A Fluctuation Relation for Weakly Ergodic Aging Systems

In collaboration with:

- Marco Picco (CNRS, LPTHE-UPMC Paris)
- Felix Ritort (U Barcelona)

Plan of the talk

- Some facts on Fluctuation Relations and Aging
- A Fluctuation Relation in the Aging state
- Numerical Test

Fluctuation Relations

At microscopic level permanent state of agitation

↓

Physical quantities undergo random fluctuations

↓

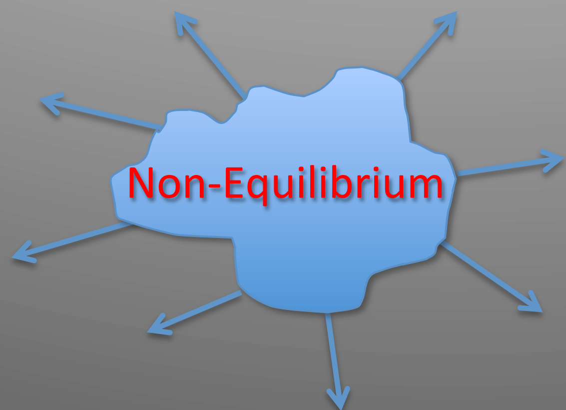
Statistical properties described by Statistical Mechanics

Restrictions on the PDF of Fluctuating quantities ⟷ Fluctuation Relations

$$\frac{{}^{F}P(X)}{{}^{R}P(-X)} = \exp\Big[a(X-b)\Big]$$

Non-Equilibrium Systems

Non-Equilibrium system → Net energy transfer to the environment



Fluctuation Relations → Relate probabilities of absorbing/releasing a given amount of energy

Aging Systems
(Quench)

Aging systems are characterized by two time-scales

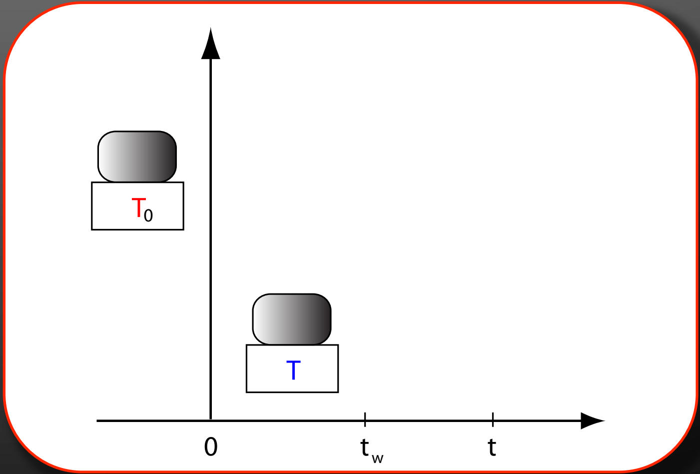
The age or waiting time t_w

The time $t > t_w$ of the measurement

Quenching Protocol:

At time $t = 0$ the system is quenched from high temperature T_0 down to low temperature T

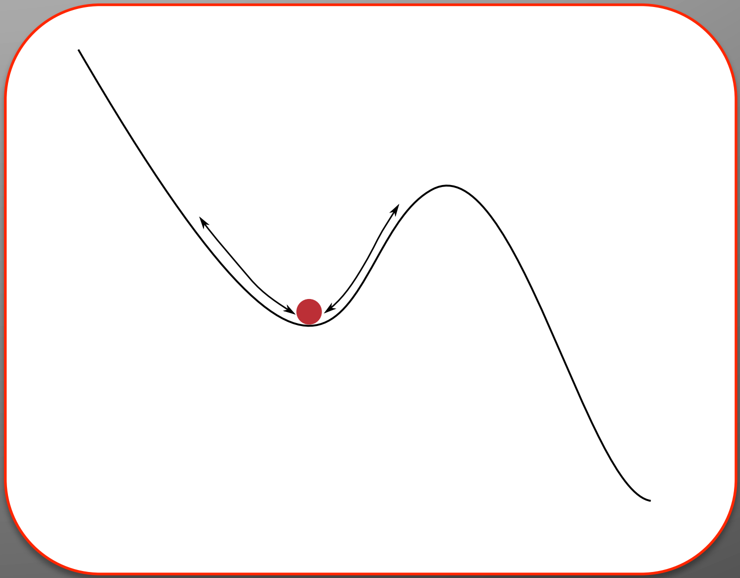
Non-Equilibrium (relaxation) state characterized by a net energy flux



Energy Transfer: Stimulated Process

- For times $t - t_w << t_c \sim t_w$

Heat Q is exchanged back-and-forth
but net heat flow vanishingly small



The system looks as *equilibrated*
at the bath temperature T

We call this process ***Stimulated***
as it originates from processes
thermally excited by the bath

PDF of Q: Gaussian of zero mean and
T-dependent variance

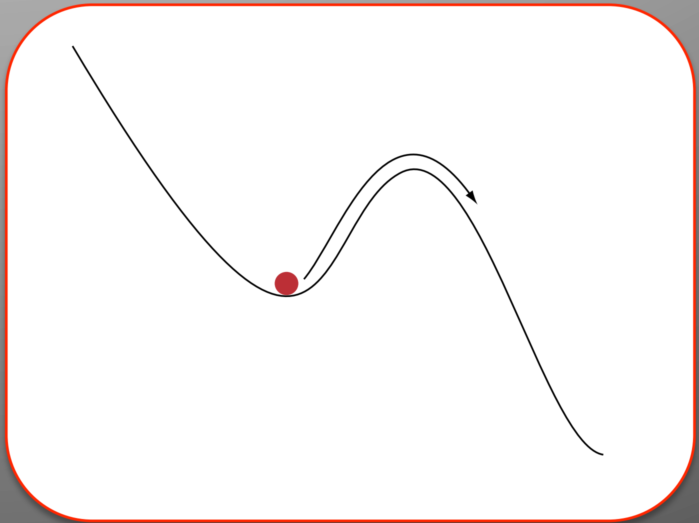
Energy Transfer: Spontaneous Process

- For times $t - t_w >> t_c \sim t_w$

Intermittent exchange of larger than typical amounts of heat Q

↓

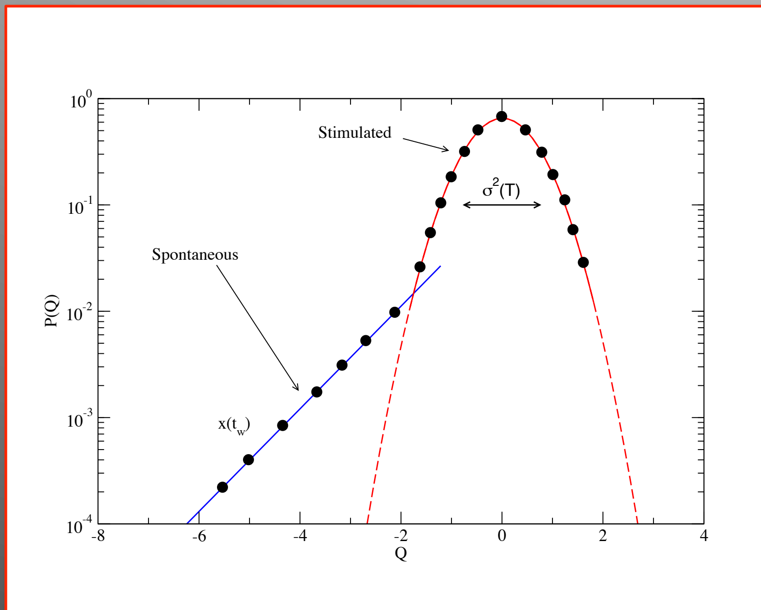
Finite net heat flow



We call this process *Spontaneous* as it originates because the system was in a non-equilibrium state at t_w

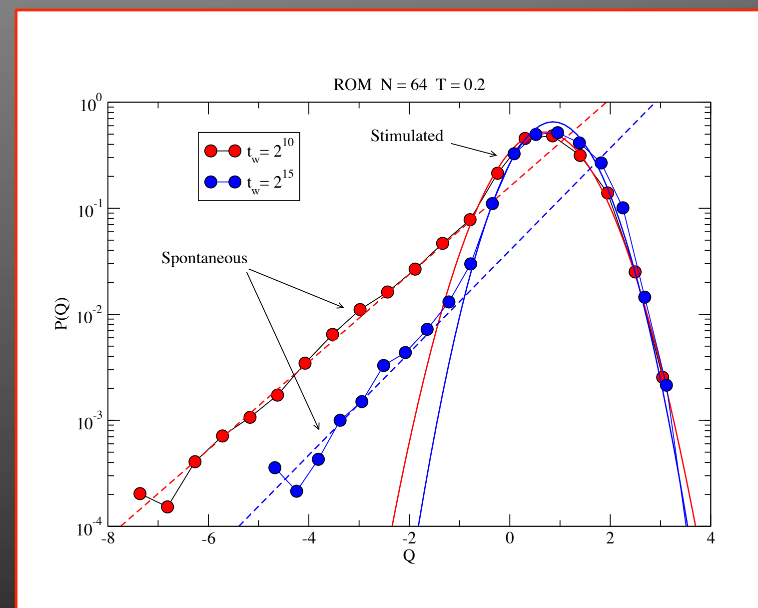
PDF of Q: exponential tail with an age-dependent slope

Stimulated and Spontaneous Processes



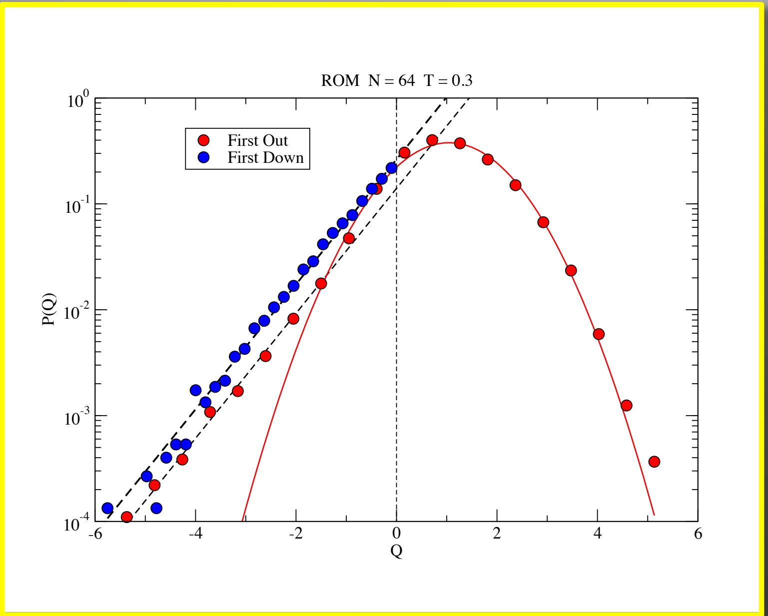
Theoretical

Experimental
(Numerical)



AC and FR, *Europhys. Lett*. **66**, 253 (2004)

Stimulated and Spontaneous Processes



Aging Fluctuation Relation

(Bochkov-Kuzovlev)

Protocol:

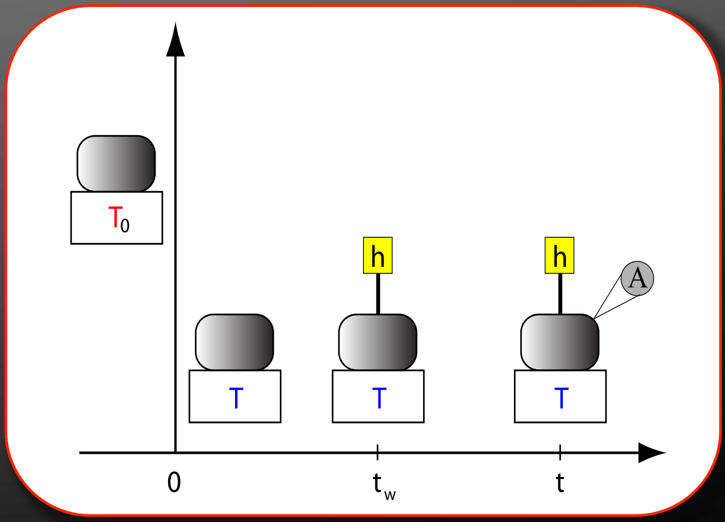
- $t = 0$ quench to low temperature T
- t_w apply a constant external perturbation of strength h coupled to the (macroscopic) observable A
- $t = \Delta t + t_w$ measure the entropy production during Δt

$$\Delta S_{t_w,t} = Q_{t_w,t}/T$$
$$= \beta h \big[A(t) - A(t_w)\big]$$
$$= \beta \mathcal{W}_0(t_w, t)$$

Exclusive Work

- Build the PDF $P_{t_w,t}(\Delta S)$

$$\frac{{}^F P_{t_w,t}(\Delta S)}{{}^R P_{t_w,t}(-\Delta S)} = \; ?$$



The Model

Langevin Equation

$$\Gamma^{-1}\frac{d\varphi}{dt} = F(\varphi) + h + \xi$$

$$\langle \xi(t)\,\xi(t')\rangle = \frac{2\,T}{\Gamma}\,\delta(t-t')$$

$$F(\varphi) = -\frac{\delta}{\delta\varphi}\,H(\varphi)$$

The Model

External forcing

Langevin Equation

$$\Gamma^{-1}\frac{d\varphi}{dt} = F(\varphi) + h + \xi$$

$$\langle \xi(t)\,\xi(t')\rangle = \frac{2\,T}{\Gamma}\,\delta(t-t')$$

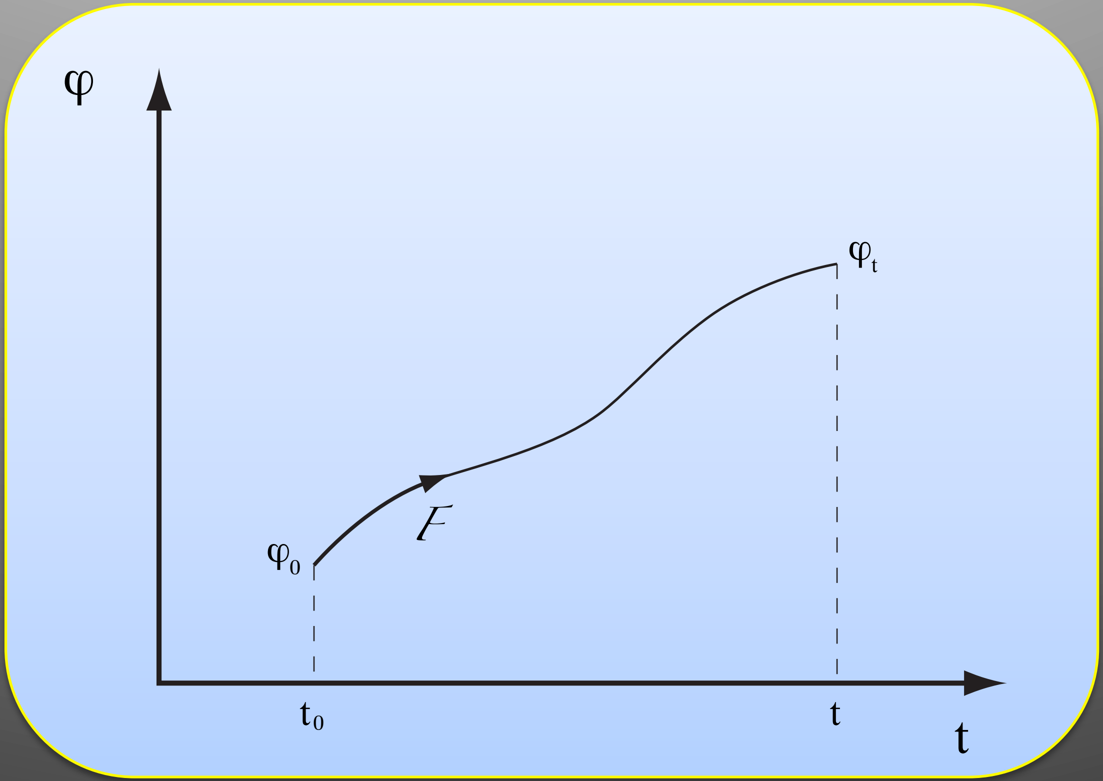
$$F(\varphi) = -\frac{\delta}{\delta\varphi}\,H(\varphi)$$

$$\lim_{t\to\infty} P(\varphi,t) = P^{\mathrm{eq}}(\varphi) = \frac{e^{-\beta H(\varphi)}}{Z}$$

Forward Process

Forward Path

$$\{\varphi_s\}_{s\in[t_0,t]}$$



Path Integral Formulation

$$P(\varphi_t, t) = \int d\varphi_0 \, P(\varphi_t, t|\varphi_0, t_0) \, P(\varphi_0, t_0)$$

$$P(\varphi_t, t|\varphi_0, t_0) = \int_{\varphi_0}^{\varphi_t} \mathcal{D}\varphi \, \exp\left[\int_{t_0}^{t} ds \, \mathcal{L}(\dot{\varphi}, \varphi; h)\right]$$

$$\mathcal{L}(\dot{\varphi}, \varphi; h) = -\frac{\beta}{4\Gamma}\Big[\dot{\varphi} - \Gamma F(\varphi) - \Gamma h\Big]^2$$

Path Integral Formulation

$$P(\varphi_t, t) = \int d\varphi_0 \, P(\varphi_t, t|\varphi_0, t_0) \, P(\varphi_0, t_0)$$

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Path Integral Formulation

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$\mathcal{P}\left[\{\varphi_s\}_{s\in[t_0,t]}\right] :=$ Probability of the single path $\{\varphi_s\}_{s\in[t_0,t]}$

Equilibrium Distribution (h = 0)

If the force: $$F(\varphi) = -\frac{\delta}{\delta\varphi} H(\varphi)$$

Then

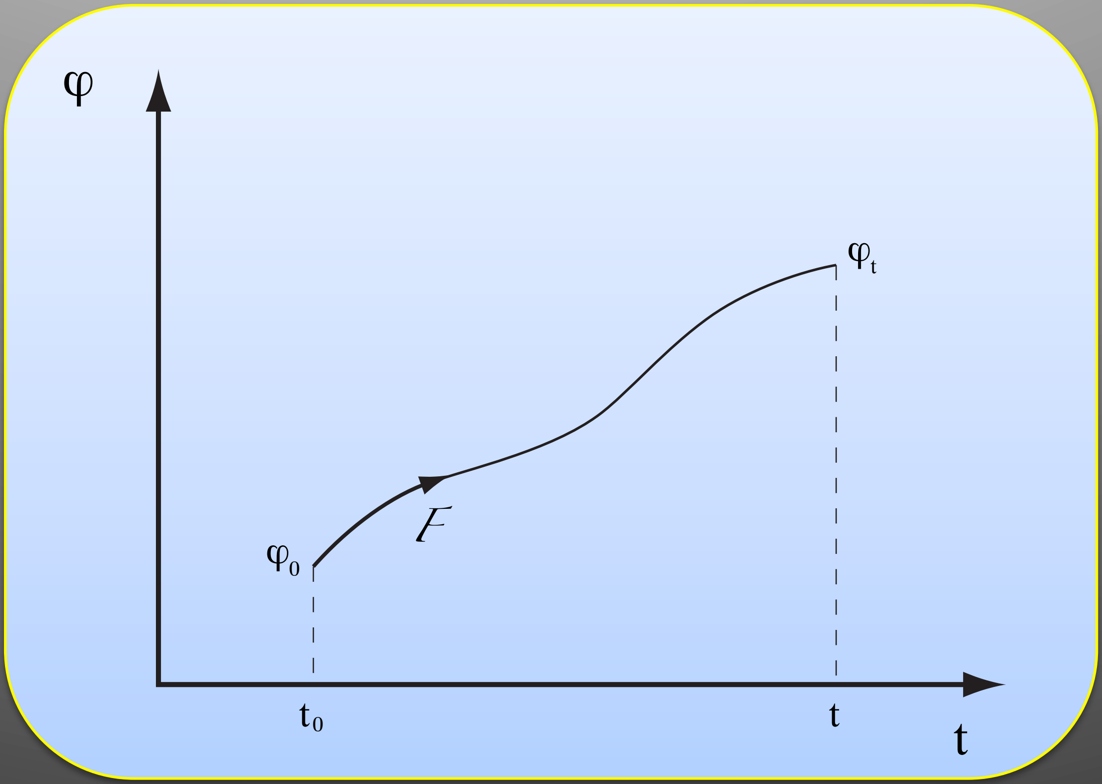
$$\lim_{t\to\infty} P(\varphi, t) = P^{\mathrm{eq}}(\varphi) = \frac{e^{-\beta H(\varphi)}}{Z}$$

$$Z = \int d\varphi\, e^{-\beta H(\varphi)}$$

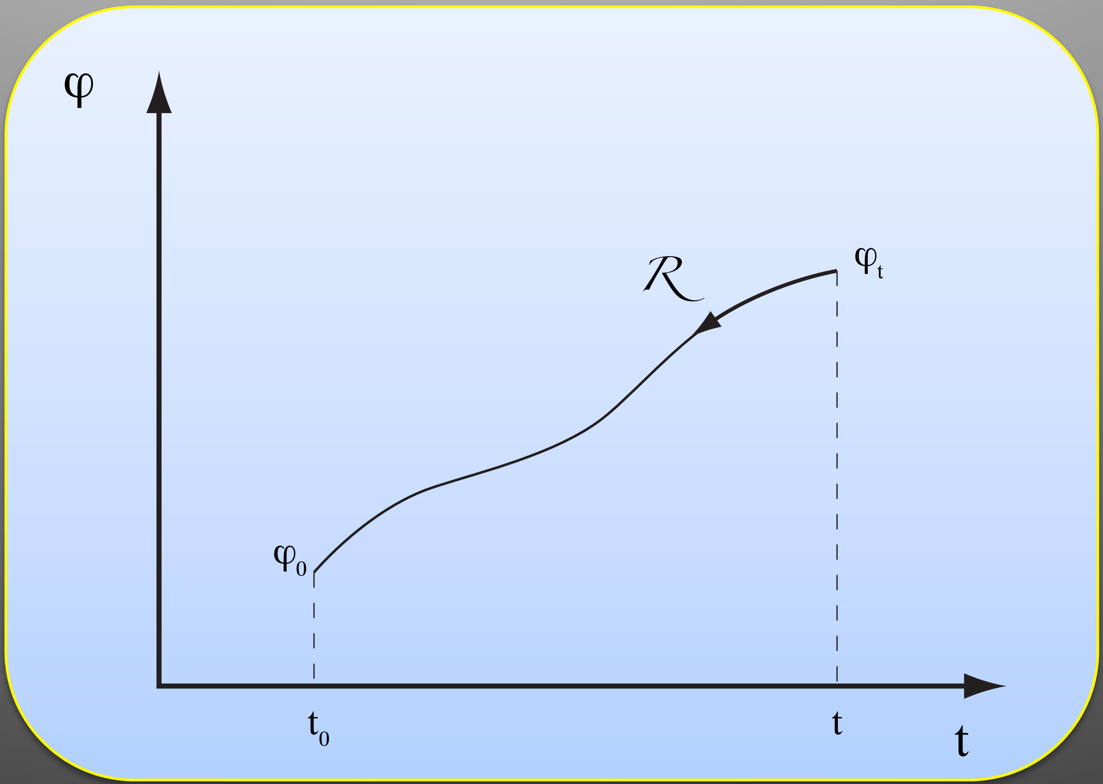
Forward/Reverse

Forward Path

$\{\varphi_s\}_{s\in[t_0,t]}$



Reverse Process



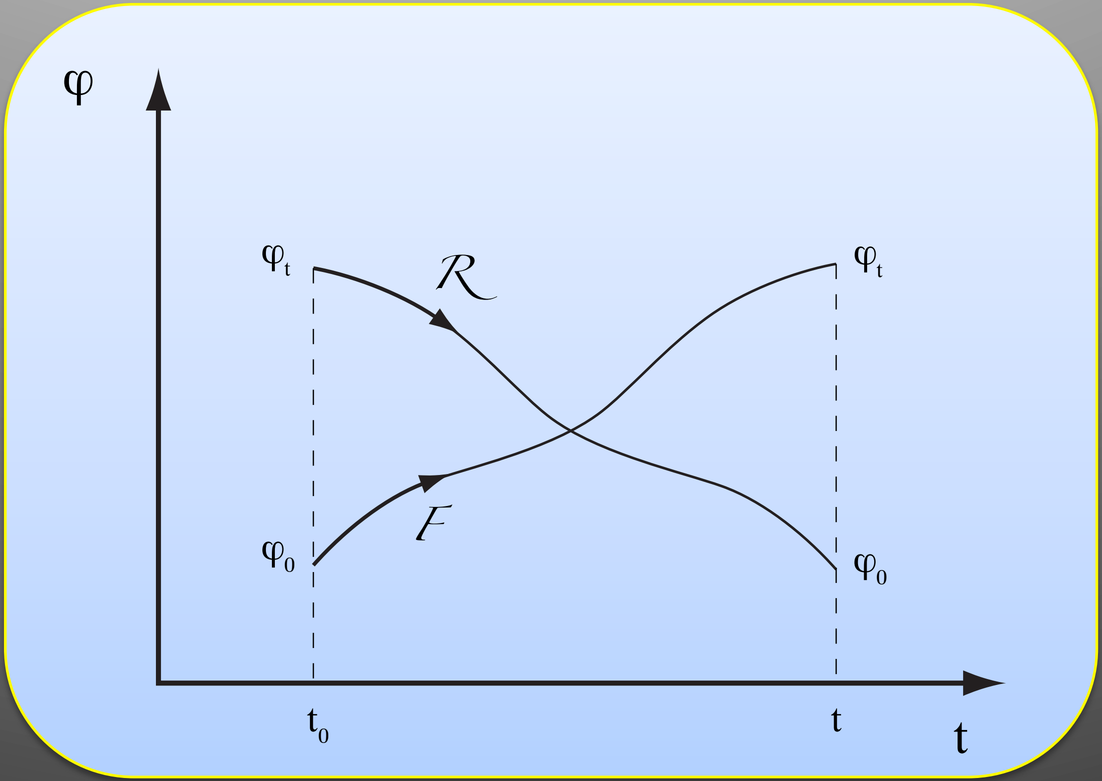
Reverse Path

$$\{\widetilde{\varphi}_s\}_{s\in[t_0,t]} = {}^{R}\{\varphi_s\}_{s\in[t_0,t]}$$

Reverse Process

Forward Path

$\{\varphi_s\}_{s\in[t_0,t]}$



Reverse Path

$$\{\widetilde{\varphi}_s\}_{s\in[t_0,t]} = {}^R\{\varphi_s\}_{s\in[t_0,t]} \equiv \{\varphi_{t+t_0-s}\}_{s\in[t_0,t]}$$

Path Integral Formulation

Reverse Path:

$$P(\widetilde{\varphi}_t, t|\widetilde{\varphi}_0, t_0) = \int_{\widetilde{\varphi}_0}^{\widetilde{\varphi}_t} \mathcal{D}\widetilde{\varphi} \, \exp\left[\int_{t_0}^{t} ds\, \mathcal{L}(\dot{\widetilde{\varphi}}, \widetilde{\varphi}; h)\right]$$

Path Integral Formulation

Reverse Path:

$$P(\widetilde{\varphi}_t, t|\widetilde{\varphi}_0, t_0) = \int_{\widetilde{\varphi}_0}^{\widetilde{\varphi}_t} \mathcal{D}\widetilde{\varphi} \, \exp\left[\int_{t_0}^{t} ds \, \mathcal{L}(\dot{\widetilde{\varphi}}, \widetilde{\varphi}; h)\right]$$

$$P(\varphi_0, t|\varphi_t, t_0) = \int_{\varphi_0}^{\varphi_t} \mathcal{D}\varphi \, \exp\left[\int_{t_0}^{t} ds \, \mathcal{L}(-\dot{\varphi}, \varphi; h)\right]$$

Path Integral Formulation

Reverse Path:

$$P(\widetilde{\varphi}_t, t|\widetilde{\varphi}_0, t_0) = \int_{\widetilde{\varphi}_0}^{\widetilde{\varphi}_t} \mathcal{D}\widetilde{\varphi} \exp\left[\int_{t_0}^{t} ds\, \mathcal{L}(\dot{\widetilde{\varphi}}, \widetilde{\varphi}; h)\right]$$

$$P(\varphi_0, t|\varphi_t, t_0) = \int_{\varphi_0}^{\varphi_t} \mathcal{D}\varphi \exp\left[\int_{t_0}^{t} ds\, \mathcal{L}(-\dot{\varphi}, \varphi; h)\right]$$

$$\mathcal{P}\left[\{\widetilde{\varphi}_s\}_{s\in[t_0,t]}\right]$$ Probability Reverse Path

Forward/Reverse

$$\int_{t_0}^{t} ds\, \mathcal{L}(-\dot{\varphi}, \varphi; h) = \int_{t_0}^{t} ds\, \mathcal{L}(\dot{\varphi}, \varphi; h)$$

$$+\beta\left[H(\varphi_t) - H(\varphi_0)\right] - \beta\mathcal{W}_0(\varphi_t, \varphi_0)$$

$$\mathcal{W}_0(t, t_0) = \int_{t_0}^{t} ds\, h\, \dot{\varphi}$$

$$= h\,(\varphi_t - \varphi_0) \equiv \mathcal{W}_0(\varphi_t, \varphi_0)$$

Exclusive Work

Forward/Reverse

$$e^{-\beta\mathcal{W}_0(\varphi_t,\varphi_0)}\mathcal{P}\left[\{\varphi_s\}_{s\in[t_0,t]}\right]P^{\mathrm{eq}}(\varphi_0) = \mathcal{P}\left[\{\widetilde{\varphi}_s\}_{s\in[t_0,t]}\right]P^{\mathrm{eq}}(\varphi_t)$$

(Detailed-Balance relation)

$$e^{-\beta\mathcal{W}_0(\varphi_t,\varphi_0)}P(\varphi_t,t|\varphi_0,t_0)P^{\mathrm{eq}}(\varphi_0) = P(\varphi_0,t|\varphi_t,t_0)P^{\mathrm{eq}}(\varphi_t)$$

Integral Fluctuation Relation

$$\frac{P(\varphi_t, t|\varphi_0, t_0)\, P_0(\varphi_0)}{P(\varphi_0, t|\varphi_t, t_0)\, P_1(\varphi_t)}$$

Forward/Reverse

$$\frac{P(\varphi_t, t|\varphi_0, t_0)\, P_0(\varphi_0)}{P(\varphi_0, t|\varphi_t, t_0)\, P_1(\varphi_t)} = e^{\beta \mathcal{W}_0(\varphi_t,\varphi_0) - \Delta S^{\mathrm{eq}}(\varphi_t,\varphi_0) + \Delta S_{\mathrm{b}}(\varphi_t,\varphi_0)}$$

$$\Delta S^{\mathrm{eq}}(\varphi_t, \varphi_0) = \beta\big[H(\varphi_t) - H(\varphi_0)\big] = -\ln \frac{P^{\mathrm{eq}}(\varphi_t)}{P^{\mathrm{eq}}(\varphi_0)}$$

$$\Delta S_{\mathrm{b}}(\varphi_t, \varphi_0) = -\ln \frac{P_1(\varphi_t)}{P_0(\varphi_0)}$$

Forward/Reverse

$$-\Delta S^{\mathrm{eq}}(\varphi_y,\varphi_0)+\beta\mathcal{W}_0(\varphi_t,\varphi_0)$$
$$=\beta\int_{t_0}^{t} ds\left[F[\varphi(s)]+h\right]\dot{\varphi}(s)$$
$$=\beta\mathcal{Q}(\varphi_t,\varphi_0)$$
Dissipated Heat
$$=\Delta S_{\mathrm{m}}(\varphi_t,\varphi_0)$$
Medium Entropy Change

$$\frac{P(\varphi_t,t|\varphi_0,t_0)\,P_0(\varphi_0)}{P(\varphi_0,t|\varphi_t,t_0)\,P_1(\varphi_t)}=e^{\Delta S_{\mathrm{tot}}(\varphi_t,\varphi_0)}$$

U Seifert,
PRL **95**, 040602 (2005)

$$\Delta S_{\mathrm{tot}}(\varphi_t,\varphi_0)=\Delta S_{\mathrm{m}}(\varphi_t,\varphi_0)+\Delta S_{\mathrm{b}}(\varphi_t,\varphi_0)$$

Integral Fluctuation Relation

$$\left\langle F(\varphi_t, \varphi_0)\, e^{-\Delta S_{\rm tot}(\varphi_t, \varphi_0)} \right\rangle_{t,t_0} = {}^R\langle F(\varphi_t, \varphi_0)\rangle_{t,t_0}$$

$$\left[F(\varphi_t, \varphi_0) = \delta(W_0 - \mathcal{W}_0(\varphi_t, \varphi_0)) \right]$$

$$\left\langle \delta(W_0 - \mathcal{W}_0(\varphi_t, \varphi_0; h))\, e^{-\Delta S_{\rm tot}(\varphi_t, \varphi_0)} \right\rangle_{t,t_0} = P(-W_0; t, t_0)$$

Equilibrium Fluctuation Relation

Assume: $P_0(\varphi) = P_1(\varphi) = P^{\mathrm{eq}}(\varphi)$

$$\Delta S_{\mathrm{tot}} = \beta \mathcal{W}_0 - \Delta S^{\mathrm{eq}} + \Delta S_{\mathrm{b}} = \beta \mathcal{W}_0$$

$$\frac{P(W_0; t, t_0)}{P(-W_0; t, t_0)} = e^{\beta W_0}$$

$$\left\langle e^{-\beta W_0} \right\rangle = 1$$

Bochkov – Kuzovlev
Sov. Phys. JETP **45**, 125 (1977)

Aging Fluctuation Relation

Aging (Glassy) System:

- Phase space made of a set of disjoint subsets: Cages
- Number of cages depends on the age t_0 (waiting time)
- At the initial time t_0 the system is inside one cage
- It is trapped into the cage for a typical time $t_c \sim t_0$
- Microscopic relaxation time << t_c (local equilibrium)

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- Microscopic relaxation time << t_c (local equilibrium)

$$\frac{P(\Delta S; t; t_0)}{P(-\Delta S; t; t_0)} = e^{\Delta S} \qquad t - t_0 \ll t_c$$

$$\Delta S = \beta W_0$$

Aging Fluctuation Relation

What about $t - t_0 \gg t_c$?

→ The exclusive work depends on macroscopic quantities

$$\mathcal{W}_0(\varphi_t, \varphi_0) = h\left(\varphi_t - \varphi_0\right) \equiv h\left(\sum_i \varphi_{i,t} - \sum_i \varphi_{i,0}\right)$$

→ $$\mathcal{W}_0(\varphi_t, \varphi_0) = h\left(\psi_t - \psi_0\right)$$

Where: $\psi = \sum_i \varphi_i \equiv 1 \cdot \varphi$

Aging Fluctuation Relation

$$P(-W_0;t,t_0) = e^{-\beta W_0} \int d\psi_0 \int d\psi_t \, \delta\big(W_0/h - \psi_t + \psi_0\big)$$

$$\times \left\langle \delta(\psi_0 - 1\cdot\varphi_0)\, \delta(\psi_t - 1\cdot\varphi_t)\, e^{\Delta S^{\mathrm{eq}}(\varphi_t,\varphi_0) - \Delta S_{\mathrm{b}}(\varphi_t,\varphi_0)} \right\rangle_{t,t_0}$$

Average by classification

Only states of fixed $1\cdot\varphi = \psi$

Aging Fluctuation Relation

In local equilibrium

$$P(\varphi|\psi) \propto P^{\mathrm{eq}}(\varphi) \times \text{Probability of } 1 \cdot \varphi = \psi \text{ in a cage}$$

Aging Fluctuation Relation

This can be written as

$$\Rightarrow \quad P(\varphi|\psi) \propto P^{\mathrm{eq}}(\varphi)\frac{\Omega_T(\psi)}{\Omega(\psi)}$$

where

$\Omega_T(\psi)$ = number of a states in a cage with $1 \cdot \varphi = \psi$

$\Omega(\psi)$ = number of accessible states with $1 \cdot \varphi = \psi$

- Local equilibrium in a cage $\Rightarrow$ $\ln \Omega_T(\psi) = S_T(\psi)$ Thermal equilibrium entropy

Aging Fluctuation Relation

$$\Delta S^{\mathrm{eq}}(\varphi_t, \varphi_0) - \Delta S_{\mathrm{b}}(\varphi_t, \varphi_0) = \Delta S_T - \Delta S$$

$$S(\psi) = \ln \Omega(\psi)$$

$$P(-W_0; t, t_0) = e^{-\beta x W_0} \int d\psi_0 \int d\psi_t \, \delta(W_0/h - \psi_t + \psi_0) \times \left\langle \delta(\psi_0 - 1 \cdot \varphi_0) \, \delta(\psi_t - 1 \cdot \varphi_t) \right\rangle_{t,t_0}$$

$$\frac{dS_T(\psi_0)}{d\psi_0} = \beta h$$

$$\frac{dS(\psi_0)}{d\psi_0} = x\beta h$$

→ $x < 1$ phase space contraction factor

Aging Fluctuation Relation

$$\Delta S^{\mathrm{eq}}(\varphi_t, \varphi_0) - \Delta S_{\mathrm{b}}(\varphi_t, \varphi_0) = \Delta S_T - \Delta S$$

$$S(\psi) = \ln \Omega(\psi)$$

$$P(-W_0; t, t_0) = e^{-\beta x W_0} \int d\psi_0 \int d\psi_t \, \delta(W_0/h - \psi_t + \psi_0) \times \langle \delta(\psi_0 - 1 \cdot \varphi_0) \, \delta(\psi_t - 1 \cdot \varphi_t) \rangle_{t,t_0}$$

$$P(W_0; t; t_0)$$

$$\frac{dS_T(\psi_0)}{d\psi_0} = \beta h$$

$$\frac{dS(\psi_0)}{d\psi_0} = x\beta h$$

$x < 1$ phase space contraction factor

Aging Fluctuation Relation

(AFR)

$$\frac{P(\Delta S; t; t_0)}{P(-\Delta S; t; t_0)} = e^{x\Delta S}$$

$$t - t_0 \gg t_c$$

$$\Delta S = \beta W_0$$

Numerical Test AFR

ROM

- Random Orthogonal Model (ROM)

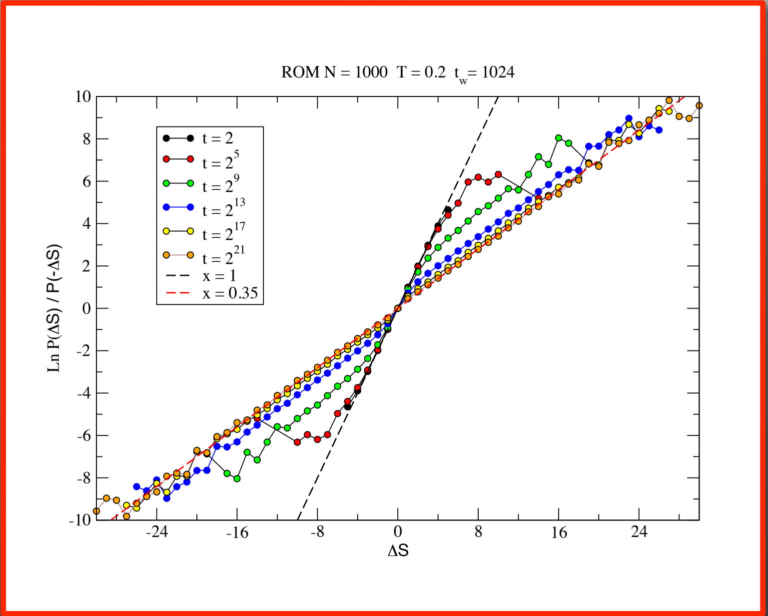
$$H = -\sum_{1\leq i<j\leq N} J_{ij}\sigma_i\sigma_j \qquad \sigma_i = \pm 1$$

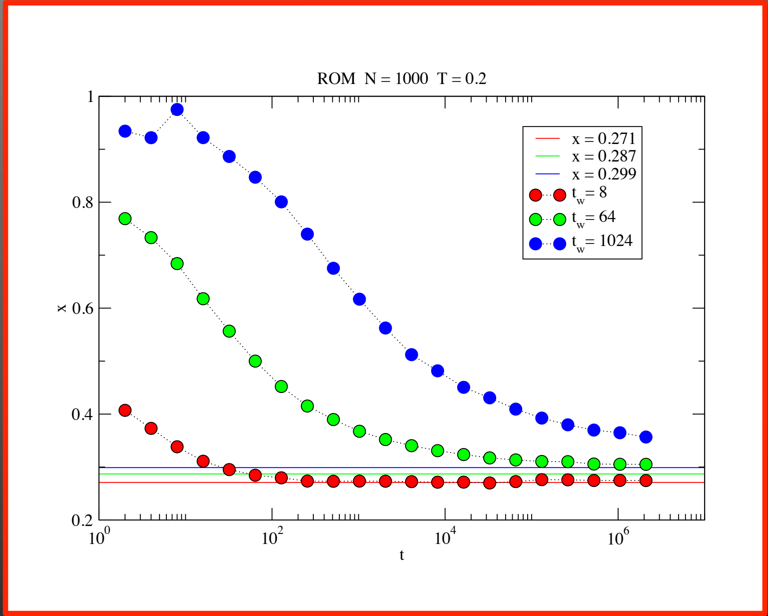
J_{ij} Random Orthogonal Matrix

$$\sum_k J_{ik}J_{kj} = \delta_{ij} \qquad J_{ii} = 0$$

Numerical Test AFR

ROM





Numerical Test AFR

- $\Delta S_{t_0,t}$ Strongly intermittent

$$\Delta S_{t_0,t} = \Delta S$$

Broad time interval $t - t_0$

Define:

$\overline{P}_{\Delta t}(\Delta S; t_0)$ = Probability of observing $\Delta S_{t_0,t} = \Delta S$ in the time interval $[t_0, \Delta t + t_0]$

Numerical Test AFR

- $|\Delta S| < \Delta S^*$ Stimulated processes dominated

$$\ln \frac{\overline{P}_{\Delta t}(\Delta S; t_0)}{\overline{P}_{\Delta t}(-\Delta S; t_0)} \simeq \Delta S$$

- $|\Delta S| > \Delta S^*$ Spontaneous processes dominated

$$\ln \frac{\overline{P}_{\Delta t}(\Delta S; t_0)}{\overline{P}_{\Delta t}(-\Delta S; t_0)} \simeq x\Delta S$$

Numerical Test AFR

$$\overline{P}_{\Delta t}(\Delta S; t_0) = \frac{1}{\Delta t}\int_0^{\Delta t} ds\, P(\Delta S; s + t_0, t_0)$$

$$\frac{P(\Delta S; t; t_0)}{P(-\Delta S; t; t_0)} = e^{x\Delta S}$$

$$\frac{\overline{P}_{\Delta t}(\Delta S; t_0)}{\overline{P}_{\Delta t}(-\Delta S; t_0)} = \frac{\int_0^{\Delta t} ds\, P(\Delta S; s + t_0, t_0)}{\int_0^{\Delta t} ds\, P(\Delta S; s + t_0, t_0) e^{-x\Delta S}}$$

$$= \exp\left[- \ln \left[e^{-x\Delta S}\right]_{\Delta t}\right]$$

Where:

$$[(\cdots)]_{\Delta t} = \frac{\int_0^{\Delta t} ds\, P(\Delta S; s + t_0, t_0)\,(\cdots)}{\int_0^{\Delta t} ds\, P(\Delta S; s + t_0, t_0)}$$

Numerical Test AFR

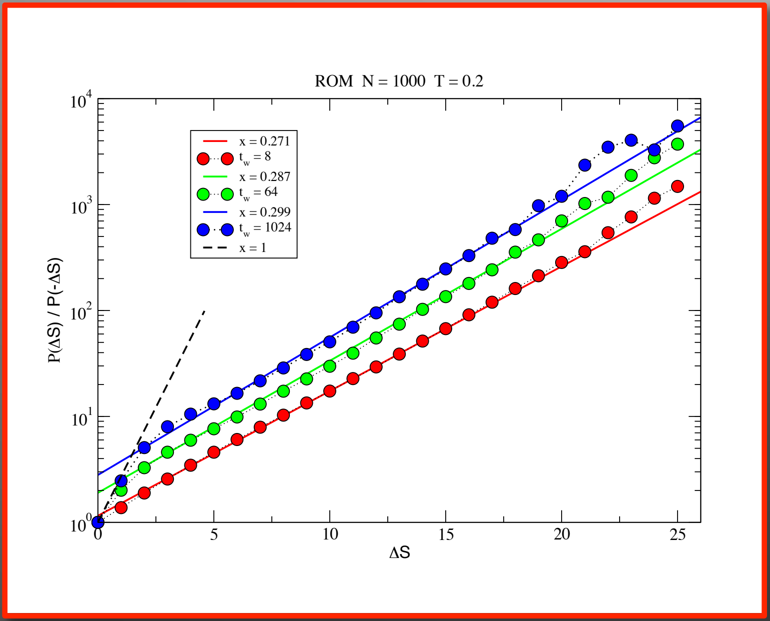
$$\ln \frac{\overline{P}_{\Delta t}(\Delta S; t_0)}{\overline{P}_{\Delta t}(-\Delta S; t_0)} \simeq x_{\min} \Delta S \qquad \Delta S \gg 1$$

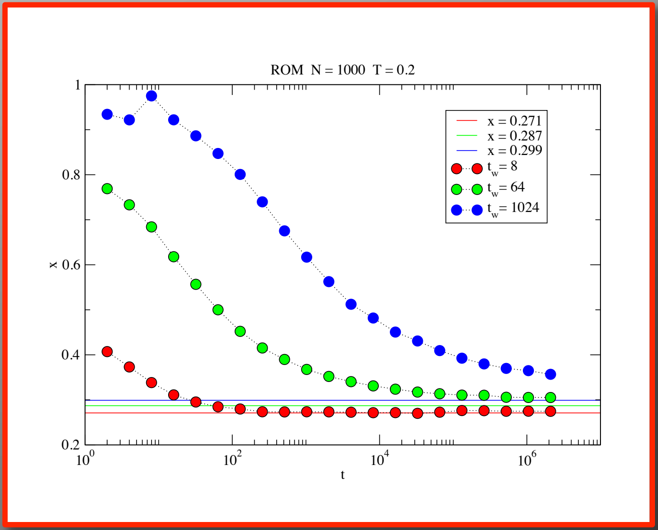
$$\ln \frac{\overline{P}_{\Delta t}(\Delta S; t_0)}{\overline{P}_{\Delta t}(-\Delta S; t_0)} \simeq \Delta S \qquad t - t_0 \ll t_0$$

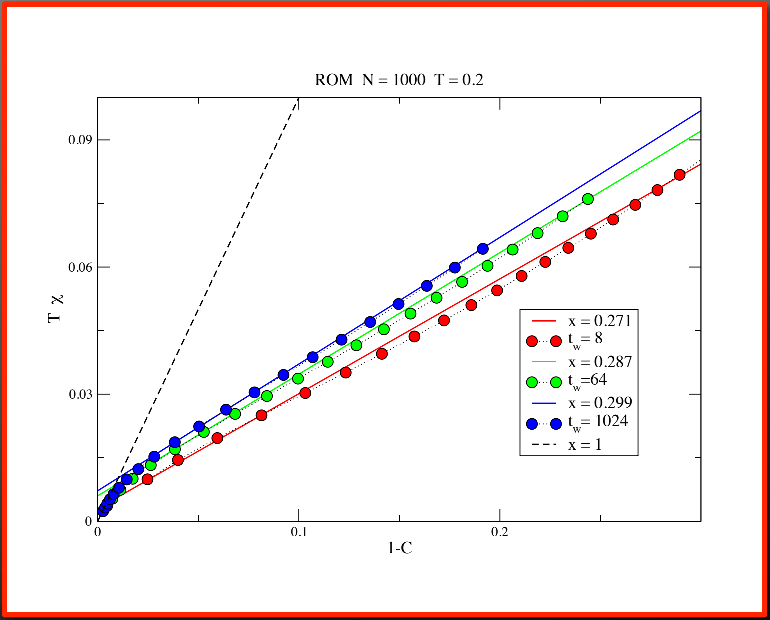
$$\ln \frac{\overline{P}_{\Delta t}(\Delta S; t_0)}{\overline{P}_{\Delta t}(-\Delta S; t_0)} \simeq x \Delta S \qquad t - t_0 \gg t_0$$

Numerical Test AFR

ROM

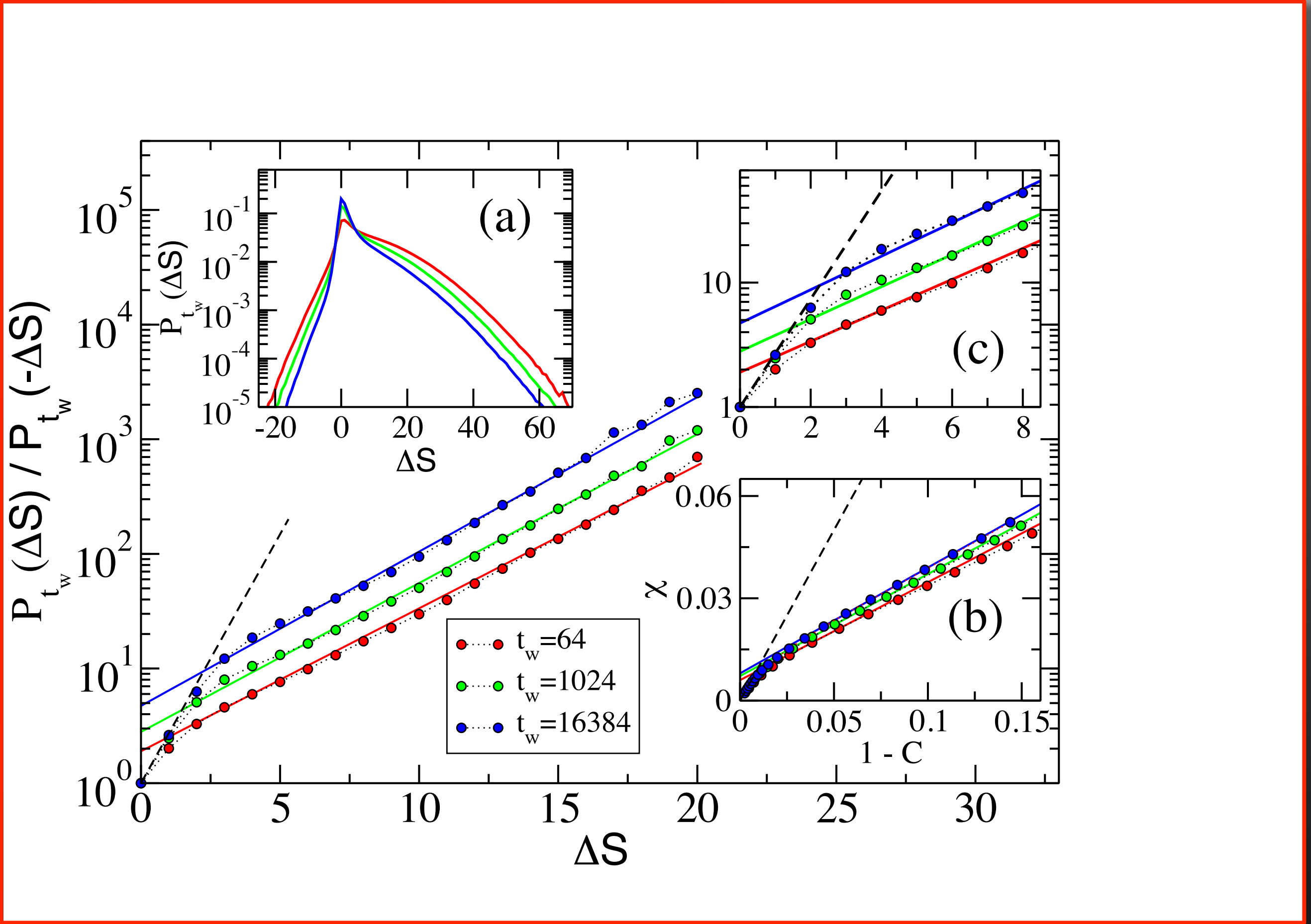






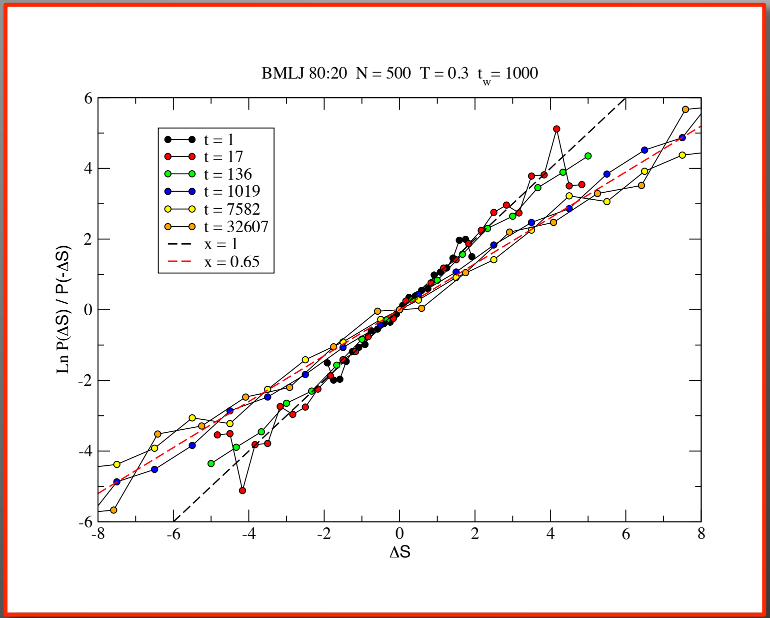
Numerical Test AFR

ROM

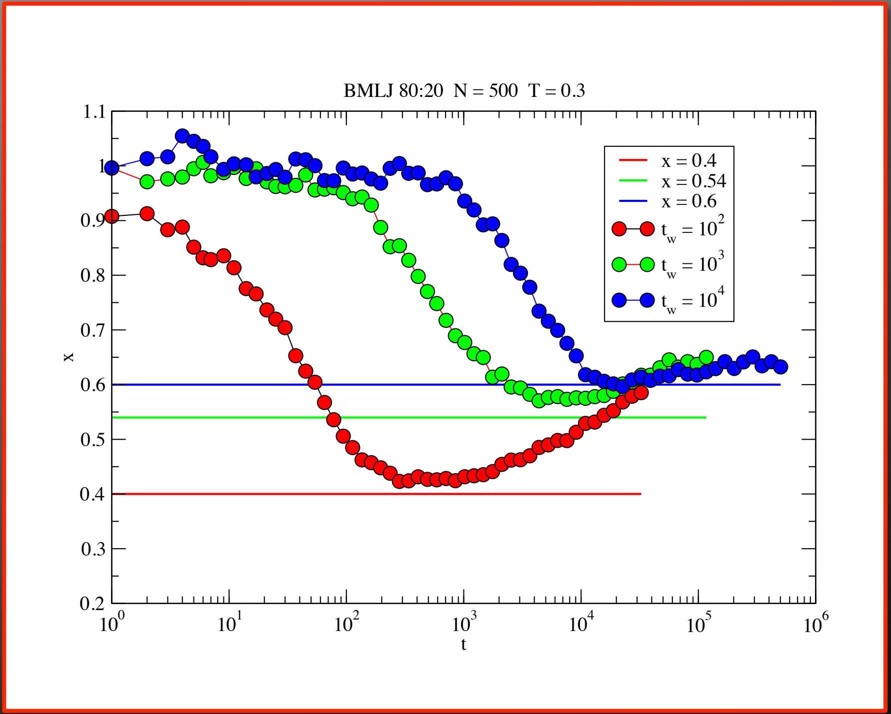


Numerical Test AFR

BMLJ 80:20



$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right]$$



Numerical Test AFR

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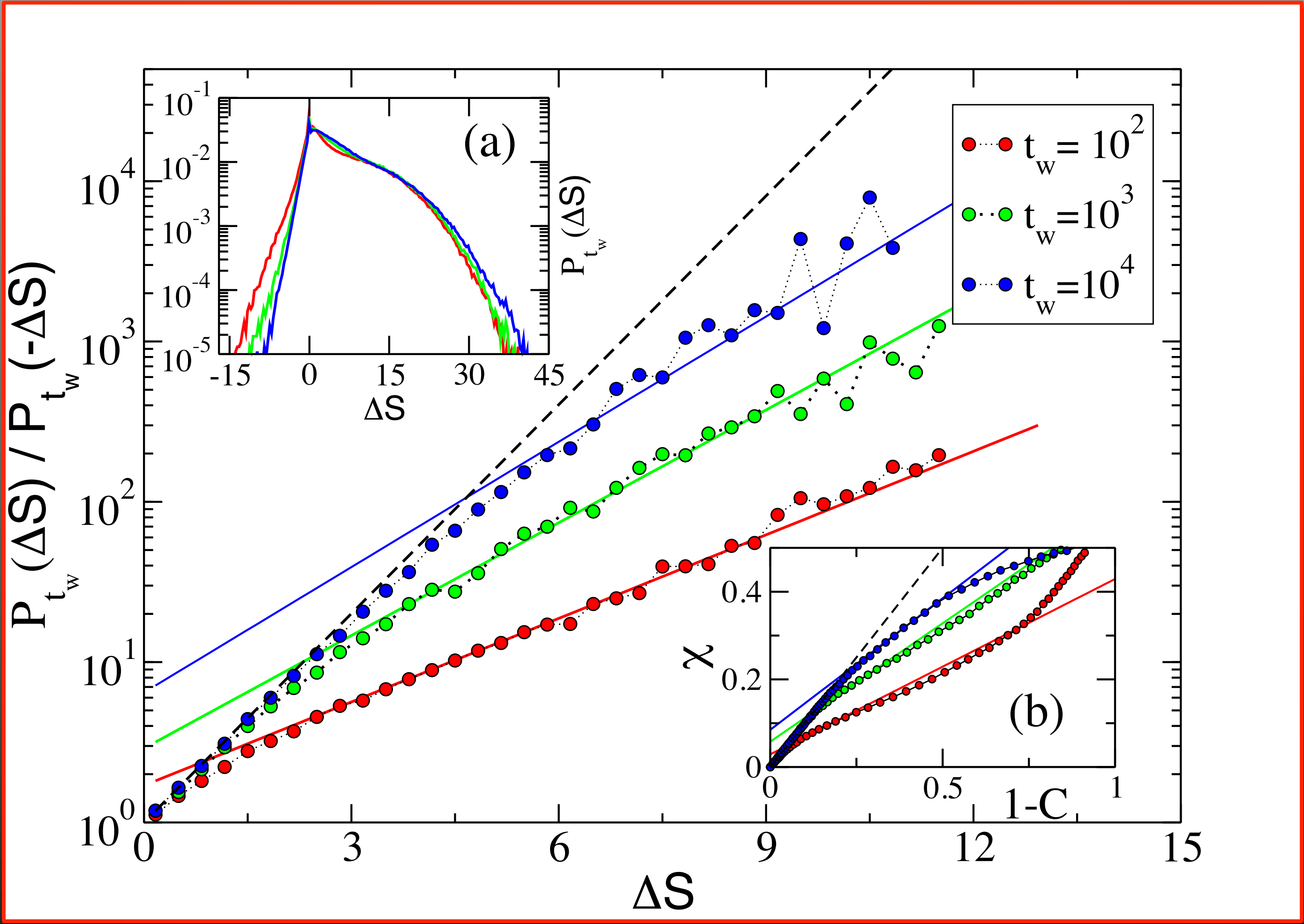

Numerical Test AFR

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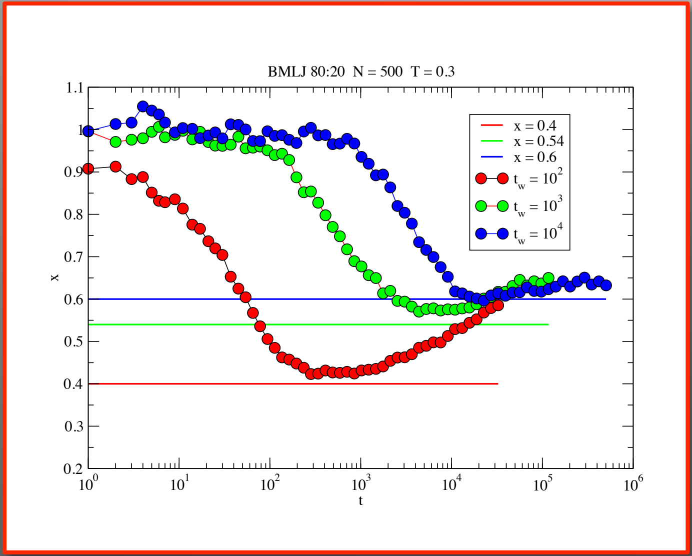
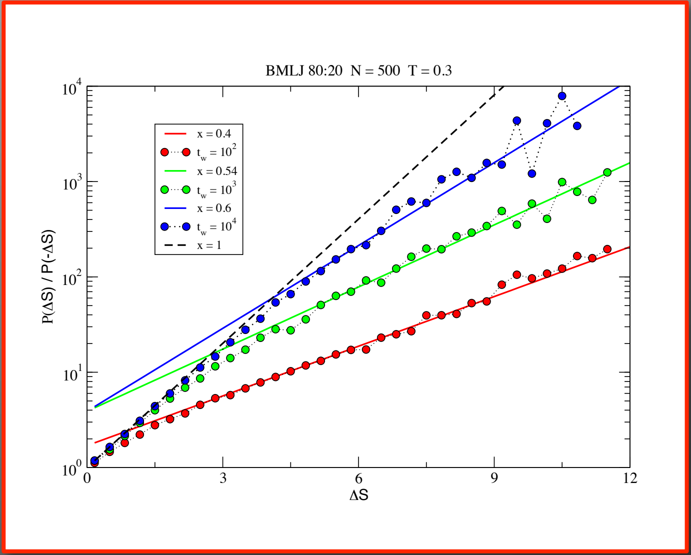
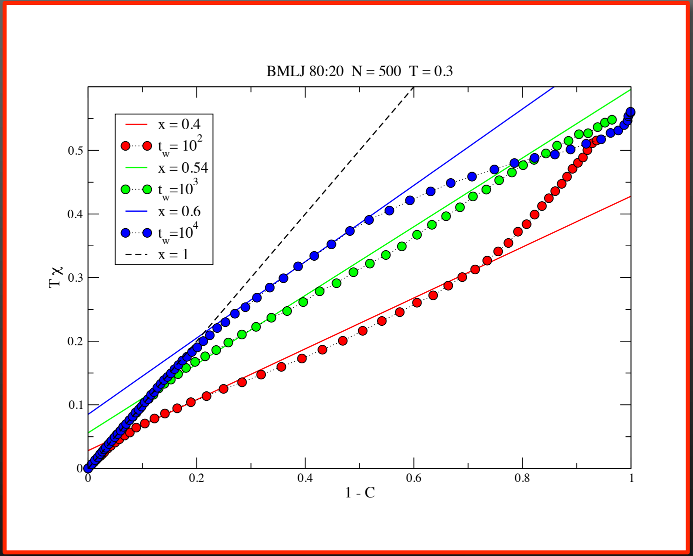




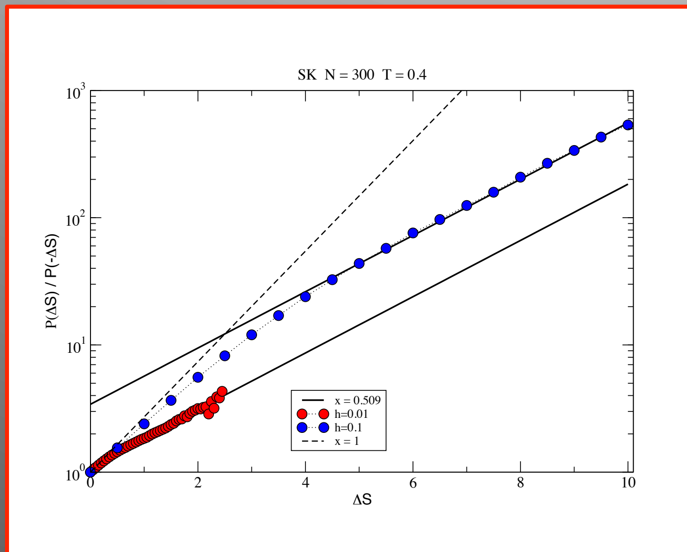


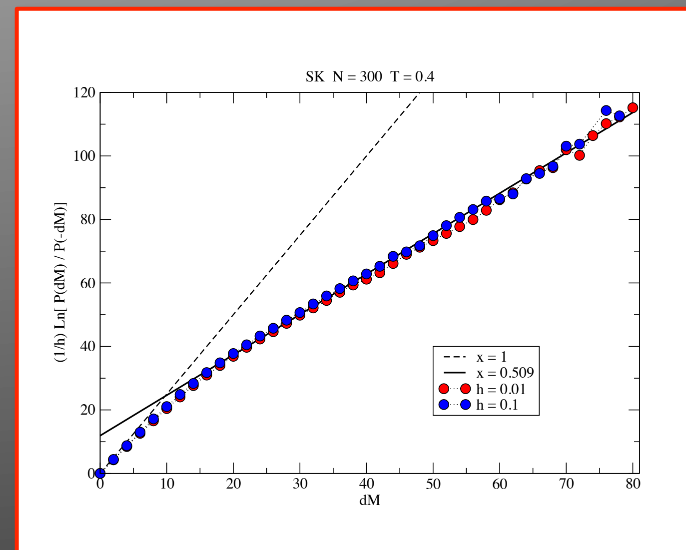
Numerical Test AFR

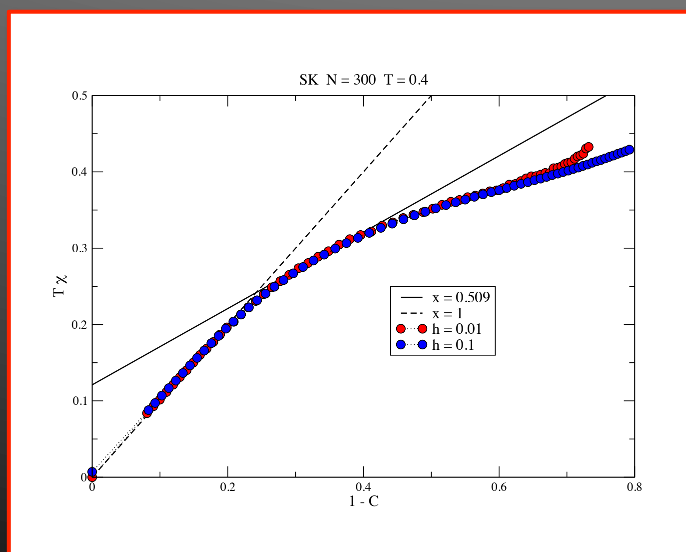
SK

$$H = - \sum_{1 \leq i < j \leq N} J_{ij} \sigma_i \sigma_j$$

J_{ij} Random Gaussian Matrix





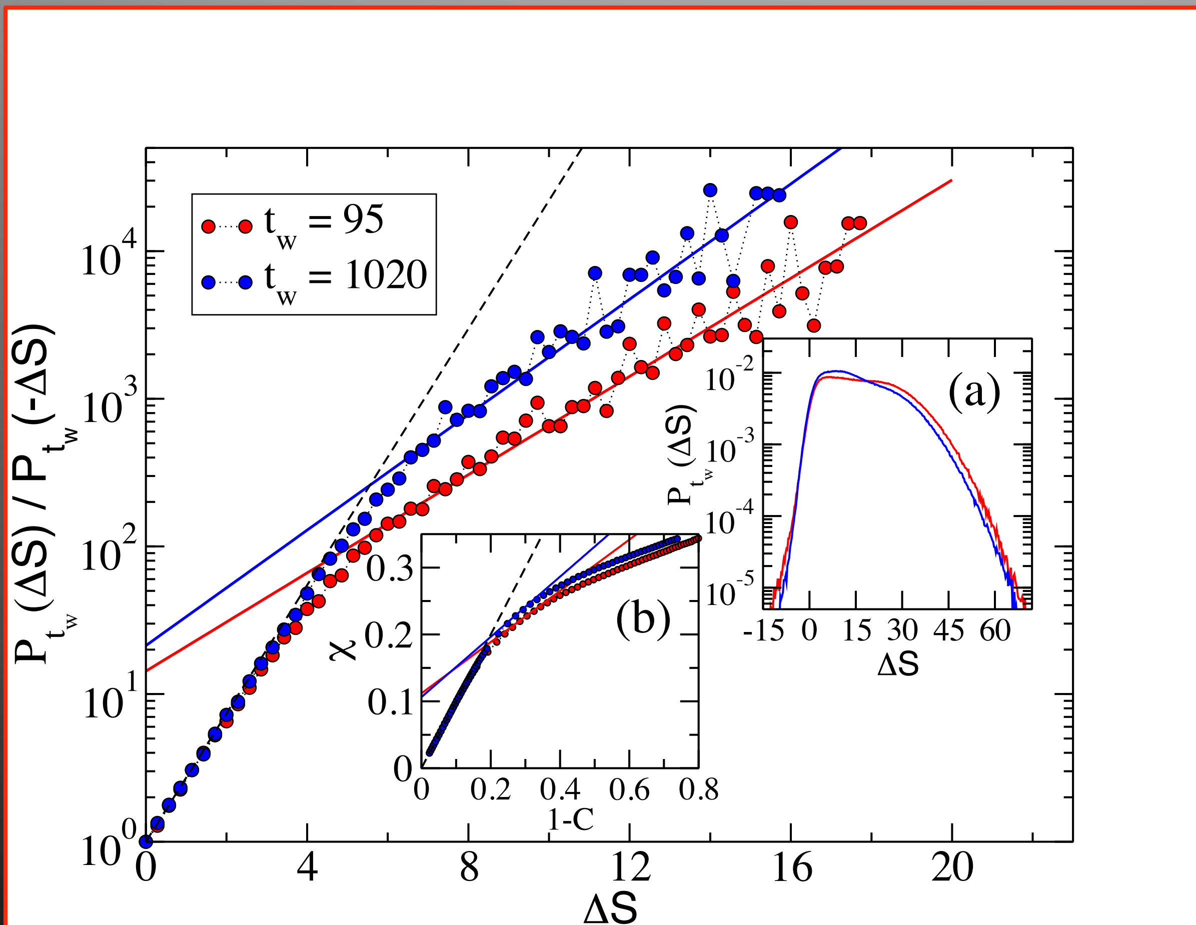


Numerical Test AFR

3D +/-J EA

$$H = -\sum_{1 \le i < j \le N} J_{ij}\sigma_i\sigma_j$$

J_{ij} Random +/-1 NN

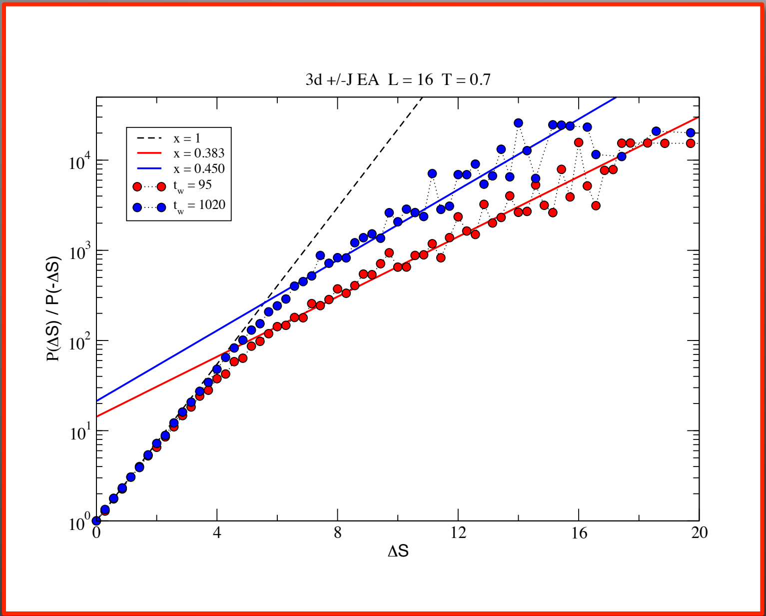


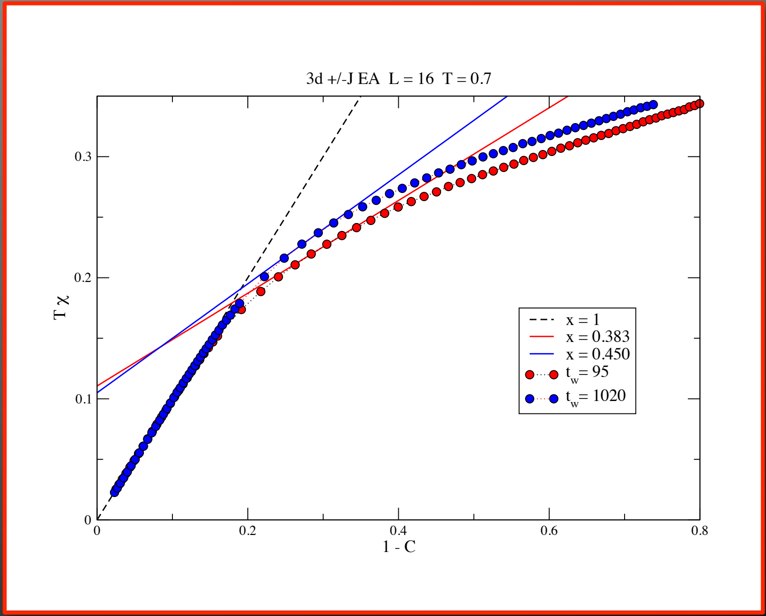
Numerical Test AFR

3D +/-J EA

$$H = -\sum_{1\leq i<j\leq N} J_{ij}\sigma_i\sigma_j$$

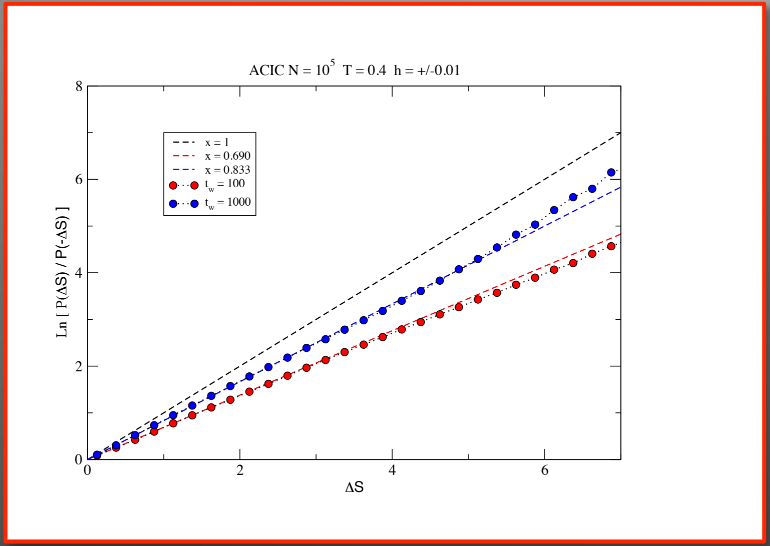
J_{ij} Random +/-1 NN Matrix

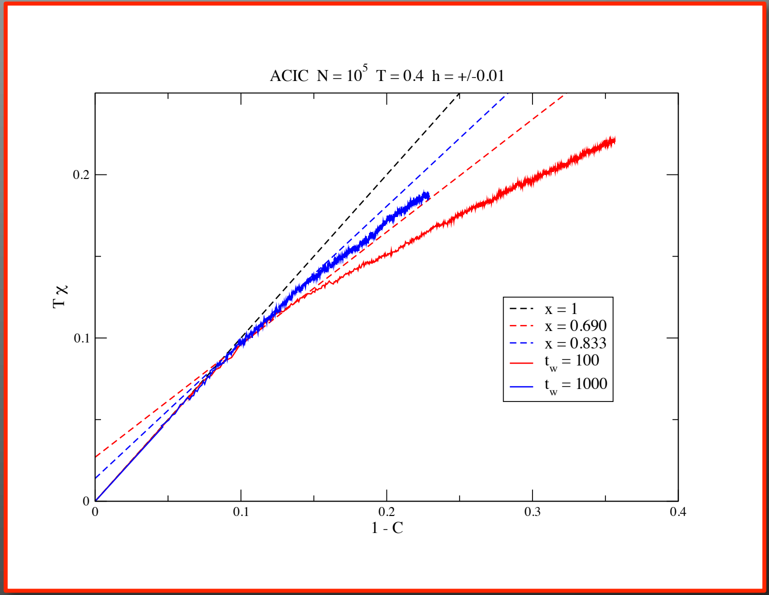




Numerical Test AFR

Asymmetrically Constraint Ising Chain (ACIC)



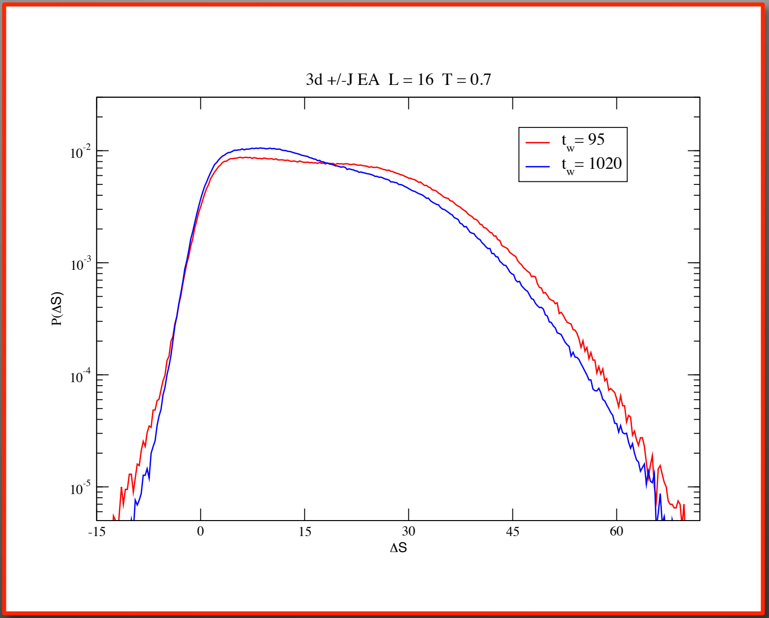


$$E = -\sum_{i=1}^{N} \sigma_i \qquad \sigma_i = 0, 1$$

$$\mathcal{W}(\sigma_i \to 1 - \sigma_i) = \min[1, \exp(-\beta \Delta E)] \times \delta_{\sigma_{i-1},0}$$

Numerical Test AFR

3D +/-J EA



Some Final Remarks…

- Proposed a Fluctuation Relation in the Aging regime
- Presented arguments
- Numerical Evidence

What Next…

- ….
- ….