Nonequilibrium dynamics of glassy materials

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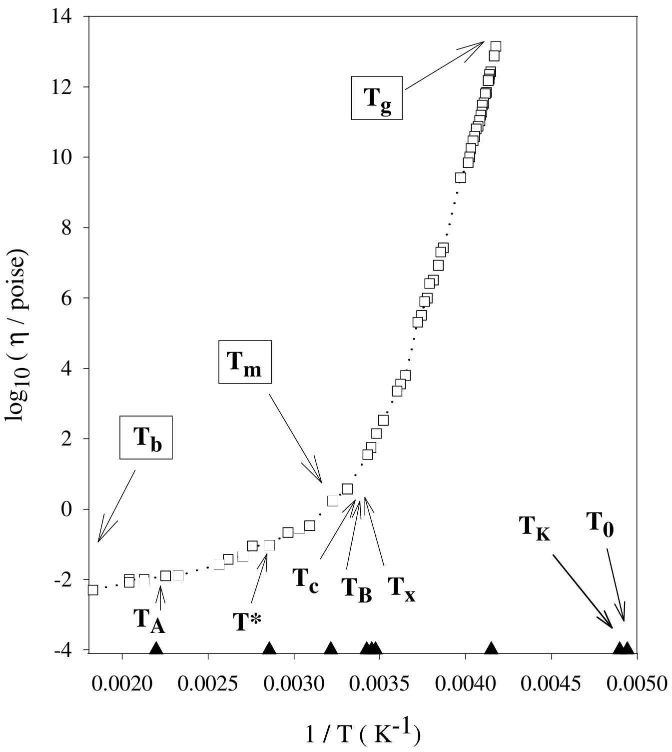
• Introduction

CAUTION: This talk contains experimental data

Slow dynamics – 'Glassy systems'



[Tarjus & Kivelson ('00)]

- Definition : $\boxed{t_{\rm rel} \gtrsim t_{\rm exp}}$

- Below the 'glass transition',

$$t_{\rm exp} \ll t_{\rm rel} \simeq \infty$$

$\boxed{\text{Out of equilibrium dynamics}}$

('glassy dynamics')

Aging, Hysteresis, Memory, Rejuvenation, Fictive or effective temperatures, Violations of equilibrium properties, etc.

- $\boxed{\text{Glassy systems are everywhere!}}$

Structural glasses, Spin glasses, Complex fluids (e.g. colloids, emulsions, etc.), Foams, Granular materials, Charge density waves, High-T_c superconductors, Electron glass, Proteins, etc.

- Both fundamental and practical interests.

What is the phenomenology?
What is the theoretical description?

Out of equilibrium dynamics – Aging

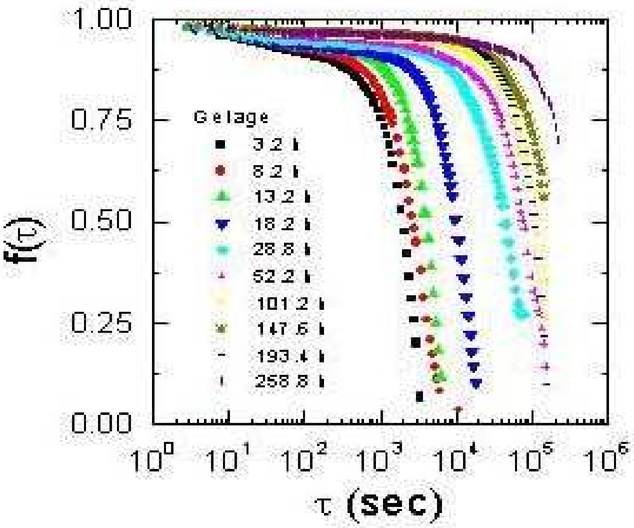
- $t_{\rm rel} \gg t_{\rm exp} \Rightarrow$ All the history (thermal, mechanical) is important.

- A well-defined experimental protocol [Struik ('78), Lundgren et al, PRL ('83)]

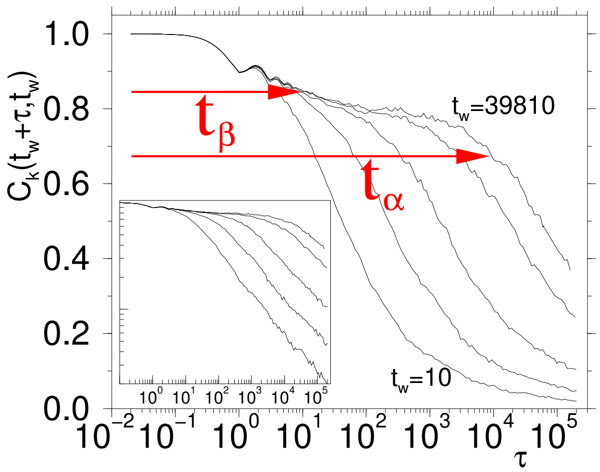
(i) 'Quench' in the glassy phase at $t_w = 0$.

(ii) Let the system 'age' during t_w ('age').

(iii) Compute at two-time quantity: $C(t, t_w) \neq C(t - t_w)$.



Fractal gel (Exp.) [Cipeletti et al, PRL ('00)]



Lennard-Jones (Num.) [Kob & Barrat, PRL ('97)]

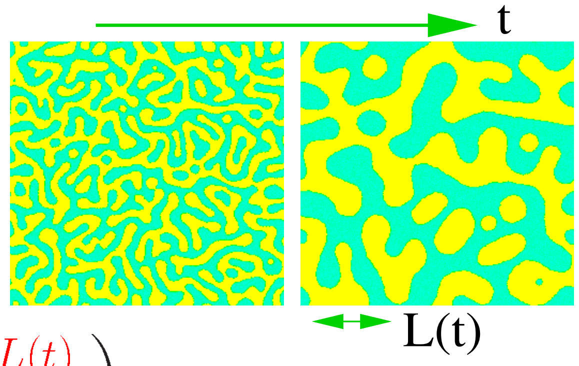
- Universality? In many systems,

$$C(t, t_w) \simeq C_{\rm stat}(t - t_w) + C_{\rm aging}\left(\frac{t}{t_w}\right)$$

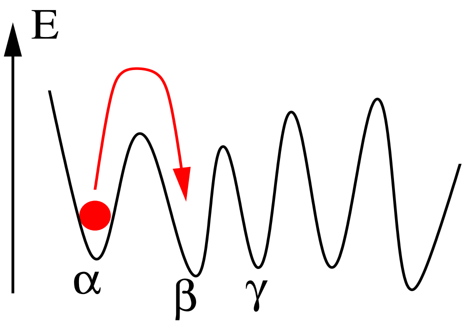
$$\chi''(\omega, t_w) \simeq \chi''_{\rm stat}(\omega) + \chi''_{\rm aging}(\omega t_w)$$

Four families of theoretical approaches

(1) 'Aging in real space'.
Aging = Domain growth (binary mixtures, ferromagnets).
Spatial description.
Scaling regime $L(t) \gg \xi_{\rm eq}(T)$



$$\Rightarrow C(t,t_w) \simeq C_{\rm stat}(t-t_w) + C_{\rm aging}\left(\frac{L(t)}{L(t_w)}\right).$$



(2) 'Aging in phase space'.
Aging = Looking for deepest traps in a 'complex' energy landscape.
Phenomenological description.

(3) 'Aging in an infinite-dimensional space'.
Study of exactly solvable models (mean-field). Microscopic description.
Quantitative predictions for (1) Structural glasses (2) Spin glasses.

Aging of two-time correlation and response functions, modification of the fluctuation-dissipation theorem as

$$R(t,t') = \frac{1}{T_{\sf eff}} \frac{\partial C(t,t')}{\partial t'},$$

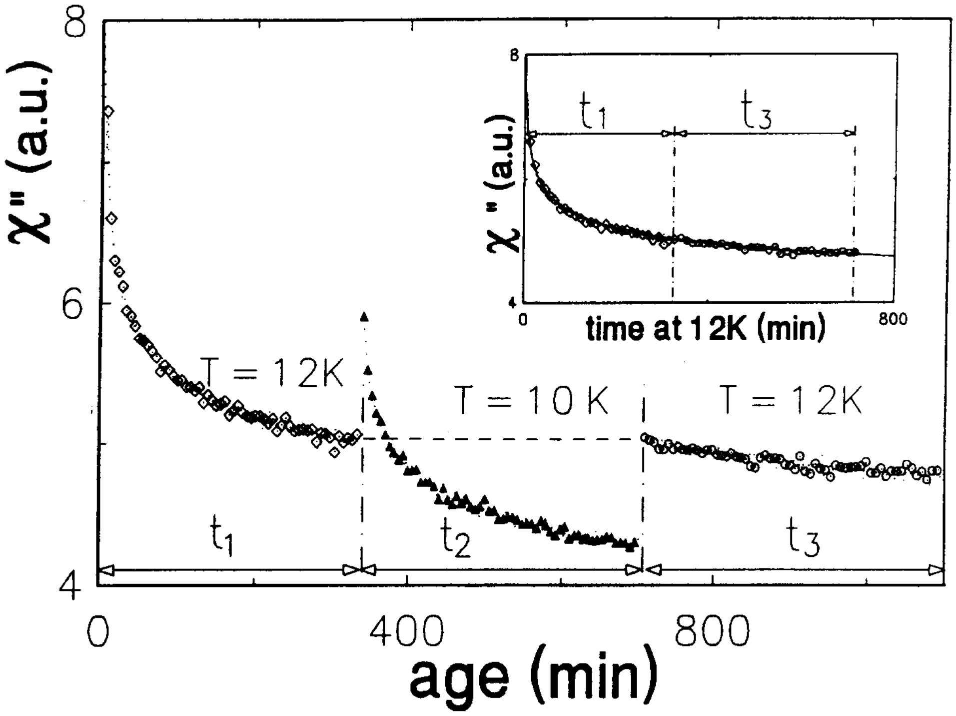
and link with the statics

$$x(q) \equiv \frac{T}{T_{\sf eff}(q)} = \int_0^q {\rm d}q' P(q')$$

(4) Exactly solvable models in finite dimensions. Cf JM Luck.

T-cycling experiments: ‘Memory’ and ’rejuvenation’

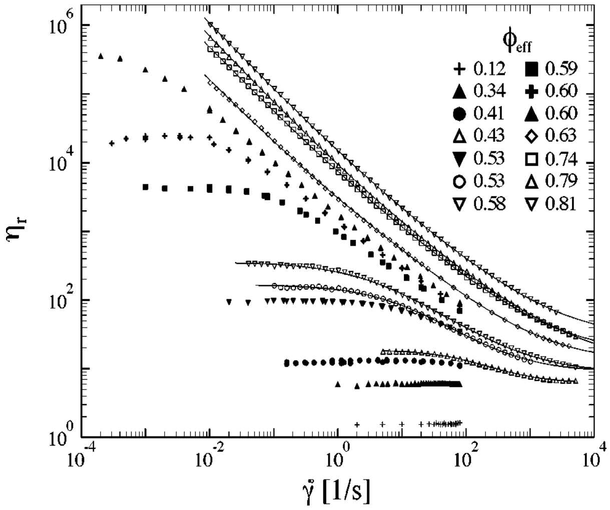
• More elaborated protocols to (1) refine experimental descriptions, (2) discriminate models.

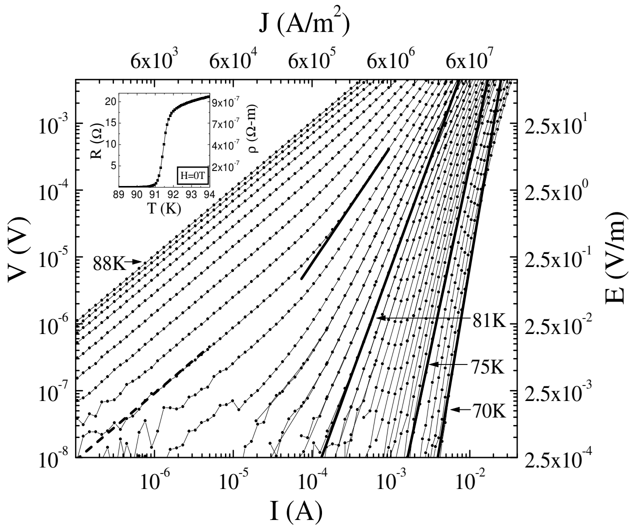


[Refregier et al., J Phys I (’87)]

Driven dynamics of glassy systems

• Aging is not the (only) relevant experimental situation.
Rheology of complex fluids, Vortex dynamics in superconductors, Phase separation in a flow, Driven directed polymer, Dry-friction, etc.





Suspension silica/PDMS [Nommensen et al, PRE ('99)] H-Tc Superconductor [Strachan et al, ('00)]

• The driving force introduces a new time scale (e.g. $t \sim \gamma^{-1}$). Competition slow dynamics / driving force.

• Drive may stop aging, $t_{\rm rel} = t_{\rm rel}(\text{forcage}) < \infty$.

Shear-thinning, $t_{\rm rel} \propto \eta = \eta(\gamma) \approx \dfrac{1}{\gamma^\alpha}$,

Creep, $t_{\rm rel} \propto V^{-1} \approx \exp\left[\dfrac{U}{T}\left(\dfrac{I_0}{I}\right)^\mu\right]$.

• Two good reasons not to be at equilibrium...

Mean-field approach

- Microscopic dynamics for ϕ_i $(i = 1, \cdots, N \to \infty)$.

$$\frac{\partial \phi_i}{\partial t} = -z(t)\phi_i - \frac{\delta H[\boldsymbol{\phi}]}{\delta \phi_i} + \zeta_i + \varepsilon f_i(t)^{\mathrm{DRIVE}}$$

$$H_p = \sum_{i_1,\cdots,i_p} J_{i_1\cdots i_p}\phi_{i_1}\cdots\phi_{i_p} \qquad \sim \text{Structural glass } (p-\text{spin})$$

$$H = H_2 + H_4 \qquad \sim \text{Spin Glass (SK)}$$

- Closed and exact dynamical equations in terms of

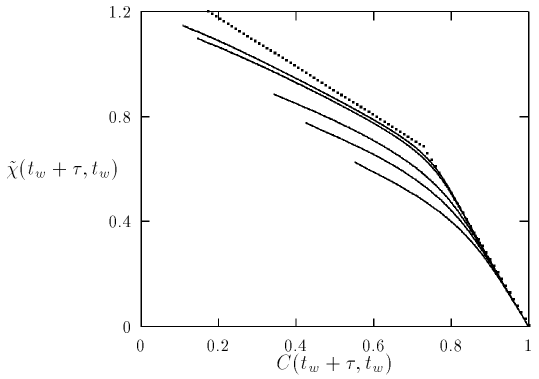
$$C(t,t') = \langle \boldsymbol{\phi}(t)\boldsymbol{\phi}(t')\rangle, \quad \chi(t,t') = \int_{t'}^{t} \mathrm{d}t'' \, \frac{\delta\langle \boldsymbol{\phi}(t)\rangle}{\delta \boldsymbol{\zeta}(t'')} = \int_{t'}^{t} \mathrm{d}t'' R(t,t'')$$

- Relaxational (aging) dynamics, $\varepsilon = 0$.

Equilibrium for $T > T_c$ $(t_{\mathrm{rel}} < \infty)$: $\quad R(t-t') = \dfrac{1}{T}\dfrac{\partial C(t-t')}{\partial t'}$

Fluctuation-Dissipation Theorem (FDT)

Aging for $T < T_c$ $(t_{\mathrm{rel}} = \infty)$. For $t, t' \to \infty$,



$$R(t,t') = \frac{1}{T_{\mathrm{eff}}(C)}\frac{\partial C(t,t')}{\partial t'}$$

T_{eff} is the 'effective temperature'.

$X \equiv T/T_{\mathrm{eff}}$ is the 'fluctuation-dissipation ratio'.

Dynamic equations

- p-spin model with constant driving force of amplitude ε.

$$
\begin{aligned}
\frac{\mathrm{d}C(t)}{\mathrm{d}t} =& - \mu C(t) + \int_0^t \mathrm{d}t' \Sigma(t-t')C(t') \\
& + \int_0^\infty \mathrm{d}t' \left[\Sigma(t+t')C(t') + D(t+t')R(t')\right] \\
\frac{\mathrm{d}R(t)}{\mathrm{d}t} =& - \mu R(t) + \int_0^t \mathrm{d}t' \Sigma(t-t')R(t') \\
\mu =& T + \int_0^\infty \mathrm{d}t' \left[D(t')R(t') + \Sigma(t')C(t')\right] \\
D(t) =& \frac{p}{2} C(t)^{p-1} + \varepsilon^2 \frac{k}{2} C(t)^{k-1} \\
\Sigma(t) =& \frac{p(p-1)}{2} C(t)^{p-2} R(t)
\end{aligned}
$$

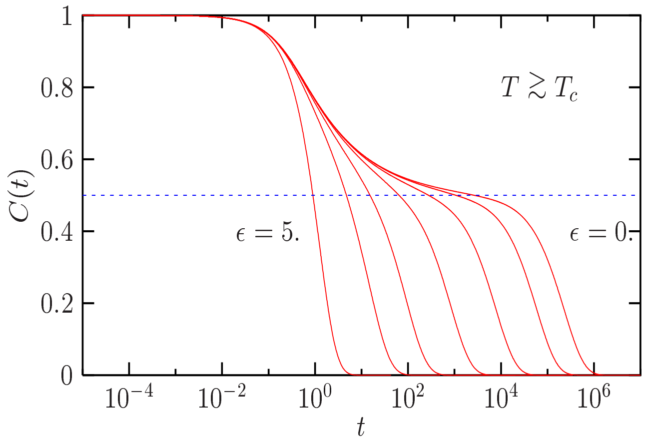
- For $\varepsilon = 0$ and $T > T_c$, one gets:

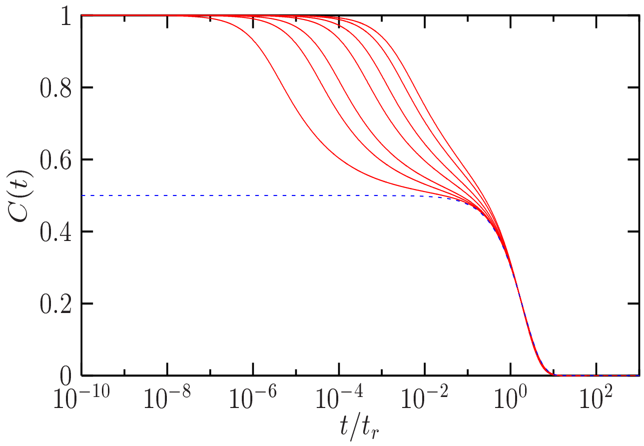
$$
\frac{\mathrm{d}C(t)}{\mathrm{d}t} = -TC(t) - \int_0^t \mathrm{d}t' \frac{\mathrm{d}C(t')}{\mathrm{d}t'} D(t-t')
$$

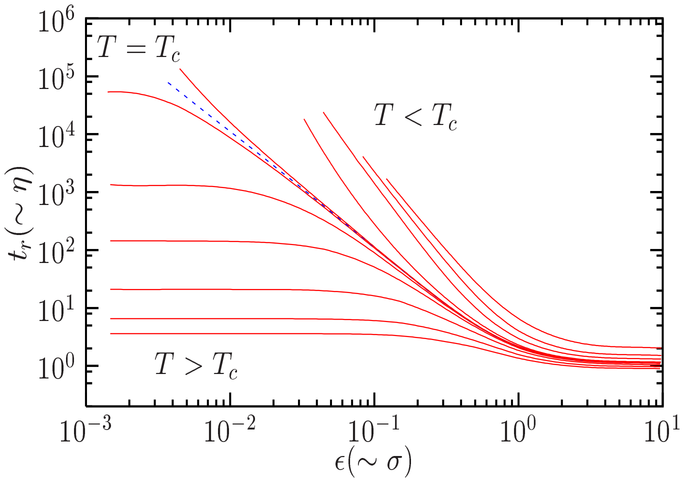
This is the schematic mode-coupling theory.

Nonlinear rheology – 2 time scales

- p-spin + constant drive. Numerical ($\varepsilon > 0$) and analytical ($\varepsilon \to 0$) solution of the dynamical equations. [Berthier, Barrat & Kurchan, PRE ('00)]



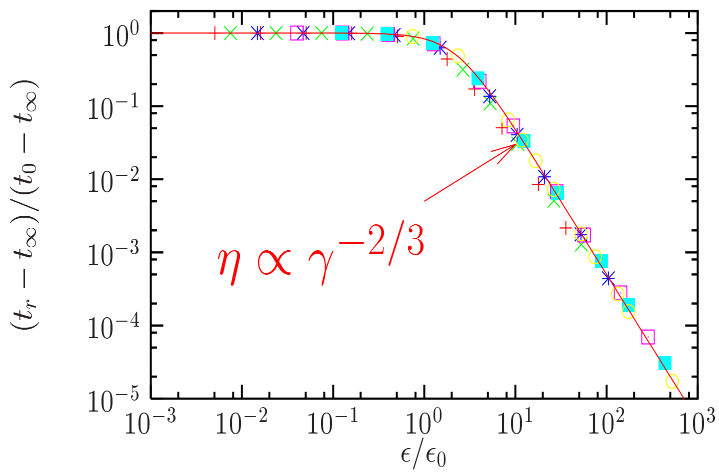




- $t_{\rm rel} \sim \eta$, $\varepsilon \sim \sigma$, $\dfrac{\varepsilon}{t_{\rm rel}} \sim \gamma$.

- $T > T_c$: Newtonian regime, then shear-thinning.

$$\eta \sim \gamma^{-2/3}$$



- $T = T_c$: $\eta \sim \gamma^{-2/3}$

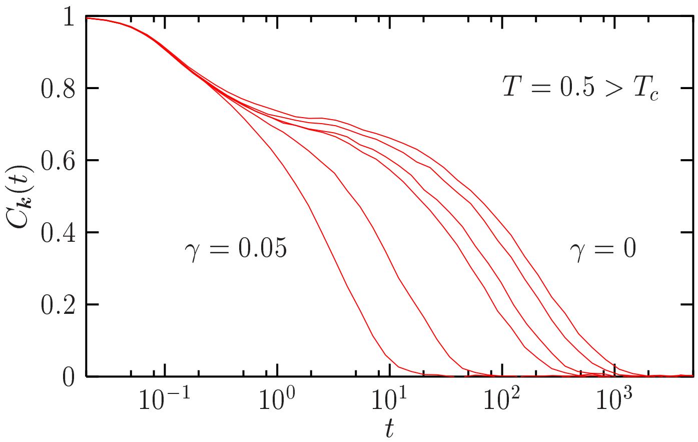
- $T < T_c$: No linear regime, shear-thinning.

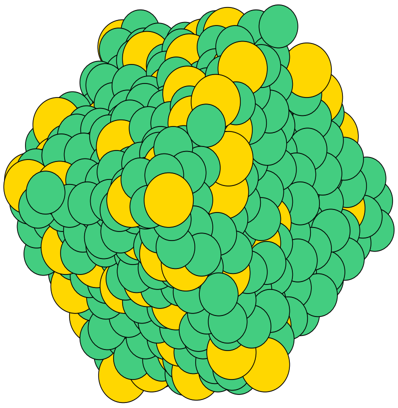
$$\eta \sim \gamma^{-\alpha(T)}, \ \frac{2}{3} < \alpha(T) < 1$$

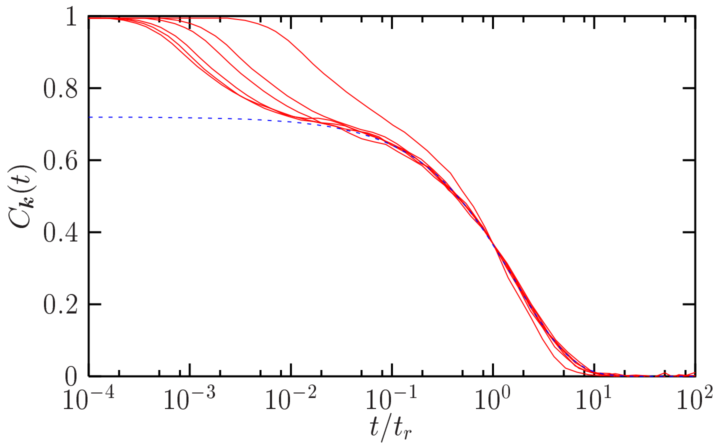
Glassy rheology by molecular dynamics

• 3D molecular dynamics simulation of a simple (binary Lennard-Jones) glassy liquid under shear.

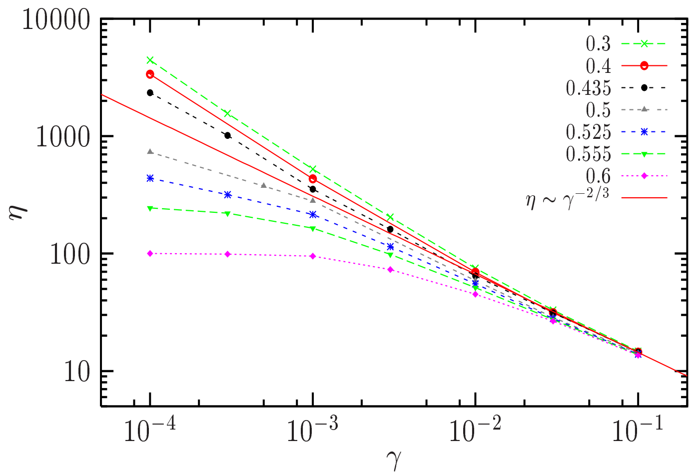
[Barrat & Berthier, PRE ('01), JCP ('02)]







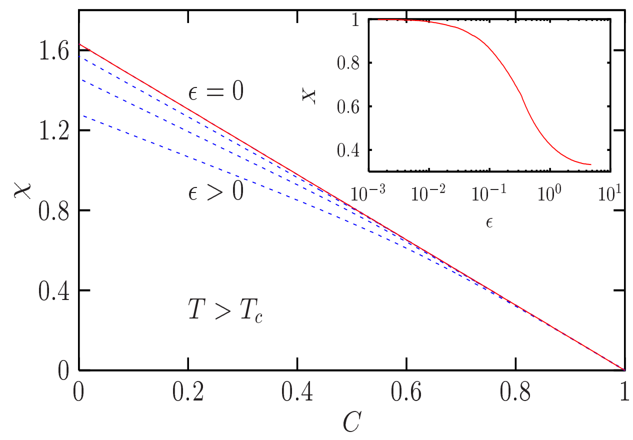
• 'Microscopic' model in very good agreement with the behavior observed in sheared supercooled liquids...

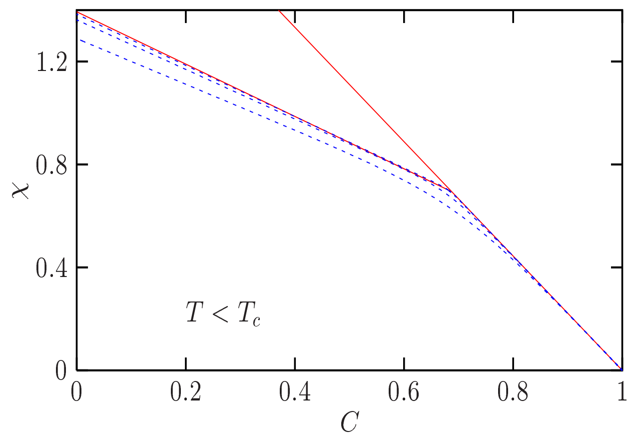


• ... and in many complex fluids.

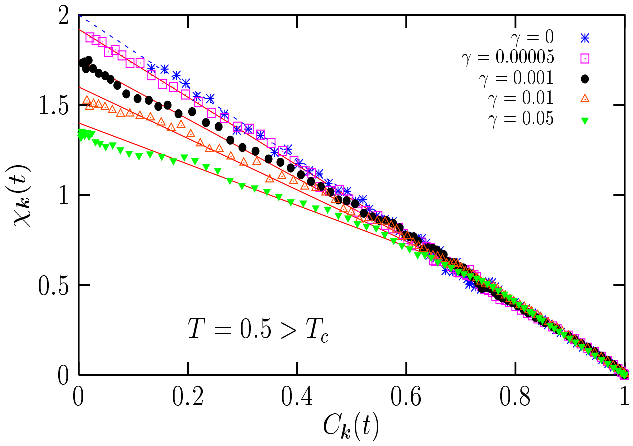
Nonlinear rheology – 2 Temperatures...

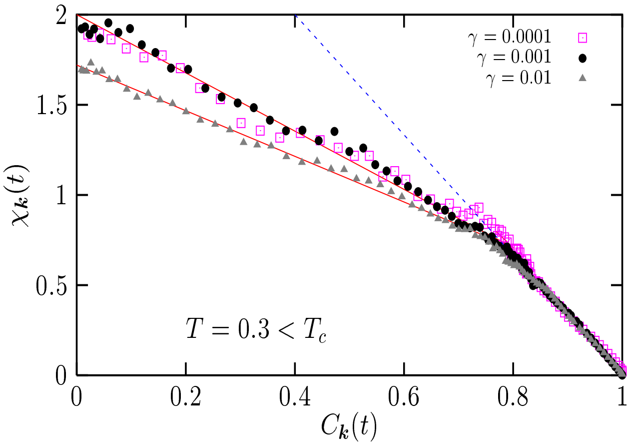
- ... in the mean-field model beyond the Newtonian regime.



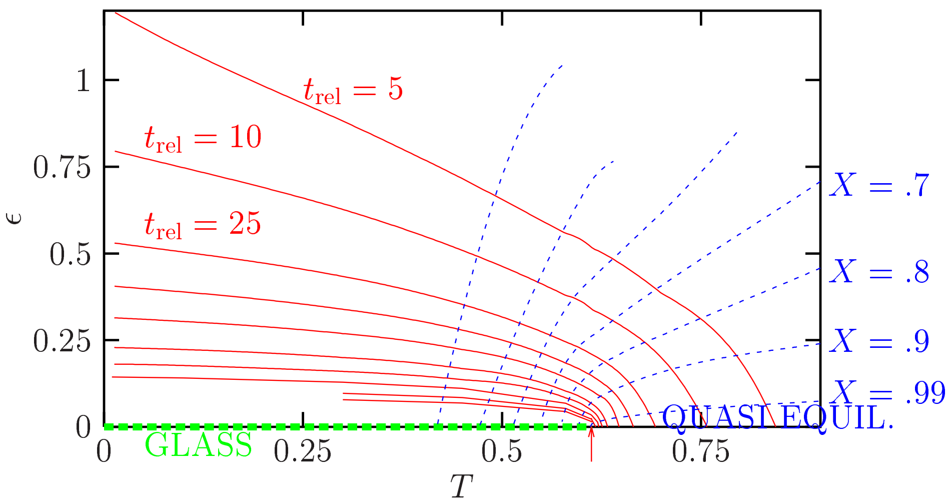


- ... in the sheared liquid. FDT associated to the density fluctuations.



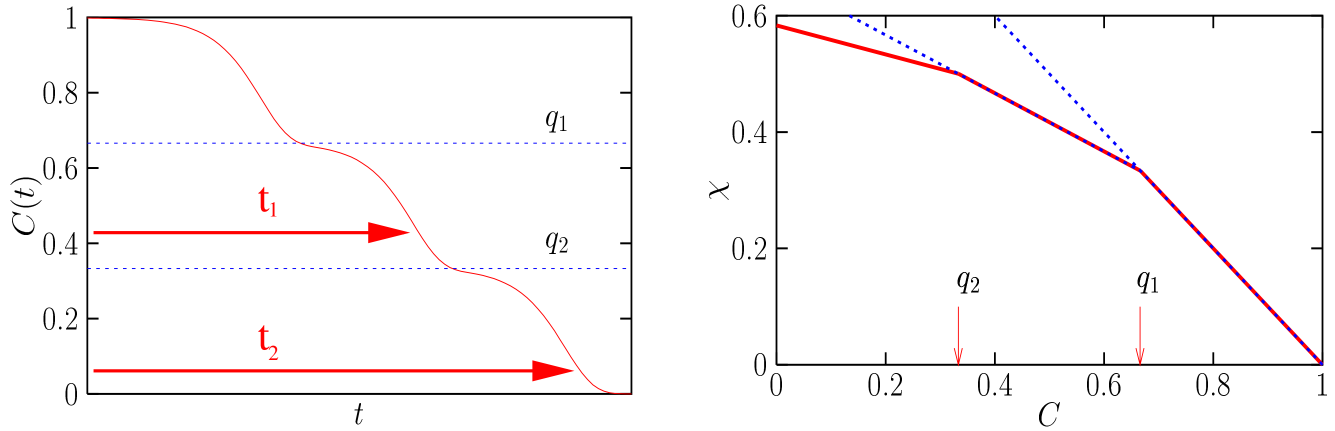


- To summarize: 2D-view of the glass transition.



Dynamic ultrametricity

- What if 2 slow time scales, with $\dfrac{t_1}{t_2} \underset{\varepsilon \to 0}{\longrightarrow} \infty$?



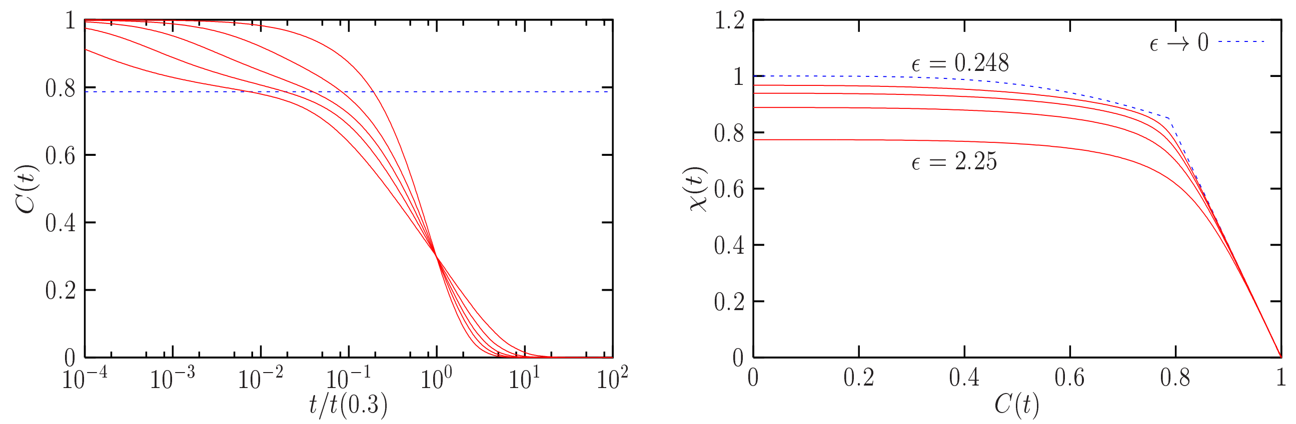
- Mean-field spin glasses ($\sim$ Sherrington-Kirkpatrick): generalisation to an infinity ('hierarchy') of time scales: dynamic ultrametricity.

- Driven dynamics:

$$\forall\, q_2 < q_1 < q_{EA} \qquad \frac{t(q_2)}{t(q_1)} \underset{\varepsilon \to 0}{\longrightarrow} \infty \quad \Leftrightarrow \quad C(t,\varepsilon) \neq \mathcal{C}\left(\frac{t}{t_{\rm rel}(\varepsilon)}\right)$$

- How to see it? Driven dynamics of a mean-field spin glass.

[Berthier, Barrat & Kurchan, PRE ('01)]



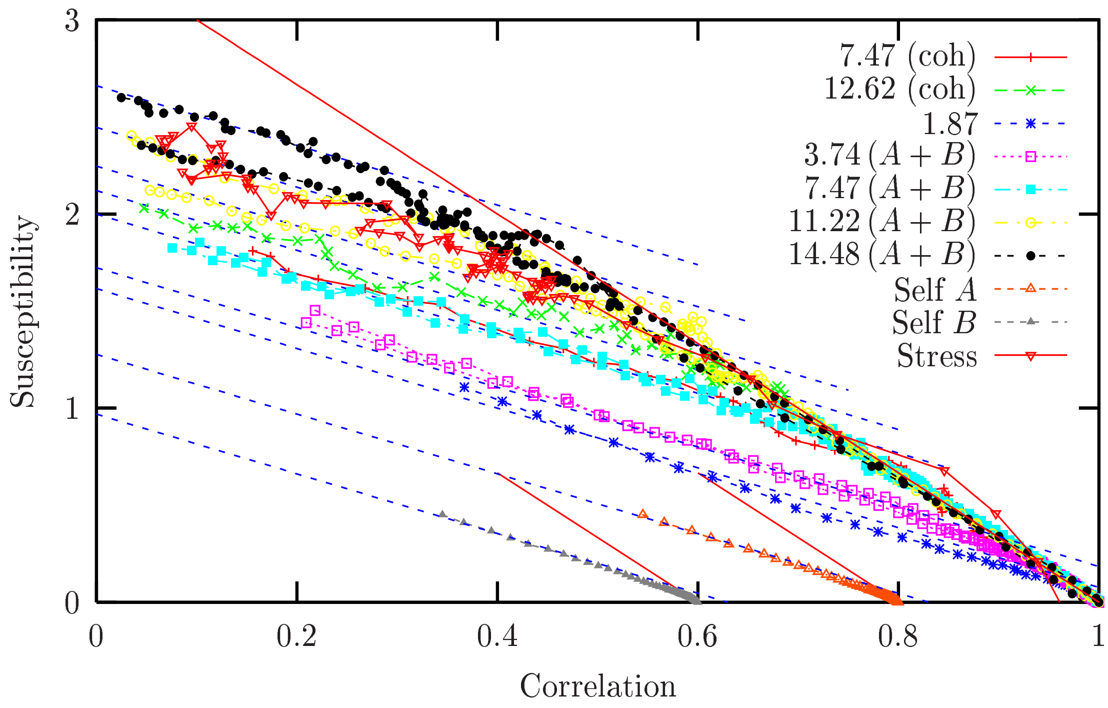
Meaning of FDT violations?

• T_{eff} is a 'real' temperature. [Cugliandolo, Kurchan & Peliti, PRE ('97)]

(1) Temperature measured by a thermometre coupled to any observable of the system.

(2) Fixes the direction of the heat flows. 'Zeroth law' of thermodynamics.

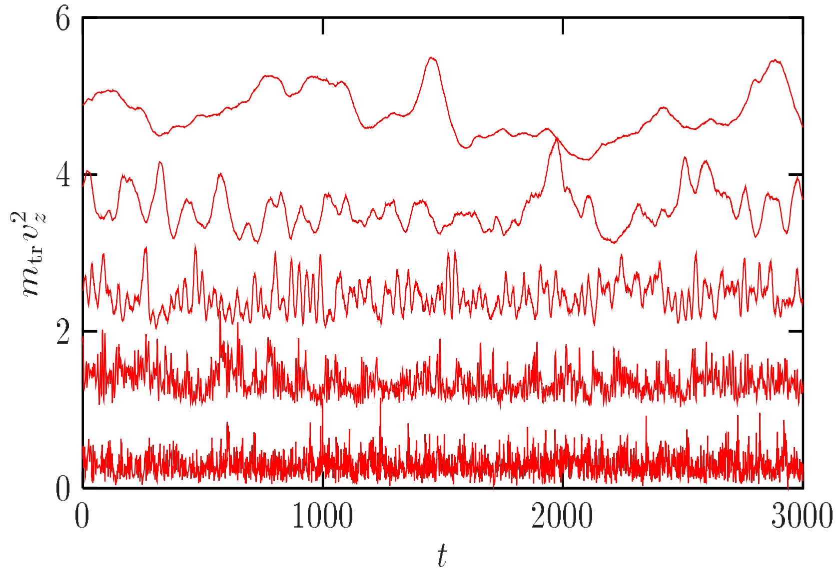
• Observable independance in the sheared Lennard-Jones liquid: 14 identical FDT plots. [Berthier, Barrat, PRL ('02)]



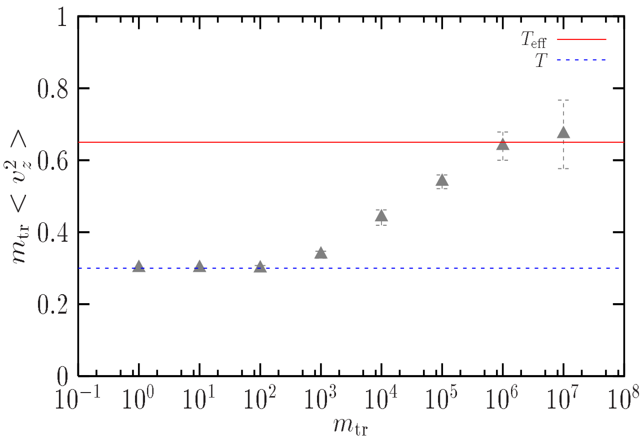
An 'effective thermometer'

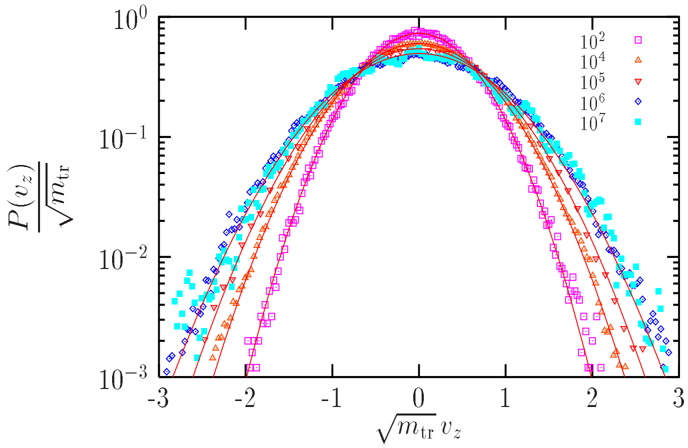
- Thermometer = 'Heavy' tracers, mass $m_{\rm tr}$. Frequency $\omega \sim 1/\sqrt{m_{\rm tr}}$.

[Berthier, Barrat, J. Chem. Phys. (2002)]



- Reading of the temperature: Measure of $\frac{1}{2} m_{\rm tr} v_z^2$.

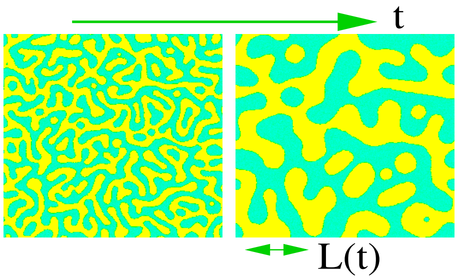




- Nonequilibrium equipartition theorem and Maxwell distribution

$$\frac{1}{2} m_{\rm tr} v_z^2 = \frac{1}{2} k T_{\rm eff} \qquad P(E) \sim \exp(-\beta_{\rm eff} E)$$

Back to domain growth processes



- Ferro, $P(q) = \delta(q - m^2)$.

$$x(C < m^2) = \int_0^C \mathrm{d}q\, P(q) = 0 \Leftrightarrow T_{\mathrm{eff}} = \infty$$

- Interpretation [Berthier, Barrat & Kurchan, EPJB ('99)]

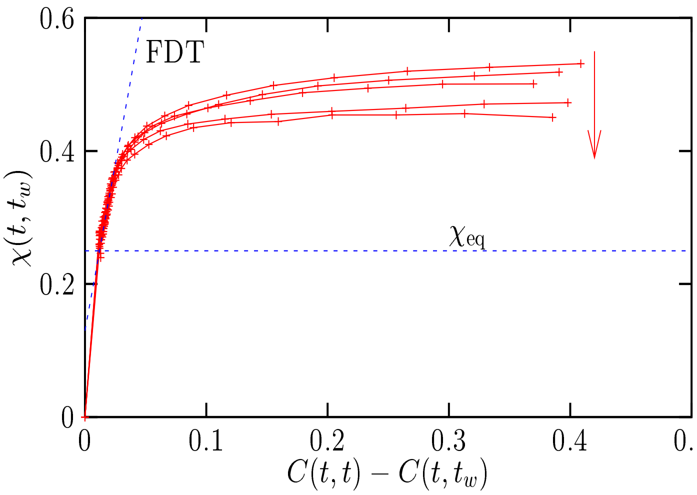
$$\chi = \chi_{\mathrm{bulk}} + \chi_{\mathrm{interf}} \text{ with } \chi_{\mathrm{interf}}(t, t_w) \sim \frac{1}{L(t_w)} \mathcal{F}\left(\frac{L(t)}{L(t_w)}\right) \to 0 \ (d > 2)$$

- $\ell \ll L(t)$

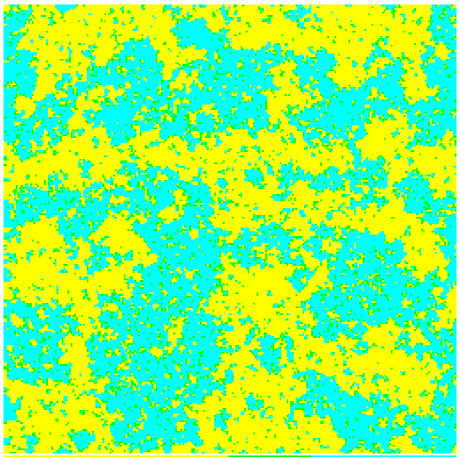
'Quasi-equilibrated' system.

- $\ell \gg L(t)$

Still disordered system.



- This argument breaks down at the critical point. No distinction between bulk and interfaces.



Nonequilibrium critical dynamics

- Analytical and numerical study of the 2D XY model in the Kosterlitz-Thouless phase. [Berthier, Holdsworth & Sellitto, JPA ('01)]

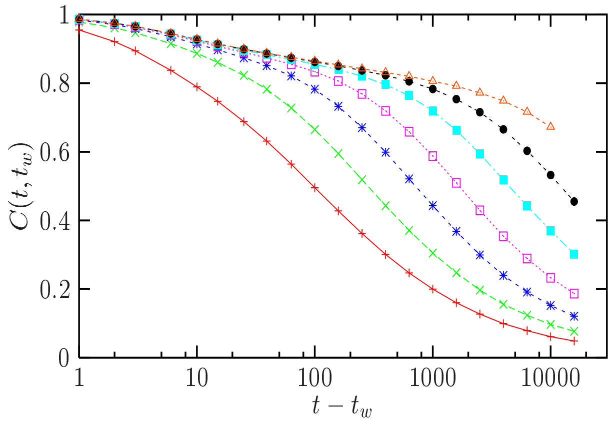
- Aging at the critical point: growth of the dynamic correlation length, $\xi(t) \sim t^{1/z}$. Successive equilibration of critical fluctuations, $t_{\rm rel}(k) \sim k^{-z}$.

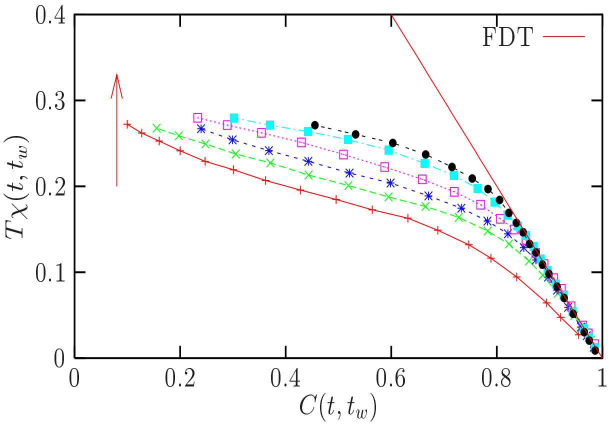
- Scaling laws:

$$C(t,t_w) \sim \frac{1}{(t-t_w)^{2\beta/\nu z}} \mathcal{C}\left(\frac{\xi(t)}{\xi(t_w)}\right)$$

$$R(t,t_w) \sim \frac{1}{(t-t_w)^{2\beta/\nu z+1}} \mathcal{R}\left(\frac{\xi(t)}{\xi(t_w)}\right)$$

- Single slow time scale, an 'infinity' of effective temperatures.





- Aging different from mean-field models and standard domain growth.

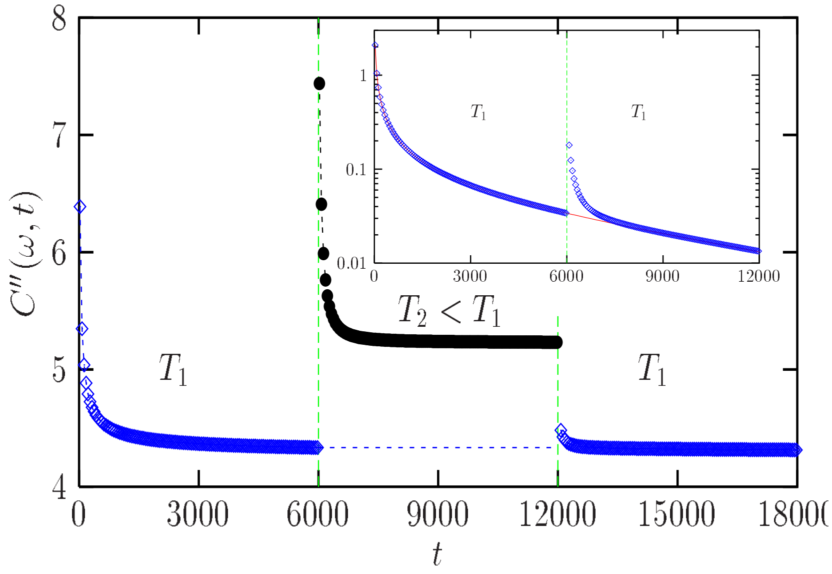
- Aging is quantitatively similar to 3D spin glasses.

Surfing on a critical line

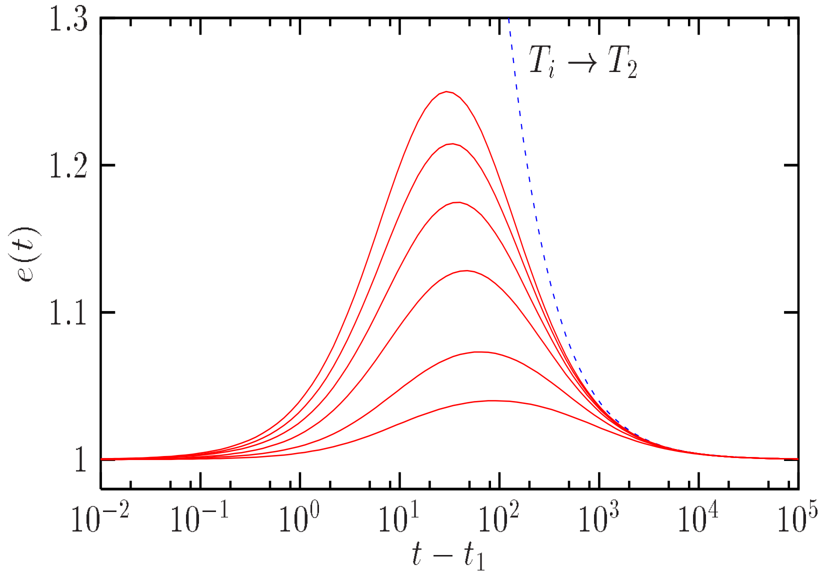
- Nonequilibrium dynamics of the 2D XY model $\left(\int_{-\infty}^{\infty} \mathrm{d}x \, e^{-\alpha x^2} = ? \right)$

[Berthier, Holdsworth, Europhys. Lett. (2002)]

- Temperature cycles



- Kovacs effect



A conjecture

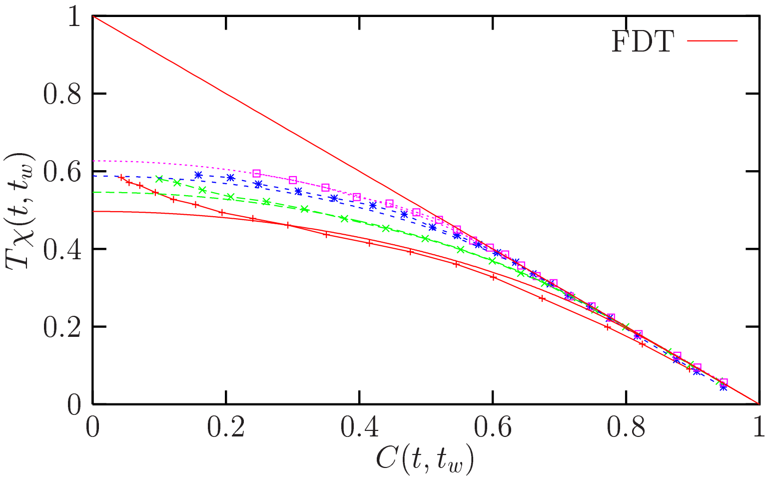
- Spatial interpretation of the statics / dynamics relation.

$$x(C) = \int_0^C \mathrm{d}q \, P(q)$$

At time t_w, the aging system may be viewed as an assembly of 'quasi-equilibrated' subsystems of size $\xi(t_w) \sim t_w^{1/z}$.
Dynamic measurement $\approx$ Ensemble average.

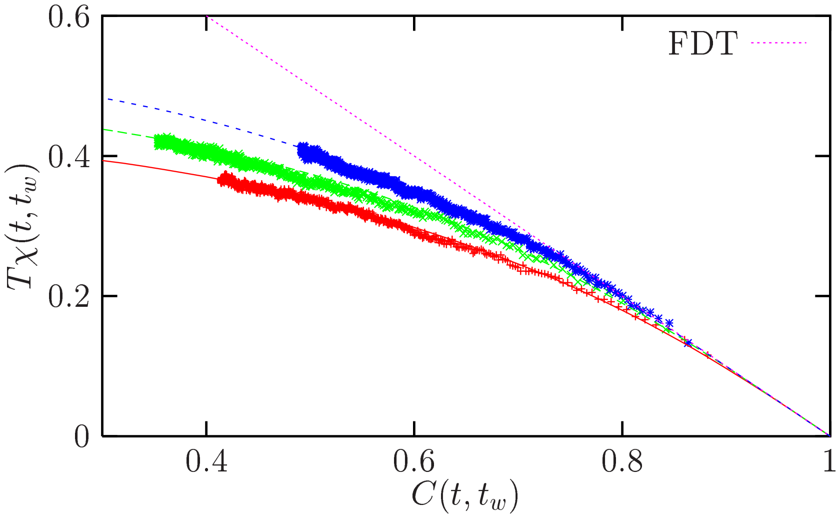
$$\boxed{x\big(C(t,t_w)\big) = \int_0^{C(t,t_w)} \mathrm{d}q' \, P\big(q', \xi(t_w)\big)}$$

- Test in the 2D XY model.

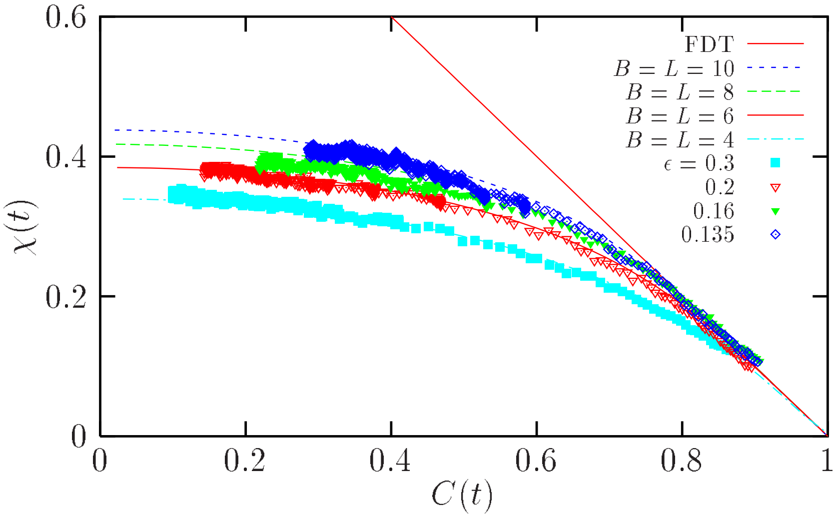


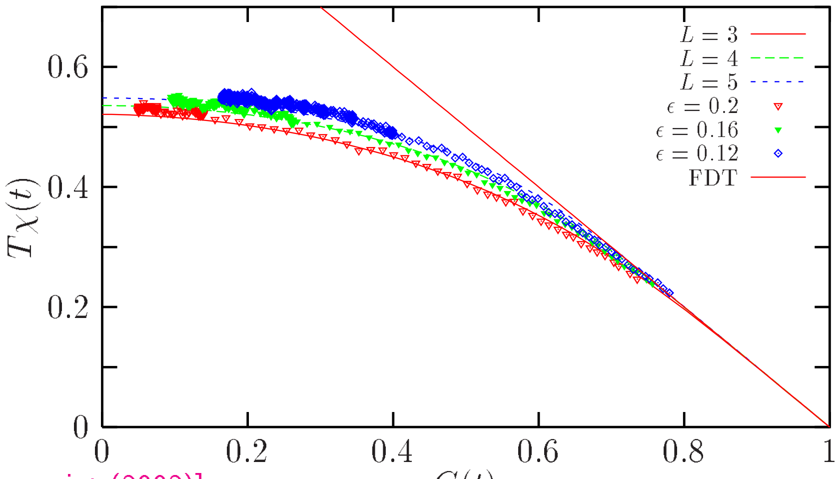
- Fundamental role played by the Parisi function, beyond the physics of spin glasses.

The conjecture in spin glasses



d=2 [Barrat, Berthier, PRL ('01)]





d=3,4 [Berthier, preprint (2002)]

Conclusion

- Glassy materials are everywhere.

- Experiments, simulations, theory (phenomenology and nonequilibrium stat. mech.).

- Thanks to: Alain Barrat, Jean-Louis Barrat, Lyderic Bocquet, Jean-Philippe Bouchaud, Leticia Cugliandolo, Juan Pedro Garrahan, Peter Holdsworth, Jose-Luis Iguain, Jorge Kurchan, Peter Mayer, Mauro Sellitto, Peter Sollich, Fathollah Varnik.

- Papers at: `http://www-thphys.physics.ox.ac.uk/users/LudovicBerthier/`