Slow energy relaxation in linear and non-linear systems

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EPF-Lausanne, Switzerland

NLDD05 Sevilla, March 3-4, 2005

Overview of the talk

- Slow energy relaxation of local or distributed energy fluctuations: examples from simple and complex systems.
- Non-linear systems: stretched exponential relaxation in chains of coupled rotors. Relation with energy localization (rotobreathers).
- Conclusions 1
- Linear systems: complex energy relaxation in simple models of biological macromolecules and metallic nanoclusters…. Where does it come from?
- Conclusions 2

Slow energy relaxation: some examples

- Well-known slow kinetics in glasses

- Slow relaxation of local energy fluctuations in proteins (e.g. after photo-dissociation of CO group in Myoglobin)
  (Sabelko et al. PNAS 1999)

- Slow relaxation of global heat transfer after pump-probe experiments in metallic nanoclusters
  (Hu & Hartland, J.Phys.Chem. B 2002)

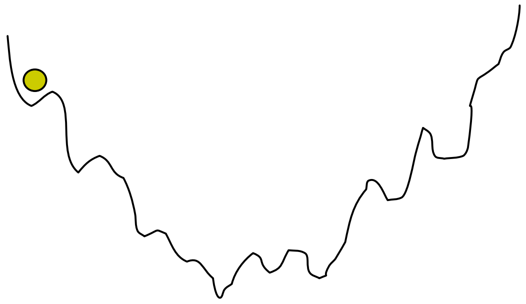
The natural explanation…

There exists a **spectrum** of relaxation rates associated with the degrees of freedom of the system, which relax exponentially…

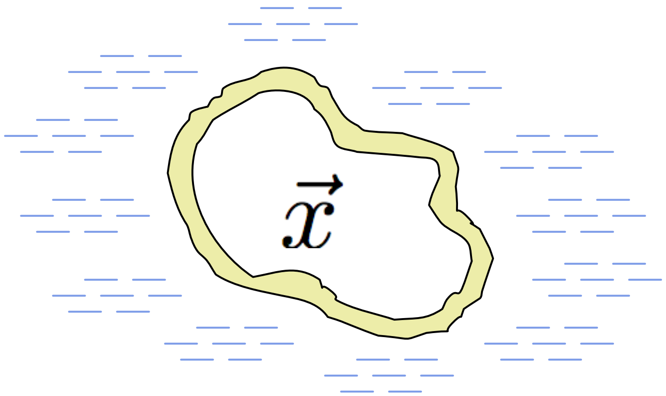
$$\mathcal{O}(t) = \int \langle \mathcal{O} | \vec{x} \rangle g(\vec{x}) e^{-t/\tau(\vec{x})} \, d\vec{x}$$

… intrinsic hierarchy of d.o.f
(high correlations among them)

… ruggedness of the energy landscape



...or

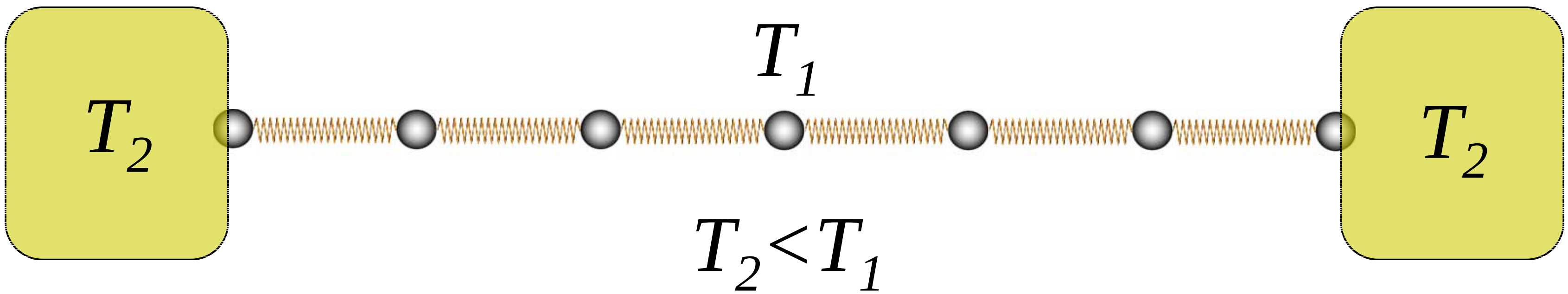


Systems with sizeable surface fraction are characterized by a natural inhomogeneity of coupling with the environment, which under general conditions results in a spectrum of decay rates $\tau(\vec{x})$

The simplest example:

an harmonic chain at equilibrium at $T=T_1$ is put in contact at its edges with a thermal bath at a lower temperature T_2

Slow energy relaxation in a 1D harmonic chain



The Langevin problem is equivalent to that of a deterministic system linearly damped at its edges from an initial energy $E(0) = k_B(T_1 - T_2)$

Asymptotically $\Longrightarrow$ $E(t)/E(0) = t^{-1/2}$ $\Longrightarrow$

Cross over to $\exp[-2t/\tau_N]$ on a time scale $\tau_N \propto N^3$

Cooling non-linear systems: disentangling localization and slow relaxation

Edge cooling in non-linear systems quite generally results in non-exponential relaxation, together with spontaneous energy localization.

Emergence of localized, long-lived objects reminiscent of Discrete Breathers.

What is the role of localized vibrations in slowing down the energy decay?

Some phenomenology

Systems with high dynamical discreteness (strong non-linear on-site potential) seem to display stretched-exponential relaxation → role of Breathers…

ϕ_4 potential

(Tsironis & Aubry, PRL 1996)

Systems with only nearest-neighbour interactions relax to a pseudo-stationary state following a power law $t^{-D/2}$

FPU $1D$ and $2D$

…. as the harmonic chain

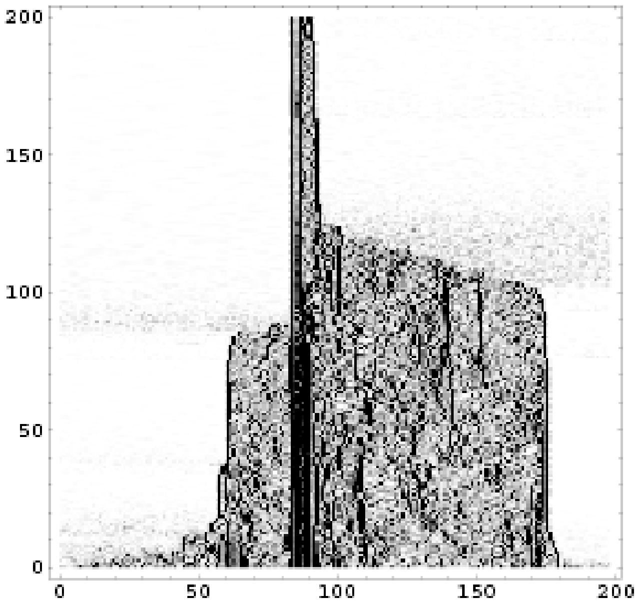
(Piazza, Lepri & Livi, J. Phys. A 2001, Chaos 2003, Reigada *et al*., PRE 2002)

Chain of coupled rotators damped at the edges

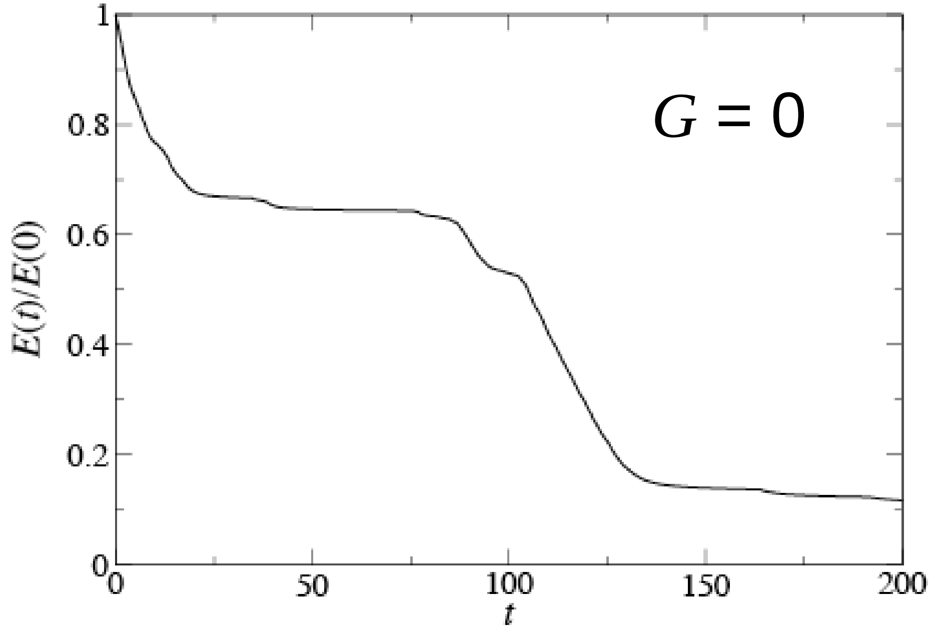
$$I_i \ddot{\phi}_i = -G \sin \phi_i$$
$$+K \left[\sin(\phi_{i+1} - \phi_i) + \sin(\phi_{i-1} - \phi_i) \right] - \gamma \dot{\phi}_i \left[\delta_{i,1} + \delta_{i,N} \right]$$

We study both the system with on-site potential ($G = 1$) and
The system with pure nearest-neighbour coupling ($G = 0$)

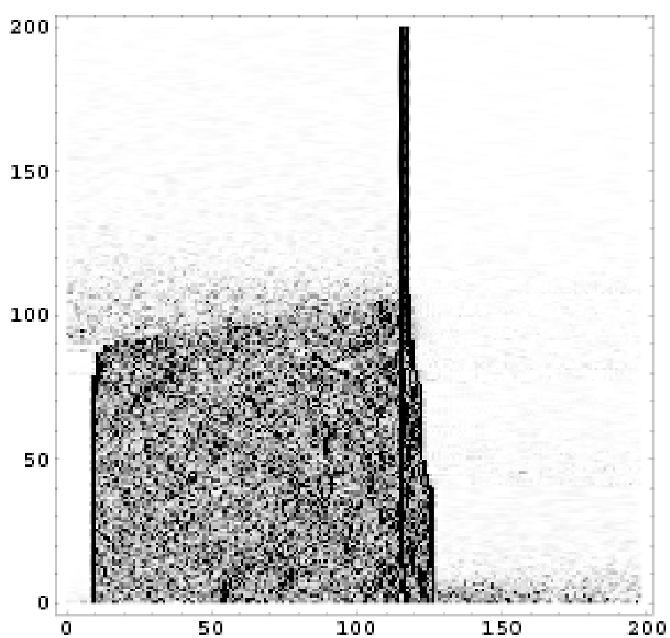
The energy decays as a stretched exponential, no matter the value of G



0
50
100
150
200



$G = 0$
$E(t)/E(0)$
t
0
0.2
0.4
0.6
0.8
1
50
100
150
200



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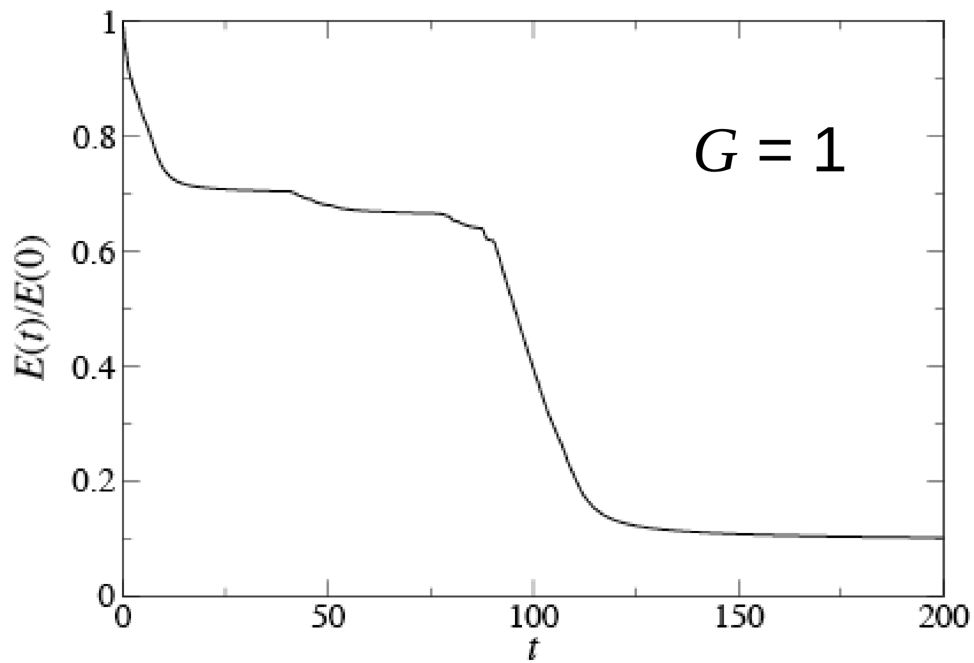

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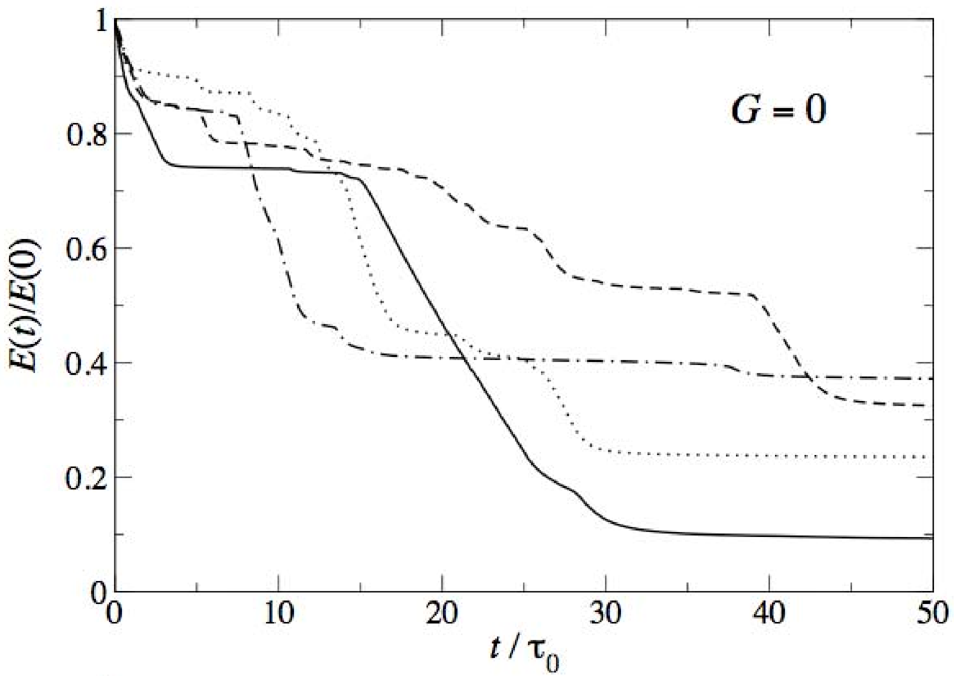
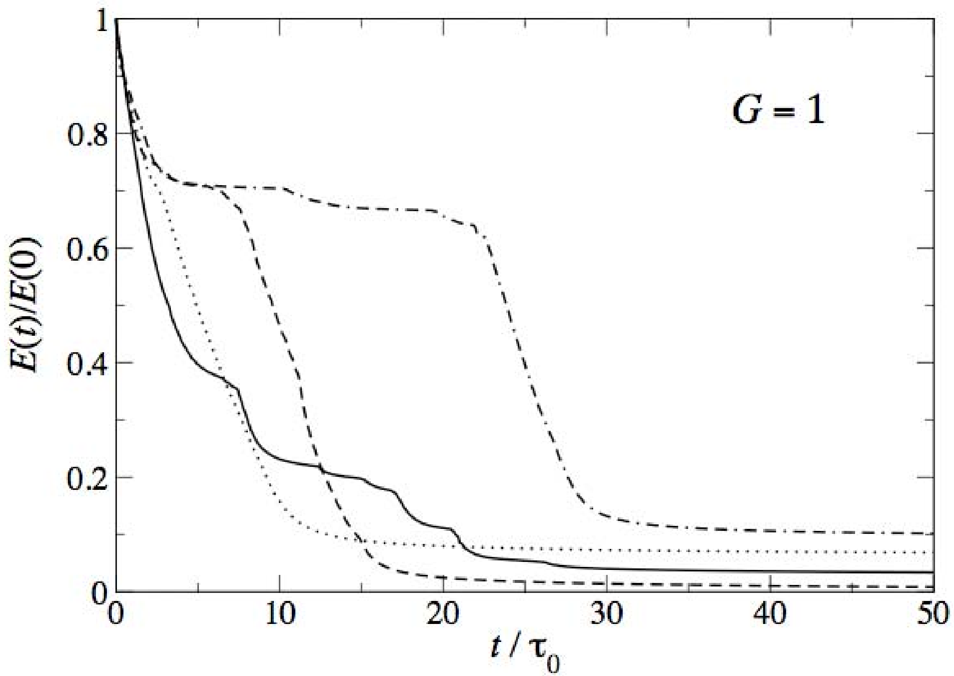




$$\tau_0 = N/2\gamma$$

Relaxation from equilibrium:

Characteristic step-wise trend of energy decay. Long plateaus followed by sudden jumps

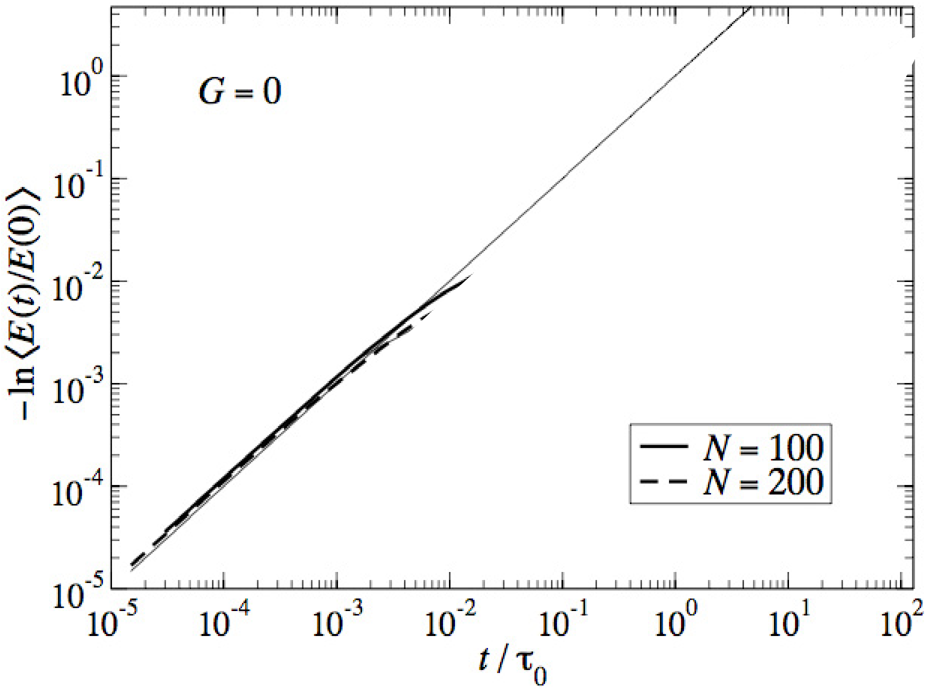
Decay of a central hot core, bounded by localized librating roto-breathers

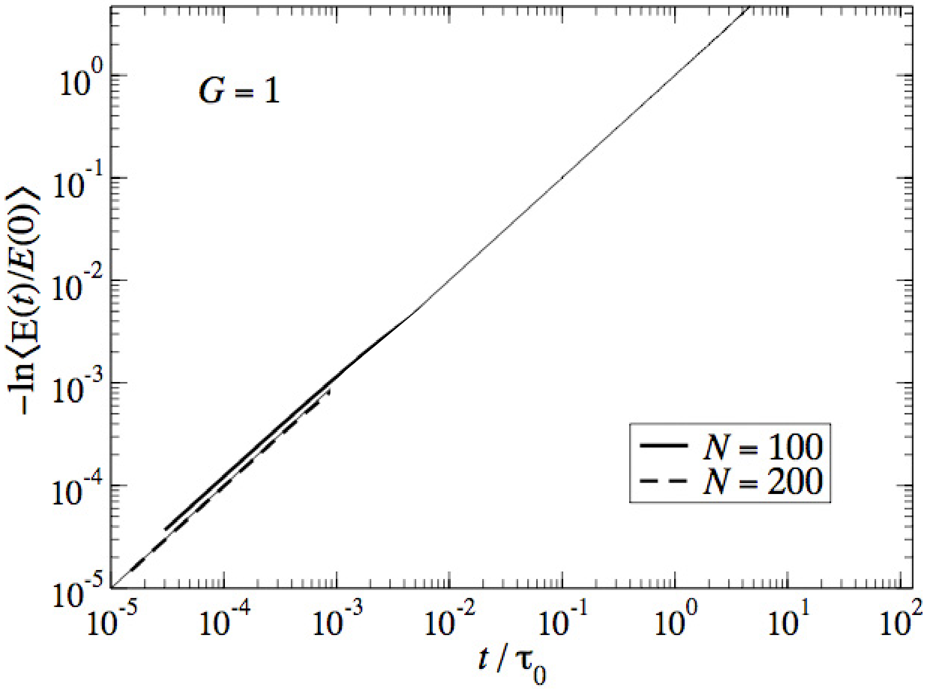
Boundary collapse –-> jump

The “integrated” decay is non-exponential

First exponential stage …

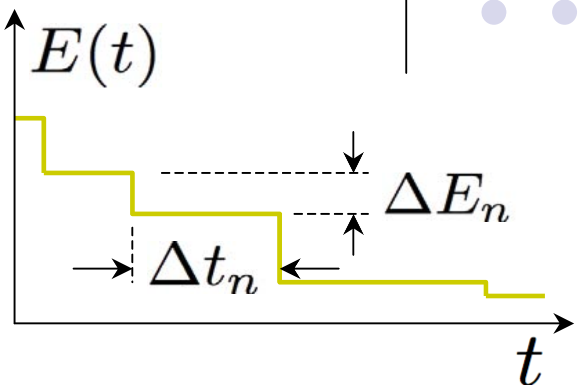
Crossover to a slower, stretched-exponential decay



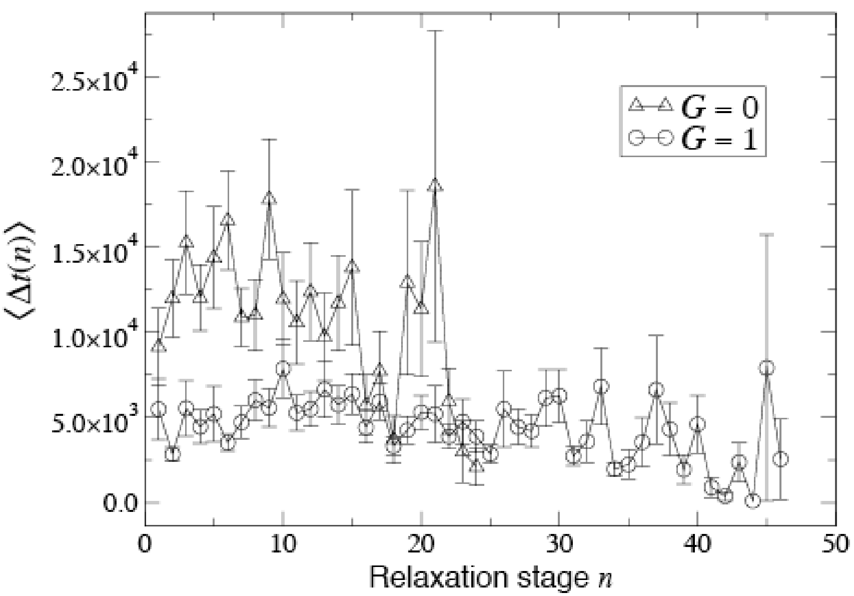


Statistical analysis of the relaxation pathway

$$\frac{E(t)}{E(0)} = 1 - \sum_{n=1}^{N_p} \Delta E_n \Theta \left(t - \sum_{m=0}^{n-1} \Delta t_m \right)$$



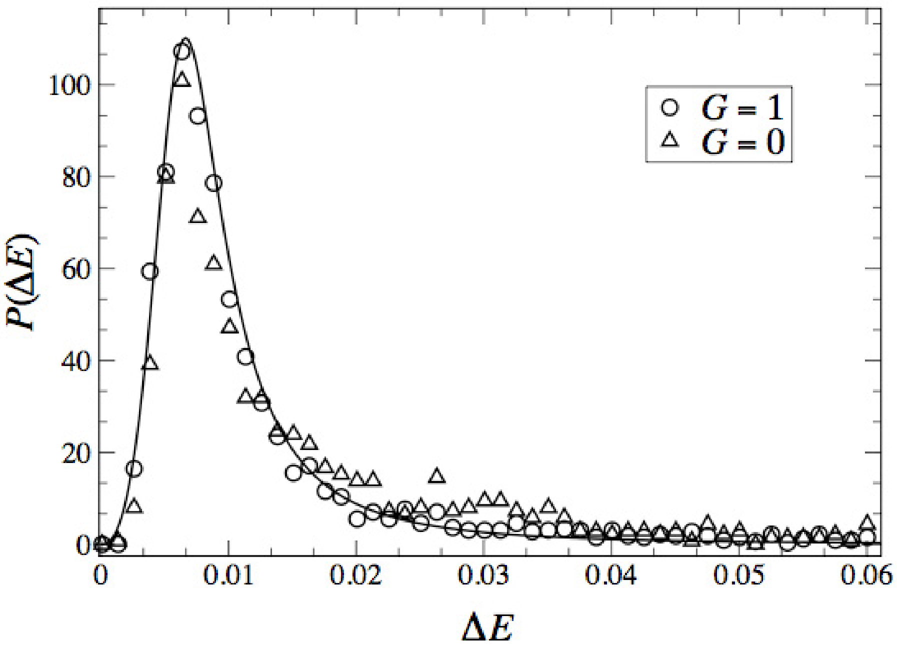
Is it just an effect of non-stationarity (growing $\langle \Delta t_n \rangle$)?

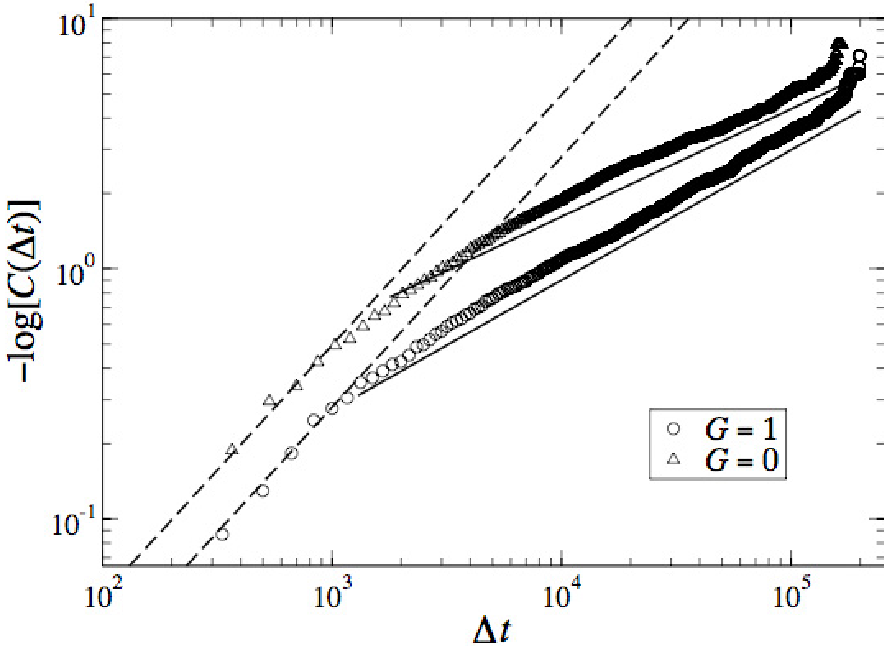


No, the average duration of plateaus does not change with relaxation stage

The statistics of plateau durations is intrinsically stretched exponential…

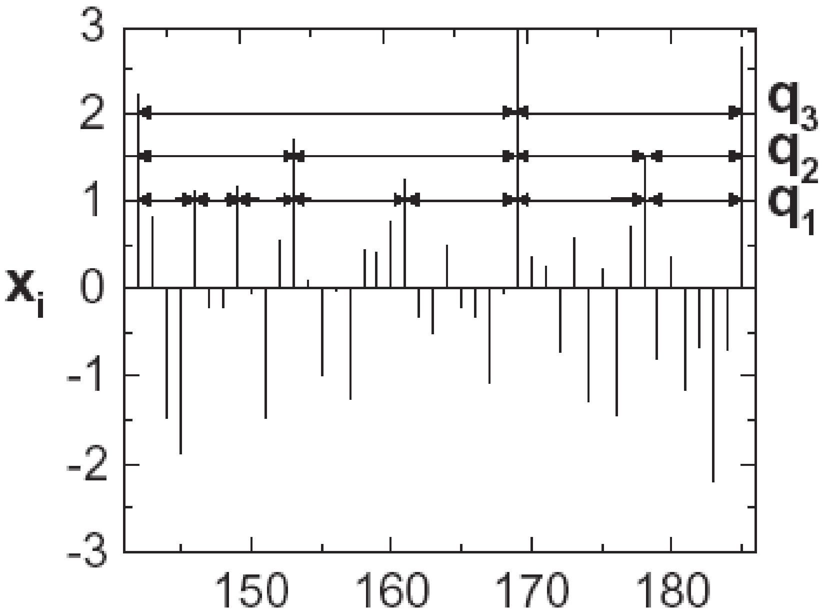
It is possible to find a rationale for that by drawing an analogy with the statistics of return periods of rare events





Return periods of rare events

(A. Bunde et al., Physica A, 330, 1 (2003))



$$x(i) = \text{Time series}$$

$$q = \text{threshold}$$

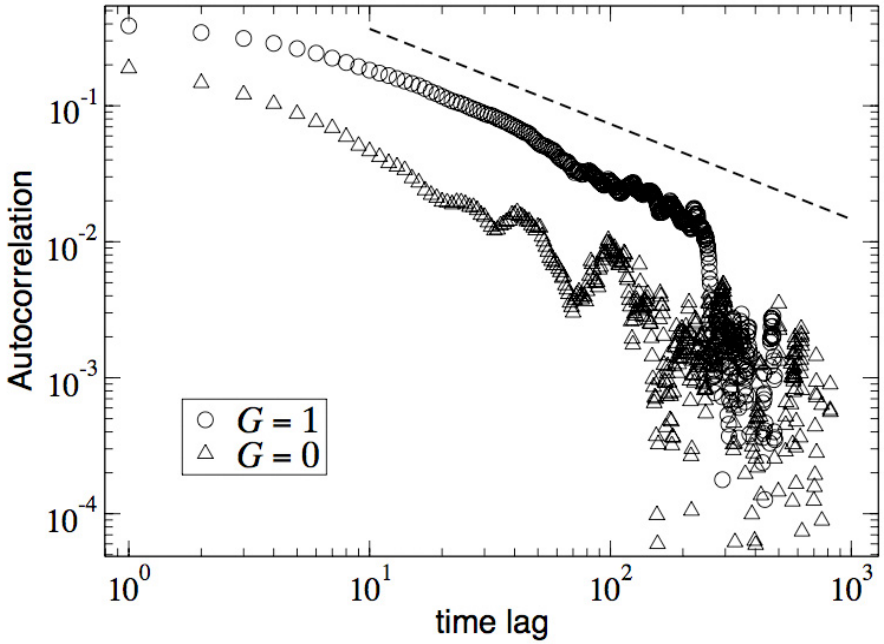
$$x(i) > q \Rightarrow$$ **event is "rare"**

$$\langle x(t)x(0)\rangle \propto t^{-\gamma} \;\; (0 < \gamma < 1) \Rightarrow$$

Stretched-exponential statistics of return periods $P(\Delta t) \propto \exp[-t^{\gamma'}] \;\; (\gamma' \approx \gamma)$

Collapse of a rotobreather as a rare event

$$J(t) = E(t + t_s) - E(t) > q \Rightarrow \text{Energy jump}$$



Physically J is the energy flux integrated over a sampling interval

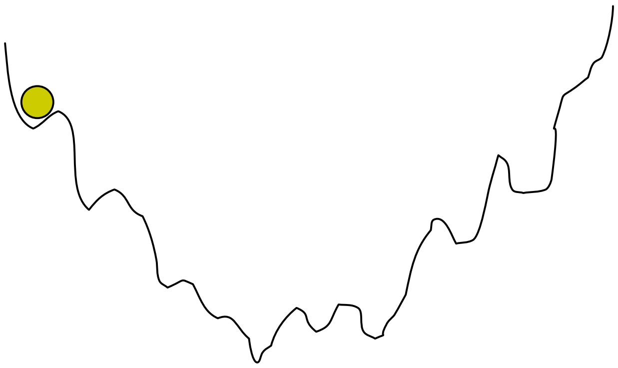
In the FPU lattice (no stretched exponential) the flux autocorrelation decays exponentially

Conclusions

- Energy relaxation in chains of coupled rotators proceeds in a characteristic, step-wise fashion: plateaus followed by jumps. This reflects the spatial segregation of a central, hot core in the chain.
- The “integrated” energy decay is stretched exponential, with and without on-site coupling: same picture.
- Connection with return periods of rare events. Collapse of a rotobreather is a “rare” event in the series of energy flux.
- Accordingly, the autocorrelation of the energy flux decays slower than exponentially (a general signature of stretched-exponential relaxation?)

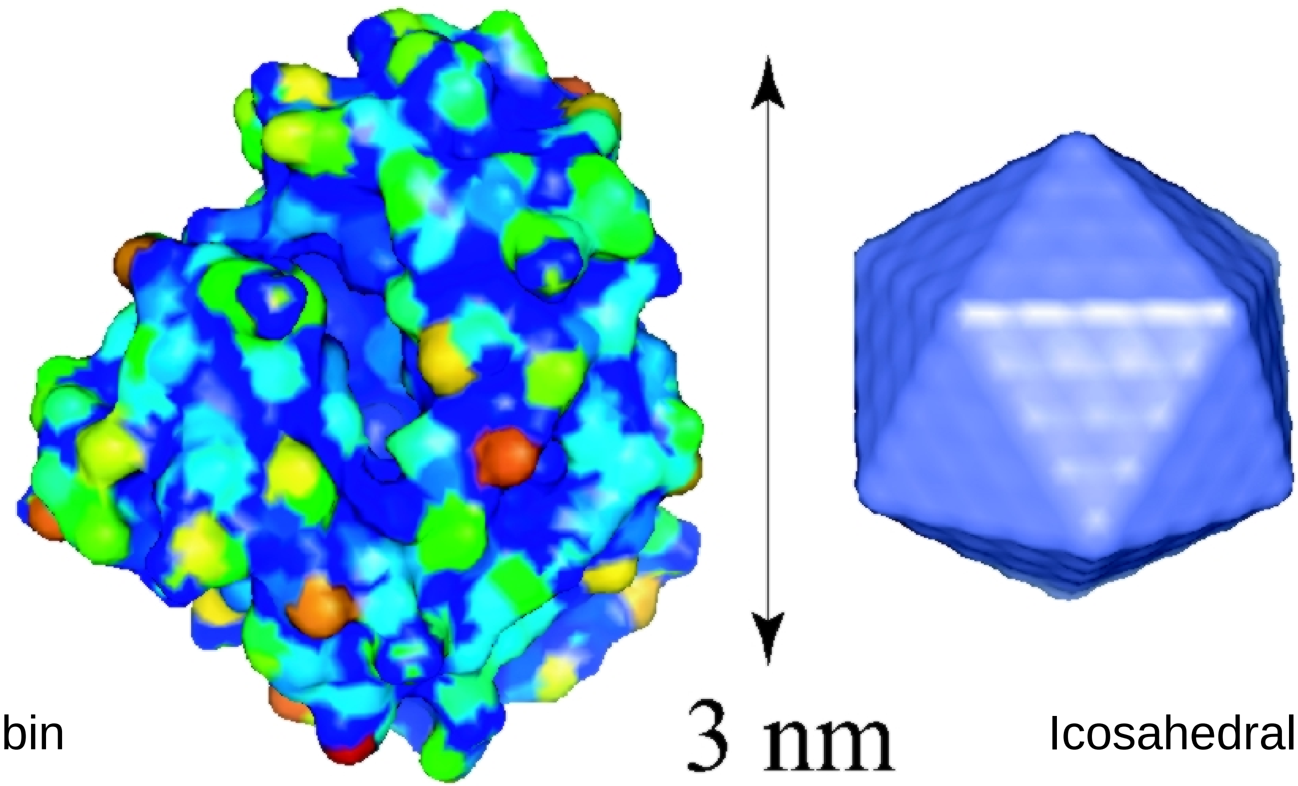
Slow energy relaxation in complex systems

Challenging the picture of Potential ruggedness



Many systems from the nano-world have sizeable surface fractions…

…and live immersed in a viscous solvent



Myoglobin

Icosahedral nano-cluster

The problem

We want to study the relaxation of the system from a temperature T_1 to a lower temperature T_2

The individual units (residues, atoms) are assigned a “local” surface fraction ***f*** (**bulk** and **surface**)

We describe the stochastic dynamics à la Langevin. The damping constants are taken to be proportional to ***f***

The amplitudes of the fluctuating forces are set accordingly, in obeyance to the FD theorem.

The simplest dynamical model: a network of beads and springs

$$V(\vec{r}_i, \vec{r}_j) = k_{ij}/2(|\vec{r}_i - \vec{r}_j| - |\vec{r}_{i0} - \vec{r}_{j0}|)^2$$

$$k_{ij} = k\ \theta(|\vec{r}_{i0} - \vec{r}_{j0}| - r_c)$$

$$k_{ij} = k\ \exp(-|\vec{r}_{i0} - \vec{r}_{j0}|^2/r_c^2)$$

$$U = \frac{1}{2}(X - X^0)^T K\,(X - X^0)$$

The matrix K is the Hessian of the potential energy function evaluated at the equilibrium structure

We can define a damping matrix Γ (diagonal)

$$\Gamma_{ij} = \gamma \delta_{ij} S_i$$

The vector S specifies the surface fractions ($0 < S_i < 1$)

Fokker-Planck formulation of the problem

$$\frac{\partial P(Y,t|Y(0))}{\partial t} = \sum_{i,j=1}^{6N} \left[-\mathbb{A}_{i,j} \frac{\partial}{\partial Y_i} Y_j + \mathbb{B}_{i,j} \frac{\partial^2}{\partial Y_i \partial Y_j} \right] P(Y,t|Y(0)) \quad (6)$$

where $Y = (X - X^0, \dot{X})$ is the $6N$–dimensional vector of displacements and velocities, and the matrices $\mathbb{A}$ and $\mathbb{B}$ are given by

$$\mathbb{A} = \left(\begin{array}{c|c} 0 & \mathbb{I}_{3N} \\ \hline -K & -\Gamma \end{array} \right) \qquad \mathbb{B} = k_B T \left(\begin{array}{c|c} 0 & 0 \\ \hline 0 & \Gamma \end{array} \right) \quad . \quad (7)$$

The solution

$$P(Y,t|Y(0)) = (2\pi)^{-3N}|\det C(t)|^{-1/2}$$
$$\times \exp\left\{-\frac{1}{2}[Y-G(t)Y(0)]^T C^{-1}(t)[Y-G(t)Y(0)]\right\}$$

where G is the propagator matrix and

$$C_{i,j}(t) = \langle Y_i(t)Y_j(t)\rangle = \left(\begin{array}{c|c} C_{XX} & C_{X\dot{X}} \\ \hline C_{X\dot{X}} & C_{\dot{X}\dot{X}} \end{array}\right)$$

The evolution law for the correlation matrix

$$C(t) = C(\infty) + G^T(t)[C(0) - C(\infty)]G(t)$$

where

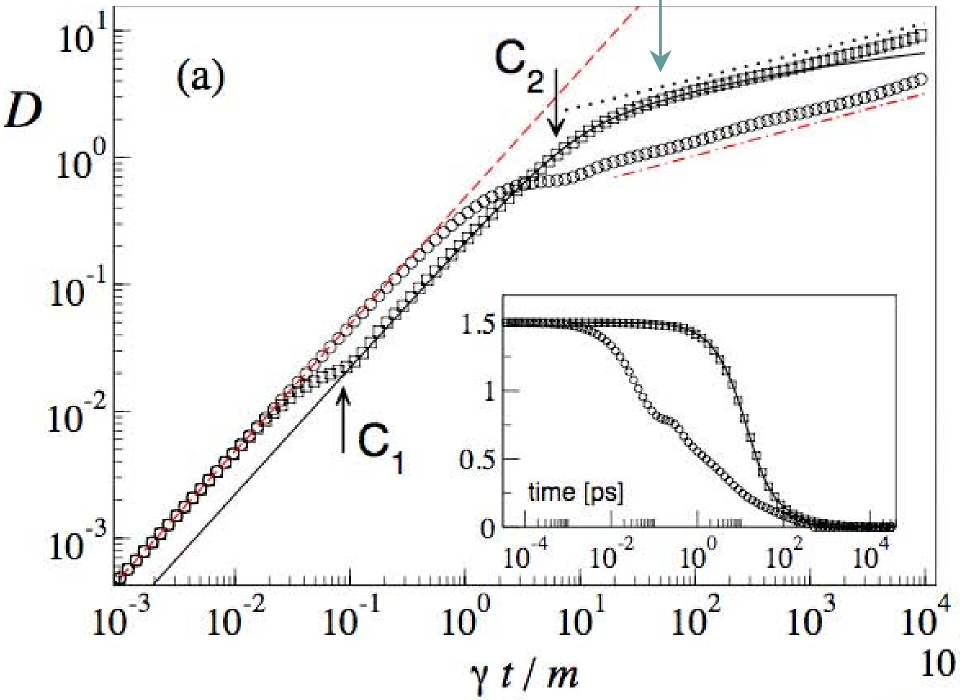
$$C(\infty) = k_B T \left(\begin{array}{c:c} K^{-1} & 0 \\ \hdashline 0 & \mathbb{I}_{3N} \end{array} \right)$$

The energy decay

$$\langle E(t)\rangle = \frac{1}{2}\mathrm{Tr}\left[C_{\dot{X}\dot{X}}(t) + KC_{XX}(t)\right]$$

$$\mathcal{D}(t) = -\log\left[\frac{\langle E(t)\rangle - \langle E(\infty)\rangle}{\langle E(0)\rangle - \langle E(\infty)\rangle}\right]$$

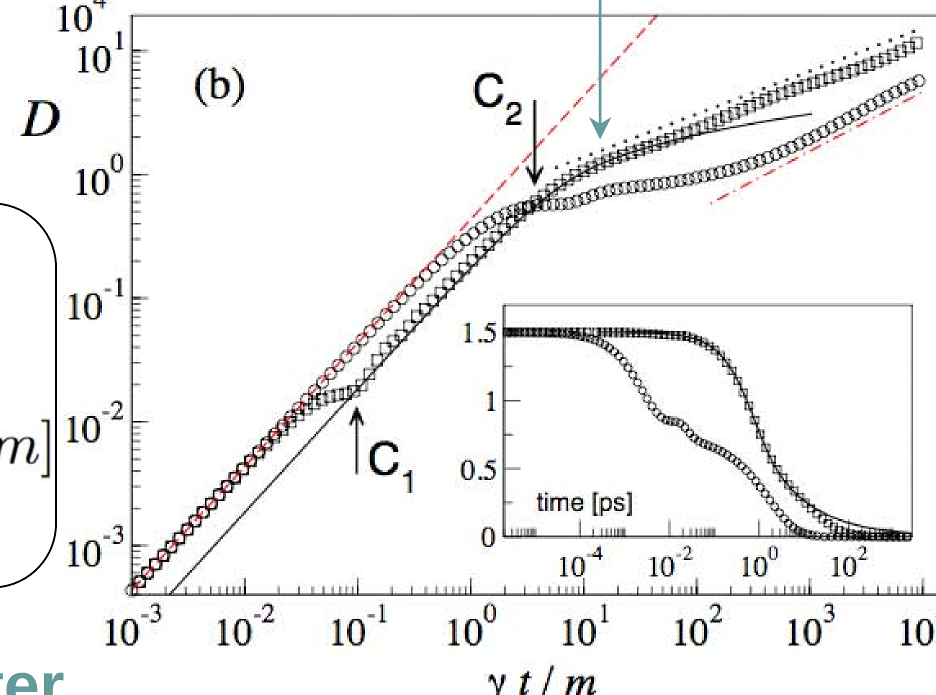
In log-log scale D is straight line with slope one if E(t) decays exponentially



Myoglobin

Stretched exponentials

$$f_{\text{eff}} = \frac{1}{N}\sum_i S_i$$



dashed line - - - - - - - - - -

$$\frac{\langle E(t)\rangle - \langle E(\infty)\rangle}{\langle E(0)\rangle - \langle E(\infty)\rangle} = \exp[-2 f_{\text{eff}} \gamma t / m]$$

Sample nano-cluster

Conclusions

- Systems with sizeable surface fractions immersed in a viscous medium are characterized by a natural hierarchy of relaxation times, even in smooth energy landscapes.

- Systems as different as Myoglobin and a metal nano-cluster, even in the harmonic approximation, show complex relaxation dynamics.

Credits

- Maria Eleftheriou (Athens)
- Stefano Lepri, Roberto Livi (Florence)

- Paolo De Los Rios (EPFL)
- Yves-Henri Sanejouand (ENS-Lyon)