Fluctuation Relations for systems far from equilibrium

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Do fluctuation relations need to be modified in the far from equilibrium regime?

Plan

- Fluctuation Relations
- Types of Fluctuation Relations
- Motivation for this work
- Adjustments to Fluctuation Relations far from Equilibrium?
  - **Numerical results**
- Conclusions

Fluctuation Relations

- In general describes the ratio of the probability of observing trajectory segments with the values of a phase function with equal magnitude, but opposite sign:

$$\frac{p(\bar{\Phi}_t = A)}{p(\bar{\Phi}_t = -A)} = \ldots \qquad \lim_{t\to\infty} \frac{1}{t} \ln \frac{p(\bar{\Phi}_t = A)}{p(\bar{\Phi}_t = -A)} = \ldots$$

- In some special cases:

$$\frac{p(\bar{\Phi}_t = A)}{p(\bar{\Phi}_t = -A)} = e^{At} \qquad \lim_{t\to\infty} \frac{1}{t} \ln \frac{p(\bar{\Phi}_t = A)}{p(\bar{\Phi}_t = -A)} = A$$

- Notation: $\bar{\Phi}_t = \frac{1}{t}\int_0^t \Phi(\Gamma(s))ds$

$$p(\bar{\Phi}_t = A) \qquad p(A - dA < \bar{\Phi}_t < A + dA)$$

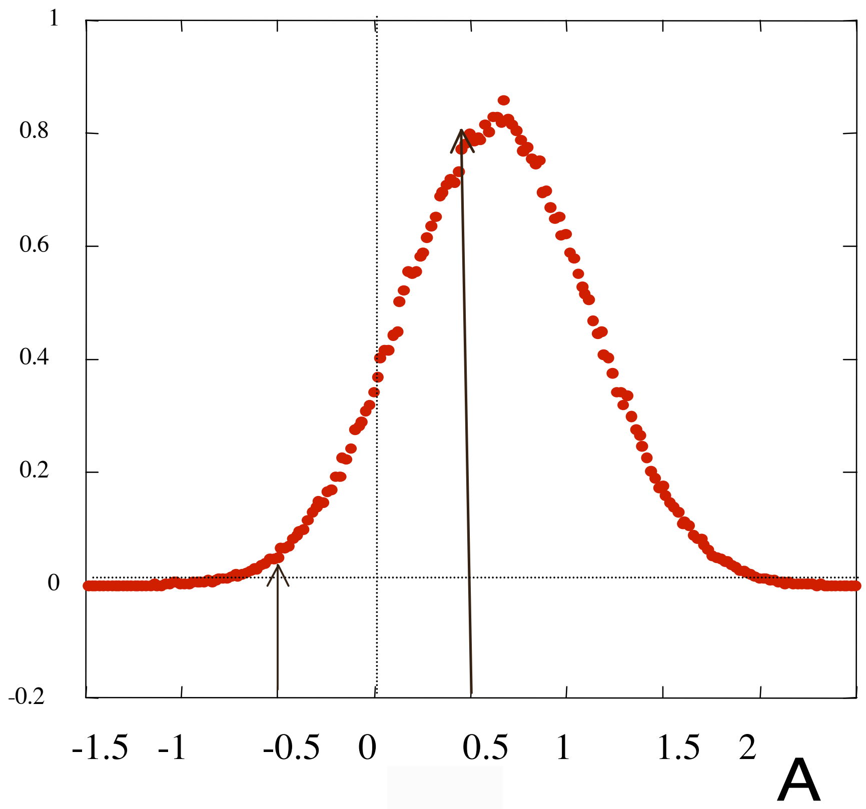
Evans & Searles, Ad. Phys. **51**, 1529-1585 (2002)

Fluctuation Relations

$$\frac{p(\bar{\Phi}_t = A)}{p(\bar{\Phi}_t = -A)} = \dots$$

$$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(\bar{\Phi}_t = A)}{p(\bar{\Phi}_t = -A)} = \dots$$

$$p(\bar{\Phi}_t = A)$$



Types of Fluctuation Relation

- Focus here on nonequilibrium steady state systems, or systems approaching a steady state from a known state

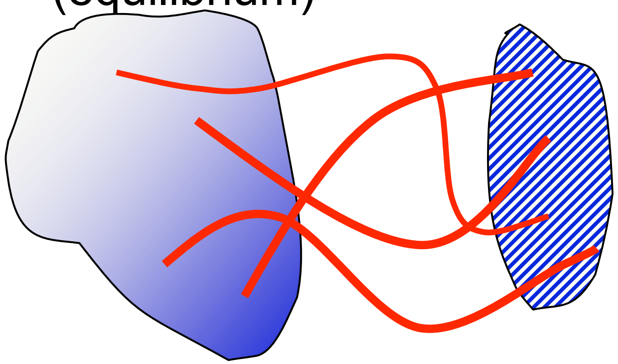
- How the segments are sampled:
  - Transient
  - Ensemble of Steady States
  - Segments from a single steady state trajectory
- The argument of the relation
- The way in which they are derived

Sampling

Transient relations

known distribution (equilibrium)

steady state

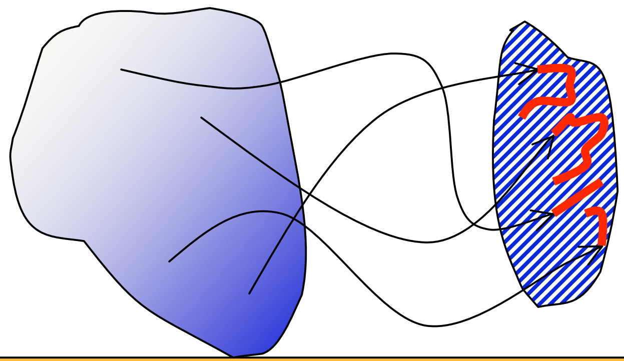


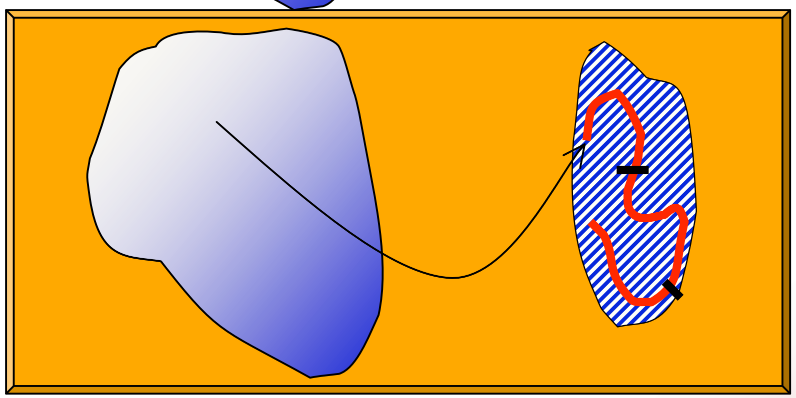
True at all t

Steady state relations

known distribution (equilibrium)

steady state





True at long t

Steady State Fluctuation Relations

- Dissipation function fluctuation relation:

Dissipation function

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = A \qquad p(\bar{\Omega}_t = A) \neq 0; p(\bar{\Omega}_t = -A) \neq 0$$

- Phase space expansion fluctuation relation

Phase space expansion

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = A \qquad -A^* < A < A^*$$

Differences

$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = A$	$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = A$
Derived from the transient fluctuation relation which is obtained from the Liouville measure (also Lyapunov measure) (Evans Searles)	For systems that are Anosov or satisfy the chaotic hypothesis (Gallavotti Cohen)
Argument is the dissipation function: which is proportional to the dissipative flux for systems that satisfy AIΓ.	Argument is the phase space expansion rate
Applies for all A provided p(A)≠0 and p(-A)≠0	Applies for a restricted range of A: but at least $-\langle A \rangle < A < \langle A \rangle$

Similarities

$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = A$	$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = A$
Require chaos; steady state exists	
When dynamics is isoenergetic: $\bar{\Lambda}_t = -\bar{\Omega}_t$ and the relations are identical (but might apply over different domains, and aren't derived in the same way)	

Differences

$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = A$	$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = A$
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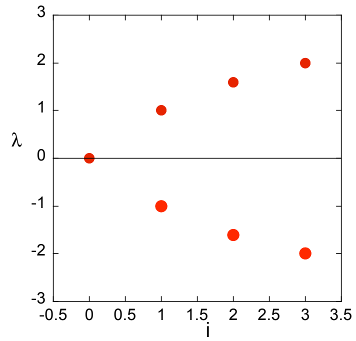
Argument is the dissipation function: which is proportional to the dissipative flux for systems that satisfy AIΓ.	Argument is the phase space expansion rate
Applies for all A provided p(A)≠0 and p(-A)≠0	Applies for a restricted range of A: but at least $-\langle A \rangle < A < \langle A \rangle$
Applies at all fields (provided only one steady state exists)	**Breaks down at high fields, when the equality of number of ± Lyapunov exponents is broken (dimension of the attractive set smaller than that of the full phase space)**

High Field Fluctuation Relation

- At high fields it has been proposed that the FR gives[a]

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = XA$$



X is ~ the ratio of number of ± pairs to the number of pairs of Lyapunov exponents

- Furthermore, it has been argued that from this relationship the dissipative flux relation can be obtained[b] (**not** just for isoenergetic systems) and therefore

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = XA$$

a) F. Bonetto, G. Gallavotti, and P. L. Garrido, Physica D **105**, 226 (1997).

b) A. Giuliani, F. Zamponi, and G. Gallavotti, J. Stat. Phys. **119**, 909 (2005).

Motivation

- For some range of A, the two different approaches lead to two different relationships for the same system (unless A*=0). Both cannot apply

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = A \qquad \lim_{t\to\infty}\frac{1}{t}\ln\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = XA$$

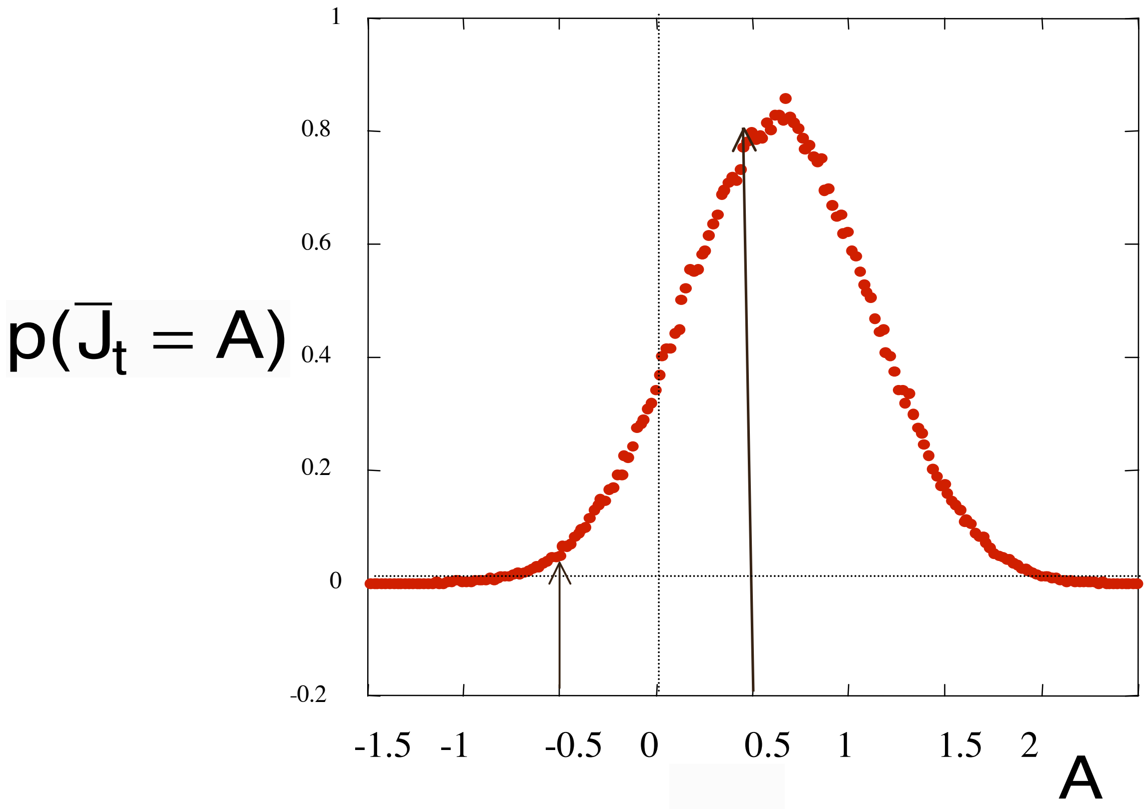
- Can we test which one applies to a simple system that represent the nonequilibrium steady state dynamics that we are interested in?

S. R. Williams, D. J. Searles and D. J. Evans, J. Chem. Phys., 124, 194102 (2006)

System to study

- Need fields high enough that the numbers of +ve and -ve Lyapunov exponents do not match
- Need to still be able to observe trajectory segments with ±A
- Need systems with few degrees of freedom so that X is significant.
- Need to select a system for which both expressions would be expected to apply, according to theory or systems studied previously
- Selected a simple Nosé-Hoover thermostatted dynamics - model of heat conduction

Fluctuation Relations



System to study

- Equations of motion:

$$\dot{q} = p$$

$$\dot{p} = -q - \alpha_1 p - \alpha_3 p^3 - \alpha_5 p^5$$

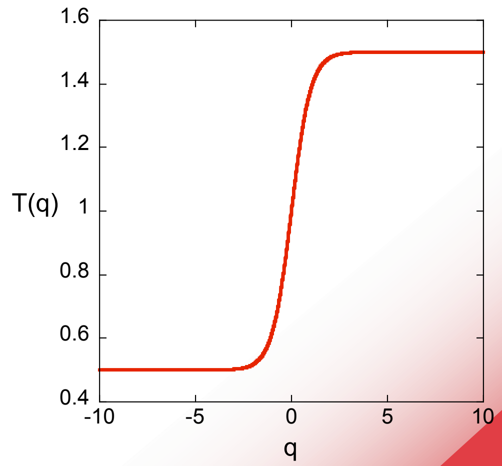
$$\dot{\alpha}_1 = \frac{(p^2 - T(q))}{\tau_1^2}$$

$$\dot{\alpha}_3 = \frac{(p^4 - 3p^2 T(q))}{\tau_3^2}$$

$$\dot{\alpha}_5 = \frac{(p^6 - 3p^4 T(q))}{\tau_5^2}$$

$$T(q) = 1 + \varepsilon \tanh(q)$$

Drives system out of eq.



Equilibrium distribution function

$$H = H_0 + \tfrac{1}{2}\left(\tau_1^2 \alpha_1{}^2 + \tau_3^2 \alpha_3{}^2 + \tau_5^2 \alpha_5{}^2\right) = \tfrac{1}{2}\left(q^2 + p^2 + \tau_1^2 \alpha_1{}^2 + \tau_3^2 \alpha_3{}^2 + \tau_5^2 \alpha_5{}^2\right)$$

$$f\left(q, p, \alpha_1, \alpha_3, \alpha_5\right) \sim \frac{\tau_1 \tau_3 \tau_5}{\left(2\pi\right)^{5/2}} \exp\left(-H\left(q, p, \alpha_1, \alpha_3, \alpha_5\right)\right)$$

Dissipation function and Phase space expansion rate

$$\Omega\left(q,p,\alpha_1,\alpha_3,\alpha_5\right)=\dot{H}-\Lambda=\left(1-T\left(q\right)\right)\left(\alpha_1+3\alpha_3 p^2+5\alpha_5 p^4\right)$$

$$\begin{aligned}\Lambda\left(p,\alpha_1,\alpha_3,\alpha_5\right)&=\frac{\partial\dot{q}}{\partial q}+\frac{\partial\dot{p}}{\partial p}+\frac{\partial\dot{\alpha}_1}{\partial\alpha_1}+\frac{\partial\dot{\alpha}_3}{\partial\alpha_3}+\frac{\partial\dot{\alpha}_5}{\partial\alpha_5}\\&=-\alpha_1-3\alpha_3 p^2-5\alpha_5 p^4\\&=-\Omega-T(q)(\alpha_1+3\alpha_3 p^2+5\alpha_5 p^4)\end{aligned}$$

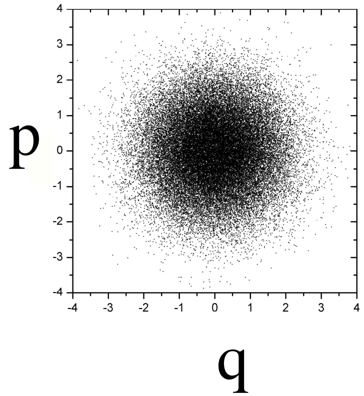
$$\left\langle\dot{H}\right\rangle=0\qquad\Rightarrow\qquad\left\langle\Lambda\right\rangle=-\left\langle\Omega\right\rangle$$

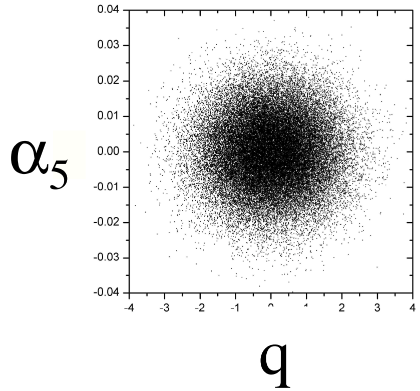
Lyapunov exponents

ε	λ_1	λ_2	λ_3	λ_4	Error in exponents (~2 SE)	
0	0.0173	0.0025	-0.0025	-0.0173	0.0001	X=1
0.1	0.0195	0.0028	-0.0032	-0.0199	0.0001	.
0.2	0.0190	0.0018	-0.0055	-0.0226	0.0001	.
0.3	0.0131	0.0010	-0.0089	-0.0288	0.0001	. .
0.4	0.0080	0.0008	-0.0082	-0.0320	0.0001	X=1
0.43	0.0063	-0.0009	-0.0088	-0.0222	0.0001	X=1/2
0.45	0.00130	-0.00400	-0.01330	-0.02310	0.00003	X=1/2

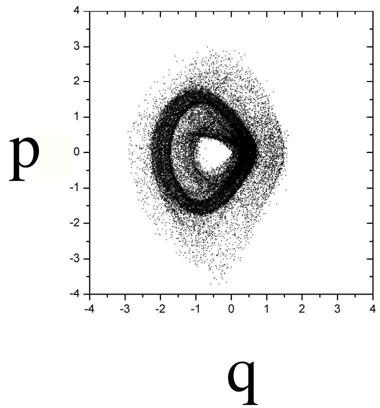
Phase space projections

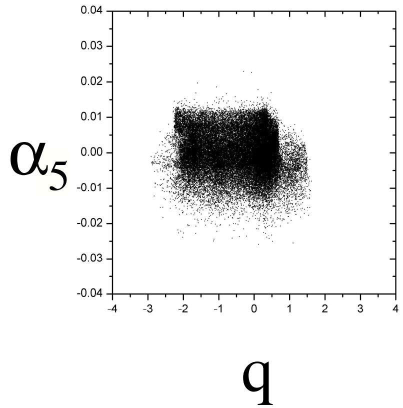
$\varepsilon = 0$



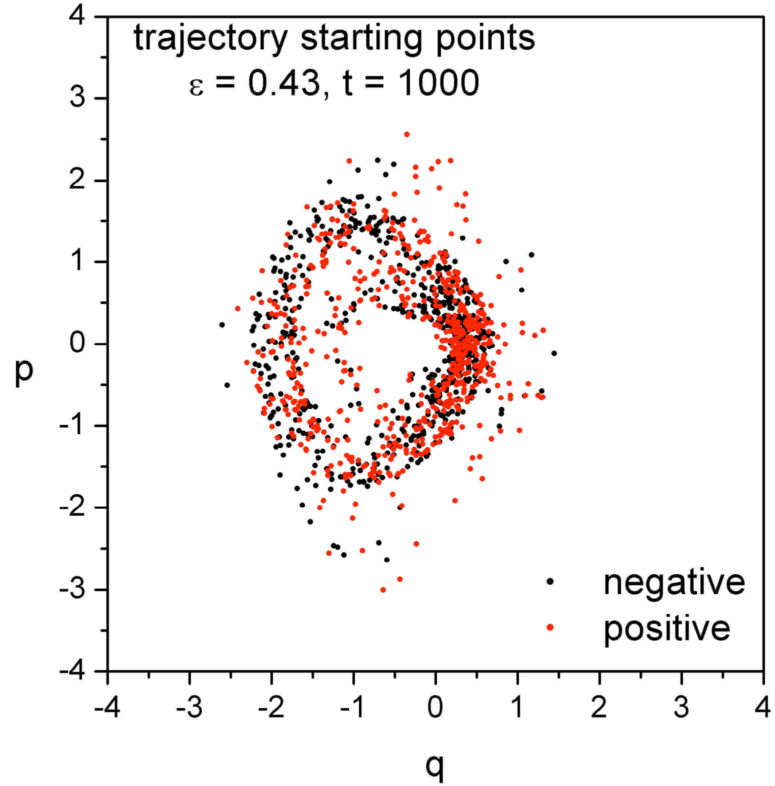


$\varepsilon = 0.43$





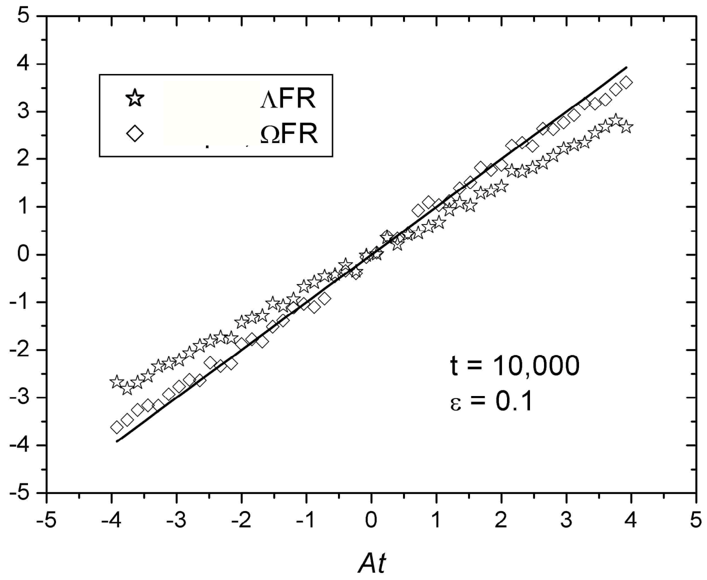
Phase space projections

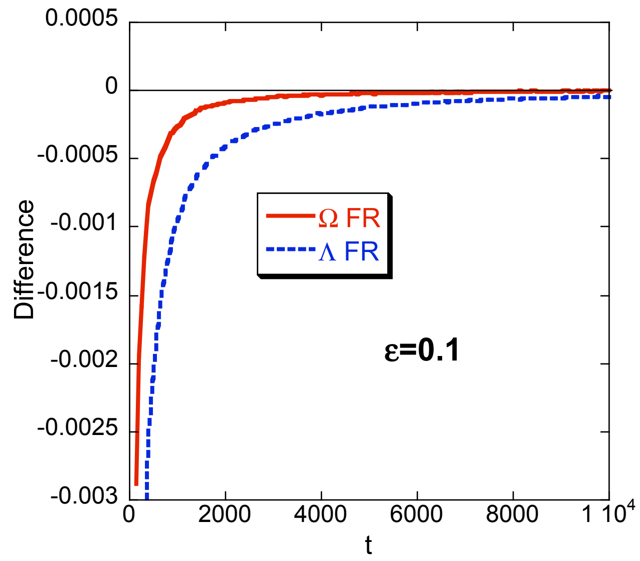


Steady State FR ε = 0.1

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = A$$

$$\lim_{t\to\infty}\frac{1}{t}\left(\ln\frac{p(\bar{\Omega}_t < 0)}{p(\bar{\Omega}_t > 0)} - \ln\left\langle e^{-\bar{\Omega}_t t}\right\rangle_{\bar{\Omega}_t > 0}\right) = 0$$



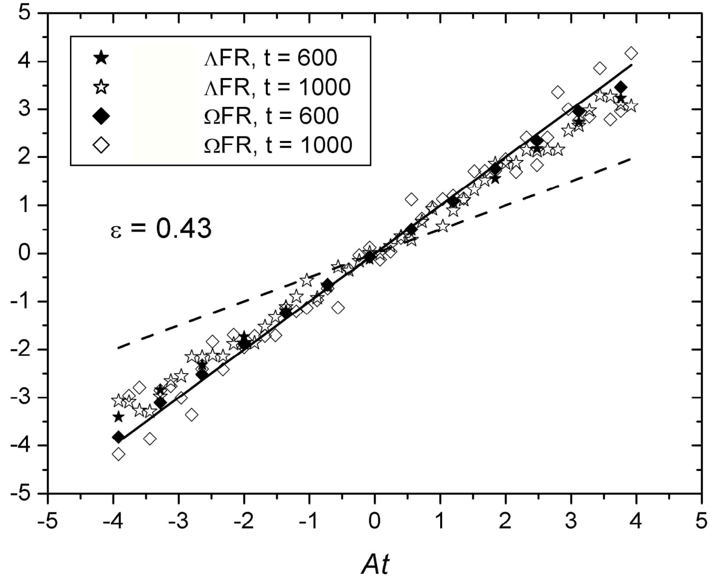


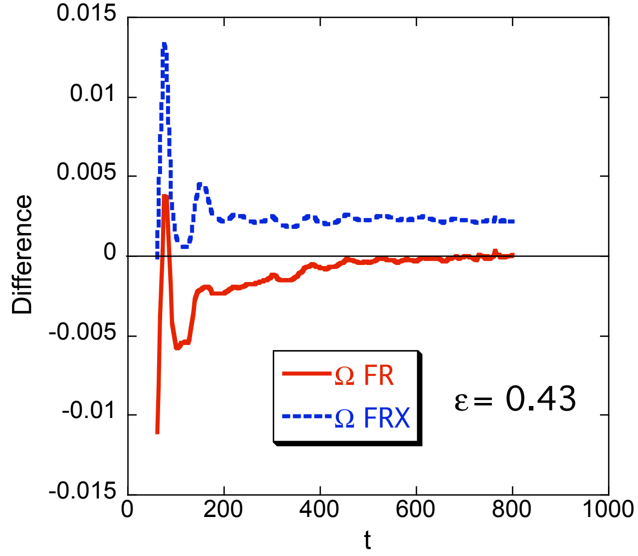
$$\langle A\rangle t = 8.0$$

Steady State FR ε = 0.43

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = XA$$

$$\lim_{t\to\infty}\frac{1}{t}\left(\ln\left\langle e^{-X\bar{\Omega}_t t}\right\rangle_{\bar{\Omega}_t>0} - \ln\frac{p(\bar{\Omega}_t<0)}{p(\bar{\Omega}_t>0)}\right) = 0$$



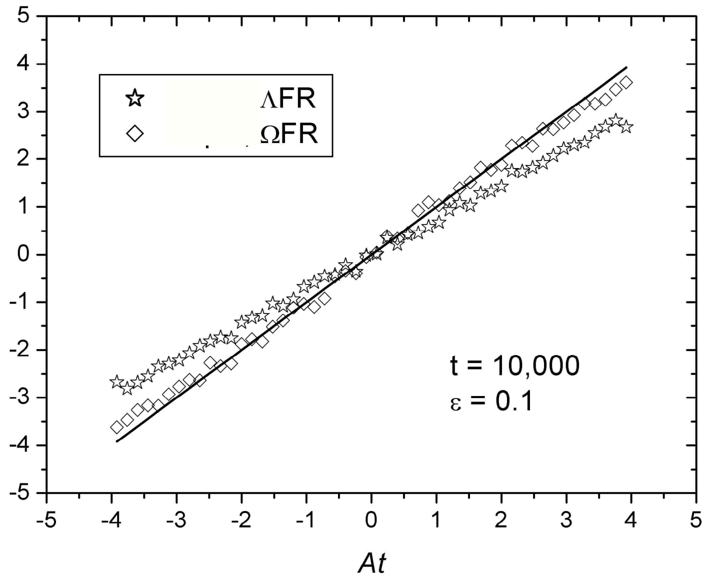


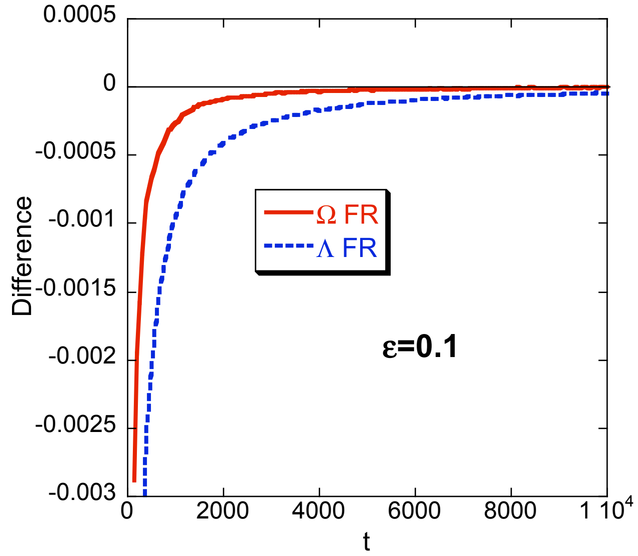
No X is required

Steady State FR $\varepsilon = 0.1$

$$\lim_{t\to\infty} \frac{1}{t} \ln \frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = XA$$

$$\lim_{t\to\infty} \frac{1}{t}\left(\ln \left\langle e^{X\bar{\Lambda}_t t} \right\rangle_{\bar{\Lambda}_t > 0} - \ln \frac{p(\bar{\Lambda}_t > 0)}{p(\bar{\Lambda}_t < 0)} \right) = 0$$

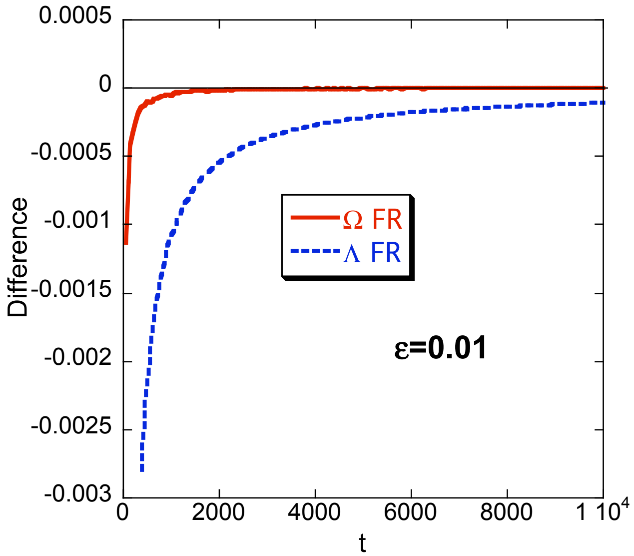




$$\langle A \rangle t = 8.0$$

Steady State FR ε = 0.01

$$\lim_{t\to\infty}\frac{1}{t}\left(\ln\left\langle e^{\bar{\Lambda}_t t}\right\rangle_{\bar{\Lambda}_t>0} - \ln\frac{p(\bar{\Lambda}_t>0)}{p(\bar{\Lambda}_t<0)}\right)=0$$

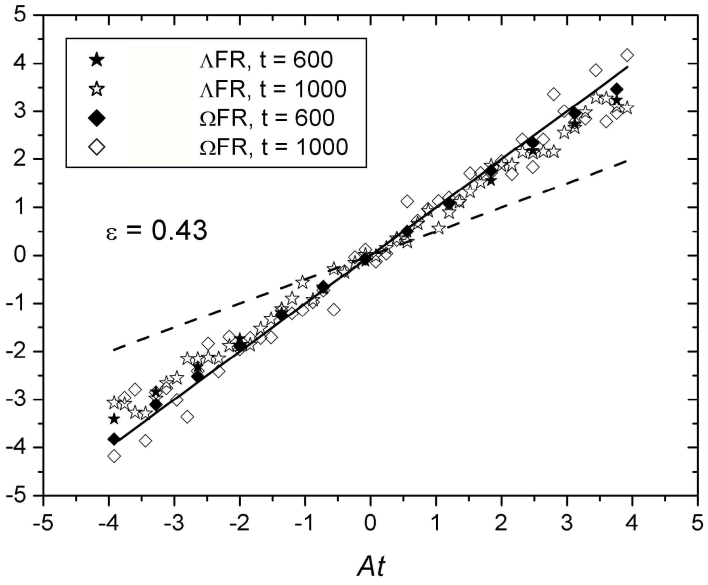


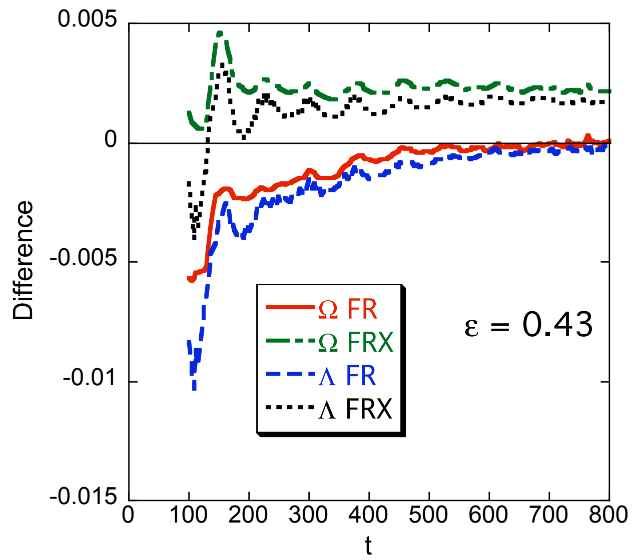
D. J. Evans, D. J. Searles and L. Rondoni, , Phys. Rev. E, **71**, 056120/1-13 (2005)

Steady State FR $\varepsilon = 0.43$

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{p(-\bar{\Lambda}_t = A)}{p(-\bar{\Lambda}_t = -A)} = XA$$

$$\lim_{t\to\infty}\frac{1}{t}\left(\ln\left\langle e^{X\bar{\Lambda}_t t}\right\rangle_{\bar{\Lambda}_t>0} - \ln\frac{p(\bar{\Lambda}_t > 0)}{p(\bar{\Lambda}_t < 0)}\right) = 0$$





$\langle A \rangle 1000 = 25.6$

Numerical observations : $X \sim 1$

convergence faster $\varepsilon \to$ large

Steady State FR - Conclusions

- **Ω-FR: No X required.** As expected from theory, at fields that as so high that the number of +ve and -ve exponents do not match, the FR is robust - no factor X has to introduced.
- Since Ω-FR and Λ-FR become equivalent in **isoenergetic systems,** expect that X=1 for Λ-FR (at least in that case) too.
- For this system, behaviour of Λ-FR is inconclusive: at the timescales considered, it is not conclusively obeyed at low field (X is expected to be 1), and X~1 at high field. This might be because
  - Timescale much too short
  - Chaotic hypothesis does not apply to this system (can we test it for a system that is Anosov at low fields?)
  - Conjecture leading to inclusion of a factor, X, needs reconsideration

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