet \mathbf{L}^{T-1} \bullet \mathbf{J}^T$$

From the eigenvalue equation

$(\mathbf{L} \bullet \mathbf{x})^{\mathrm{T}} = \mathbf{x}^{\mathrm{T}} \bullet \mathbf{L}^{\mathrm{T}} = \lambda \mathbf{x}^{\mathrm{T}}$

and

$\mathbf{x}^{\mathrm{T}} \bullet \mathbf{L}^{\mathrm{T}-1} = \lambda^{-1} \mathbf{x}^{\mathrm{T}}$

Substituting gives,

$(\mathbf{J} \bullet \mathbf{x})^{\mathrm{T}} \bullet \mathbf{L} = \lambda^{-1} \mathbf{x}^{\mathrm{T}} \bullet \mathbf{J}^{\mathrm{T}} = \lambda^{-1} (\mathbf{J} \bullet \mathbf{x})^{\mathrm{T}}$

and $(\mathbf{J} \bullet \mathbf{x})^{\mathrm{T}}$ is an eigenvector of $\mathbf{L}$ with eigenvalue $\lambda^{-1}$

$\Rightarrow \mathbf{J} \bullet \mathbf{x}$ is an eigenvector of $\mathbf{L}^{\mathrm{T}}$ with eigenvalue $\lambda^{-1}$

$\Rightarrow \lambda^{-1}$ is an eigenvalue of $\mathbf{L}$

## Conjugate Pairing Rule for Lyapunov Exponents

The Lyapunov exponents are the logarithms of the eigenvalues of the real symmetric matrix $\mathbf{\Lambda}(t) = \left[\mathbf{L}^{\dagger}(t) \bullet \mathbf{L}(t)\right]^{1/2t}$, and $\mathbf{\Lambda} = \lim_{t \to \infty} \mathbf{\Lambda}(t)$. If $\mathbf{L}$ is g-symplectic then $\Lambda$ is g-symplectic so that,

$$\mathbf{\Lambda}^{T} \bullet \mathbf{J} \bullet \mathbf{\Lambda} = \mathbf{\Lambda} \bullet \mathbf{J} \bullet \mathbf{\Lambda} = \mathbf{J}$$

Clearly therefore,

$$\mathbf{J} \bullet \mathbf{\Lambda} = \mathbf{\Lambda}^{-1} \bullet \mathbf{J}$$

If $\mathbf{u}_i$ is an eigenvector of $\Lambda$ with real eigenvalue $\nu_i$,

$$\mathbf{\Lambda} \bullet \mathbf{u}_i = \nu_i \mathbf{u}_i$$

$$\mathbf{J} \bullet \mathbf{\Lambda} \bullet \mathbf{u}_i = \nu_i \mathbf{J} \bullet \mathbf{u}_i$$

$$\mathbf{\Lambda}^{-1} \bullet \mathbf{J} \bullet \mathbf{u}_i = \nu_i \mathbf{J} \bullet \mathbf{u}_i$$

Rearranging gives that,

$$\mathbf{\Lambda} \bullet \mathbf{J} \bullet \mathbf{u}_i = \nu_i^{-1} \mathbf{J} \bullet \mathbf{u}_i$$

This implies that $\mathbf{J} \bullet \mathbf{u}_i$ is an eigenvector of $\Lambda$ with eigenvalue $\nu_i^{-1}$. The Lyapunov exponent corresponding to the eigenvector $\mathbf{u}_i$ is $\lambda_i = \ln(\nu_i)$, and that corresponding to

$\mathbf{J}\bullet\mathbf{u}_i$ is $\lambda_{i*} = -\ln(\nu_i)$. Thus for dynamical systems with an i-symplectic local stability matrix (or equivalently with a g-symplectic tangent propagator matrix **L**), ***Lyapunov exponents occur in conjugate pairs which sum to zero***.

## Thermostatted Hamiltonian systems.

$$\mathbf{L}(t) = \exp_L \int_0^t ds\mathbf{T}(s) = \exp_L \int_0^t ds[\mathbf{T'}(s) - \alpha(s)\mathbf{1}/2] \equiv \mathbf{L'}(t)e^{-t\bar{\alpha}/2}$$

where

$$\bar{\alpha} \equiv {}^1\!/_t \int_0^t \alpha(s)ds .$$

**T**' has the i-symplectic symmetry so **T**' is i-symplectic and **L**' is g-symplectic. Letting

$$\mathbf{\Lambda}' = \lim_{t\to\infty}\left[\mathbf{L}'^{\dagger}(t) \bullet \mathbf{L}'(t)\right]^{1/2t}$$

we know that $\Lambda'$ is also g-symplectic and since,

$\Lambda = \Lambda'.\exp[-\bar{\alpha}/2]$ and, $\mathbf{\Lambda}' \bullet \mathbf{J} \bullet \mathbf{\Lambda}' = \mathbf{J}$, so

$$\mathbf{\Lambda} \bullet \mathbf{J} \bullet \mathbf{\Lambda} = e^{-\bar{\alpha}}\mathbf{\Lambda}' \bullet \mathbf{J} \bullet \mathbf{\Lambda}' = e^{-\bar{\alpha}}\mathbf{J}$$

$$\mathbf{J} \bullet \mathbf{\Lambda} = e^{-\bar{\alpha}}\mathbf{\Lambda}^{-1} \bullet \mathbf{J} .$$

If

$$\mathbf{\Lambda} \bullet \mathbf{u}_i = \nu_i \mathbf{u}_i$$

$$\mathbf{J} \bullet \mathbf{\Lambda} \bullet \mathbf{u}_i = e^{-\overline{\alpha}} \mathbf{\Lambda}^{-1}(t) \bullet \mathbf{J} \bullet \mathbf{u}_i = \nu_i \mathbf{J} \bullet \mathbf{u}_i$$

$$\mathbf{\Lambda}(t) \bullet \mathbf{J} \bullet \mathbf{u}_i = \nu_i^{-1} e^{-\overline{\alpha}} \mathbf{J} \bullet \mathbf{u}_i$$

Thus if $\mathbf{u}_i$ is an eigenvector with eigenvalue $\nu_i$, $\mathbf{J}.\mathbf{u}_i$ is an eigenvector with eigenvalue $\nu_i^{-1} e^{-\overline{\alpha}}$. The Lyapunov exponent corresponding to the eigenvector $\mathbf{u}_i$ is $\lambda_i = \ln(\nu_i)$, and that corresponding to $\mathbf{J} \bullet \mathbf{u}_i$ is $\lambda_{i*} = -\ln(\nu_i) - \overline{\alpha}$. This in turn implies that if $\lambda_i$ is a Lyapunov exponent, its conjugate exponent is $\lambda_{i*} = -\lambda_i - \overline{\alpha}$ and the sum of the conjugate pairs of exponents is $-\overline{\alpha}$, independent of the pair index. This is known as the ***Conjugate Pairing Rule***.

$$L(F_e) = \frac{3nkT(\lambda_1(F_e) + \lambda_{6N}(F_e))}{F_e^2}$$