Effective temperatures

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Plan

1. Equilibrium temperature.

2. An ‘effective temperature’ for *certain* out of equilibrium systems.

LFC, J. Kurchan & L. Peliti 97

— Measurement and properties.

— Relation to entropy : Edwards’ measure.

— Fluctuation theorems.

— Ratchets

3. Quenches of isolated systems

4. Conclusions.

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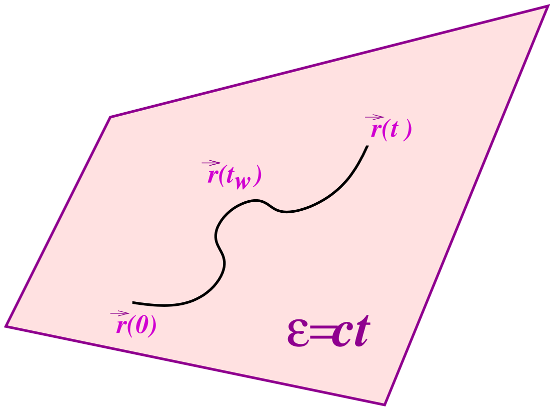
Temperature

Statistical mechanics definition



- Isolated system $\Rightarrow$ conserved energy $\mathcal{E}$
- Ergodic hypothesis

$$S = k_B \ln \mathcal{N} \qquad\qquad \beta \equiv \frac{1}{k_B T} = \left.\frac{\partial S}{\partial \mathcal{E}}\right|_{\mathcal{E}}$$

Microcanonical definition

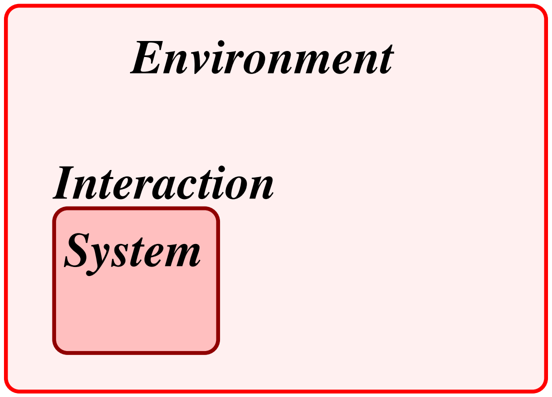
$$\mathcal{E} = \mathcal{E}_{syst} + \mathcal{E}_{env} + \mathcal{E}_{int}$$

Neglect $\mathcal{E}_{int}$ (short-range int.)

$$\mathcal{E}_{syst} \ll \mathcal{E}_{env}$$

$$p_{eq}(\mathcal{E}_{syst}) = g(\mathcal{E}_{syst}) e^{-\beta \mathcal{E}_{syst}} / Z$$

Canonical ensemble



Properties & measurement

Connection with thermodynamics

— Relation to entropy.

— Control of heat-flows : ΔQ follows ΔT.

— Partial equilibration – transitivity :

$T_A = T_B, T_B = T_C \Rightarrow T_A = T_C$.

thermometers for systems in good thermal contact (ΔQ)

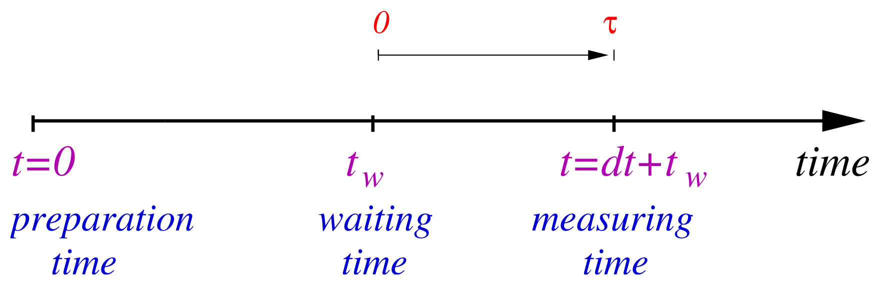
Whatever we identify with a temperature should have these properties

In and out of equilibrium

Take a **mechanical point of view** and call $\{\vec{r}_i\}(t)$ the variables

e.g. the particles' coordinates $\{\vec{x}_i(t)\}$ and momenta $\{\vec{p}_i(t)\}$

Choose an initial condition $\{\vec{r}_i\}(0)$ and let the system evolve.



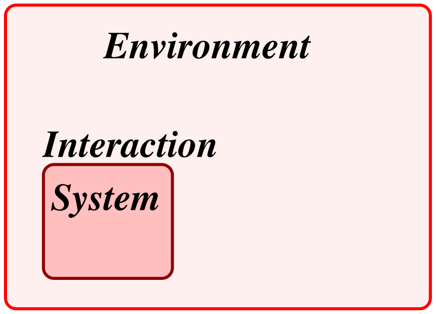
- For $t_w > t_{eq}$: $\{\vec{r}_i\}(t)$ reach the equilibrium pdf and thermodynamics and statistical mechanics apply. **Temperature** is a well-defined concept.
- For $t_w < t_{eq}$: the system remains out of equilibrium and thermodynamics and (Boltzmann) statistical mechanics **do not** apply.

Is there a quantity to be associated with a temperature ?

Dynamics in equilibrium

Conditions

Take an open system coupled to an environment



Necessary :

— The bath should be in equilibrium

same origin of noise and friction.

— Deterministic force :

conservative forces only, $\vec{F} = -\vec{\nabla} V$.

— Either the initial condition is taken from the equilibrium pdf, or the latter should be reached after an equilibration time t_{eq} :

$$P_{eq}(v, x) \propto e^{-\beta(\frac{mv^2}{2} + V)}$$

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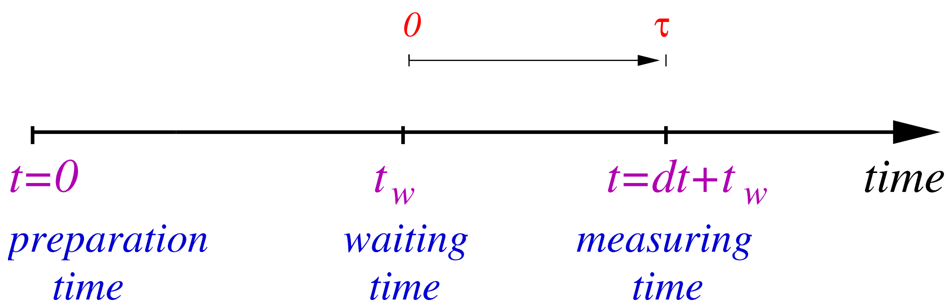
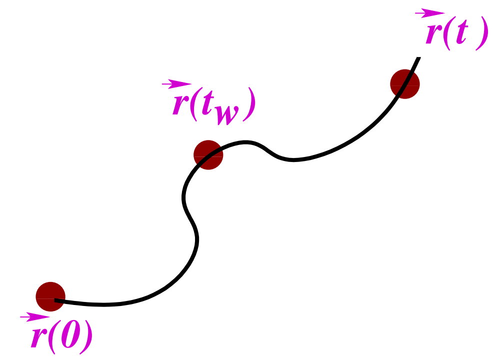
Two-time observables

Correlations





t_w not necessarily longer than t_{eq}.

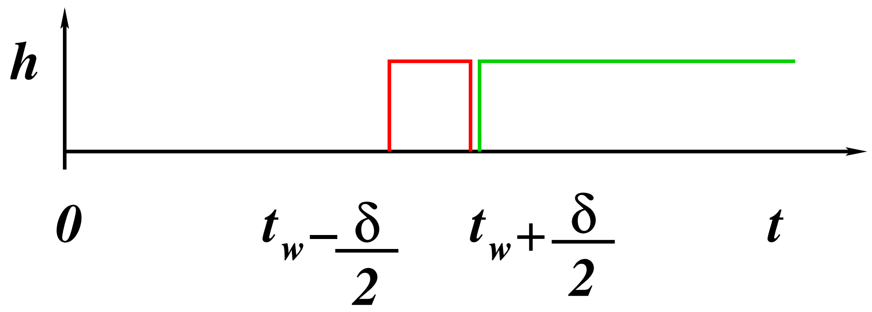
The two-time correlation between $A[\vec{x}(t)]$ and $B[\vec{x}(t_w)]$ is

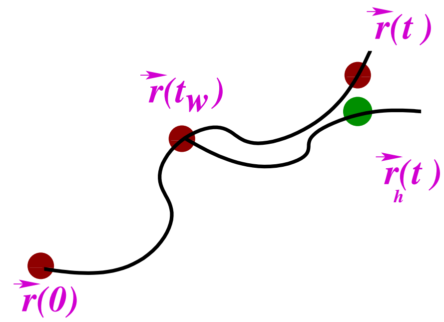
$$C_{AB}(t,t_w) \equiv \langle\, A[\vec{x}(t)] B[\vec{x}(t_w)] \,\rangle$$

average over realizations of the dynamics (initial conditions, random numbers in a MC simulation, thermal noise in Langevin dynamics, etc.)

Two-time observables

Linear response





The perturbation couples linearly to the observable $B[\vec{x}(t_w)]$

$$E \quad \to \quad E - hB[\vec{x}(t_w)]$$

The linear instantaneous response of another observable $A[\vec{x}(t)]$ is

$$R_{AB}(t,t_w) \equiv \left. \frac{\delta \langle A[\vec{x}(t)] \rangle_h}{\delta h(t_w)} \right|_{h=0}$$

The linear integrated response is

$$\chi_{AB}(t,t_w) \equiv \int_{t_w}^{t} dt' \, R_{AB}(t,t')$$

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LFC

Fluctuation-dissipation

In equilibrium

$$\boxed{P(\vec{r}, t_w) = P_{eq}(\vec{r})}$$

- The dynamics are stationary

$$C_{AB} \to C_{AB}(t - t_w) \text{ and } R_{AB} \to R_{AB}(t - t_w)$$

- The fluctuation-dissipation theorem between spontaneous (C_{AB}) and induced (R_{AB}) fluctuations

$$R_{AB}(t - t_w) = -\frac{1}{k_B T} \frac{\partial C_{AB}(t - t_w)}{\partial t} \, \theta(t - t_w)$$

holds and implies ($k_B = 1$ henceforth)

$$\boxed{\chi_{AB}(t - t_w) \equiv \int_{t_w}^{t} dt' \, R_{AB}(t, t') = \frac{1}{T}[C_{AB}(0) - C_{AB}(t - t_w)]}$$

Fluctuation-dissipation

Linear relation between χ and C

$$\boxed{P(\vec{r}, t_w) = P_{eq}(\vec{r})}$$

- The dynamics are stationary

$$C_{AB} \to C_{AB}(t - t_w) \text{ and } R_{AB} \to R_{AB}(t - t_w)$$

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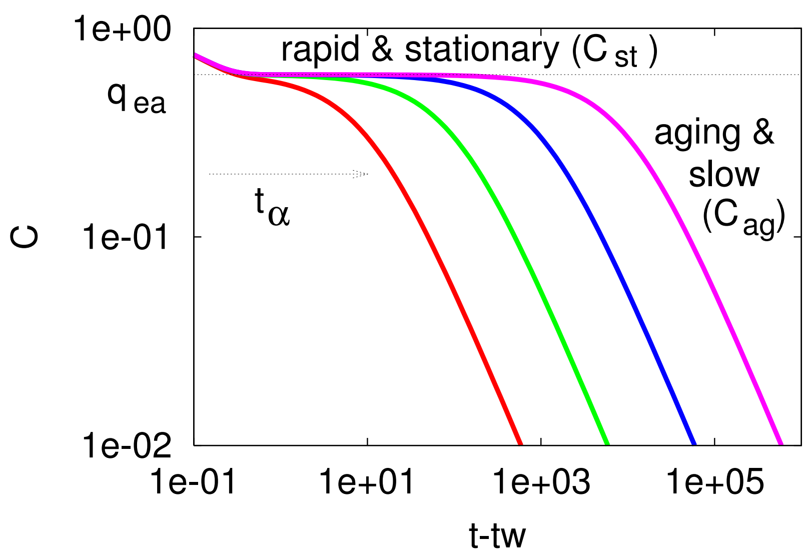
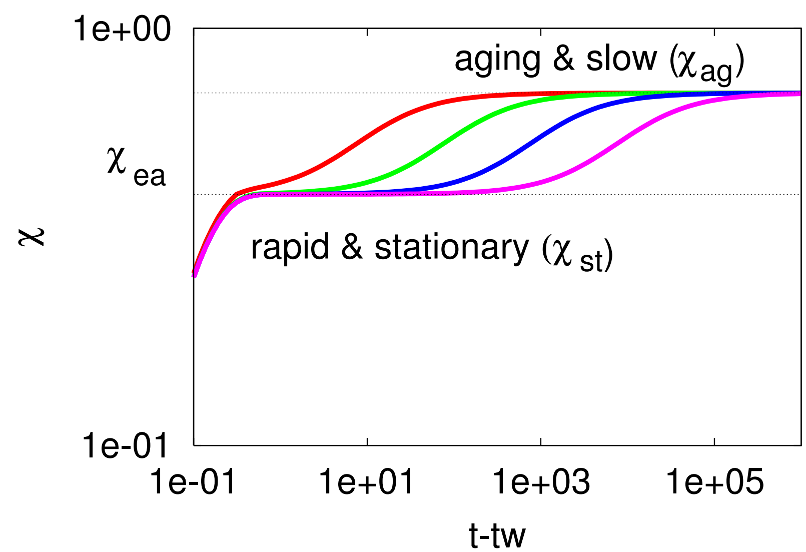
Fluctuation-dissipation

Solvable glasses: p spin-models & mode-coupling theory

- Stochastic dynamics of a particle in an *infinite dimensional* space under the effect of a quenched random potential.
- A fully-connected (Curie approximation) spin model with as many ferromagnetic as antiferromagnetic couplings.



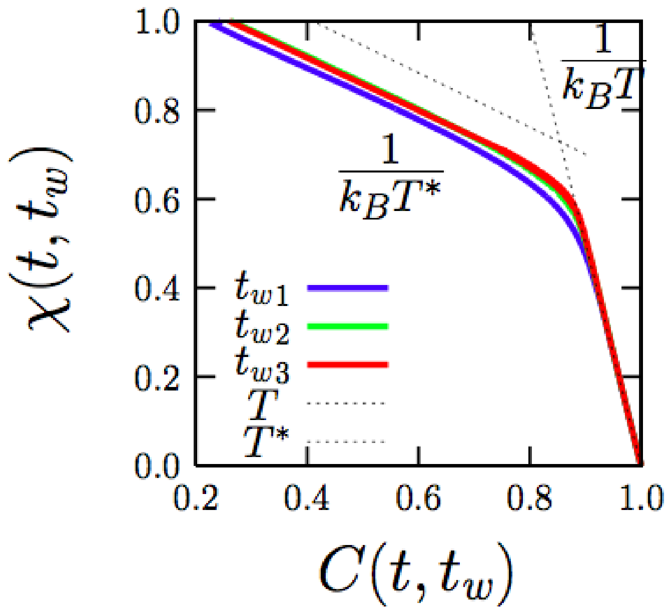


Sketch of the **separation of time-scales** in the out of equilibrium relaxation

Fluctuation-dissipation

Solvable glasses: p spin-models & mode-coupling theory

A quench from $T_0 \to \infty$ (gas) to $T < T_g$ (glass)



Parametric construction

t_w fixed

$t_{w_1} < t_{w_2} < t_{w_3}$

t : $t_w \to \infty$ or

$\tau \equiv t - t_w$: $0 \to \infty$

used as a parameter

Note that $T^* > T$

LFC & Kurchan 93

Fluctuation-dissipation

Proposal

For non-equilibrium systems, relaxing slowly towards an **asymptotic** limit (*cfr.* threshold in p spin models) such that **one-time quantities** [*e.g.* the energy-density $\mathcal{E}(t)$] **approach a finite value**

$$\lim_{\substack{\mathbf{t_w \to \infty} \\ C(t,t_w)=C}} \chi(t,t_w) = f_\chi(C)$$

For weakly forced non-equilibrium systems in the limit of **small work**

$$\lim_{\substack{\boldsymbol{\epsilon \to 0} \\ C(t,t_w)=C}} \chi(t,t_w) = f_\chi(C)$$

And the effective temperature is $$-\frac{1}{T_{\text{eff}}} \equiv \frac{\partial \chi}{\partial C}$$

LFC & Kurchan 94

A short-time regime with FDT ?

A general property proven by a bound for Langeving dynamics

$$|\chi(t,t_w) - C(t,t) + C(t,t_w)| \leq K \left(-\frac{1}{N} \frac{d\mathcal{H}(t_w)}{dt_w} \right)^{1/2}$$

with the "H-function"

$$\mathcal{H}(t_w) = \int d\vec{x} d\vec{v} \; P(\vec{x},\vec{v},t_w) \left[k_B T \ln P(\vec{x},\vec{v},t_w) + H(\vec{x},\vec{v}) \right]$$

and its time variation $\frac{d\mathcal{H}(t_w)}{dt_w} = -\langle \vec{f}(t_w) \cdot \vec{v}(t_w) \rangle - \sum_i g_i(t_w)$

where the first term is the work done by eventual non-potential forces $\vec{f}$

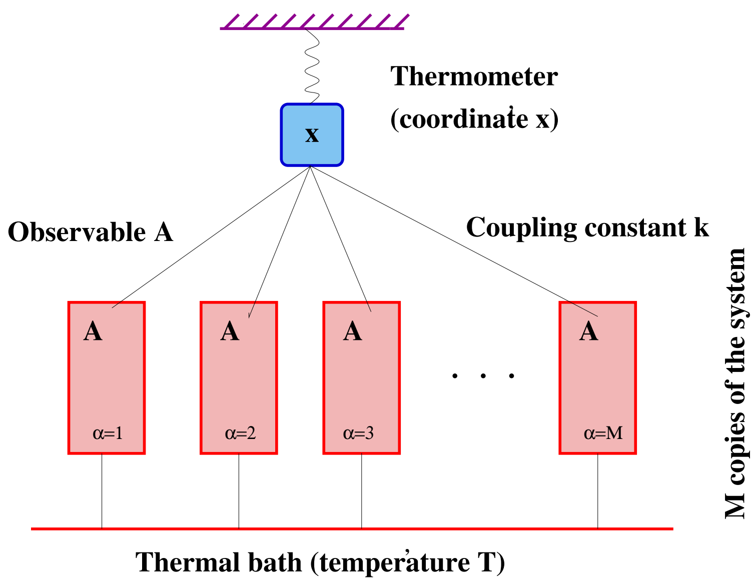
and the second term is a sum of positive terms

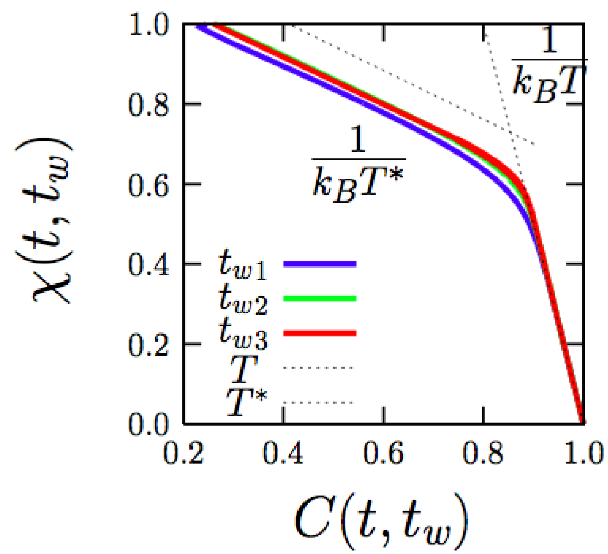
$$g_i(t_w) = \gamma_0 \int d\vec{x} d\vec{v} \; \frac{(m v_i P + T \partial_{v_i} P)^2}{m^2 P} \geq 0$$

LFC, Dean & Kurchan 97

FDT & effective temperatures

Can one interpret the slope as a temperature ?





(1) Measurement with a **thermometer** with

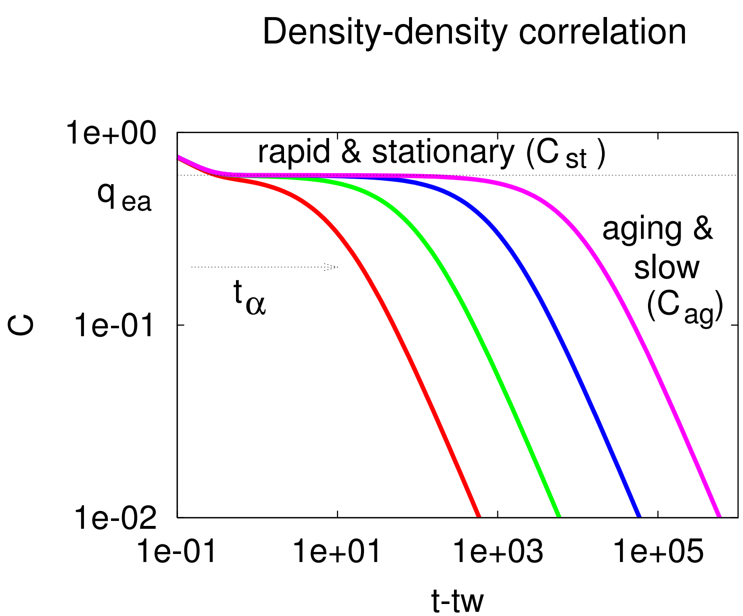
- Short internal time scale τ_0, fast dynamics is tested and T is recorded.
- Long internal time scale τ_0, slow dynamics is tested and T^* is recorded.

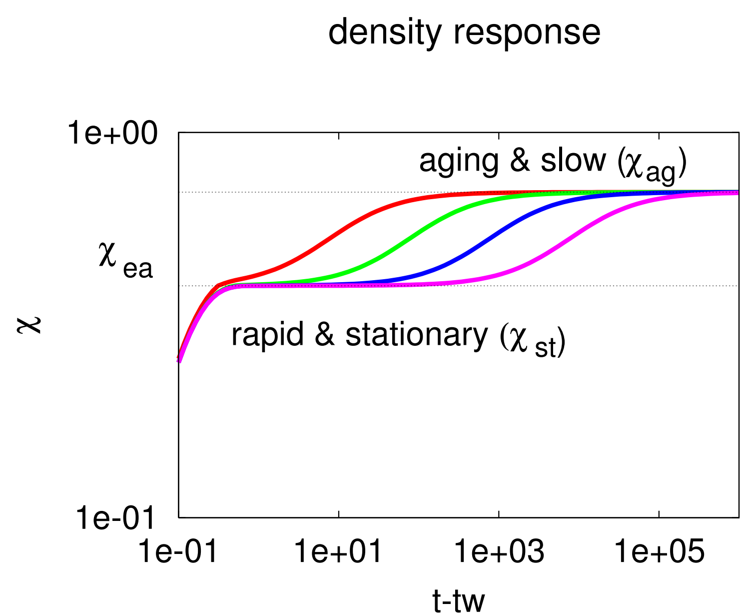
(2) **Partial equilibration** (3) **Direction of heat-flow**

LFC, Kurchan & Peliti 97

Glassy dynamics

Non stationary relaxation & separation of time-scales





$$C(t,t_w)$$

Correlation

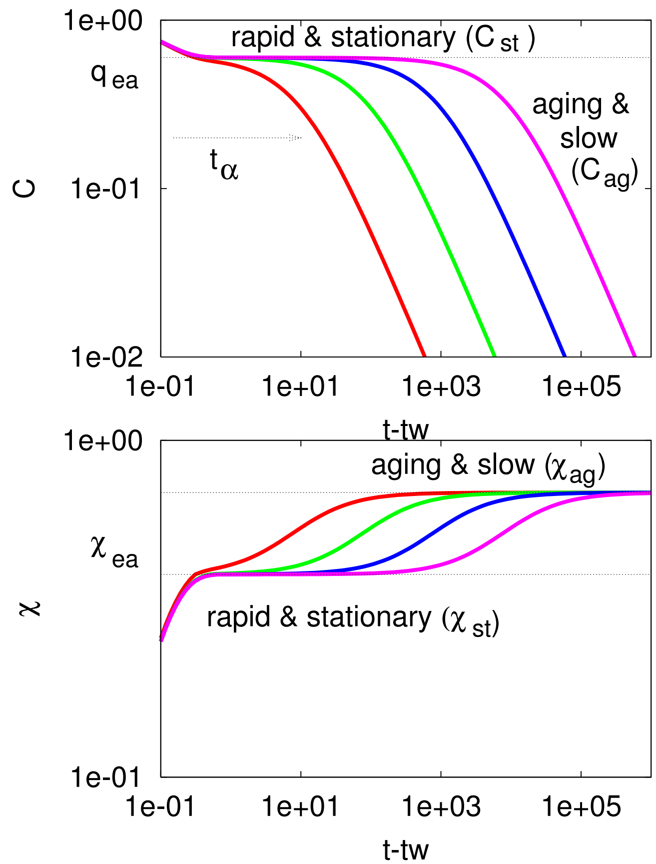
$$\chi(t,t_w) = \int_{t_w}^{t} dt' \; R(t,t')$$

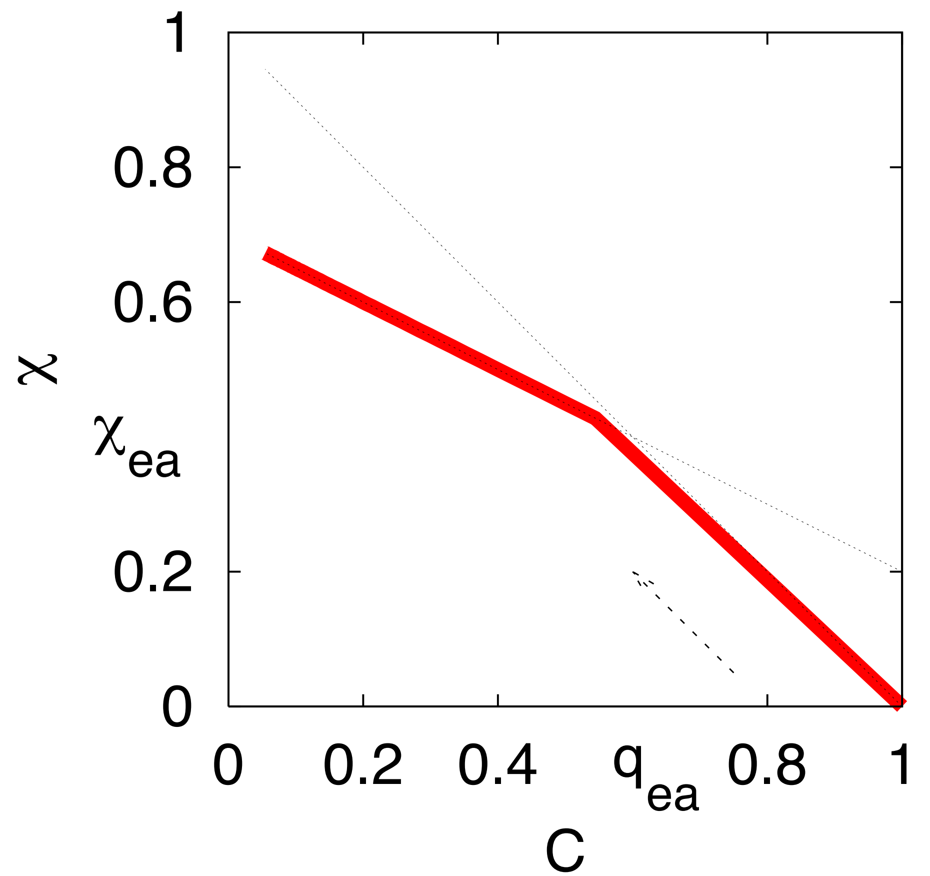
Time-integrated linear response

Analytic solution to a mean-field model **LFC & J. Kurchan 93**

Glassy dynamics

Fluctuation-dissipation relation : parametric plot

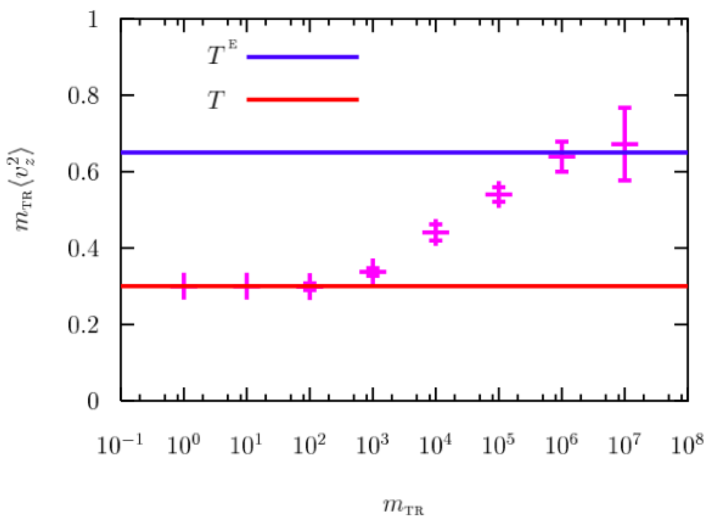


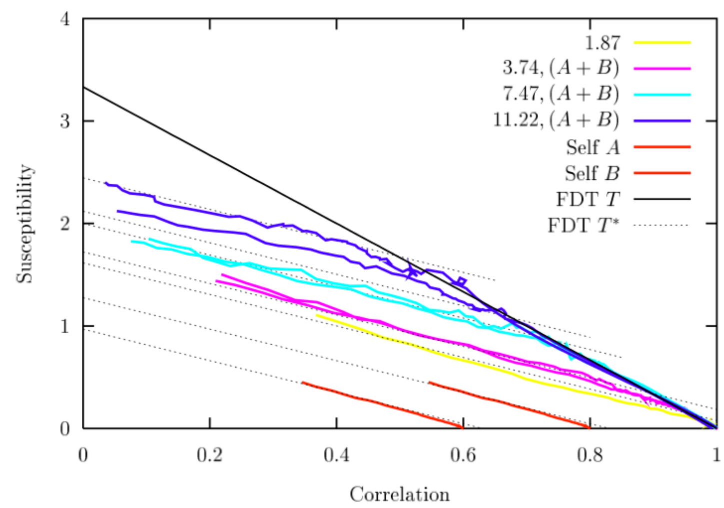


Analytic solution to a mean-field model **LFC & J. Kurchan 93**

FDT & effective temperatures

Sheared binary Lennard-Jones mixture





Left: the kinetic energy of a tracer particle (the thermometer) as a function of its mass ($\tau_0 \propto \sqrt{m_{tr}}$)

$$\frac{1}{2} m_{tr} \langle v_z^2 \rangle = \frac{1}{2} k_B T_{\text{eff}}$$

Right: $\chi_k(C_k)$ plot for different wave-vectors k, partial equilibrations.

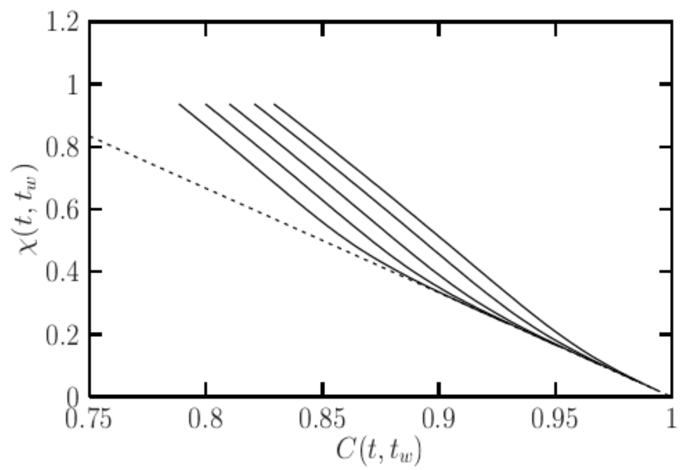
J-L Barrat & Berthier 00

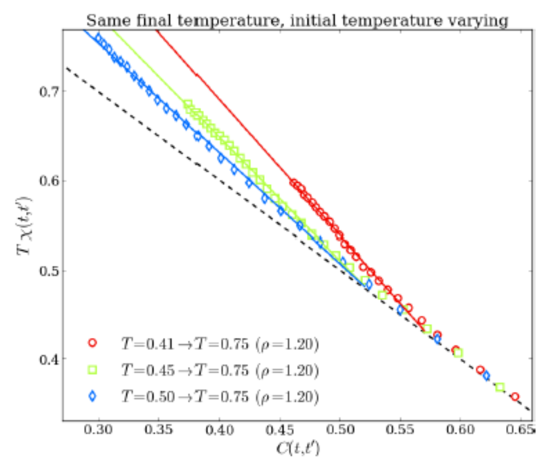
FDT & effective temperatures

Role of initial conditions

$T^* > T$ found for quenches from the disordered into the glassy phase

(Inverse) quench from an ordered initial state, $\boxed{T^* < T}$





2d XY model or O(2) field theory

Binary Lennard-Jones mixture

Berthier, Holdsworth & Sellitto 01

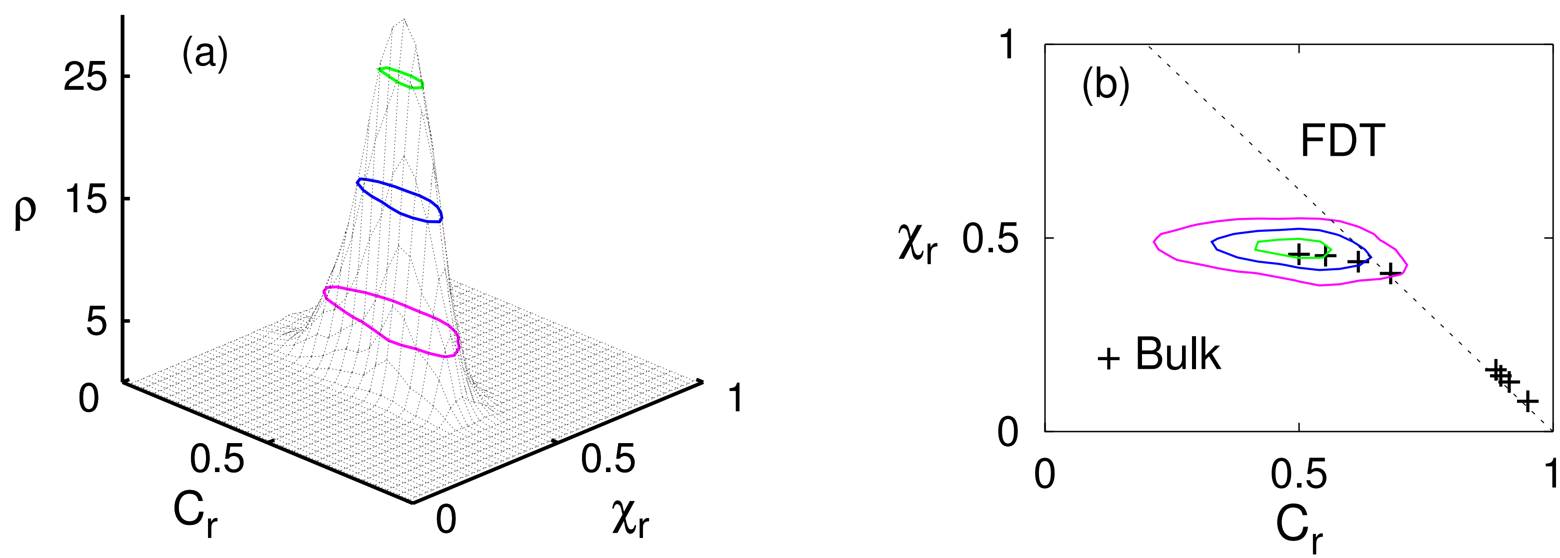
Gnan, Maggi, Parisi & Sciortino 13

Fluctuations

All subregions in space tend to have the temperature

in the same time-scale, *e.g.* $C_r < q_{ea}$

Simulations



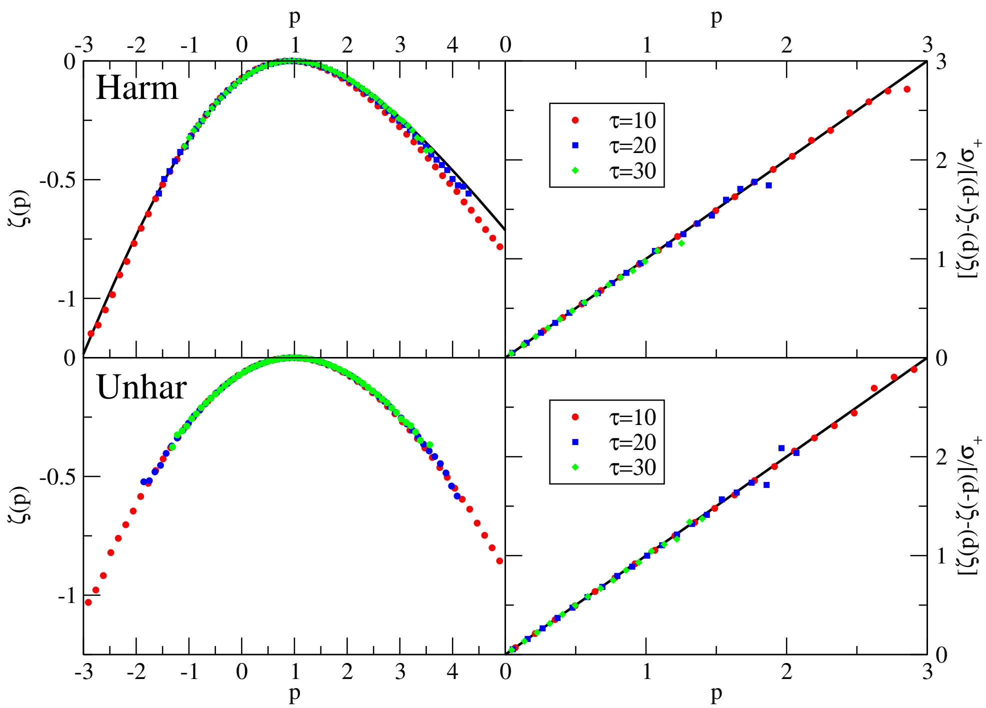
$3d$ Edwards-Anderson spin-glass

Castillo, Chamon, LFC, Iguain & Kennett 02

Teff & FTs

Driving glassy systems

A harmonic and an unharmonic oscillator driven out of equilibrium by two baths with different time-scales and temperatures.

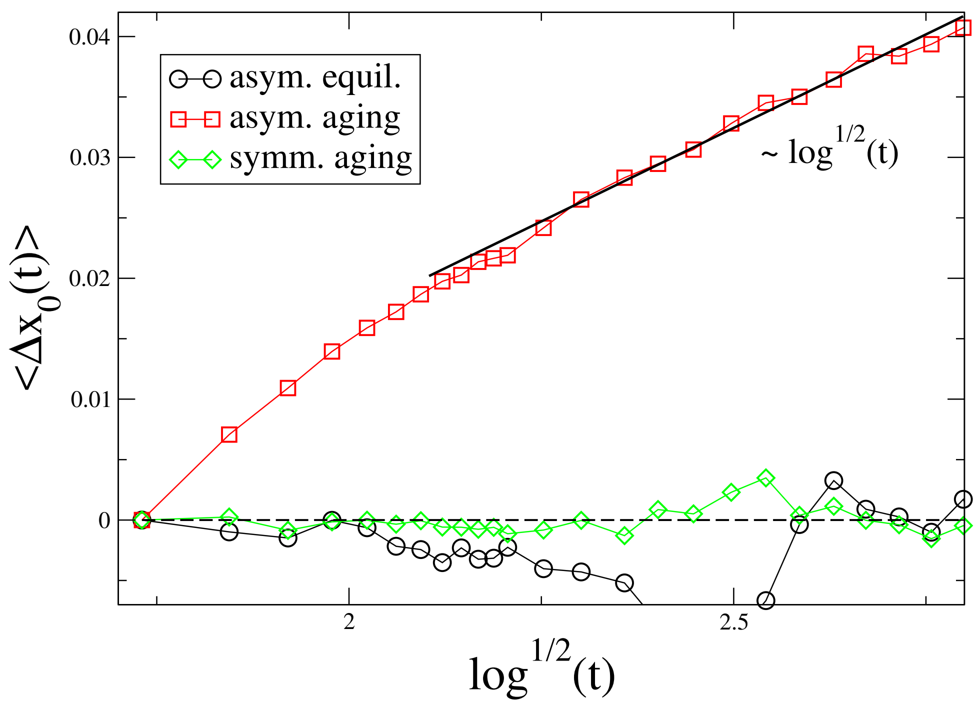


Zamponi, Bonetto, LFC & Kurchan 05

Ratchets

Asymmetric particle immersed in an ageing glass

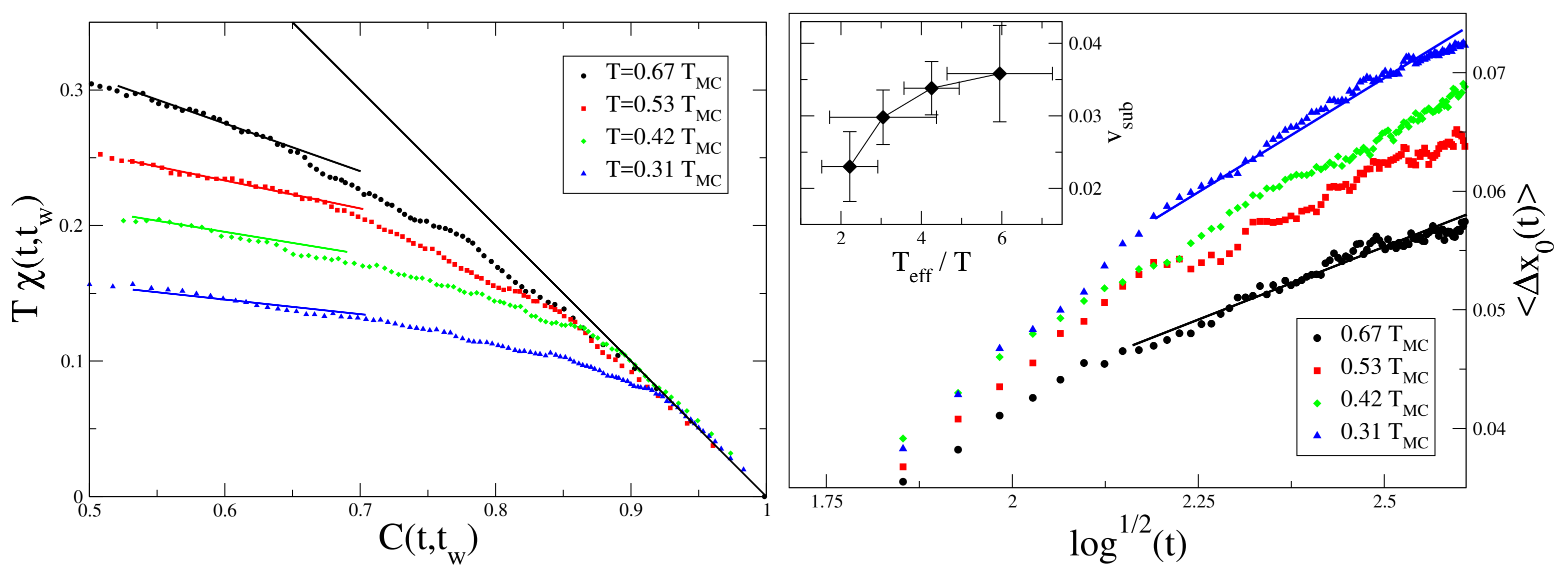
$$\langle \Delta x_0(t) \rangle \equiv \langle x_0(t) - x_0(0) \rangle$$



Gradenigo, Sarracino, Villamaina, Grigera, Puglisi 10

Ratchets

Asymmetric particle immersed in an ageing glass

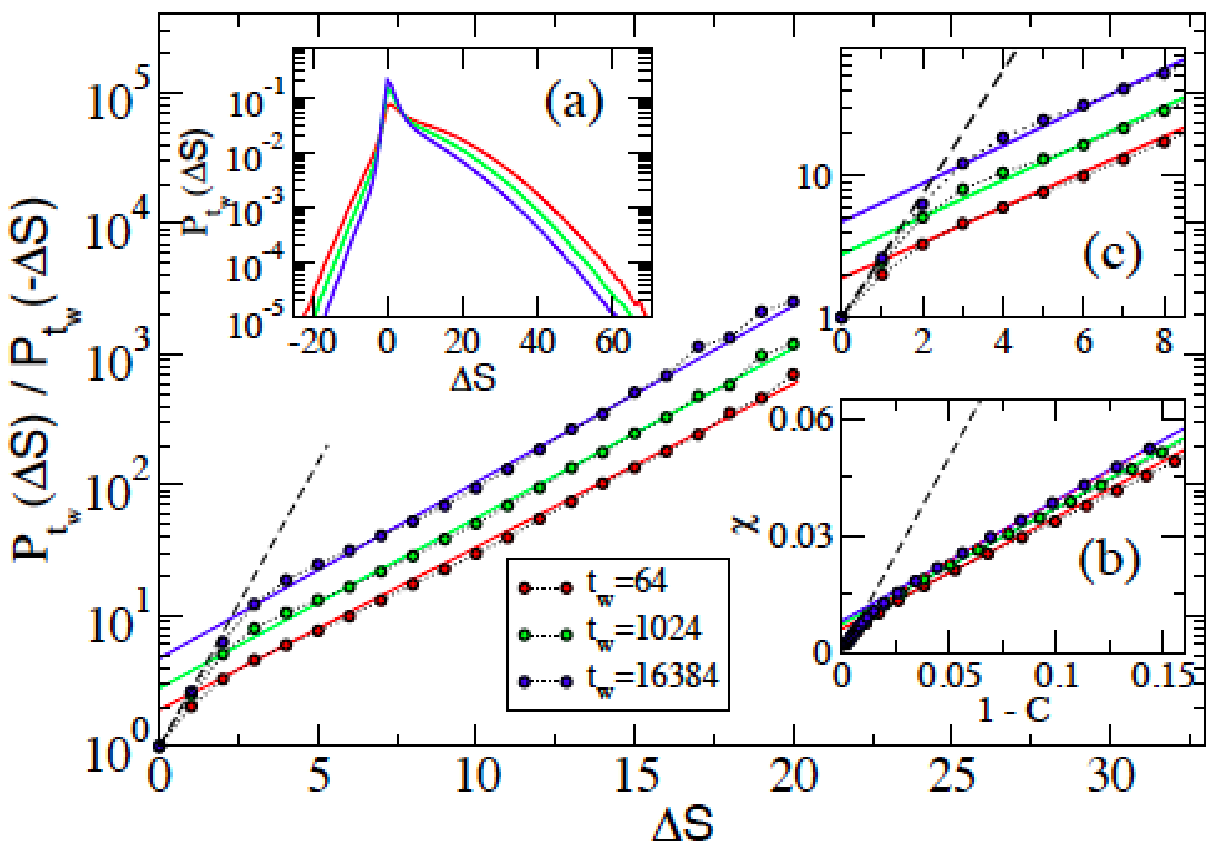


Quenches to $T = 0.67,\ 0.53,\ 0.42,\ 0.31$ $\mathrm{T_{MCT}}$

Gradenigo, Sarracino, Villamaina, Grigera, Puglisi 10

FDT & FTs

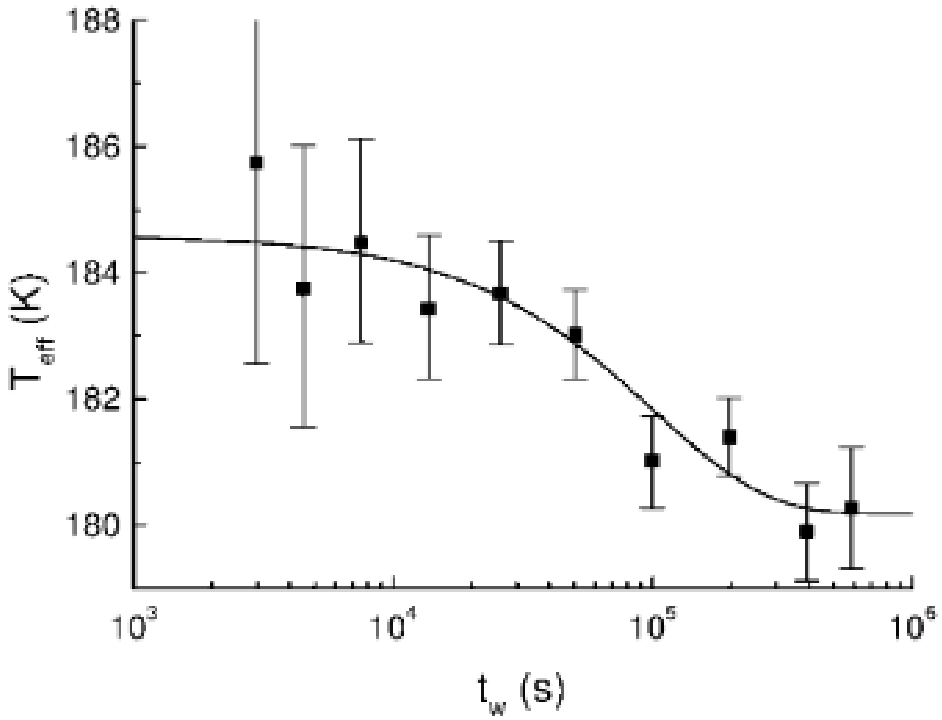
Fluctuations $\Delta s = s(t) - s(t_w)$ in ROM model



Crisanti, Picco & Ritort 13

Experiments

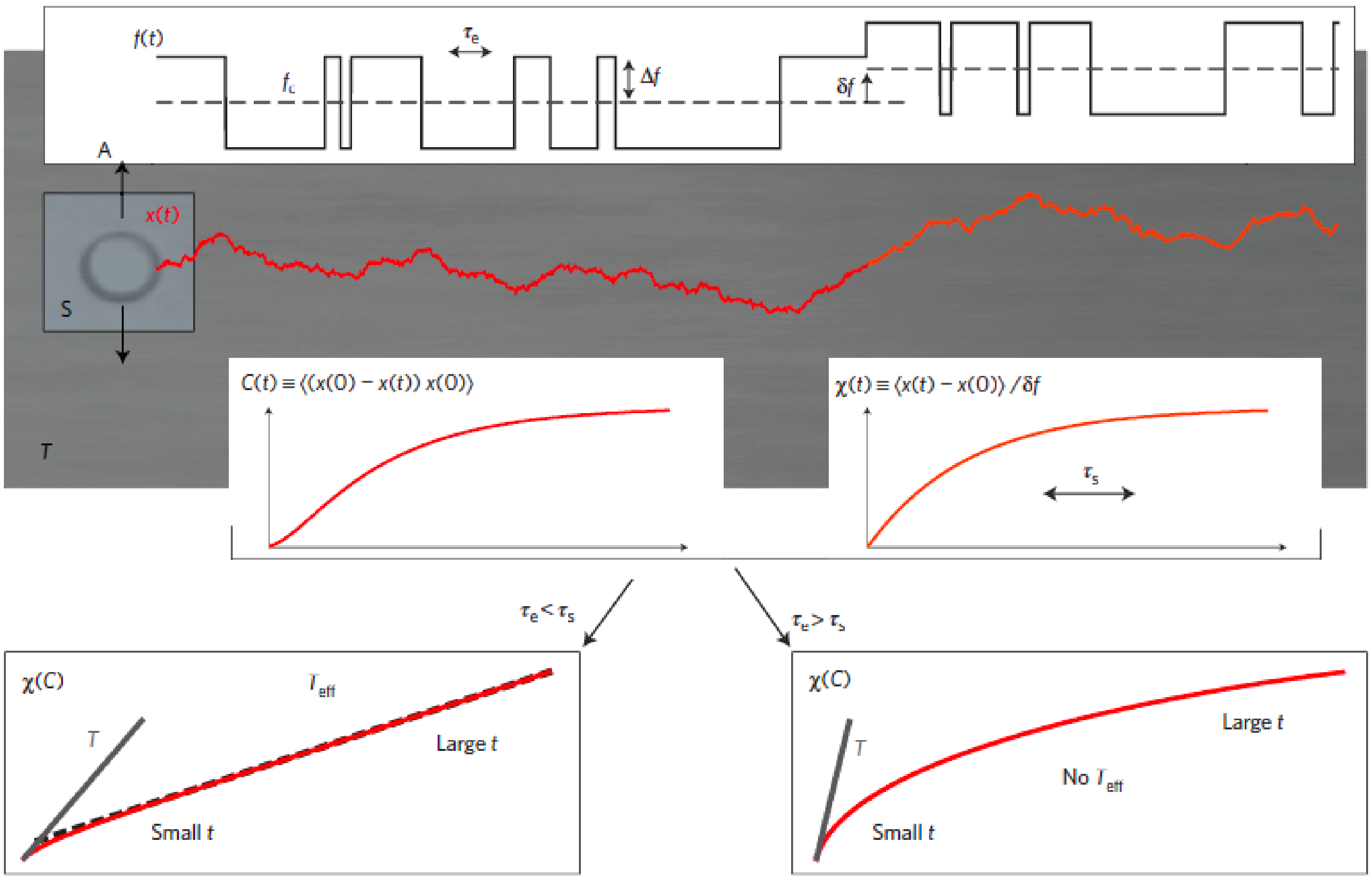
Ageing glycerol



Grigera & Israeloff 99

Experiments

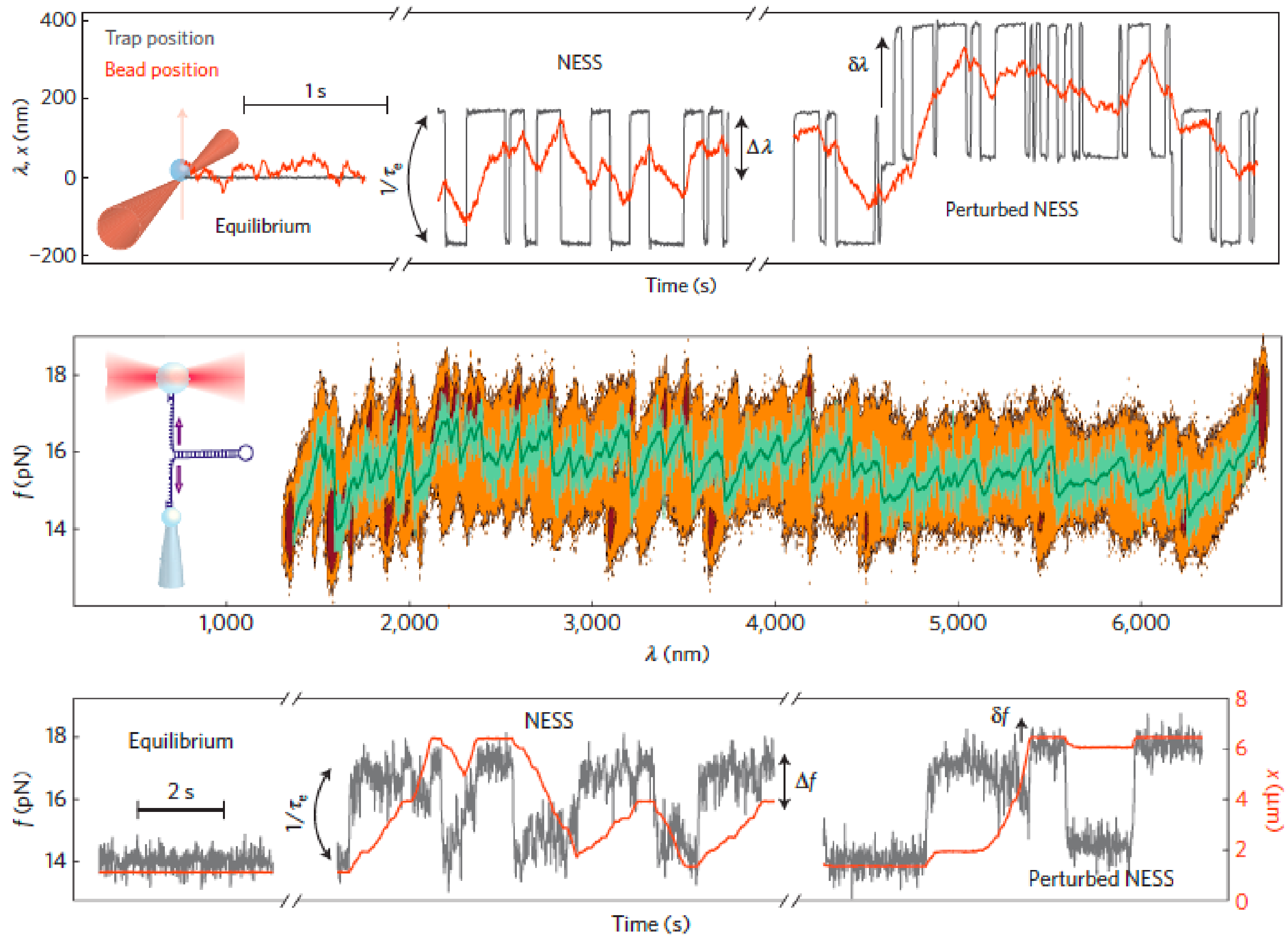
Beads and hairpins



Dietrich et al 15

Experiments

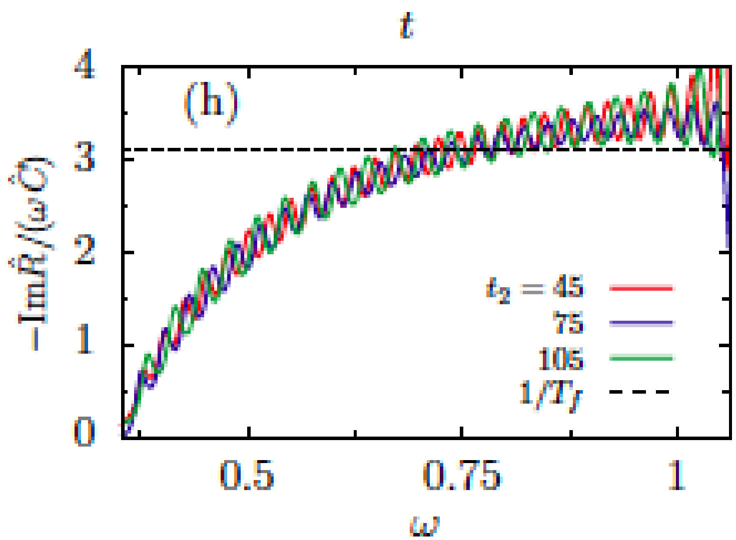
Beads and hairpins

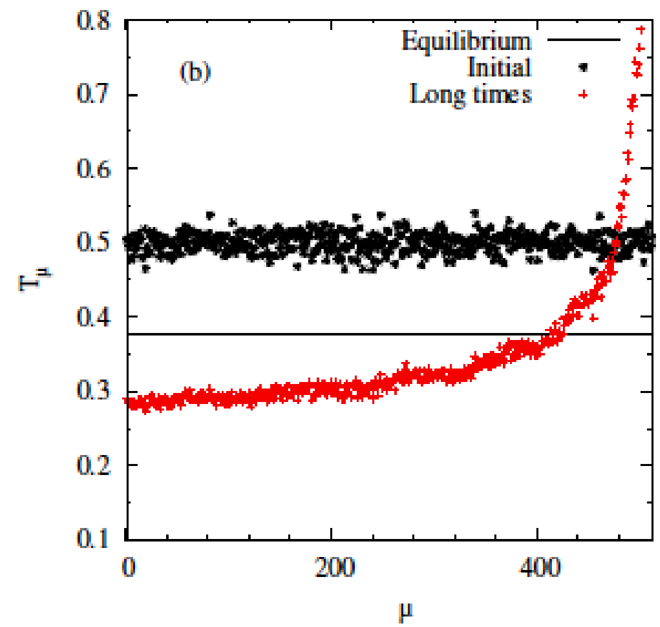


Dietrich et al 15

Closed classical system

$p = 2$ **spherical model *** preliminary *****





Foini, LFC, Gambassi, Konik 16-17

LFC, Lozano, Nessi, Picco & Tartaglia

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   LFC, J. Kurchan & L. Peliti 97

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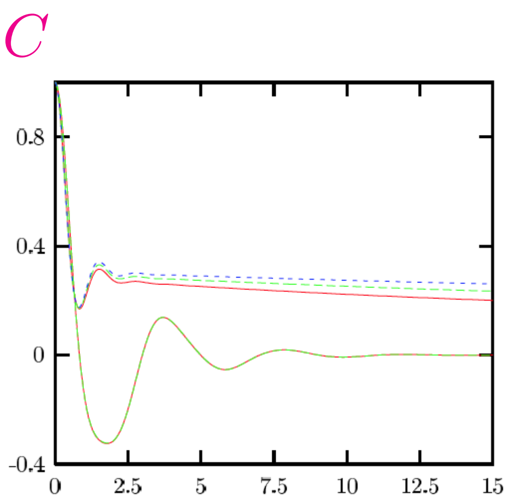
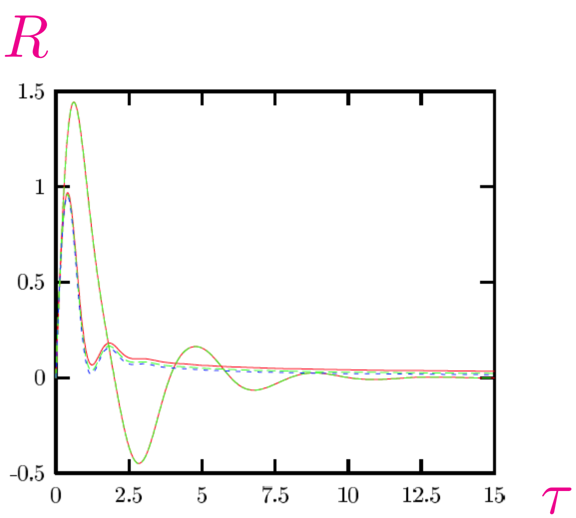
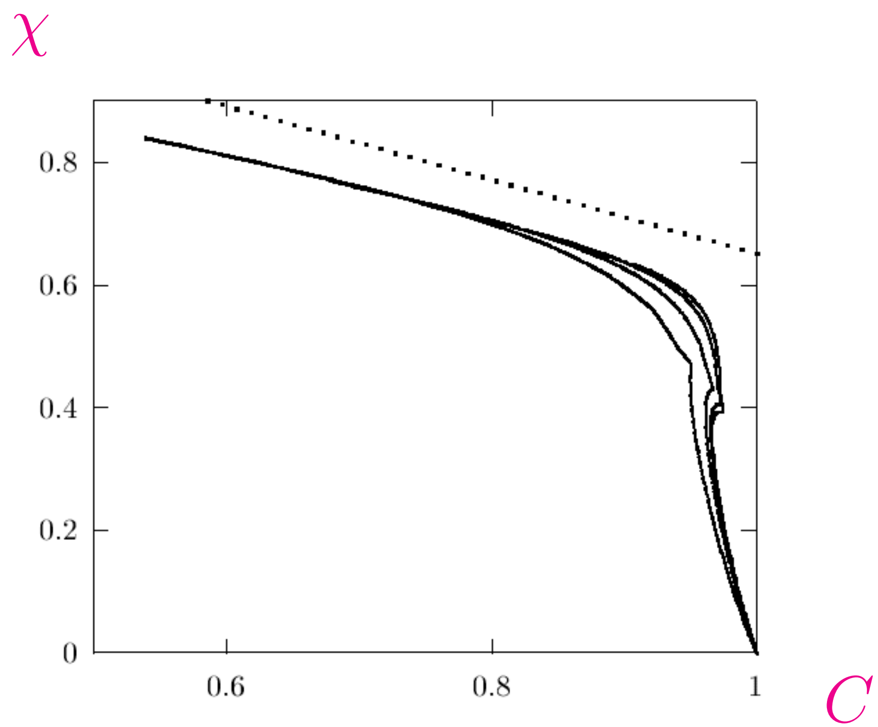
4. Conclusions.

Dissipative quantum glasses

Quantum p-spin coupled to a bath of harmonic oscillators







Out of equilibrium decoherence

LFC & Lozano 98

Isolated quantum systems

Quantum quenches

- Take an isolated quantum system with Hamiltonian H_0
- Initialize it in, say, $|\psi_0\rangle$ the ground-state of H_0.
- Unitary time-evolution with $U = e^{-\frac{i}{\hbar}Ht}$ with a Hamiltonian H.

Does the system reach some steady state ?

Note that it is the ergodic theory question posed in the quantum context.

Motivated by cold-atom experiments & exact solutions of $1d$ quantum models.

Are at least some observables described by thermal ones?

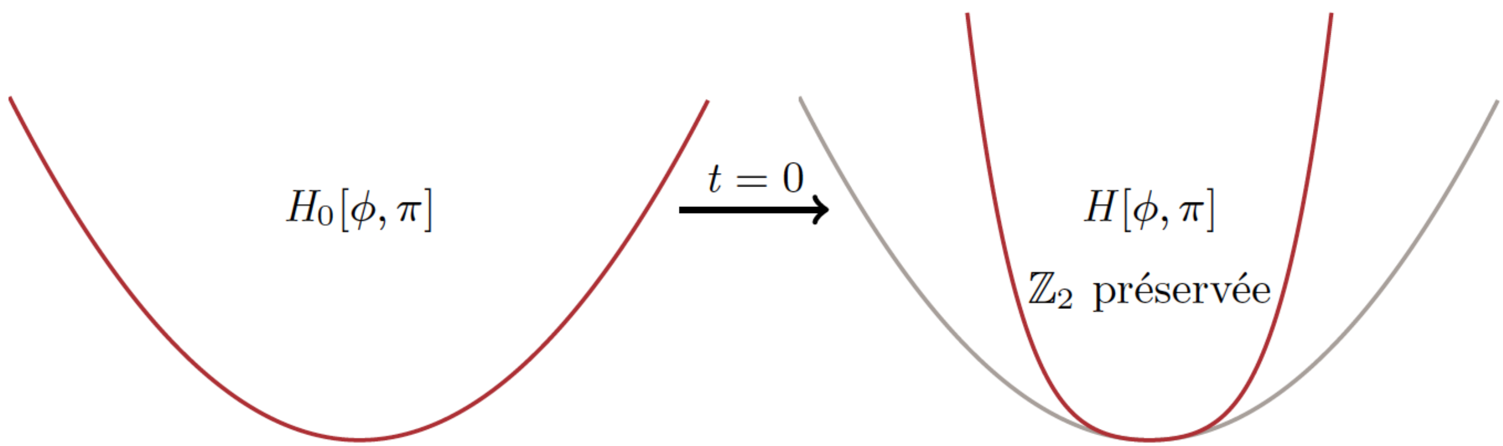
When, how, which?

Quantum quench

Setting

Take a closed system, H_0, in a given state, $|\psi_0\rangle$, and suddenly change a parameter, H. The unitary evolution is ruled by H.

e.g. $H = \int d^dx \left\{ \frac{1}{2}\pi^2 + \frac{1}{2}(\vec{\nabla}\phi)^2 + r\phi^2 + \lambda\phi^4 \right\}$



$\lambda_0 \quad \to \quad \lambda$

Quantum quench

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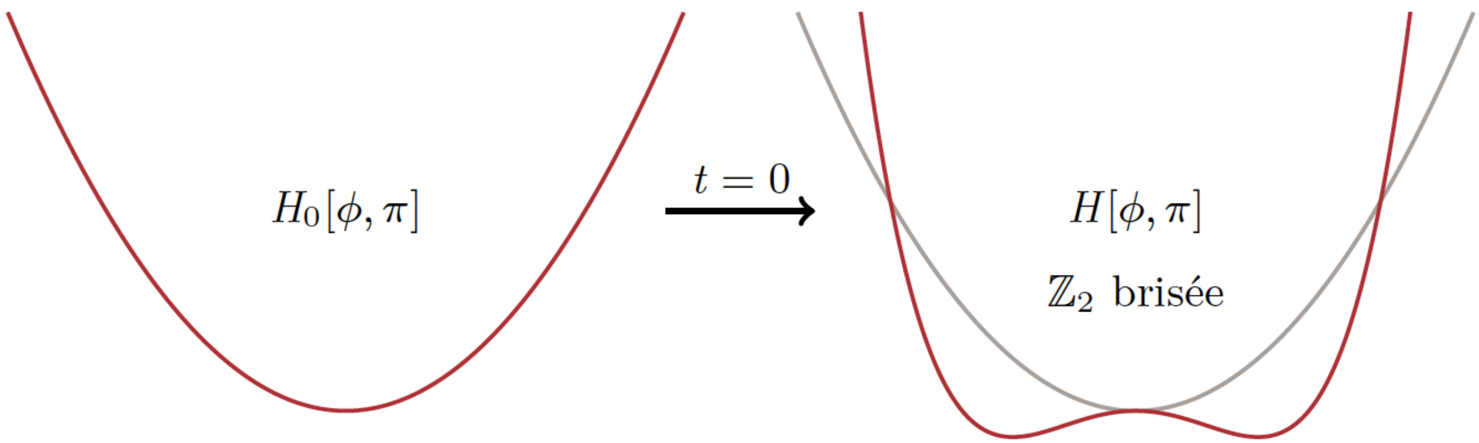


$r > 0 \quad \rightarrow \quad r < 0$

Quantum quenches

Questions

Does the system reach a thermal equilibrium density matrix ?

Under which conditions ?

non-integrable vs integrable systems ; role of initial states ; non critical vs. critical quenches

- Definition of T_e from $\langle \psi_0 | H | \psi_0 \rangle = \langle H \rangle_{T_e} = \text{Tr}\, H e^{-\beta_e H}$

Just one number, it can always be done

- Comparison of dynamic and thermal correlation functions, *e. g.*

$C(r,t) \equiv \langle \psi_0 | \phi(\vec{x},t) \phi(\vec{y},t) | \psi_0 \rangle$ vs. $C(r) \equiv \langle \phi(\vec{x}) \phi(\vec{y}) \rangle_{T_e}$.

Calabrese & Cardy ; Rigol et al ; Cazalilla & Iucci ; Silva et al, etc.

Proposal : put qFDT to the test to check whether $T_{\text{eff}} = T_e$ exists

Fluctuation-dissipation theorem

Classical dynamics in equilibrium

The classical FDT for a stationary system with $\tau \equiv t - t_w$ reads

$$\chi(\tau) = \int_0^\tau dt' \, R(t') = -\beta[C(\tau) - C(0)] = \beta[1 - C(\tau)]$$

choosing $C(0) = 1$.

Linear relation between χ and C

Quantum dynamics in equilibrium

The quantum FDT reads

$$\chi(\tau) = \int_0^\tau d\tau' \, R(\tau') = \int_0^\tau d\tau' \int_{-\infty}^{\infty} \frac{i d\omega}{\pi\hbar} \, e^{-i\omega\tau'} \tanh\left(\frac{\beta\hbar\omega}{2}\right) C(\omega)$$

Complicated relation between χ and C

Fluctuation-dissipation theorem

Quantum SU(2) Ising chain

The initial Hamiltonian $$H_{\Gamma_0} = -\sum_i \sigma_i^x \sigma_{i+1}^x + \Gamma_0 \sum_i \sigma_i^z$$

The initial state $|\psi_0\rangle$ ground state of H_{Γ_0}

Instantaneous quench in the transverse field $\Gamma_0 \to \Gamma$

Evolution with H_Γ.

Iglói & Rieger 00

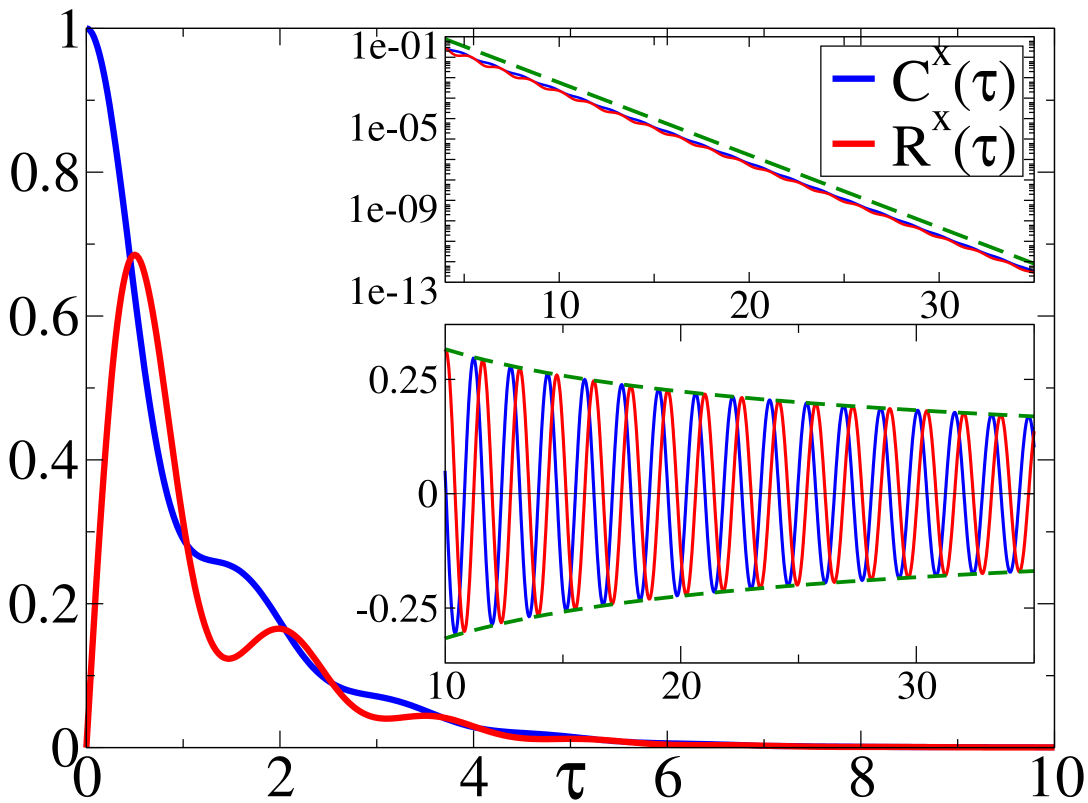
Reviews : **Karevski 06 ; Polkovnikov et al. 10 ; Dziarmaga 10**

Observables : correlation and linear response of local longitudinal and transverse spin, etc.

Specially interesting case $\Gamma_c = 1$ the critical point. **Rossini et al. 09**

Quantum quench

$T_{\rm eff}$ from FDT ? Longitudinal spin



Insets

$e^{-\tau/\tau_C}$

$\tau^{-2}\sin(4\tau+\phi)$

$$C^x(\tau) \simeq A_C e^{-\tau/\tau_C}[1 - a_C \tau^{-2}\sin(4\tau+\phi_C)]$$
$$R^x(\tau) \simeq A_R e^{-\tau/\tau_R}[1 - a_R \tau^{-2}\sin(4\tau+\phi_R)]$$

Foini, LFC & Gambassi 11

Quantum quench

$T_{\rm eff}$ from FDT ?

For sufficiently long-times such that one drops the power-law correction

$$-\beta_{\rm eff}^x \simeq \frac{R^x(\tau)}{d_\tau C_+^x(\tau)} \simeq -\frac{\tau_C A_R}{A_C}$$

A constant consistent with a classical limit but

$$T_{\rm eff}^x(\Gamma_0) \neq T_e(\Gamma_0)$$

Morever, a complete study in the full time and frequency domains confirms that $T_{\rm eff}^x(\Gamma_0, \omega) \neq T_{\rm eff}^z(\Gamma_0, \omega) \neq T_e(\Gamma_0)$ (though the values are close).

Fluctuation-dissipation relations as a probe to test thermal equilibration

No equilibration for generic Γ_0 in the quantum Ising chain

Summary

$T_{\rm eff}$ from FDT

- Analysis of **fluctuation-dissipation relations** in closed or open classical and quantum systems.

- $T_{\rm eff}$ calculated for dissipative classical and quantum *mean-field* models – large N, large d or with self-consistent closure approximations.

  A *finite dimensional* solvable model with the phenomenology discussed is missing. (This is probably the same as finding a solvable glass)

- Discussion of the **thermodynamic meaning** of $T_{\rm eff}$.

- A better understanding of the microscopic origin of $T_{\rm eff}$ is lacking.

- Use of **fluctuation-dissipation relations** to check for Boltzmann equilibrium (application to quantum quenches).

Fluctuation-dissipation

A proof

The generic **Langevin equation** for a particle in $1d$ is

$$m\ddot{x}(t) + M'[x(t)] \int_{-\mathcal{T}}^{t} dt' \, \Gamma(t-t') M'[x(t')] \dot{x}(t') = F(t) + \xi(t) M'[x(t)]$$

with the coloured noise $$\langle \xi(t)\xi(t') \rangle = T \, \Gamma(t-t')$$

The dynamic generating functional is a path-integral

$$\mathcal{Z}_{dyn}[\eta] = \int dx_{-\mathcal{T}} d\dot{x}_{-\mathcal{T}} \int \mathcal{D}x \mathcal{D}i\hat{x} \; e^{-S[x,i\hat{x};\eta]}$$

with $i\hat{x}(t)$ the 'response' variable.

$x_{-\mathcal{T}}$ and $\dot{x}_{-\mathcal{T}}$ are the initial conditions at time $-\mathcal{T}$.

Martin-Siggia-Rose-Jenssen-deDominicis formalism

Fluctuation-dissipation

A proof

The action has a deterministic part (Newton) that includes the initial condition and a dissipative part that depends upon Γ : $\boxed{S = S_{det} + S_{diss}}$

The transformation

$$\boxed{x(t) \to x(-t) \qquad\qquad i\hat{x}(t) \to i\hat{x}(-t) + \beta\dot{x}(-t)}$$

leaves S_{diss} and the path-integral measure invariant.

S_{det} is also invariant if $P(x_{-\mathcal{T}}, \dot{x}_{-\mathcal{T}}) = P_{eq}(x_{-\mathcal{T}}, \dot{x}_{-\mathcal{T}})$, and $F = V'[x]$

The **FDT** valid for Newton or Langevin dynamics

$$\boxed{R_{AB}(t, t_w) + R_{AB}(t_w, t) = \beta\partial_{t_w} C_{AB}(t, t_w)}$$

and higher-order extensions are Ward identities of this symmetry.

The fluctuation theorems can also be proven in this way.

Fluctuation theorems

Take a system *in equilibrium* and drive it into a

non-equilibrium steady state

with a perturbing force. The **fluctuations of 'entropy production rate'**

$$p \equiv (\tau\sigma_+)^{-1} \int_{-\tau/2}^{\tau/2} dt\, W(S_t)/T$$

where S_t is the trajectory of the system in phase space,

T is the temperature of the equilibrated unperturbed system,

$W(S_t)$ is the work done by the external forces, and

$T\sigma_+ \equiv \int dx P_{st}(x) W(x) \sim \lim_{\tau\to\infty} \frac{1}{\tau} \int_{-\tau/s}^{\tau/s} dt\, W(t)$ is an

average over the steady state distribution, **satisfy**

$\xi(p) - \xi(-p) = p\sigma_+$ with $\xi(p) \equiv \lim_{\tau\to\infty} \frac{1}{\tau} \ln \pi_\tau(p)$

and π_τ the probability density of p.

Cohen, Morriss & Evans 90 ; Gallavoti & Cohen 93

Fluctuation theorems

Take a glass *out of equilibrium* and take it into a

driven steady glassy state

with a perturbing force.

For which entropy production rate does a fluctuation theorem hold ?

Since there is no meaning to T but there is to $T_{\rm eff}$ the proposal is to replace

$$\int_{-\tau/2}^{\tau/2} dt \; \frac{W(t)}{T} \quad \to \quad \int_{-\tau/2}^{\tau/2} dt \; \frac{W(t)}{T_{\rm eff}(t)}$$

with $T_{\rm eff}(t)$ the effective temperature as measured from

the fluctuation-dissipation relation of the *unperturbed* relaxing system

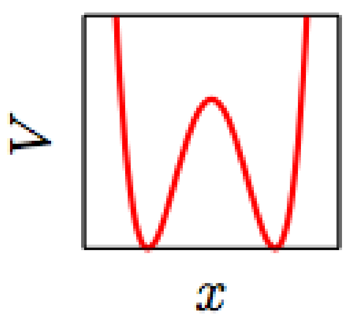
with its two values T and T^*

Zamponi, Bonetto, LFC & Kurchan 05

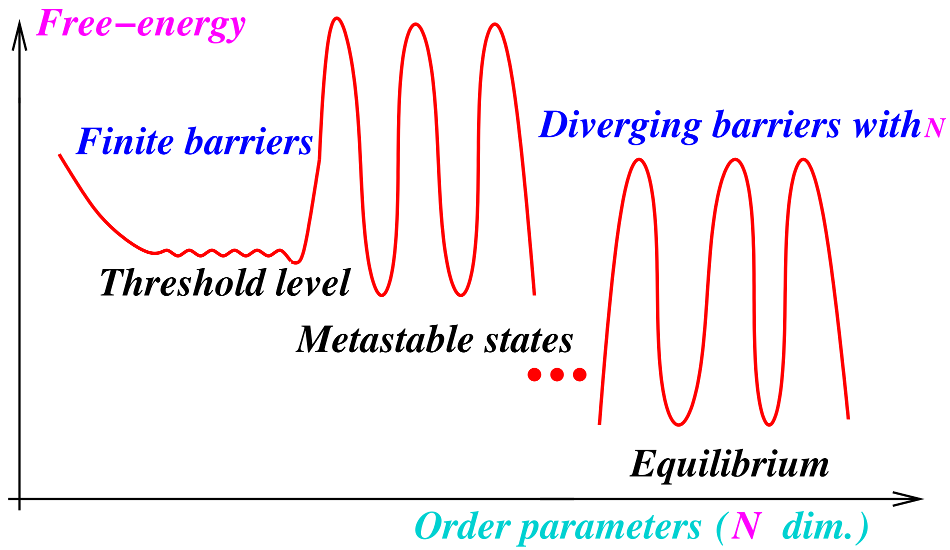
Is $T_{\rm eff}$ related to an entropy ?

Configurational entropy

An exponentially large number of metastable states is reached dynamically



Curie-Weiss (ferro)



Sketch of free-energy landscape

Threshold level is reached asymptotically

e.g. $\lim_{t_w \to \infty} \mathcal{E}(t) = \mathcal{E}_\infty > \mathcal{E}_{eq}$.

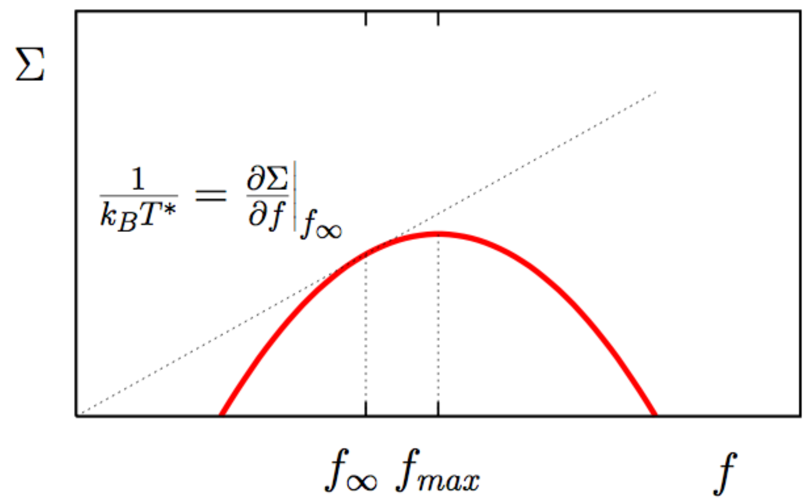
Well-understood in mean-field models with the

Thouless-Anderson-Palmer technique

Is $T_{\rm eff}$ related to an entropy ?

Configurational entropy

$$\Sigma(f) = k_B \ln \mathcal{N}(f) \qquad \Rightarrow \qquad \frac{1}{k_B T^*} = \left.\frac{\partial \Sigma(f)}{\partial f}\right|_{f_\infty}$$



NB $f_{max} \neq f_\infty \Rightarrow$ failure of 'maximum entropy principles'.

Edwards & Oakshott 89, Monasson 95, Nieuwenhuizen 98

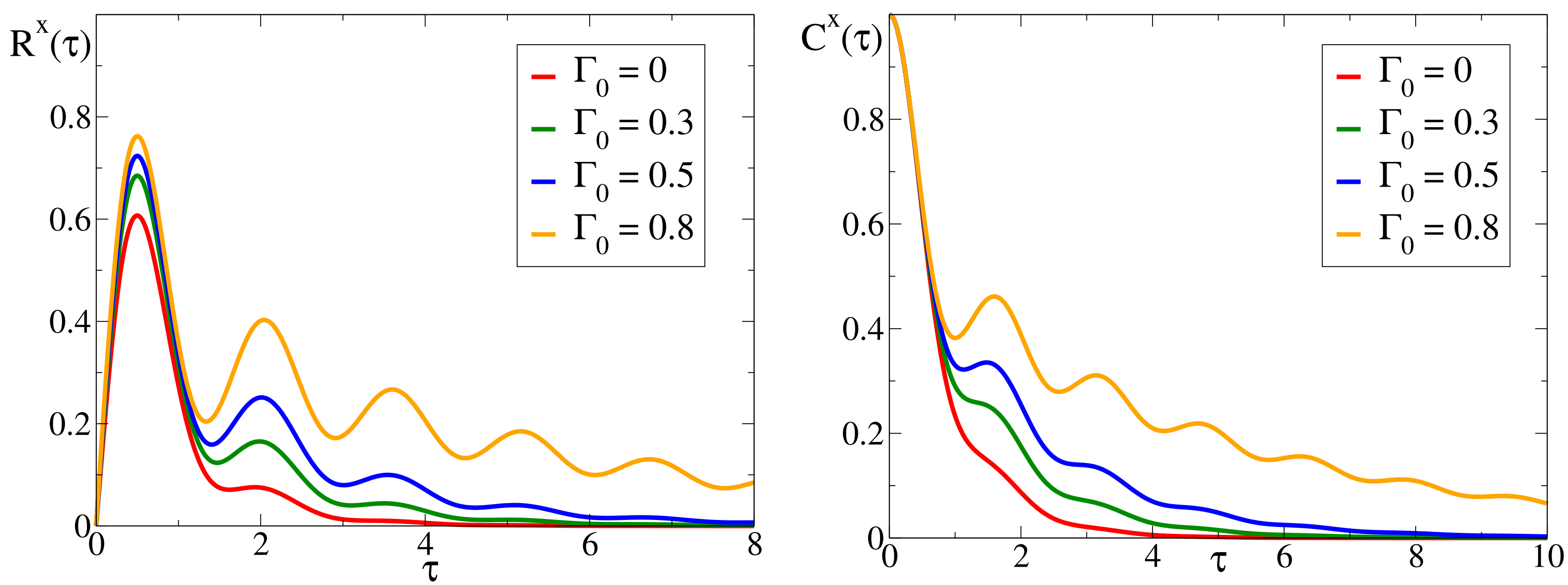
Very sketchy view : many amorphous solid configurations ($\Sigma \Leftrightarrow T^*$) and vibrations around them ($f \Leftrightarrow T$).

Quantum quench

$T_{\rm eff}$ from FDT ? Longitudinal spin

A quantum quench $\Gamma_0 \to \Gamma$ of the **isolated Ising chain**

Here : to its critical point $\Gamma = 1$



Linear response and symmetrized correlation of σ^x

Foini, LFC & Gambassi 11

Summary

- $T_{\rm eff}$ definition from the analysis of **fluctuation-dissipation relations**.

- Discussion of **thermodynamic meaning**.

  Shown for *mean-field models* – large N, large d or, in other words, within the mode-coupling approach to glassy systems.

- **Numerical evidence** *Lennard-Jones silica, soft particles ; vortex glasses granular matter ; thin magnetic films, active matter*, etc.

- Other evidence : extended Arrhenius law for activation (**Ilg & J-L Barrat**), fluctuation theorems (**Zamponi** *et al*), ratchets (**Gradenigo** *et al*), etc.

- **Experimental results** are less clear

  glycerol, laponite, spin-glasses, etc. (**Jabbari-Bonn, Abou-Gallet, Ciliberto** *et al.*, **Bartlett** *et al*, **Hérisson & Ocio**, etc.).

Summary

classical context

- The energy density approaches the equilibrium one, typically as $\Delta E \simeq t^{-b}$.
- The correlation and linear response functions have highly non-trivial time-dependencies (aging effects, non-exponential relaxations)
- There is an extended time-regime in which correlation and linear response vary "macroscopically" but the effective temperature $T_{\rm eff} = T^*$ is constant.
- T^* can be related to the variation of a configurational entropy with respect to the energy-density (*à la* micro-canonic.)
- T^* has intuitive properties : hotter for more disordered, colder for more ordered.

Cases in which this does not hold were exhibited by, *e.g.*, **Sollich et al**

in models with unbounded energy or artificial (emerging ?) dynamic rules.

Is $T_{\rm eff}$ related to an entropy ?

Granular matter

- Static granular matter : blocked states $mgd \gg k_B T$
- Hypotheses to describe weakly driven granular matter :
  – walk from blocked state to blocked state
  – blocked states are visited with equal probability working at fixed V (and $\mathcal{E}$) : $P(\{\vec{r}_i\}_{\text{blocked}}) = \text{constant}$.
  – From the entropy of blocked states

$$S(V, \mathcal{E}) = k_B \ln \# \text{ blocked states}(V, \mathcal{E})$$

define the temperature $T^{-1}_{Edw} = \frac{\partial S(V,\mathcal{E})}{\partial \mathcal{E}}$

and the compactivity $X^{-1}_{Edw} = \frac{\partial S(V,\mathcal{E})}{\partial V}$

Edwards & Oakeshott 89