Cooperative lengthscales in glass-formers: Why don't glasses flow?

with: G. Biroli, L. Berthier, E. Bertin, C. Toninelli, M. Wyart

Fragile glasses: experimental facts

- Very fast, Super-Arrhenius growth of the relaxation time:

$$\log \tau \approx \left(\frac{D T_0}{T - T_0}\right) \qquad D^{-1}: \text{ fragility}$$

  Vogel-Fulcher – increasing effective barriers.

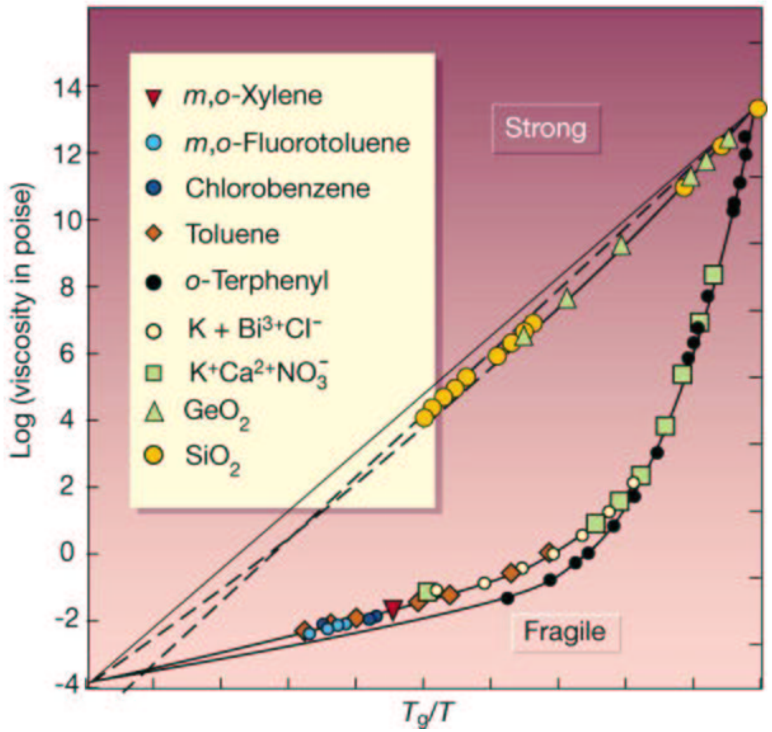
- Configurational entropy vanishes as $S_c \approx 1 - T_K/T$ with

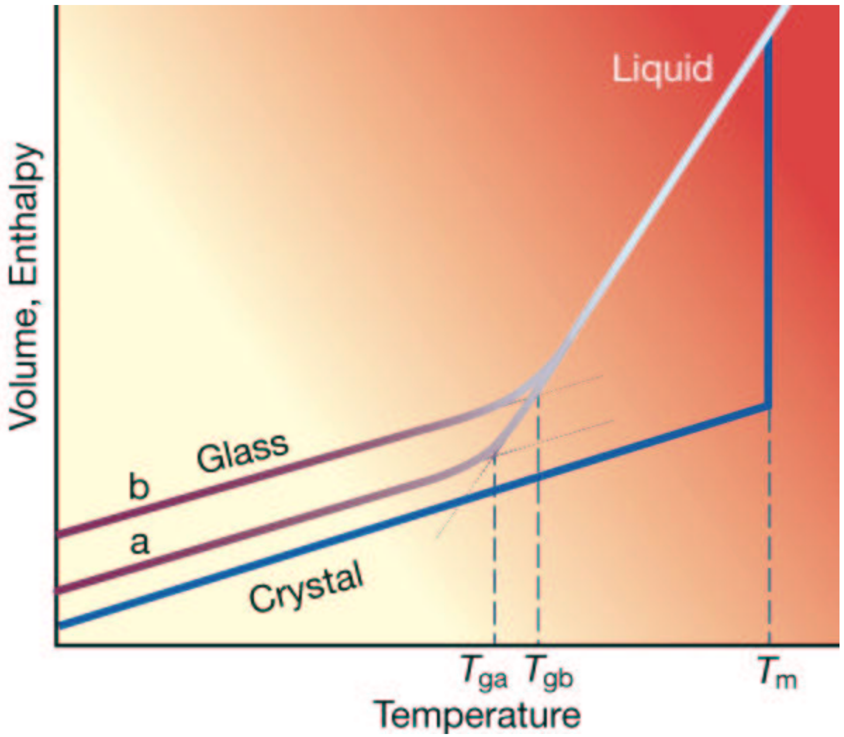
$$|T_K - T_0| < 0.1\, T_K$$

  (many different materials, $T_0 = 50 \rightarrow 1000$ K)

- An underlying phase transition?

Angell Plot and specific heat jump





Fragile glasses: experimental facts

- No latent heat, but large specific heat jump at T_g: $\Delta C_p \sim k_B$/particle, with $D \sim \Delta C_p^{-1}$: thermodynamical/kinetic duality (Adam-Gibbs)

- No latent heat, but discontinuous non-ergodic parameter: $1\frac{1}{2}$ order transition $\rightarrow$ frozen amorphous density profile

Fragile glasses: more experimental facts

- Stretched exponential relaxation $C(t) \approx \exp(-t^{\beta})$

- Dynamical heterogeneities/intermittent dynamics and viscosity/diffusion decoupling ($\mathcal{D}\eta$ increases: coexistence of fast and slow regions)

- More fragile liquids (D small) $\rightarrow$ stretching exponent β small and stronger decoupling and smaller Poisson ratio

- Note: Glasses, many siblings and friends – Granular matter, spin and Coulomb glasses, error correcting codes and combinatorial optimisation, etc..

Increasing length in glasses: general arguments

- For finite range interactions: no diverging time scale without a diverging length scale

- Maxwell's criterion for rigidity is *non local*: $d+1$ particles needed to block one, but $2d$ contacts on average to prevent *extended* soft-modes

- Why are glasses rigid and stop flowing?
  - Adam-Gibbs: dynamics become super-slow because more and more particles must be shoved around simultaneously to allow flow
  - MCT-RFOT: Unstable modes that allow particles to move without hindering each other disappear at low energy (temperature) by becoming extended

The glass conundrum: no structural signature

- Usual transitions: long range order sets in. Slowing down: dynamical correlations over a *structural* length $\xi \sim (T - T_c)^{-\nu}$

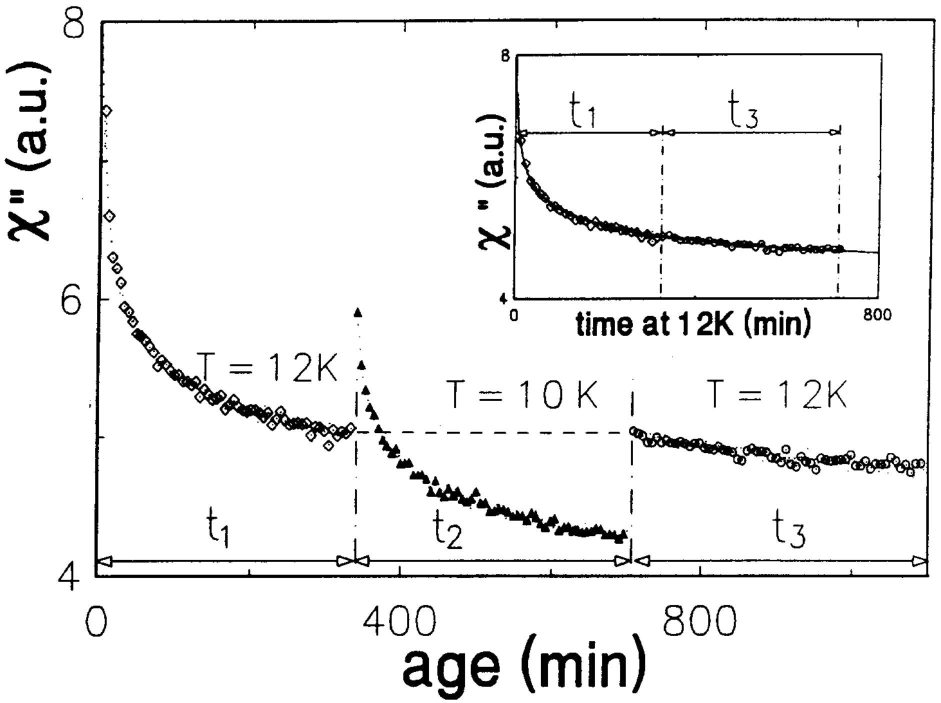
- Dynamics in the ordered phase: domain growth and coarsening

- Amorphous systems: transition towards a jammed, frozen state *without apparent order* – no growing static length

- Dynamics in the glass phase: aging, memory, rejuvenation: microscopic mechanism?

Aging and Memory

- Aging $C(t;t_w) \sim F(t/t_w)$, rejuvenation and memory for $T < T_g$



A case study: spin-glasses

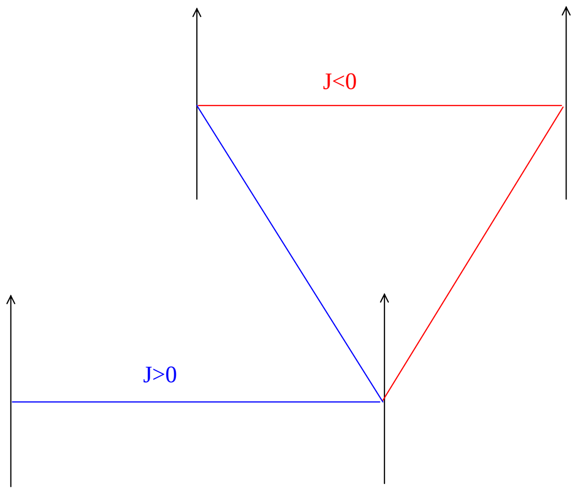
- $\langle S_i S_j \rangle \neq 0$ but of random sign $\to \chi$ regular

- $\chi_{SG} = 1/N \sum_{ij} \langle S_i S_j \rangle^2 \sim \xi^{2-\eta}$ diverges when $T \to T_g^+$: long range amorphous order! (Sounds like an oxymoron...)

- Experimentally: $\chi_{nl} \sim \chi_{SG}$ with $M = \chi H + \chi_{nl} H^3 + ...$ – direct access to a diverging amorphous correlation length

- Lesson: four-point correlations unveil non trivial information, not revealed by two-point correlations (see also intermittency in turbulence, finance)

Spin glasses: cartoon



Generalisation: dynamical susceptibilities

- Average correlation: $C(t) = \langle S_i(0) S_i(t) \rangle$

- Spatial correlation of temporal correlation:

$$G_4(|i-j|, t) = \langle S_i(0) S_i(t) S_j(0) S_j(t) \rangle - C(t)^2$$

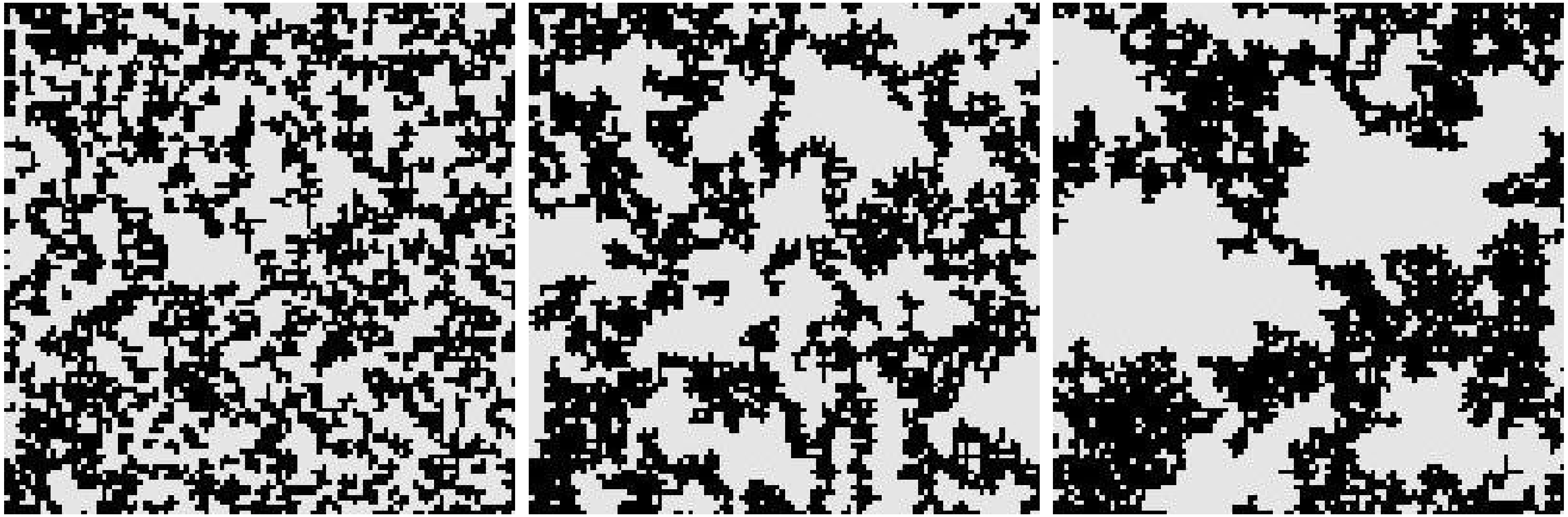
  Attempts to measure some cooperativity of the dynamics: is the motion at i necessary to trigger motion at j ?

- Temporal correlation of temporal correlation:

$$J_4(\tau, t) = \langle S_i(0) S_i(t) S_i(\tau) S_i(\tau + t) \rangle - C(t)^2$$

- Not restricted to disordered systems – Glasses: freezing of aperiodic density fluctuations $S_i \to \delta\rho(\vec{r})$

Dynamical heterogeneity in a simple model



Simulations: E. Bertin, F. Lequeux, JPB

Generalisation: dynamical susceptibility

- Dynamical susceptibility: fluctuations of correlation:

$$\chi_4(t) = \langle [\delta C(t)]^2 \rangle \equiv \sum_j G_4(|i-j|, t) \sim \xi^{2-\eta} F(t/\tau)$$

  defines a dynamic length scale

- Spin-glasses: $F(\infty) > 0$ – static long range order

- Glasses: $F(\infty) = 0$ – self-generated dynamical disorder, quenched on scale τ

- Non-linear dynamical susceptibility coupled to G_4:

  $\chi_{nl}(\omega, T) \sim \xi(T)^{2-\eta} F(\omega\tau(T))$ $\qquad$ $\chi_{nl}(\omega, t_w) \sim \xi(t_w)^{2-\eta} H(\omega t_w)$

  (experiments underway)

Dynamical length in glasses

- Numerical evidence of a growing length scale: S. Glotzer, L. Berthier,...

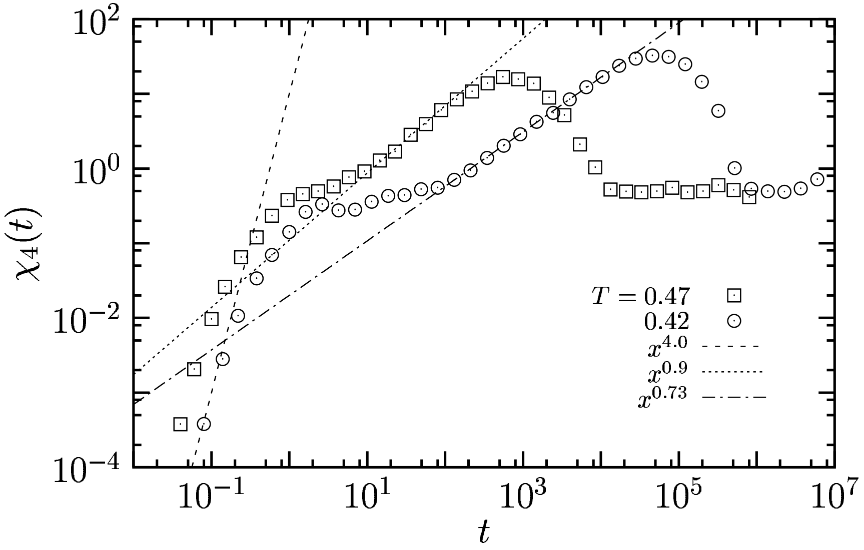
- Experimental evidence on colloids, 2d granular packings and (indirectly) molecular liquids

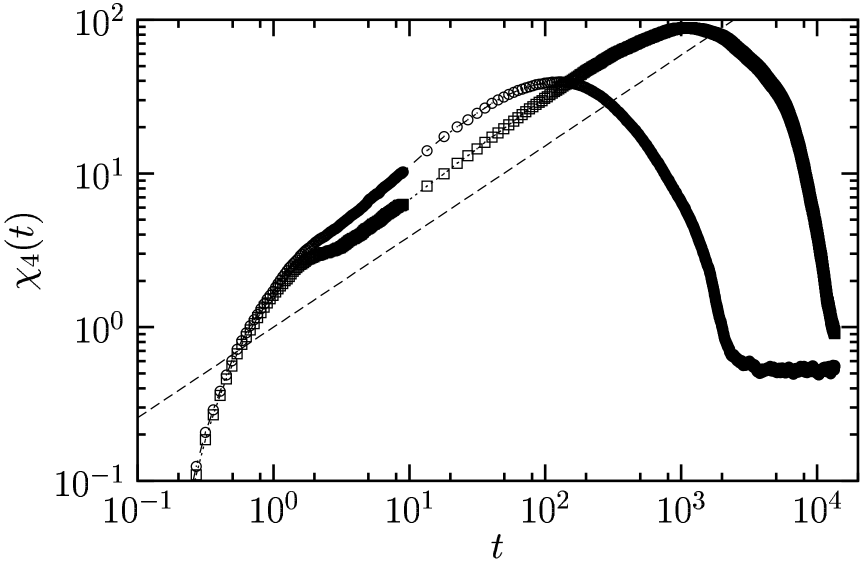
- Theoretical arguments: many scenarii lead to such a growth (see one below)

- Detailed shapes of $G_4(r,t)$ and $\chi_4(t)$ can be computed exactly in simple models, in particular $\chi_4 \sim_{t \ll \tau} t^{\mu}$ (allows to contrast different scenarii: MCT, defects; phonons, etc.)

Dynamic susceptibility: simulation

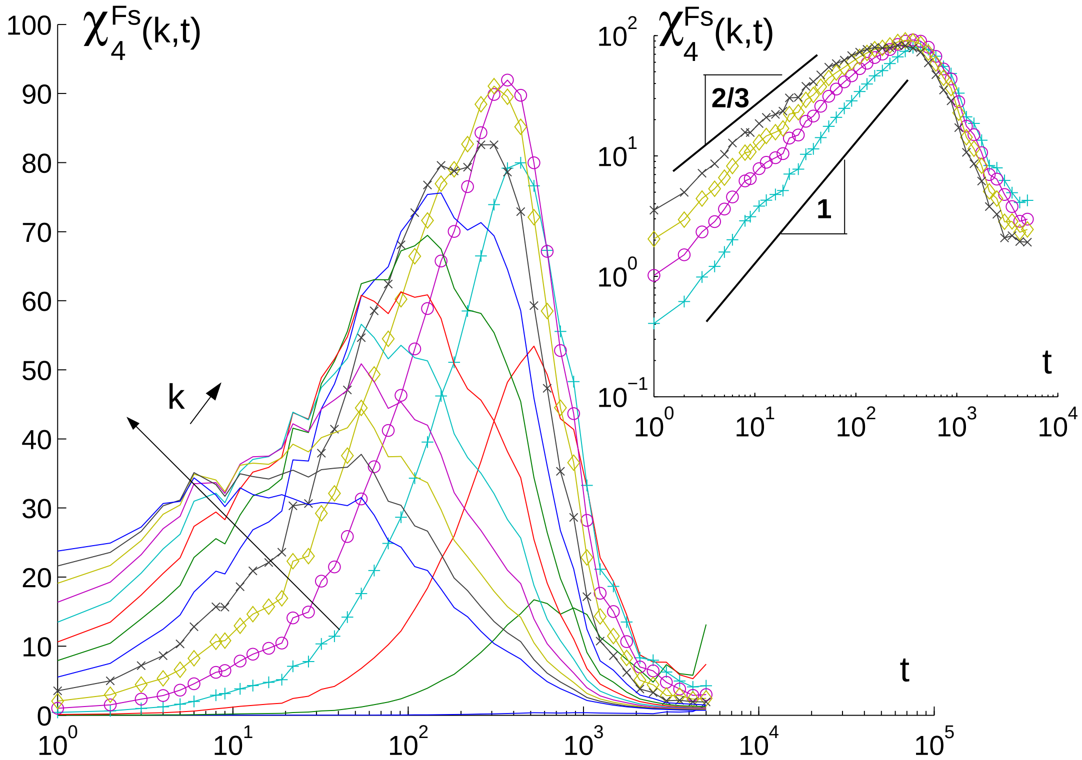
$$\chi_4(t=\tau) \sim \xi^{2-\eta}$$





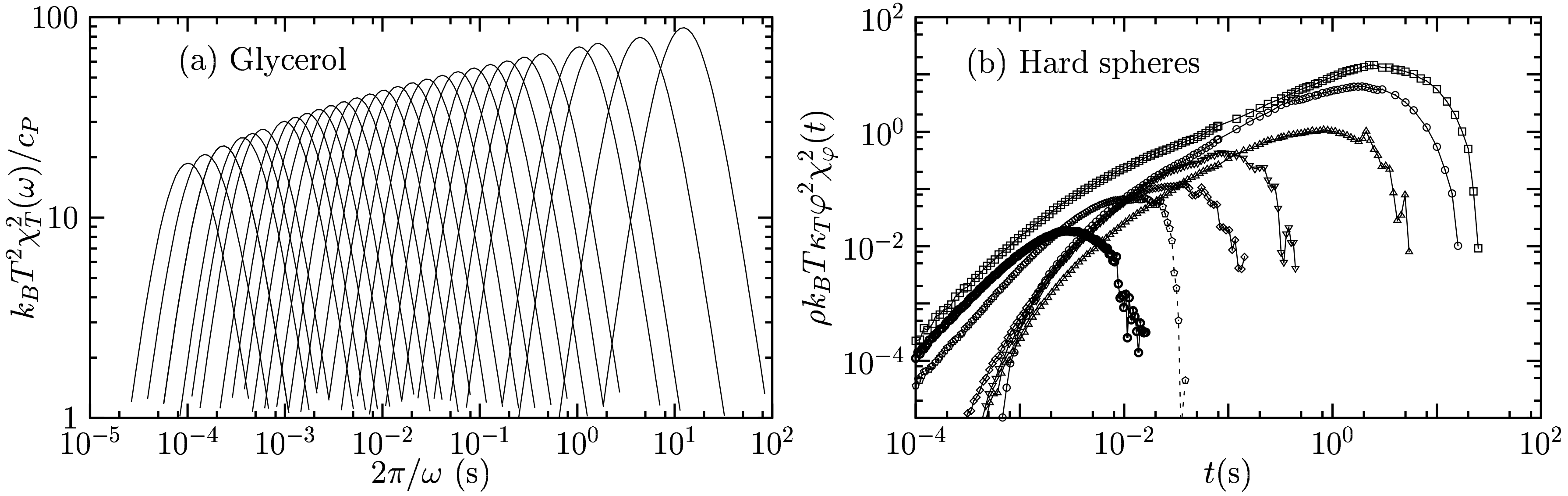
L. Berthier, D. Reichman

Dynamic susceptibility: experimental



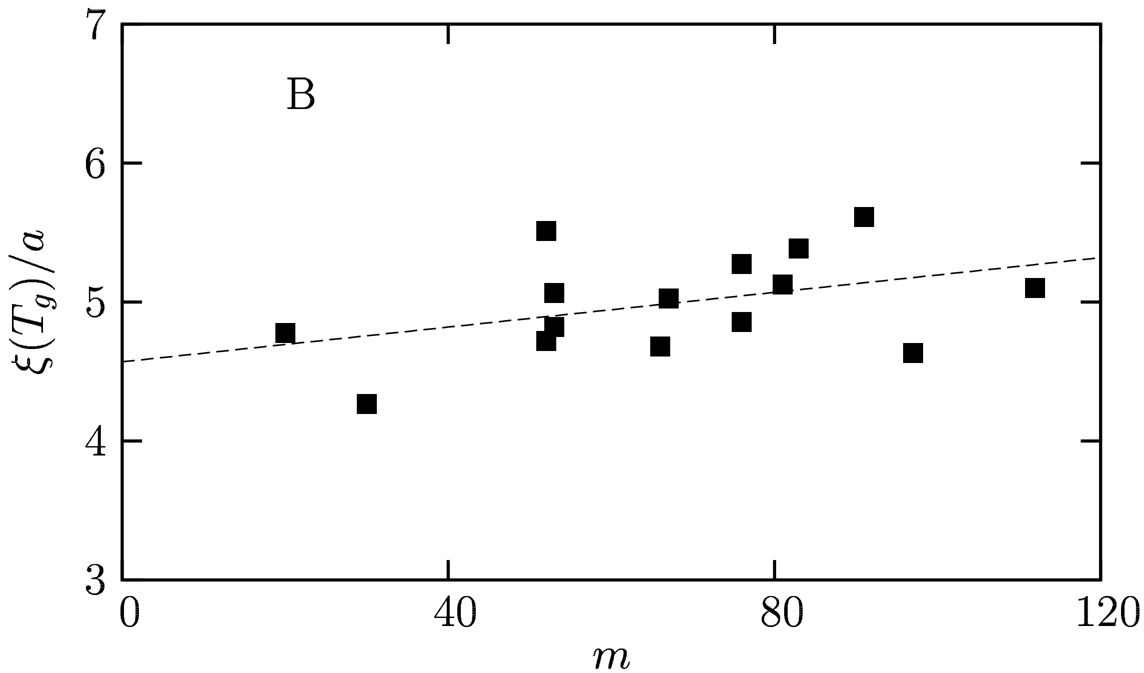
G. Marty, O. Dauchot, G. Biroli; $\xi \approx 6$ – but only one density

Dynamical susceptibility using generalized FDT



$$\chi_4(t) = \langle (\delta C)^2(t) \rangle \approx \frac{k_B T^2}{c_p} \left(\frac{dC(t)}{dT} \right)^2 \quad \text{or} \quad \rho^3 \kappa T \left(\frac{dC(t)}{d\rho} \right)^2$$

Dynamic length scale at T_g: universal?



G. Biroli, L. Berthier, J.P.B., L. Cipelletti, D. El Masri, D. L'Hote, F. Ladieu, M. Pierno. (Science, 16 Dec 2005)

A possible detailed scenario: RFOT-MCT

- Mode Coupling theory: "first principles"

$$\frac{\partial C(q,t)}{\partial t} + \Gamma_q C(q,t) = \int dt' dk V(k,q) C(k,t-t') C(q-k,t-t') \frac{\partial C(q,t')}{\partial t'}$$

- Describes 'local' dynamical freezing: self-consistent blocking of particle in their cages – finite q singularity when

$$C(q_0, t \to \infty) > 0$$

- Equivalent to mean-field $p = 3$ spin-glasses: self-generated quenched disorder

- Random First Order ($1\frac{1}{2}$) Transition

Diverging length within MCT – $T > T_c$

- Non trivial dynamic fluctuations and length scale within MCT ($T > T_c$):
  - MCT is a MF theory for the freezing of the correlation function $C(t) = \langle \rho(\vec{r}_0, t_0)\rho(\vec{r}_0, t_0 + t)\rangle$, which does not decay to zero for $T \leq T_c$.
  - The 'susceptibility' is in fact associated to the four-point correlation $G_4(r,t)$
  - $G_4(r,t)$ is in fact critical within MCT at T_c in finite dimensions (with G. Biroli), as for standard phase transitions

An intermezzo on mean-field

- For standard ferromagnets, MF is $\langle S_i S_j \rangle = \langle S_i \rangle \langle S_j \rangle$, $\to m = \tanh \beta z J m$.

- Similar to Mode-Coupling four point factorisation $\to$ MCT equations for two point $C(t)$.

- But even if correlations between two given points are neglected, $\sum_j \langle S_i S_j \rangle = \chi$ still *diverges* for $T \to T_c^+$: MF *is* compatible with a diverging length scale.

- Very same mechanism for a critical $G_4(r,t)$ in finite dimension MCT (see KTW, Franz & Parisi)

Diverging length within MCT

- A length scale *does* diverge within MCT: $\xi \sim (T - T_c)^{-\nu}$, at variance with previous claims from MCT experts

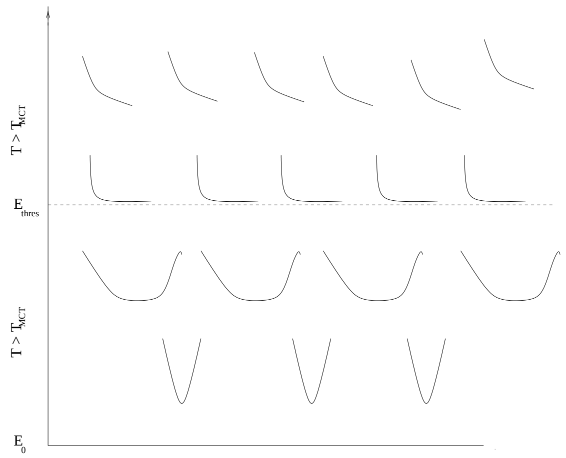
- Prediction of various scaling relations and exponents for $G_4(r, t)$ and $\chi_4(t)$, e.g. $\nu = 1/2$.

- Upper critical dimension $d_c = 6$ (or $d_c = 8$), below which MCT is quantitatively incorrect, even without 'activated' processes that blur the transition (see below)

- Critical fluctuations for $d < d_c$ necessarily lead to fluctuations of local relaxation time and viscosity/diffusion decoupling.

The Kirkpatrick-Thirumalai-Wolynes landscape

- MCT: a phase-space picture: Above T_c, only saddles; below T_c only minima. Slowing down: rarefaction of 'downhill' directions, allowing particles to move without seeing each other ($\rightarrow$ more collective moves!)



J. Kurchan- L. Laloux, A. Cavagna, I. Giardina et al...

Beyond MCT – Blurred transition

- Finite range models: transition blurred
  - saddle-minima mixing
  - barriers between minima do not diverge

- $\longrightarrow$ Difficulty: no singularity, no sharp statements

- T_c crossover between free and activated dynamics

- How to interpret mean field in that case and compute the (finite) relaxation time?

$T < T_c$: the Adam-Gibbs-KTW mosaic state I

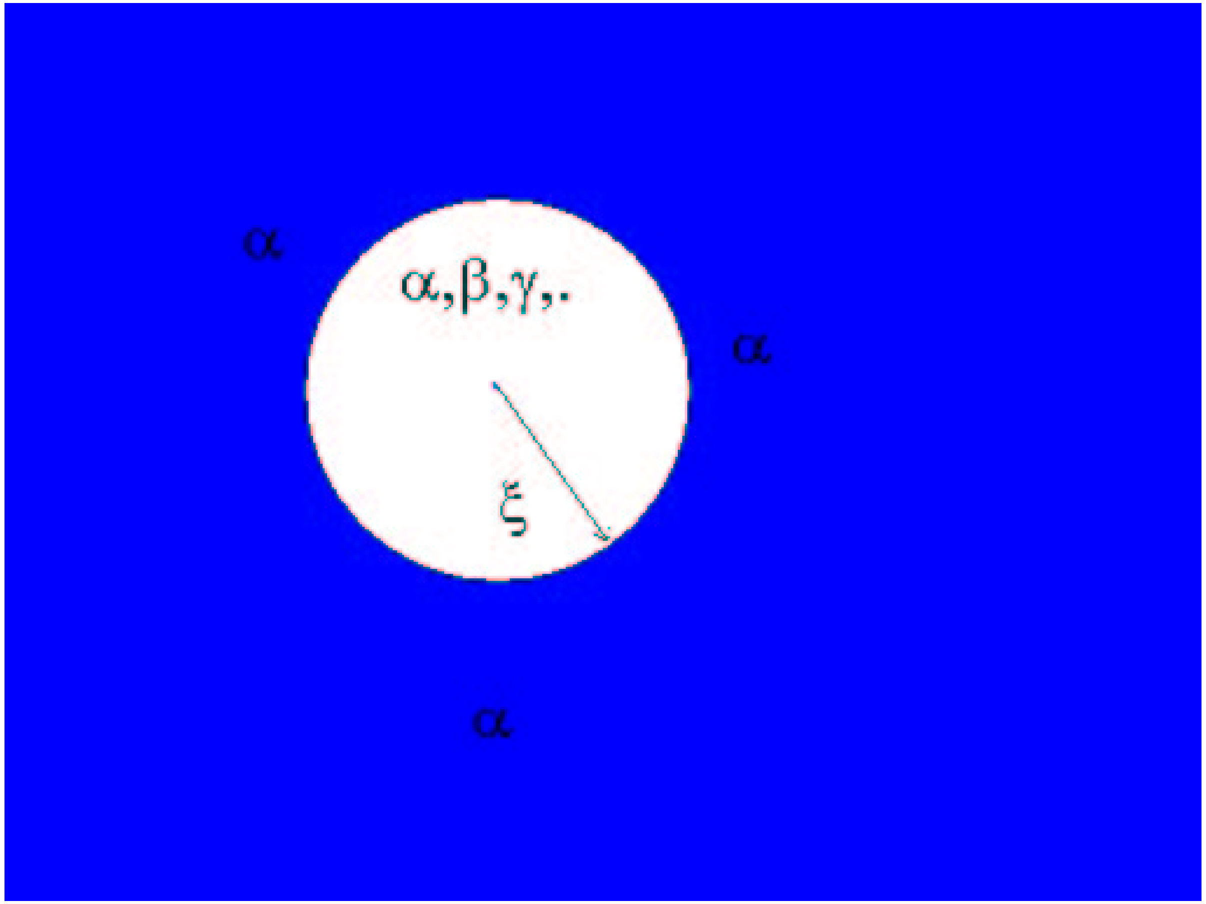
- Large degeneracy of inherent structures (below T_c): non zero configurational entropy, $S_c \sim T - T_K$. Generic: MF spin-glasses; long range interacting particles (Kac potential); DFT.

- Question: stability of a sphere of size ξ immersed in a frozen state α?

$$Z(\xi, T) \approx \sum_{\beta \neq \alpha} \exp[-\xi^d \frac{f_\beta}{k_B T}] + \exp[-\xi^d \frac{f_\alpha}{k_B T} + \frac{\Upsilon \xi^\theta}{k_B T}]$$

- The two terms balance for $\xi^{*d-\theta} \approx \Upsilon / S_c$. For $\xi \gg \xi^*$, $F \approx F_{liquid}$

Entropic instability of single inherent structures



with G. Biroli

The Adam-Gibbs-KTW mosaic state II

- ξ^* diverges when $T \to T_K$ – Note: $S_c \xi^{*3} \gg 1$!

- $\xi < \xi^*$: state α dominates (glass) – a few relevant config.

- $\xi > \xi^*$: state α is lost (liquid) – entropy melting.

- ξ^* smallest (fastest) scale able to decorrelate in time $\to$ $\ln \tau(T) = \ln \tau(\xi^*) \sim \xi^{*\psi}$

- Hops between metastable states via activation on scale ξ^* $\to$ Adam-Gibbs fragility, $\beta < 1$, heterogeneities, Stokes-Einstein decoupling,...

Open problems (theory)

- Is MCT-RFOT at all relevant?? Universal statistics for random energy landscapes??

- Dynamical cooperativity: trivial (non thermodynamical) as in mobility defect theories or non trivial (appearance of exp. many metastable states) as in p-spin??

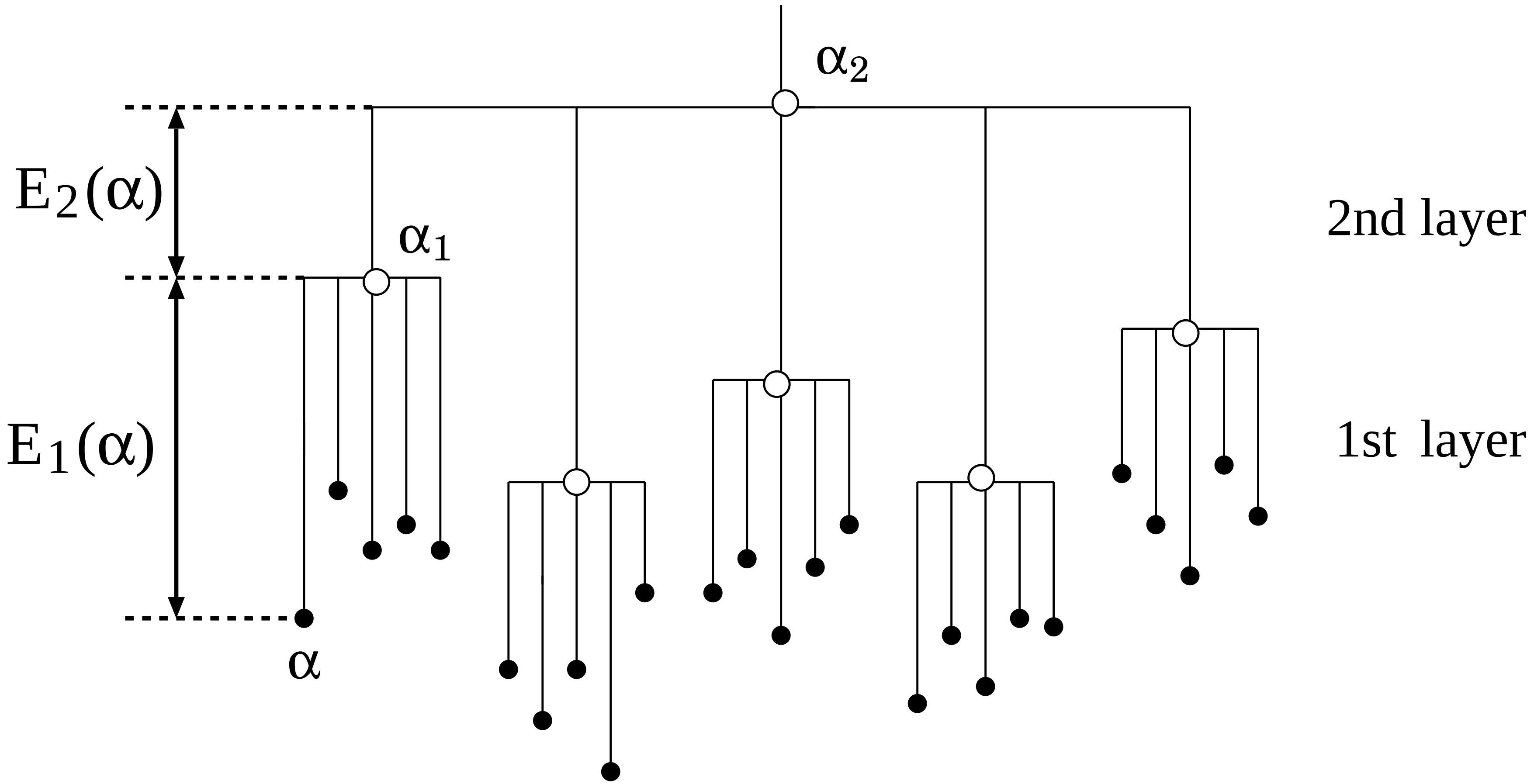
- Surface tension between inherent states (Υ, θ ??), value of the exponents (MCT in $d < d_c$, value of d_f)

- Phenomenological extension of MCT to describe the activated droplet region and rheological properties

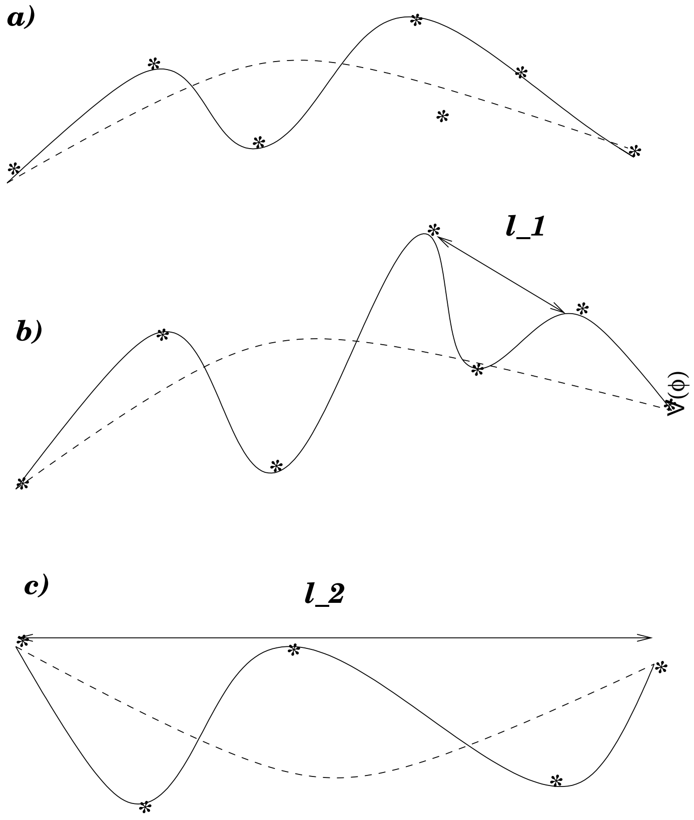
The ultimate complexity: Spin-glasses

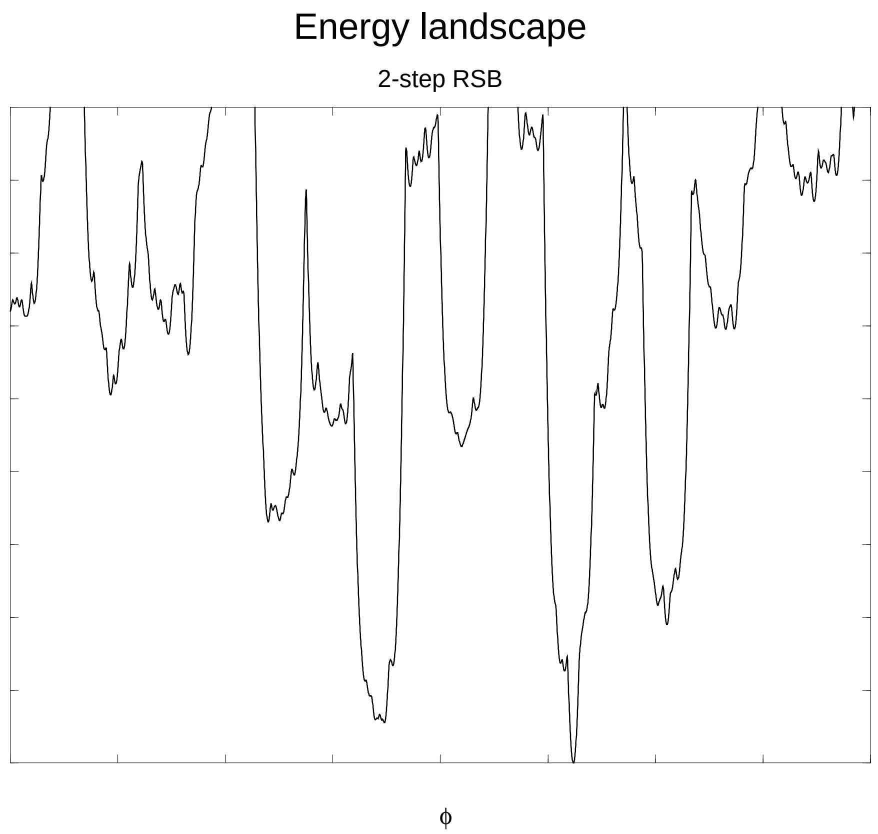
- Parisi's mean field theory
  - Hierarchical landscape picture: traps within traps with different freezing temperatures
  - Dynamical mean field + RSB $\longrightarrow$ "ultrametric" dynamics (infinite number of time domains $\neq t/t_w$).
  - Rejuvenation and memory

Hierarchical Phase Space



Multiscale dynamics

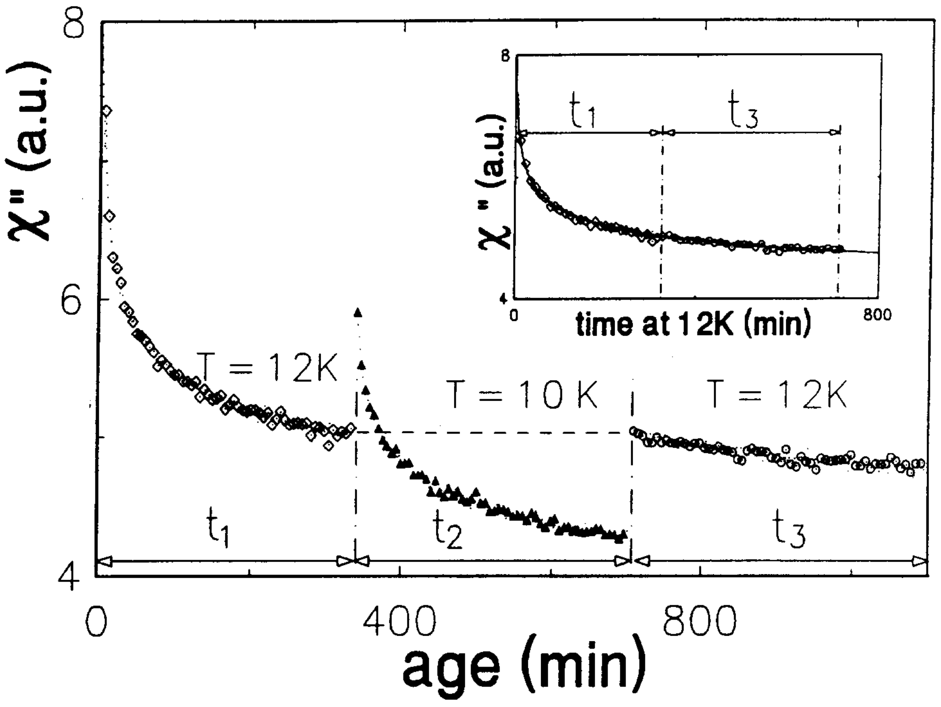




Events on scale ℓ_1 happen while conformations on ℓ_2 are *frozen*

Aging and Memory

- Aging $C(t;t_w) \sim F(t/t_w)$, rejuvenation and memory for $T < T_g$



Open problems (theory)

- What remains of the hierarchical Parisi landscape for real spin-glasses??

- Quest for a soluble, non mean-field model (glasses + SG !!)