

# OUT OF EQUILIBRIUM FLUCTUATIONS IN AGING SYSTEMS: GELS, POLYMERS

Sergio Ciliberto.

- Summary of the experimental results on the noise in aging materials
  - a) spin-glass, polymers and gels
  - b) local versus global measurements
  - c) The intermittency
  - d) The observable dependence
- The dielectric measurements in PVAc (intermittency ?)
- The local-global measurements in a gel. The quenching rate
- The quench at the critical point

# Fluctuation Dissipation Ratio (FDR) during aging

**In equilibrium**  $\chi(t, t_w) = \frac{1}{k_B T} (C_\theta(t, t) - C_\theta(t, t_w))$

$$\chi(t, t_w) = \frac{\langle \Delta \rangle}{\Gamma_{ext}} = \int_{t_w}^t R(t, t') dt' \quad C_\theta(t, t_w) = \langle \delta\theta(t) \delta\theta(t_w) \rangle$$

**Out equilibrium** (Cugliandolo and Kurchan 1992) **FDR**

$$\chi(t, t_w) = \frac{X(t, t_w)}{k_B T} (C_\theta(t, t) - C_\theta(t, t_w)) \quad X(t, t_w) = \frac{T}{T_{eff}(t, t_w)}$$

**Experimentally this idea has been tested in**

- **Spin glasses**                      Magnetic susceptibility
- **Colloids**                              Dielectric response
- **Polymers**                                Rheology

and the associated noise

# Fluctuation Dissipation Ratio (FDR) during aging

**In equilibrium**  $\chi(t, t_w) = \frac{1}{k_B T} (C_\theta(t, t) - C_\theta(t, t_w))$

$$\chi(t, t_w) = \frac{\langle \Delta \rangle}{\Gamma_{ext}} = \int_{t_w}^t R(t, t') dt' \quad C_\theta(t, t_w) = \langle \delta\theta(t) \delta\theta(t_w) \rangle$$

**Out equilibrium** (Cugliandolo and Kurchan 1992) **FDR**

$$\chi(t, t_w) = \frac{X(t, t_w)}{k_B T} (C_\theta(t, t) - C_\theta(t, t_w)) \quad X(t, t_w) = \frac{T}{T_{eff}(t, t_w)}$$

**Experimentally this idea has been tested in**

- Spin glasses
- Colloids
- Polymers

Controversial results

Need for experiments where the results can be directly compared with theoretical models

## Experimental procedure

Temperature controlled system (spin-glasses, polymères and gels)

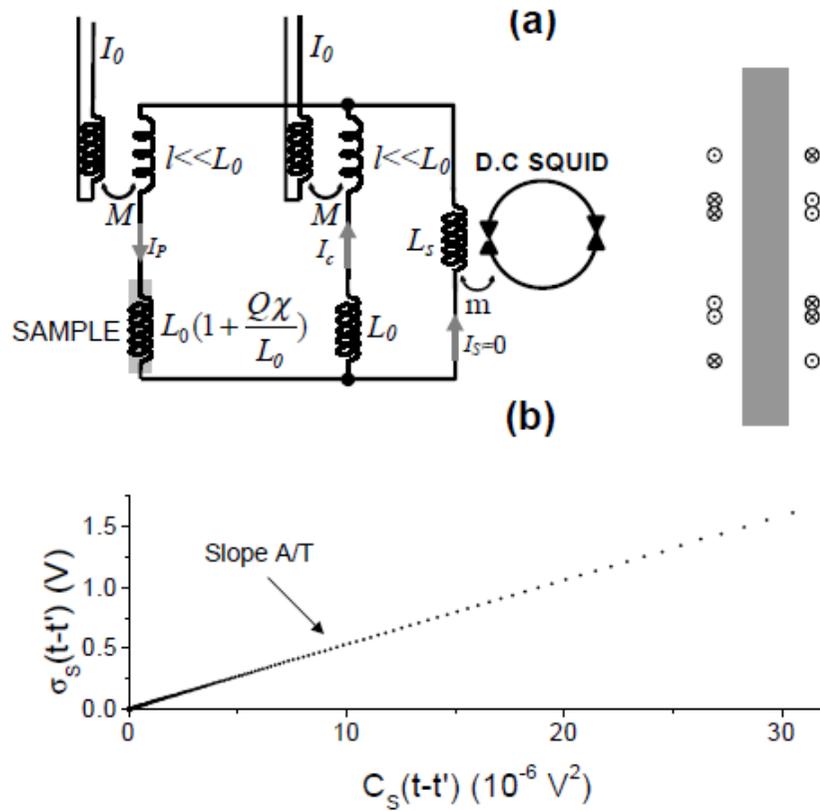
- I) The sample is prepared at a temperature  $T_i > T_g$
- II) The sample is quenched very fast at a final temperature  $T_f < T_g$
- III) The noise and the response are measured as a function of the time  $t_w$  spent by the sample at  $T_f$
- IV) The steps I)-III) are repeated many time to increase the statistics

Non thermal systems (colloids)

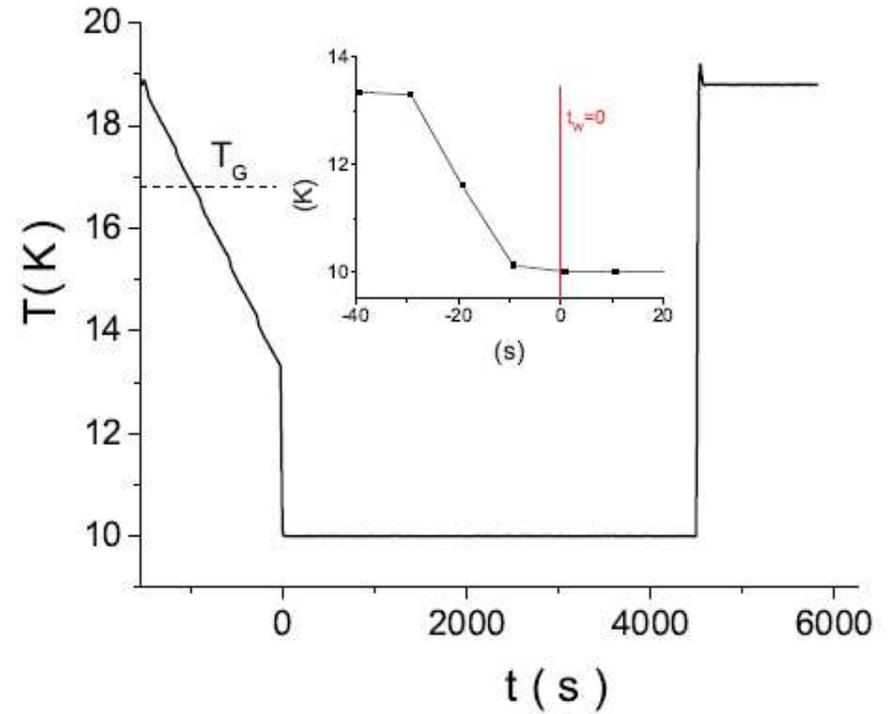
- a) Time evolution after preparation
- b) Time evolution after shearing or stirring the sample

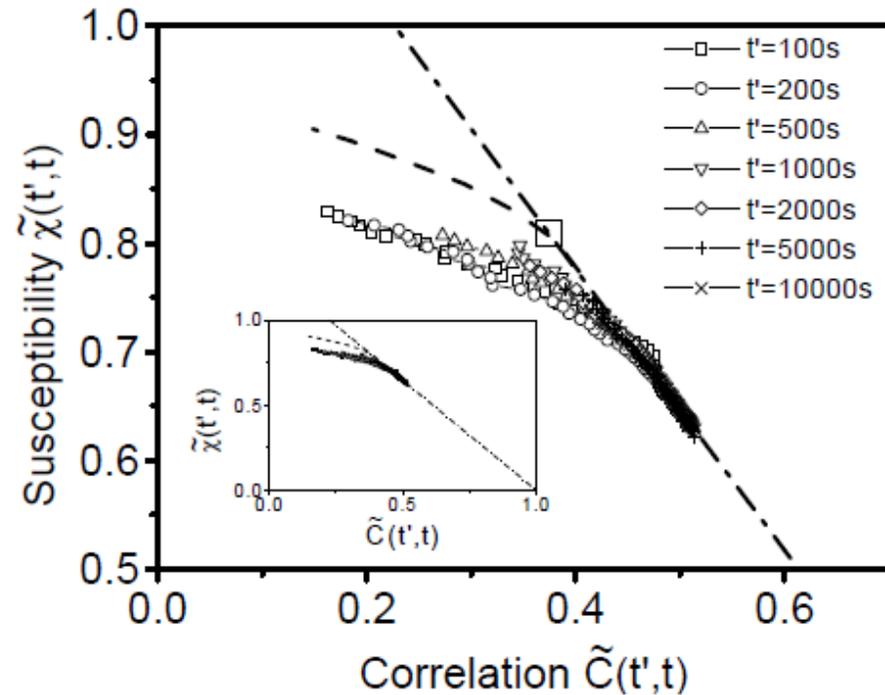
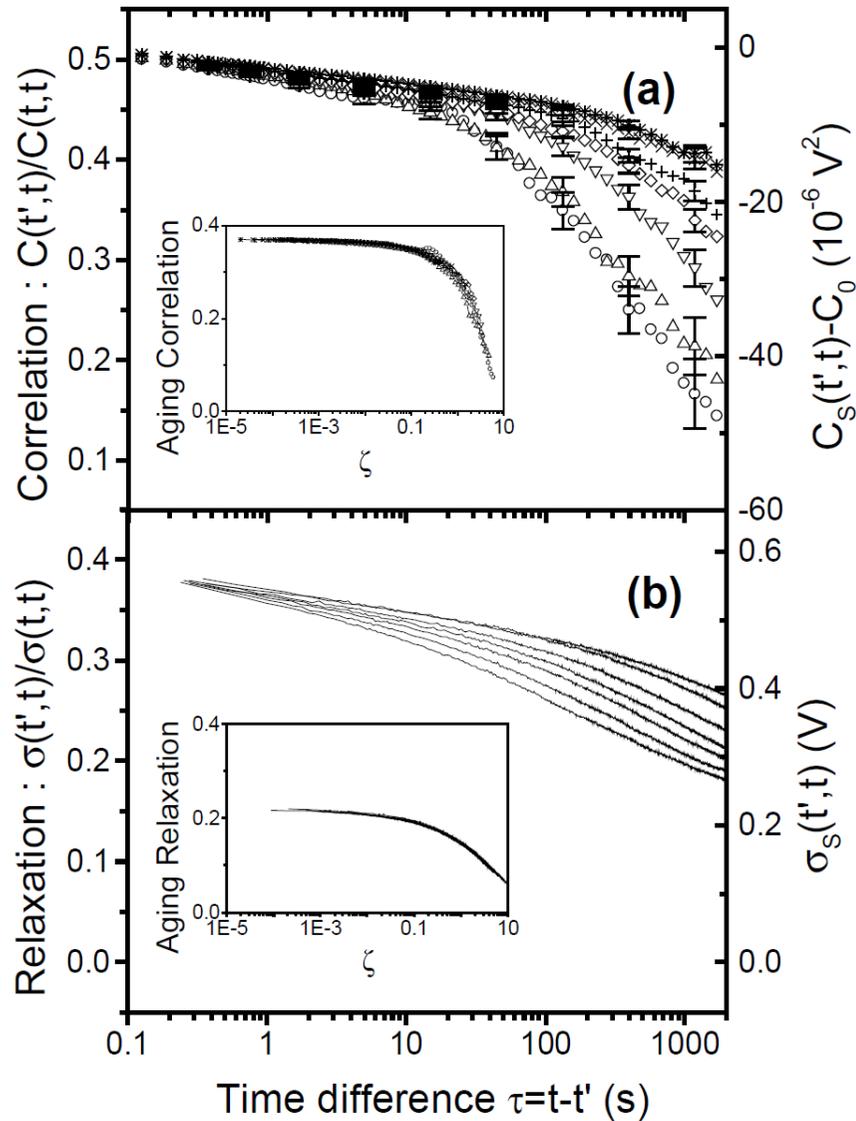
Experimental problems  
Tiny quantities : pN, fA, pm,  $\mu\text{G}$   
Several drawbacks may appear  
in out of equilibrium

## The experimental system



## The fast quench

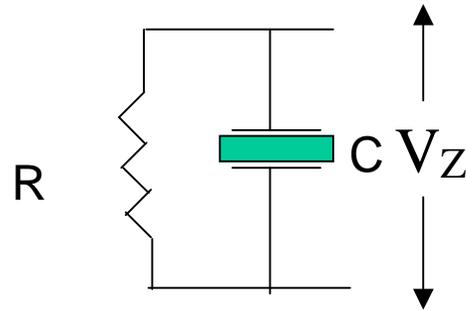
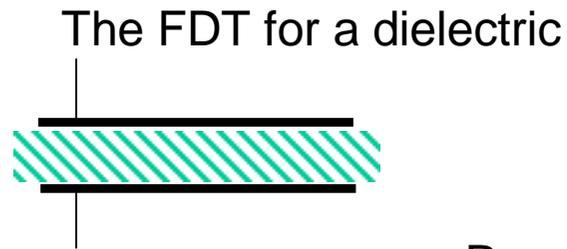




Questions :

- a) The local aspect is missed
- b) What is the statistics of the signals
- c) What does  $T_{eff}$  at very long time ?

## Dielectric measurements



$$Z(t_w, \omega) = \frac{R}{(1 + i\omega R C)}$$

$$S_Z(t_w, f) = 4 K_B T_{eff}(\omega, t_w) \text{Real}[Z(t_w, \omega)]$$

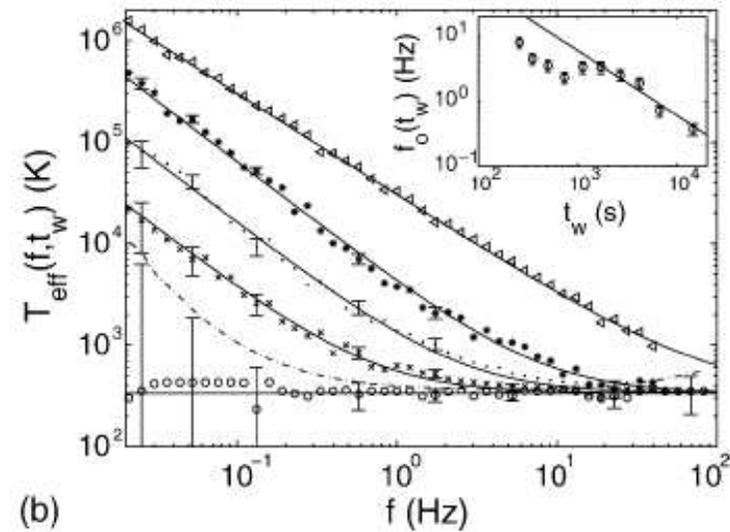
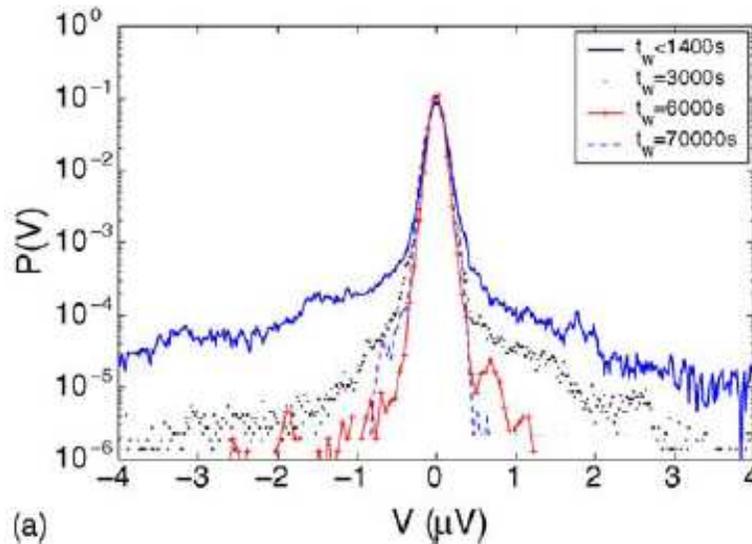
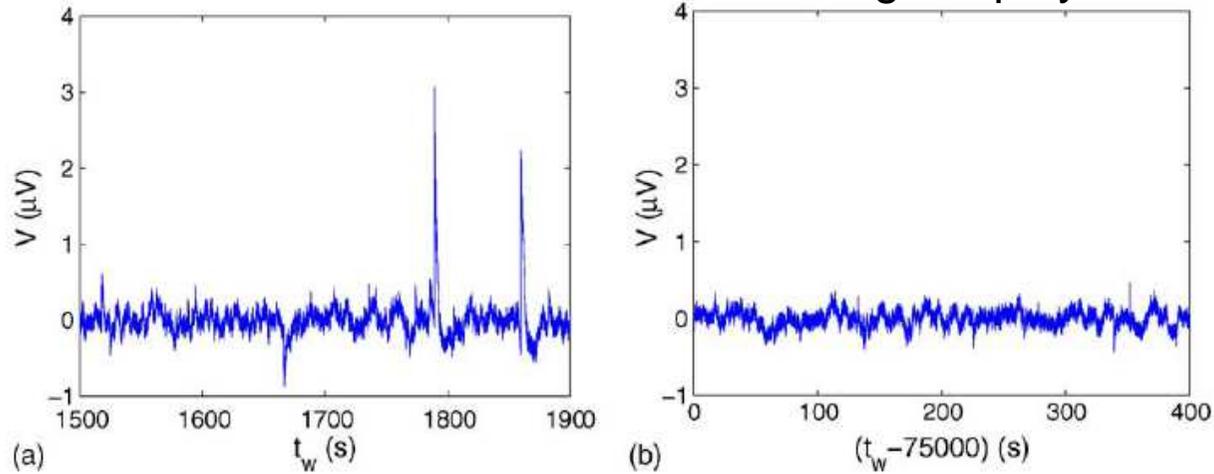
Several experimental difficulties :

- Extremely high  $Z$  at low frequencies ( $> 10G\Omega$ )
- Signal very weak ( $< 10fA$ )
- Signal to noise ratio always close to 1 at low frequencies.

**3 experiments have been performed and show strong intermittency**

Epoxy glass former, Lucchesi et al      PVAc, N. Israeloff et al  
 Polycarbonate L. Buisson et al.

## Intermittent bursts in the noise voltage of polycarbonate



# Dielectric measurements on PVAc

Comparisons of two experiments

N.E. Israeloff et al.

J. Non-Crystalline Solids 352 (2006) 4915–4919

$C=92\text{pF}$ ,

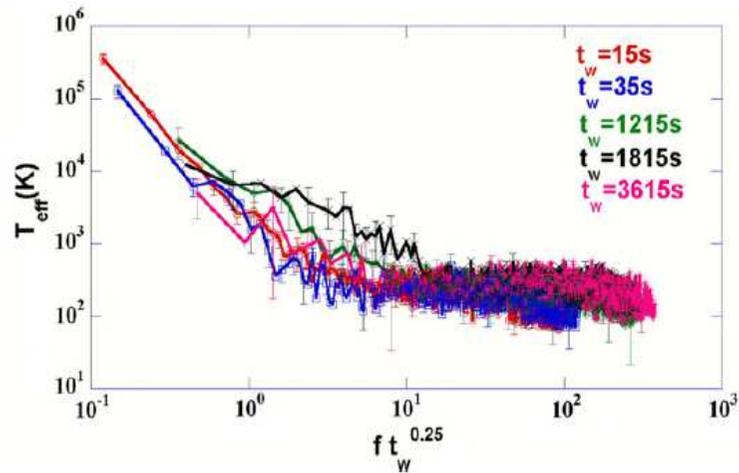
Quench

from  $55^\circ\text{C}$  to  $25^\circ\text{C}$

Quenching time = 15 sec

PVAc

$T_g=34^\circ\text{C}$



Strong intermittency

# Dielectric measurements on PVAc

## Comparisons of two experiments

N.E. Israeloff et al.

J. Non-Crystalline Solids 352 (2006) 4915–4919

C=92pF,

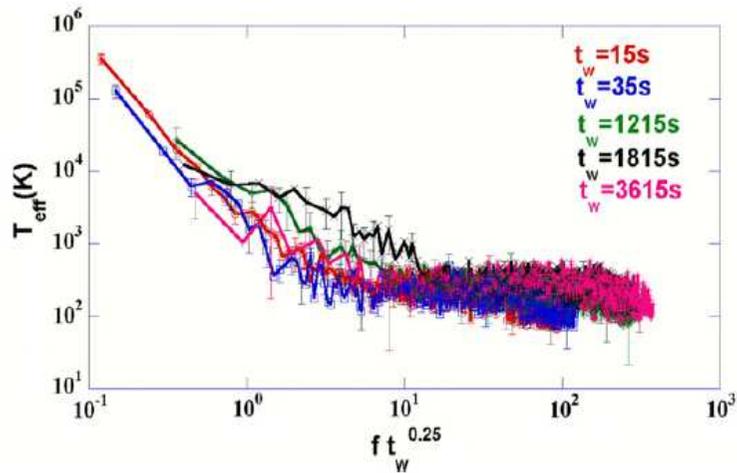
Quench

from 55°C to 25°C

Quenching time =15 sec

PVAc

T<sub>g</sub>=34°C

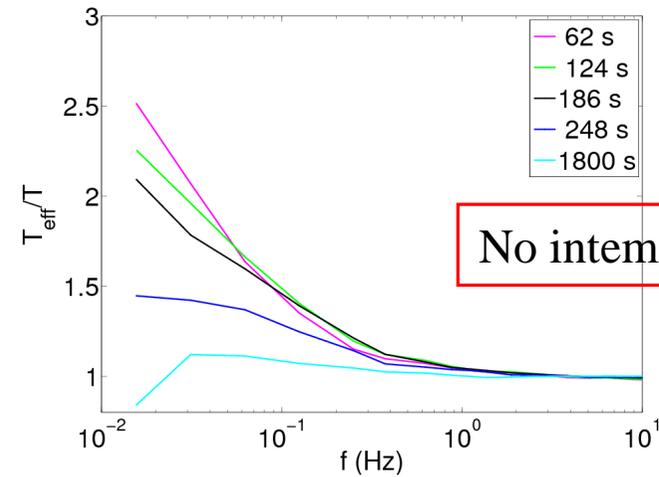


Strong intermittency

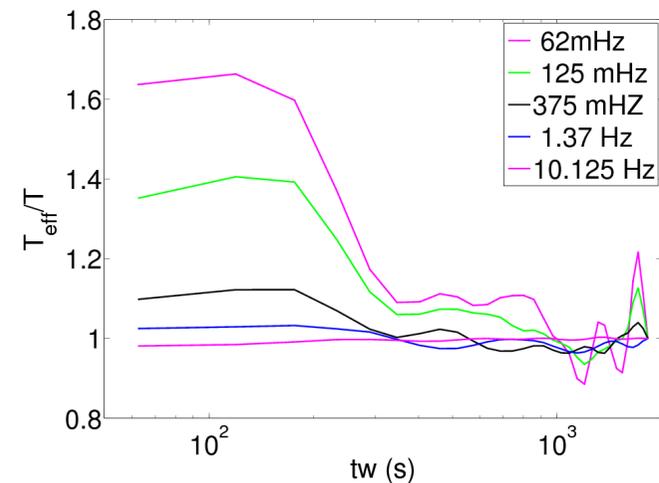
A. Naert et al., unpublished

C=5000pF

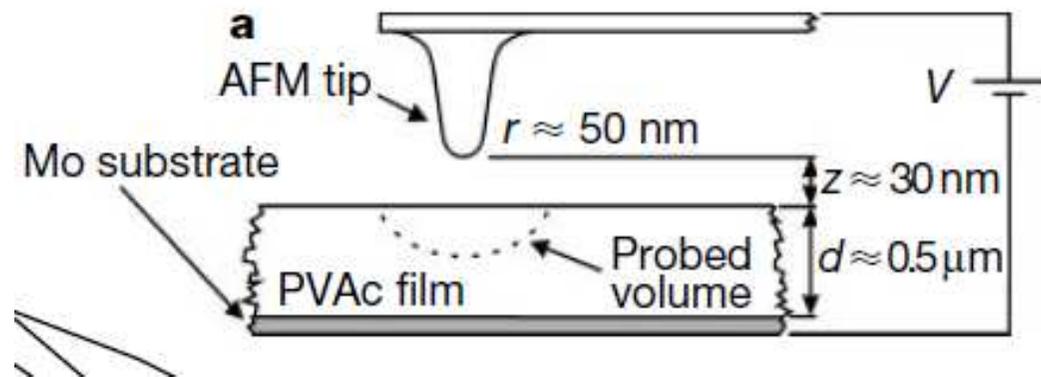
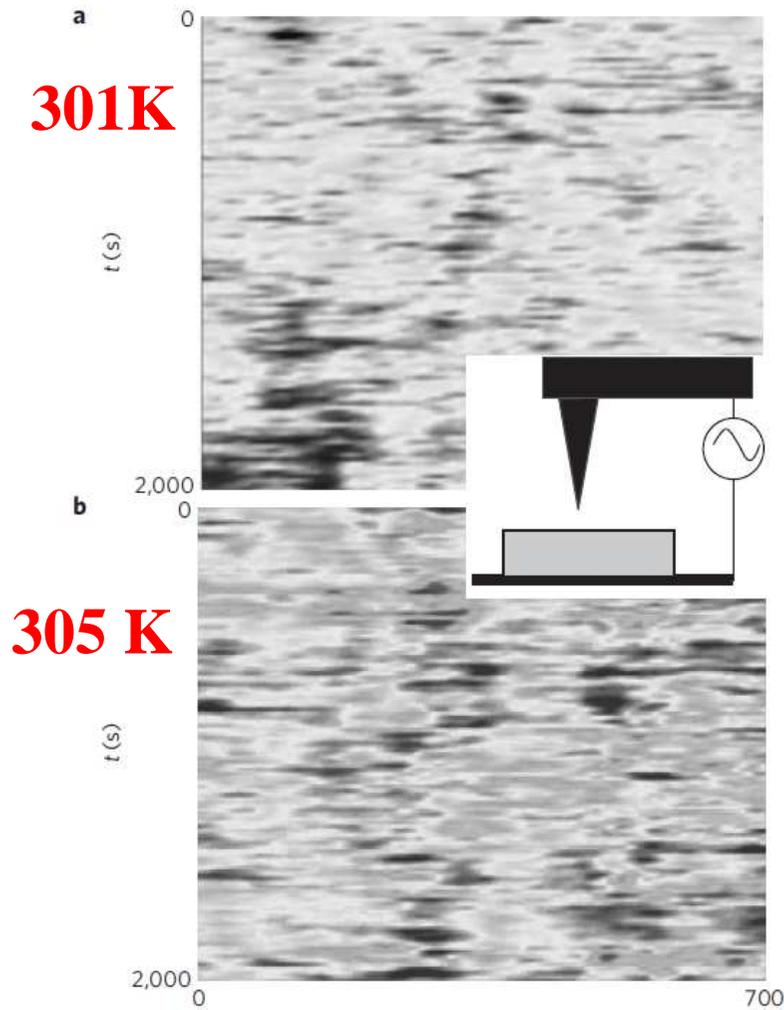
Quenching time =60sec



No intermittency

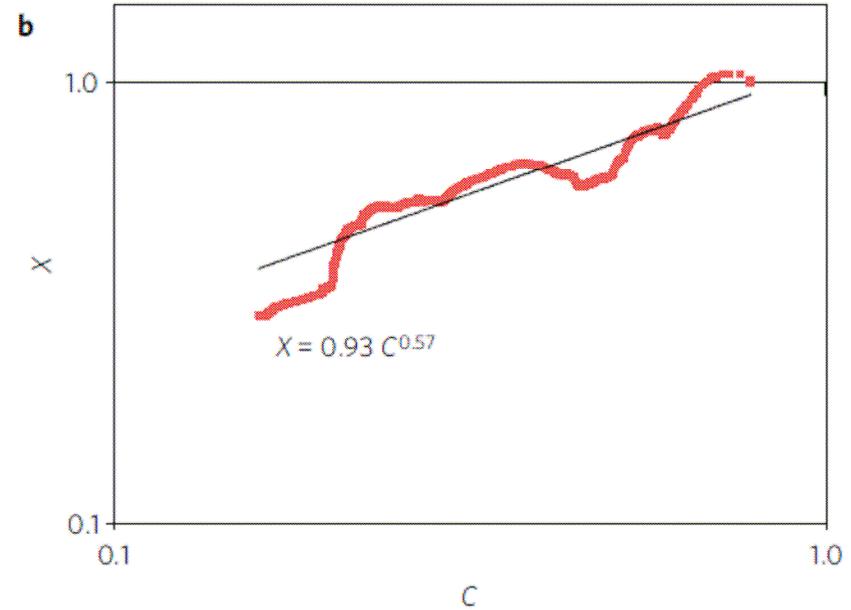
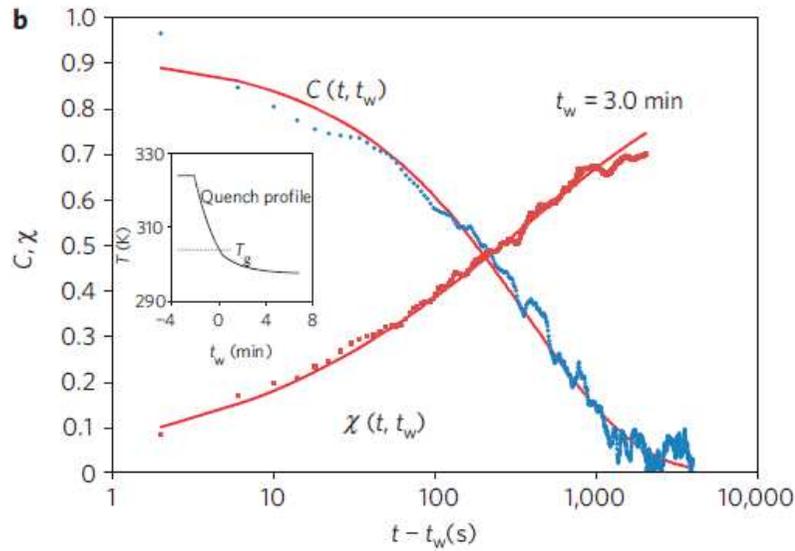
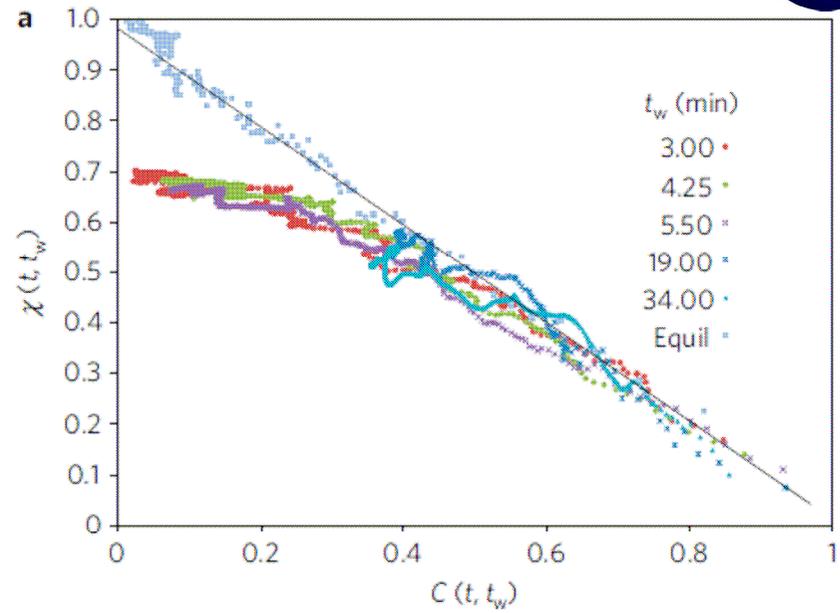
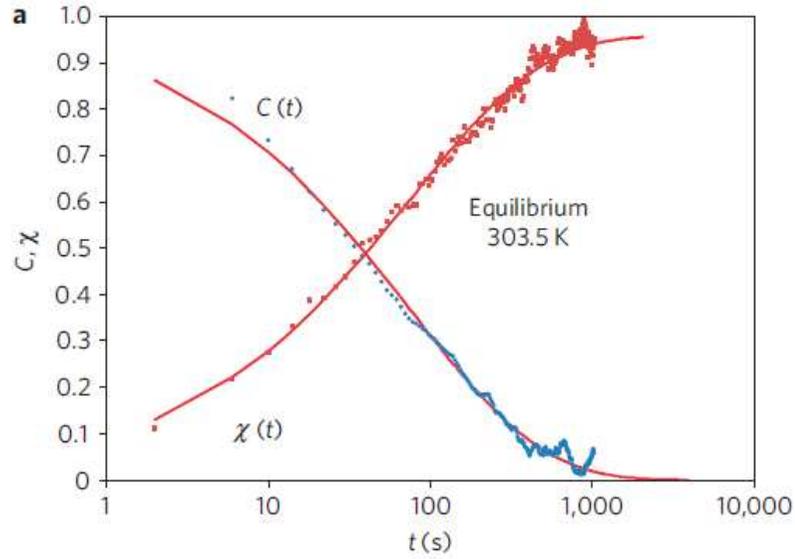


Hassan Oukris and N. E. Israeloff  
NATURE PHYSICS, 6, FEBRUARY, 2010



$$\delta f = \frac{1}{2} \frac{f_0}{k} \frac{\partial F}{\partial z} = -\frac{1}{4} \frac{f_0}{k} \frac{\partial^2 C_{\text{tip}}}{\partial z^2} (V - V_p)^2$$

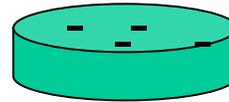
**T<sub>g</sub>=304 K**



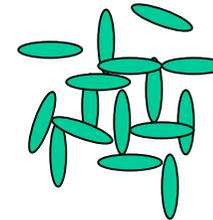
## Previous Results in Laponite

Colloidal Suspension :

discs:  $d=25$  nm,  $h=1$  nm



Fluid  $\rightarrow$  gel/colloidal glass



Fluid-Colloidal glass transition in a few hours

Prepared under  $N_2$  atmosphere

$\Phi_m = 1.2$  à  $3$  wt% in water

pH = 10

Ionic Force : I de  $10^{-4}$  à  $5 \cdot 10^{-3}$  M

## Previous Results in Laponite

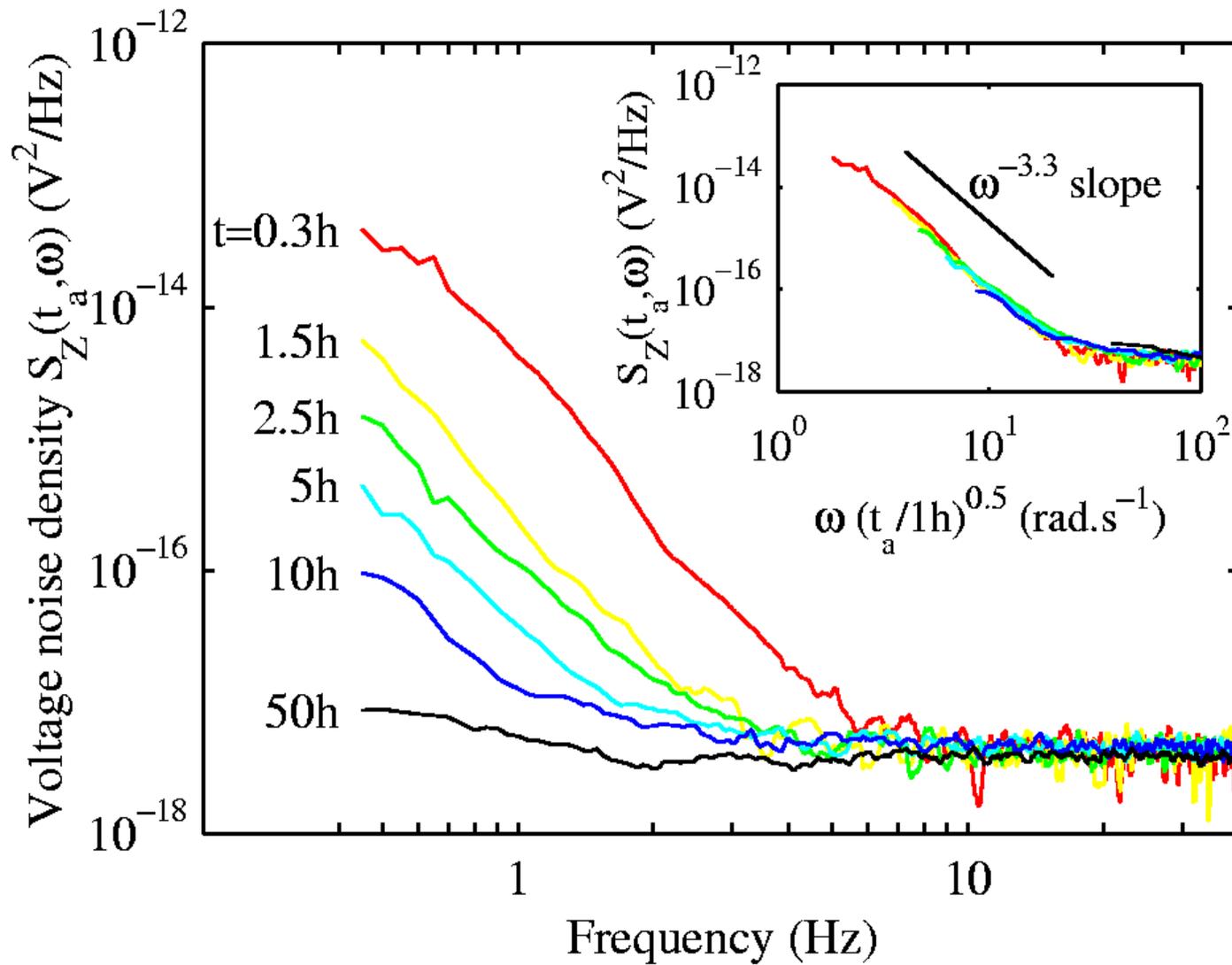
L. Bellon, S.C. Physica D 168, 325 (2002)

**Dielectric measurements**

$T_{\text{eff}} \gg T_{\text{bath}}$

Strong intermittency

# Dielectric measurements in Laponite



## Previous Results in Laponite

L. Bellon, S.C. Physica D 168, 325 (2002)

**Dielectric measurements**

$T_{\text{eff}} \gg T_{\text{bath}}$

Strong intermittency

## Rheology

L. Bellon, S.C. Physica D 168, 325 (2002)

Thermal rheometer, global measurements

$T_{\text{eff}} = T_{\text{bath}}$

S. Jabbary Farouji et al. PRL 98,108302 (2007)

Brownian particle, Active and passive micro-rheology.

B.Abou, F. Gallet, PRL 93,160603, 1-4 (2004)

Brownian particle, response and fluctuations

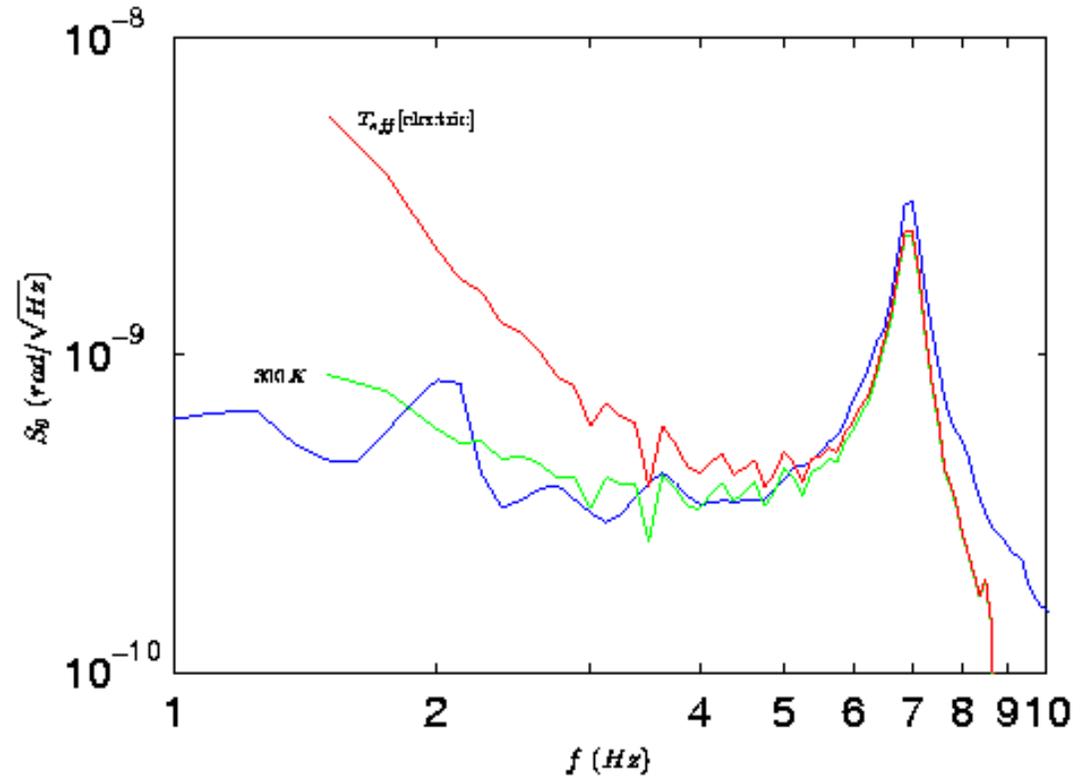
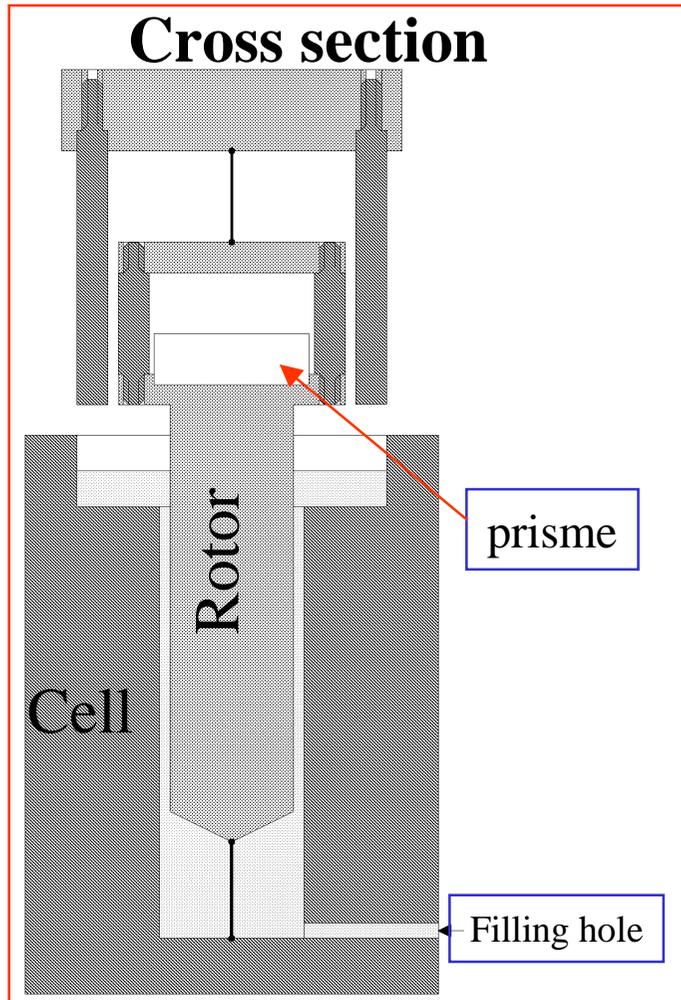
$T_{\text{eff}} > T_{\text{bath}}$

N. Greinert et al PRL 97, 265702 (2006)

Brownian particle, energy equipartition

# Thermal rheometer, global measurements

L. Bellon, S.C. Physica D 168, 325 (2002)



**Rheometer**

## Brownian particle, Active and passive micro-rheology.

S. Jabbary Farouji et al. PRL 98,108302 (2007)

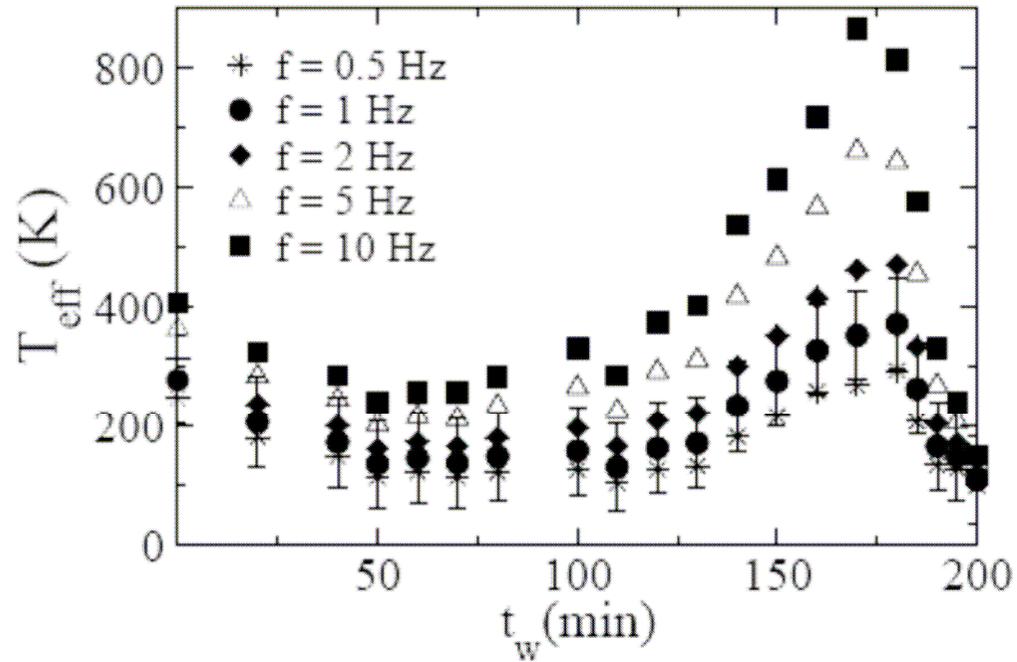
TABLE I. The effective temperature obtained for different frequencies averaged over 2 h time intervals. Within the uncertainty in the experiments,  $T_{\text{eff}}/T_{\text{bath}} = 1$ .

$t_a$	$T_{\text{eff}}/T_{\text{bath}}$				
	7.5 rad/s	68 rad/s	728 rad/s	6.5 rad/s	75 rad/s
0–2 h	$0.75 \pm 0.3$	$1 \pm 0.1$	$0.95 \pm 0.1$	$0.85 \pm 0.1$	$1.0 \pm 0.1$
2–4 h	$1.2 \pm 0.3$	$1 \pm 0.1$	$1 \pm 0.1$	$0.9 \pm 0.1$	$1.0 \pm 0.1$
4–6 h	$1.4 \pm 0.3$	$1 \pm 0.1$	$1.1 \pm 0.1$	$1.1 \pm 0.1$	$1.1 \pm 0.1$
6–8 h		$0.85 \pm 0.1$	$1.0 \pm 0.1$	$1.1 \pm 0.1$	$1.0 \pm 0.1$

2.8% Wt, Laponite XLG, filtered

# Brownian particle, response and fluctuations

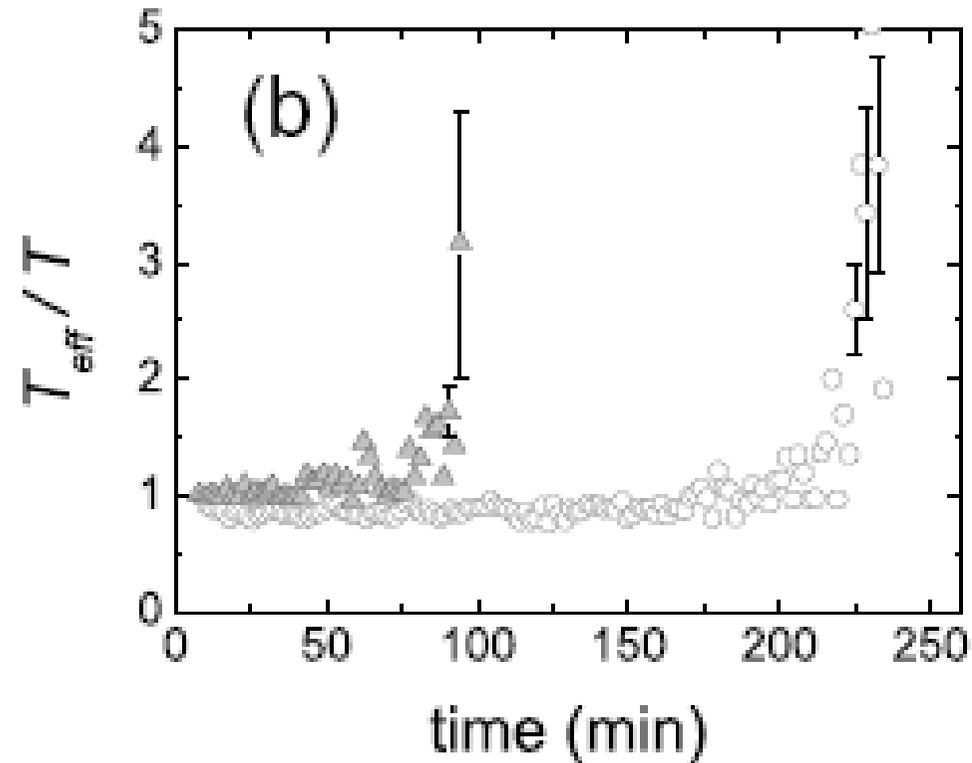
B.Abou, F. Gallet, PRL 93,160603, 1-4 (2004)



Laponite RD, 2.3 wt%, filtered, 2  $\mu\text{m}$  silica bead

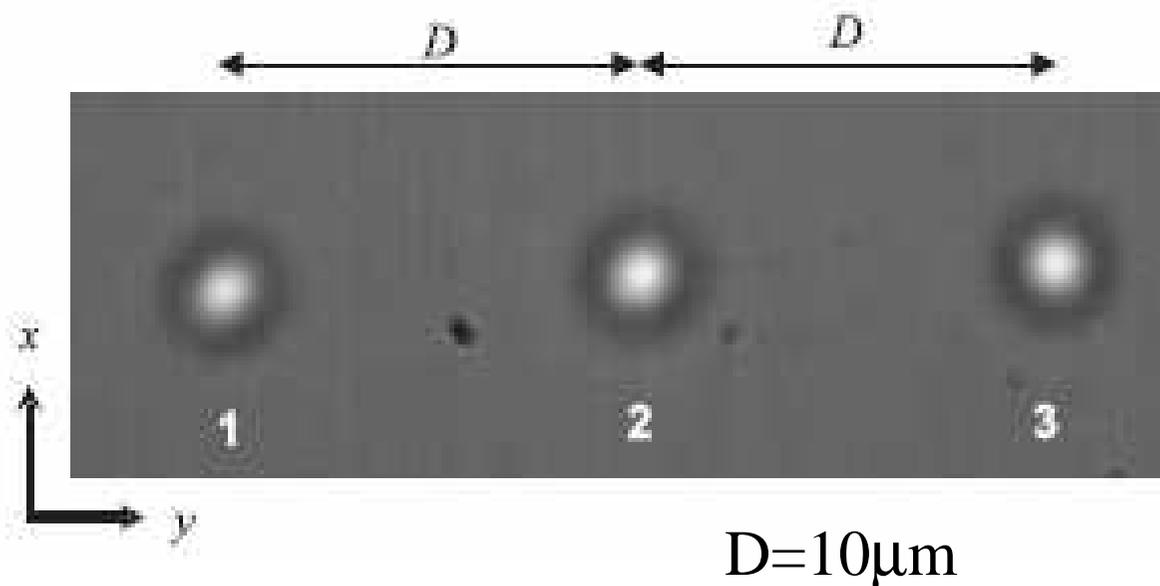
# Brownian particle, energy equipartition

N. Greinert et al PRL 97, 265702 (2006)



Laponite RD, 2.4% and 2.8%, filtered 1 um silica beads

## Simultaneous measurements of three beads in Laponite



Stiffness:

$$k_2 = k_3$$

and

$$k_1 = k_2/2$$

$$k_2 = 7.15 \text{ pN}/\mu m$$

We apply four different techniques to measure  $T_{eff}$ .

- 1) Active microrheology
- 2) Passive microrheology
  - Equipartition
  - Kramers-Kronig
  - Heat fluctuations

Do they give the same results ?

# Microrheology

Motion of a Brownian particle trapped by a laser Beam

Viscoelastic Langevin dynamics

$$\int_{-\infty}^t \Gamma(t - t', t_w) \dot{x}(t') dt' + k (x - x_o) = \xi(t),$$

The applied oscillating force  $f_o(t) = k x_o(t, \omega)$

The linear response  $\hat{\chi}(\omega, t_w) = \frac{\hat{x}(\omega, t_w)}{\hat{f}_o(\omega)}$

$$|\hat{x}(\omega, t_w)|^2 = \frac{4k_B T_{eff}(\omega, t_w) \gamma(\omega, t_w)}{\omega^2 \gamma^2(\omega, t_w) + (k + K_{gel}(\omega, t_w))^2}$$

## Passive Rheology - Measure of the $T_{eff}$

Hp:

The global potential (colloid+laser) is harmonic

Equipartition holds out of equilibrium

$$C_i = K_{Lap} + K_i \text{ and } \langle \Delta x_i^2 \rangle = \frac{K_B T_{eff}}{C_i}$$

$K_i$  is the trap stiffness

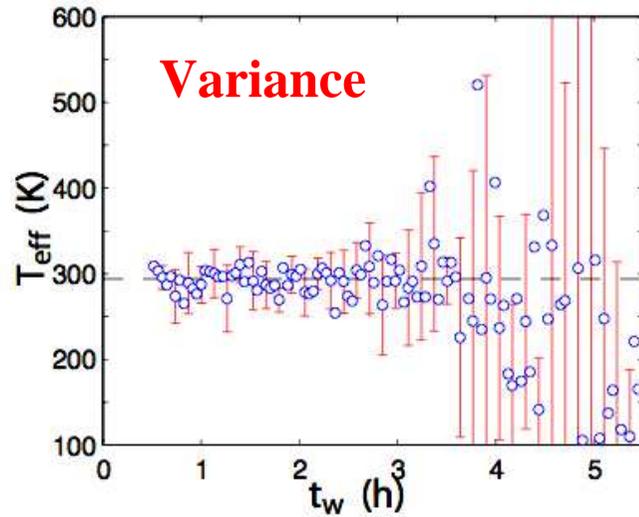
Measure of the  
fluctuations  
for 2 intensities

$$K_B T_{eff} = (K_2 - K_1) \frac{\langle \Delta x_1^2 \rangle \langle \Delta x_2^2 \rangle}{(\langle \Delta x_1^2 \rangle - \langle \Delta x_2^2 \rangle)}$$

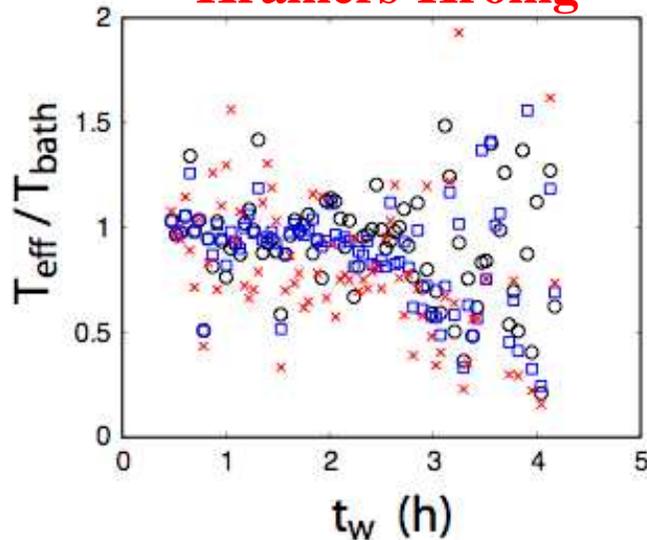
$$K_{Lap} = \frac{(K_1 \langle \Delta x_1^2 \rangle - K_2 \langle \Delta x_2^2 \rangle)}{(\langle \Delta x_1^2 \rangle - \langle \Delta x_2^2 \rangle)}$$

# Simultaneous measurements of three beads in Laponite

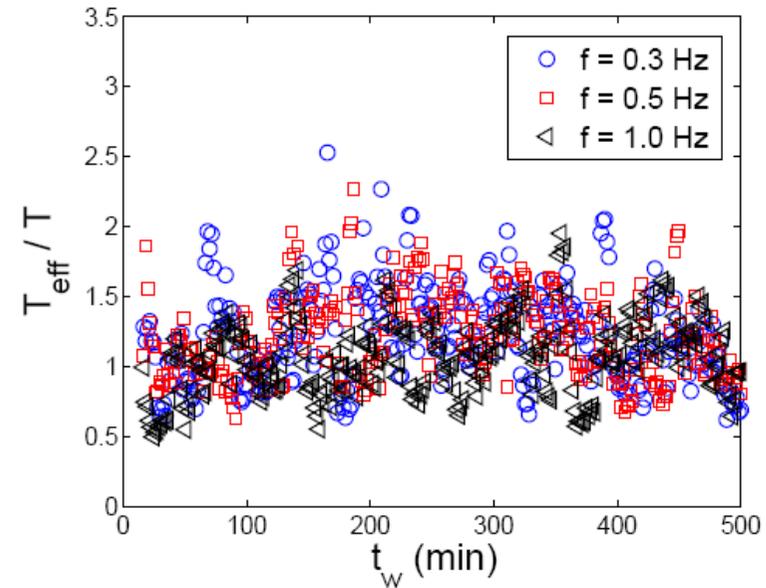
## Passive microrheology



## Kramers-Kronig



## Active microrheology



The three methods give the  
same results

$$T_{\text{eff}} = T_{\text{bath}}$$

Heat fluctuations confirm  
the result

# Conclusions on previous results on FDR in various systems

## Experiments gives controversial results

## Questions

- **Spin glasses:**  $T_{eff} > T$   
good agreement  
with theory

- a) The local aspect is missed
- b) Statistics of the signals
- c)  $T_{eff}$  at very long time

- **Colloids :** Laponite  
 $T_{eff} = T$  in rheology  
 $T_{eff} \gg T$  in dielectric

- a) Other gels
- b) Quenching rate
- c) Confinement

- **Polymers :**

Needs of a more close comparison  
of theory with experiments

- a) Local measurements :  $T_{eff} > T$
- b) Global measurements  
Intermittency,  $T_{eff} \gg T$   
 $T_{eff} > T$  only for very fast quench

## New experiments

Improved experimental design in dielectric measurements  
A. Naert, M. Tanase, L. Bellon, D. Bagchi

Aging at the critical point  
A. Caussarieu, S. Joubaud, A. Petrosyan

- a) More close comparison theory-experiment
- b) Quenching rate

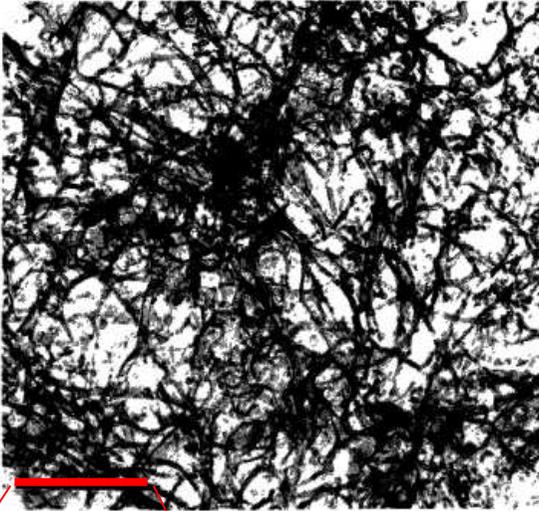
Confined liquid-gel transition  
R. Gomez Solano, A. Petrosyan

- a) Other gels
- b) Quenching rate
- c) Confinement

How is this scenario modified if

- the gel is confined in a volume comparable with the bead size ?
- a very fast quench of 1ms is performed ?
- the energy instead of the displacement is used as the relevant variable ?

R. Gomez Solano, A. Petrosyan, S.C. arXiv:1102.4750



0.5 $\mu$ m

Gelatine :

liquid for  $T_m > 32^\circ\text{C}$

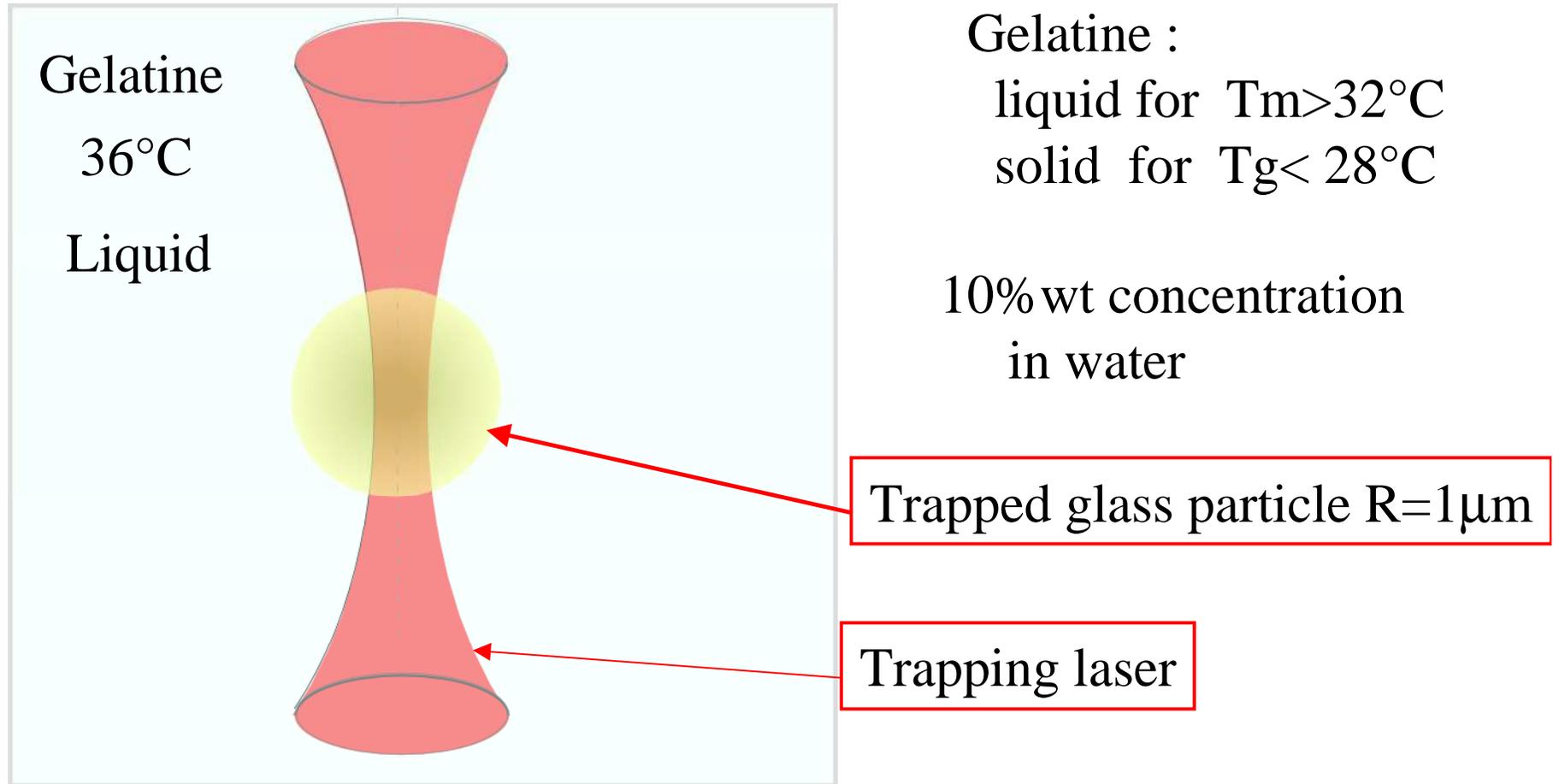
solid for  $T_g < 28^\circ\text{C}$

In our experiment we use

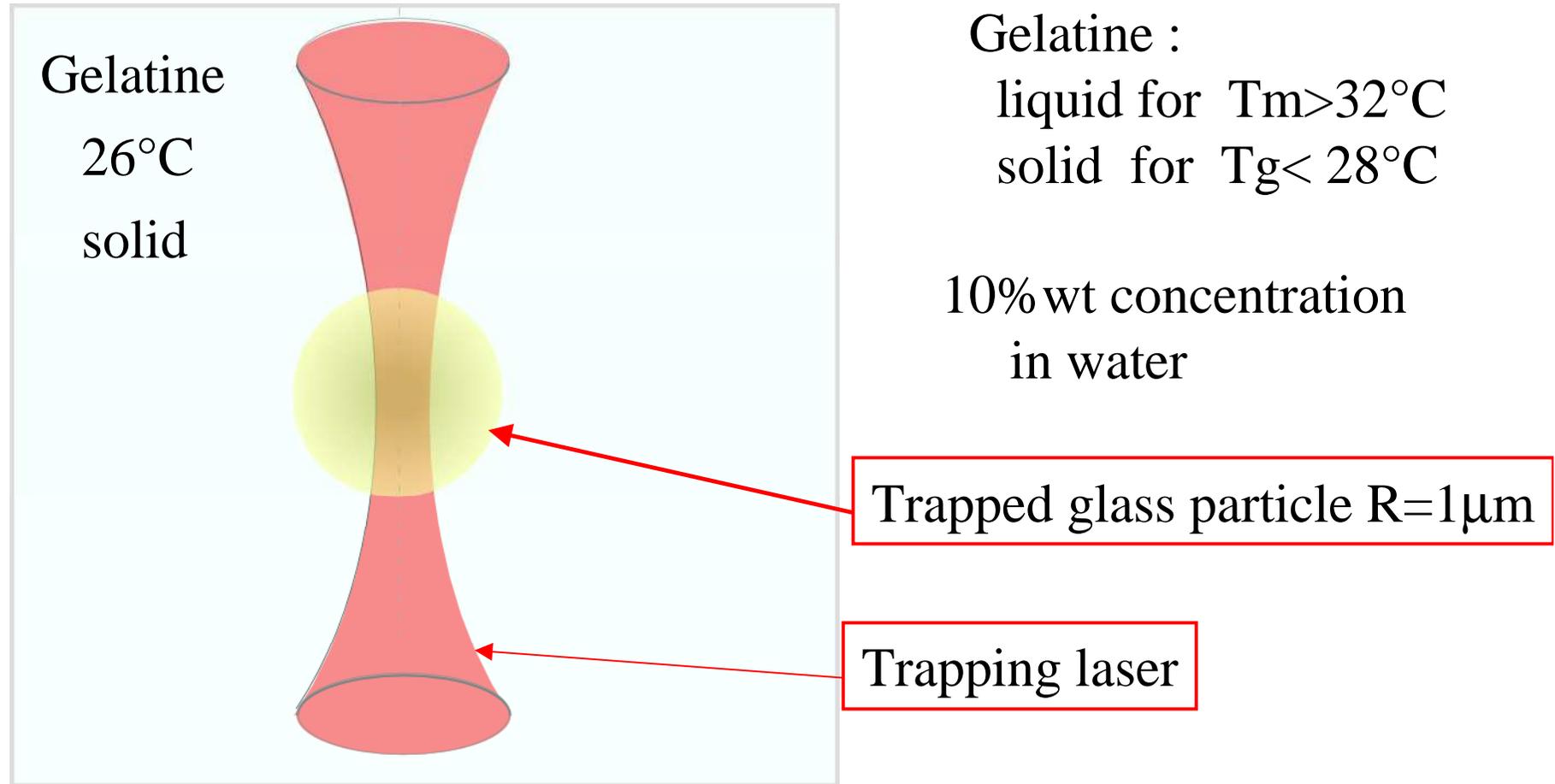
10% wt concentration in water

For  $T < T_g$  gelatine presents : aging and memory effects

at 10% wt concentration after a cooling at  $26^\circ\text{C}$  it takes  $\sim 2\text{h}$  to solidify

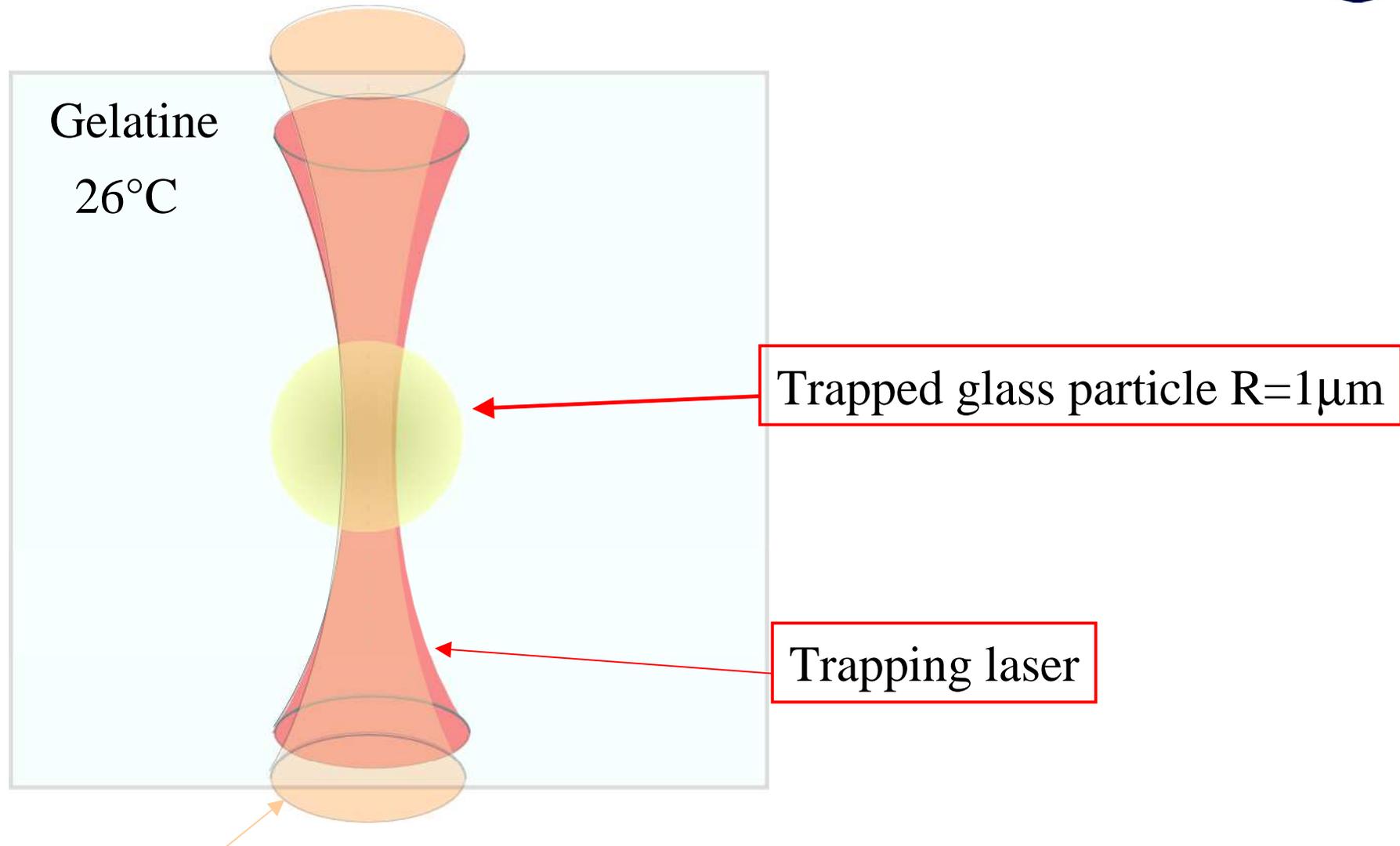


For  $T < T_g$  gelatine presents : aging and memory effects  
at 10% wt concentration after a cooling at  $26^\circ\text{C}$  it takes  $\sim 2\text{h}$  to solidify



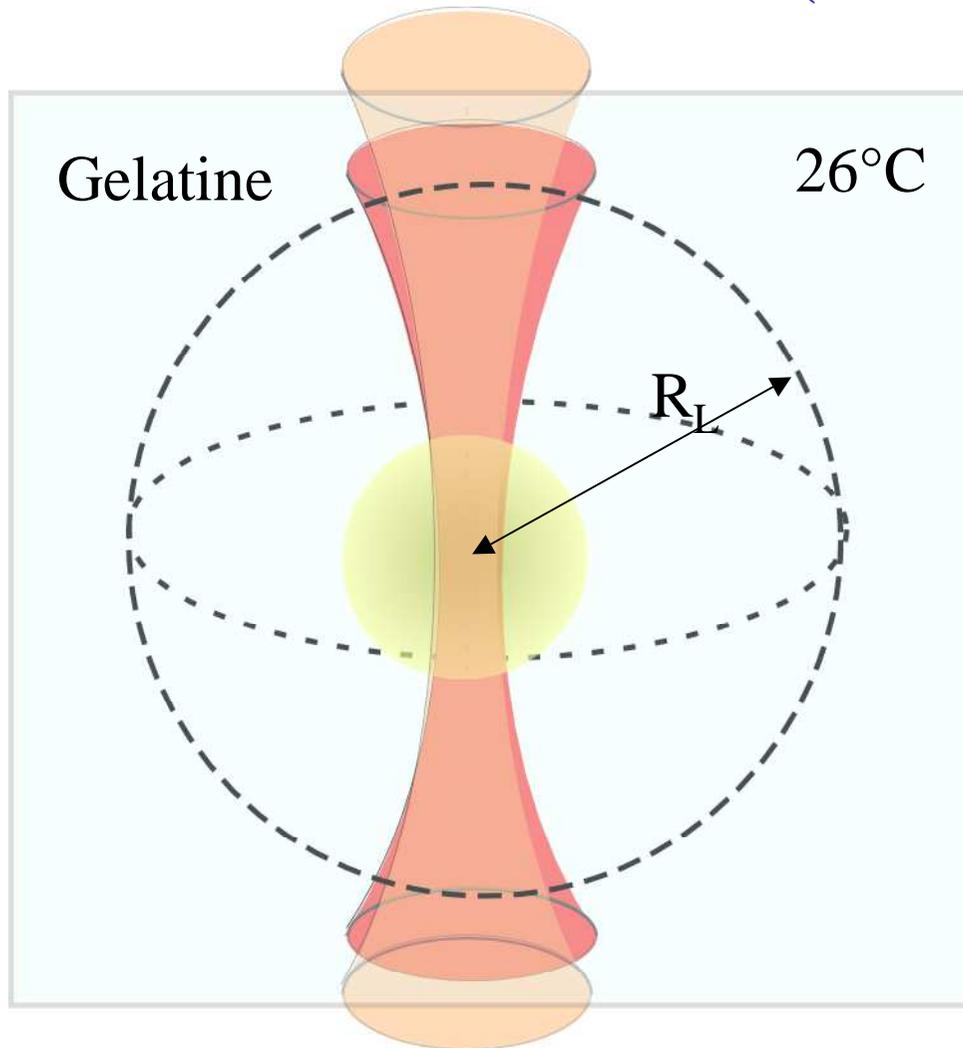
For  $T < T_g$  gelatine presents : aging and memory effects  
at 10% wt concentration after a cooling at  $26^\circ\text{C}$  it takes  $\sim 2\text{h}$  to solidify

# Gelatine liquid-solid transition (heating)



Infrared Laser switched on for a few minutes

## Gelatine liquid-solid transition (heating)



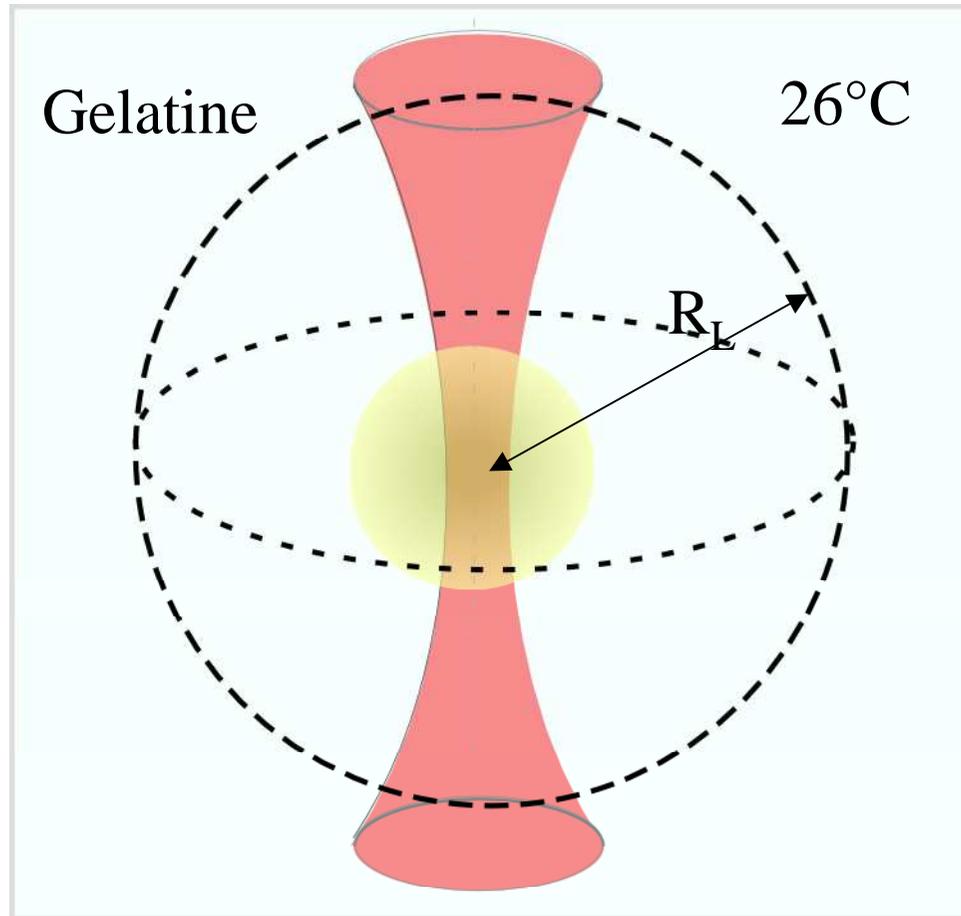
The temperature  
around the focus  
grows till 36°C

A drop of liquid of radius  
 $R_L=10\ \mu\text{m}$  is formed

After a few minutes the  
infrared laser is  
switched off

The drop cools in about 1mS

# Gelatine liquid-solid transition (quench)



At  $t=3\text{ms}$  after the switch off

Drop of an unstable liquid  
at  $26^\circ\text{C}$   
inside a stable solid

What happens ?

Does the transition start  
from the frontier ?

How long does it take  
to solidify ?

# Microrheology

Motion of a Brownian particle trapped by a laser Beam

Viscoelastic Langevin dynamics

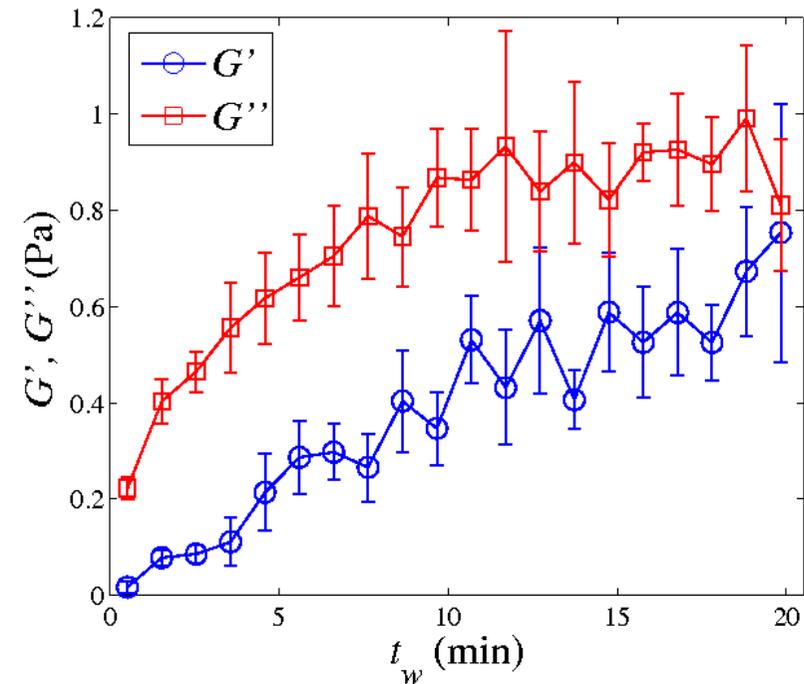
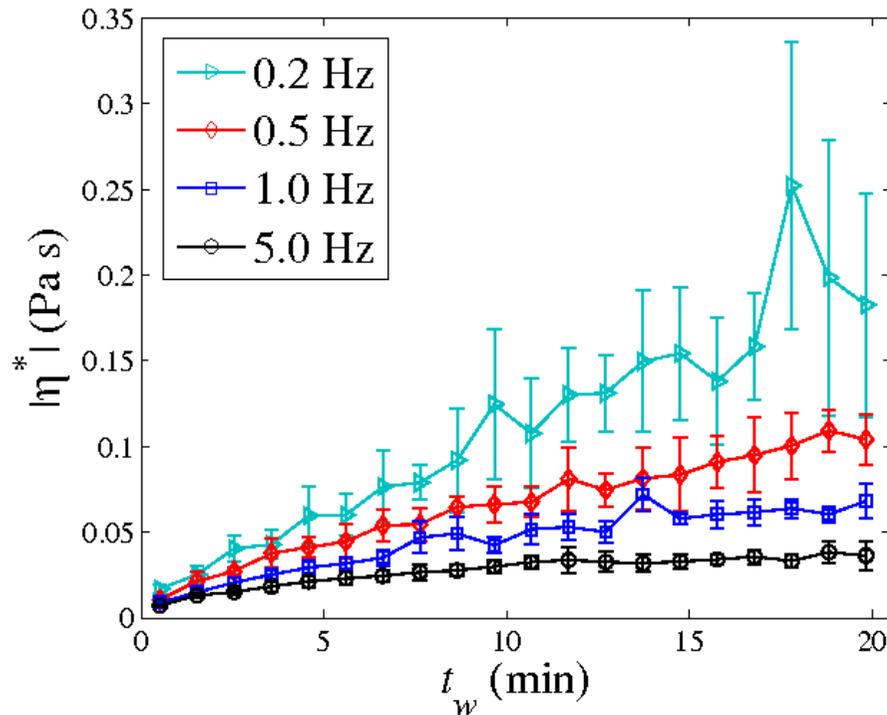
$$\int_{-\infty}^t \Gamma(t - t', t_w) \dot{x}(t') dt' + k (x - x_o) = \xi(t),$$

The applied oscillating force  $f_o(t) = k x_o(t, \omega)$

The linear response  $\hat{\chi}(\omega, t_w) = \frac{\hat{x}(\omega, t_w)}{\hat{f}_o(\omega)}$

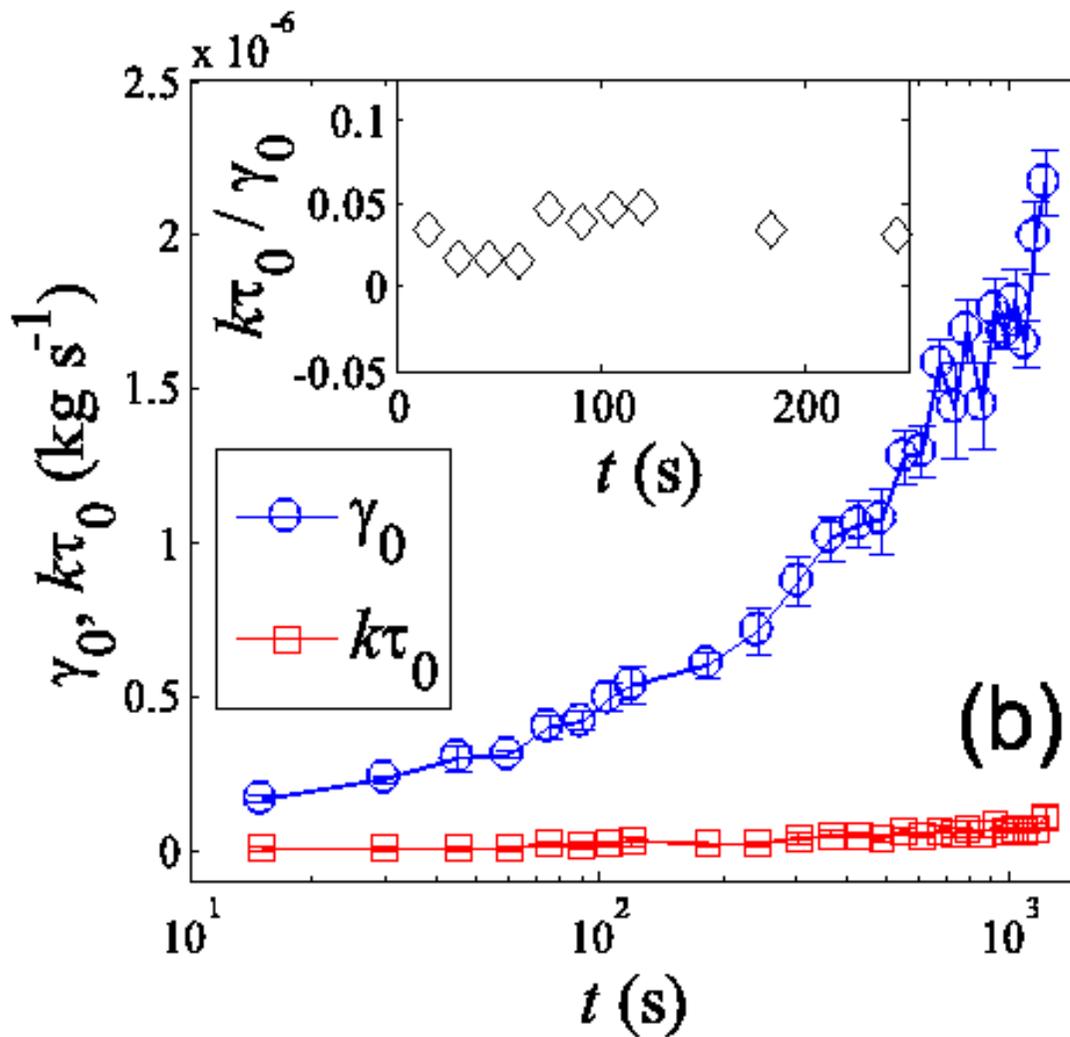
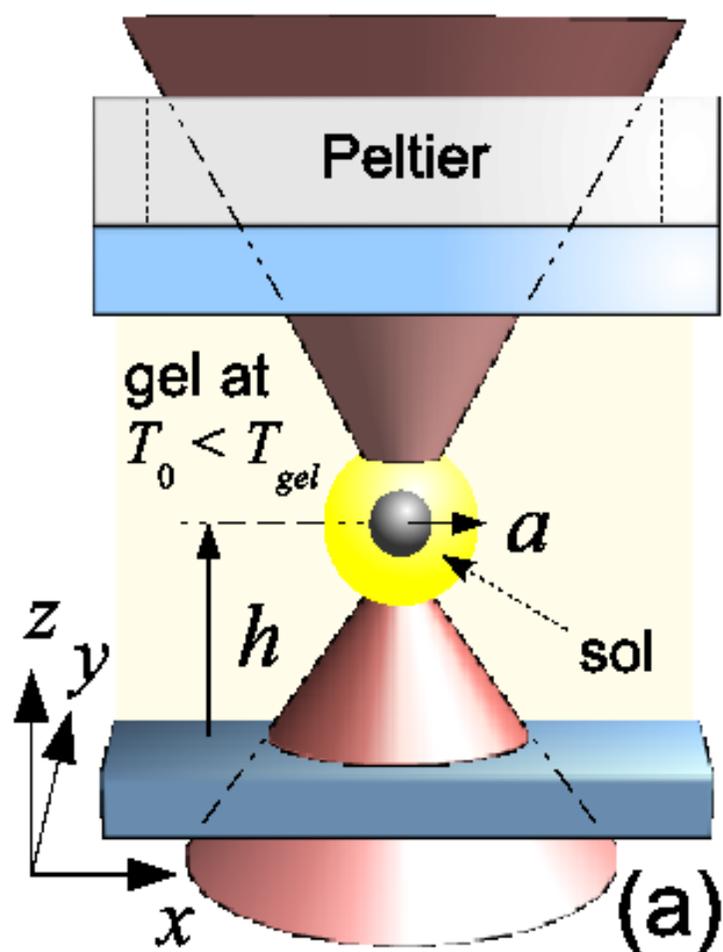
$$|\hat{x}(\omega, t_w)|^2 = \frac{4k_B T_{eff}(\omega, t_w) \gamma(\omega, t_w)}{\omega^2 \gamma^2(\omega, t_w) + (k + K_{gel}(\omega, t_w))^2}$$

## Time evolution of the viscosity and elastic modulus

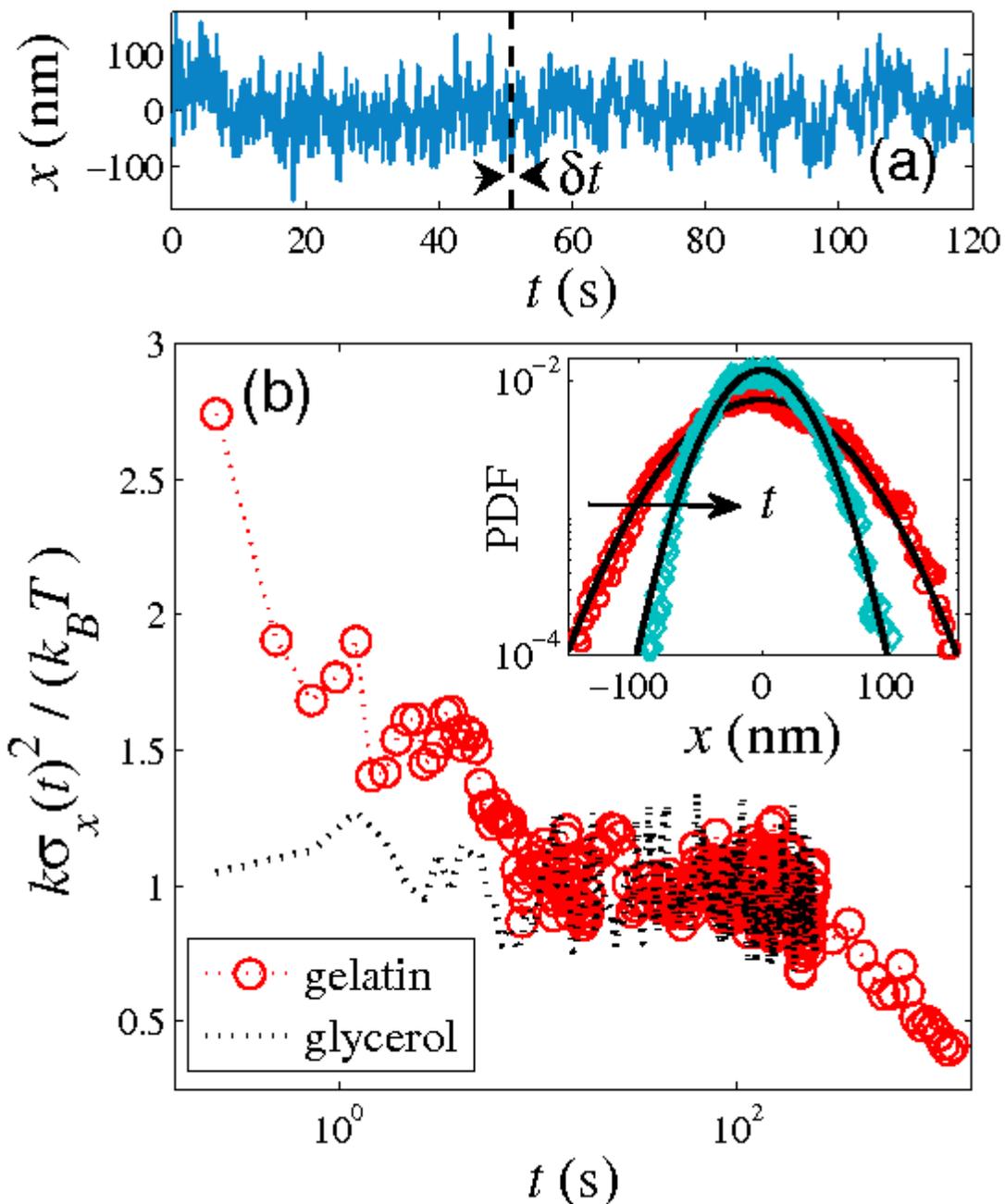


The gel forms in about 30 min

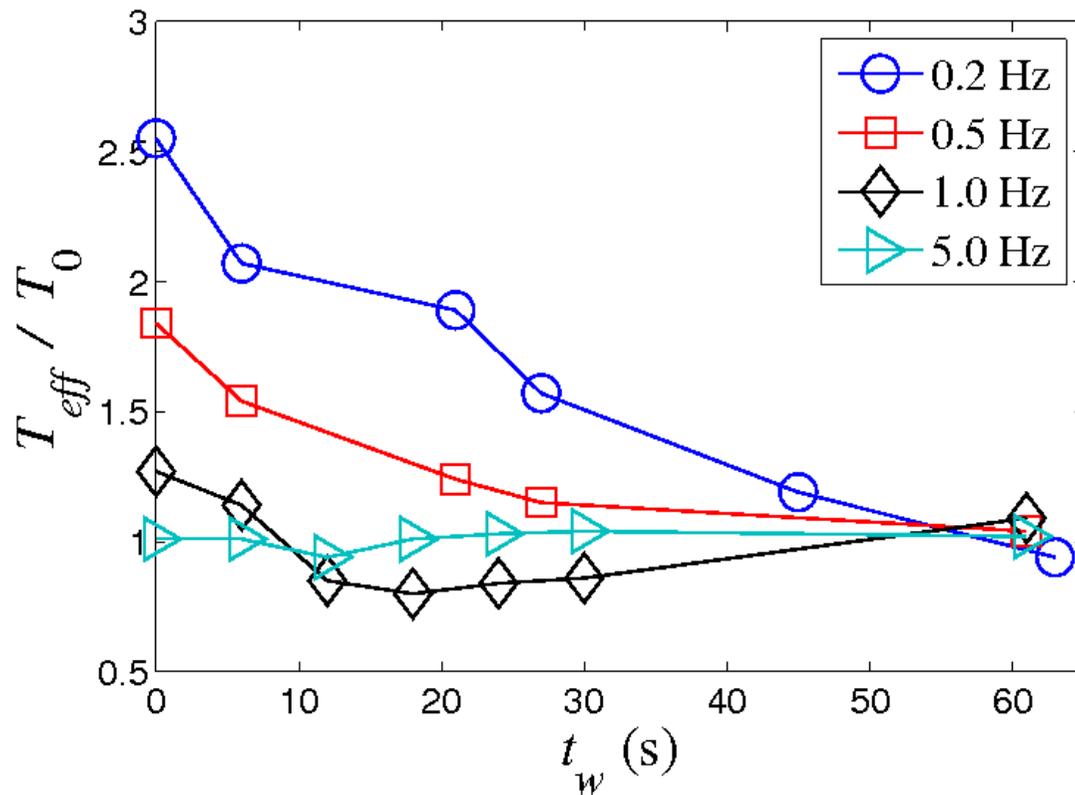
This time evolution is independent of the distance from the boundary of the drop



# Gelatine liquid-solid transition



# Effective Temperature after the quench



Experiment in gelatine  
at 10% wt  
sol-gel transition at 28°C

## Energy balance in Langevin equation

Sekimoto K, Progress of Theoretical Phys. supplement (130), 17 (1998).

$$\int_{-\infty}^t \Gamma(t-t', t_w) \dot{x}(t') dt' + kx = F + \xi(t),$$

Multiplying by  $\dot{x}(t)$  and integrating for a time  $\tau$  starting at  $t_w$ :

$$\Delta U_\tau(t_w) - W_\tau = Q_\tau(t_w),$$

$$\Delta U_\tau(t_w) = \frac{1}{2}k(x(t_w + \tau)^2 - x(t_w)^2) + \int_{t_w}^{t_w + \tau} \dot{x}(t)(K_t * x)(t, t_w) dt,$$

$$Q_\tau(t_w) = \int_{t_w}^{t_w + \tau} \xi(t') \dot{x}(t') dt' - \int_{t_w}^{t_w + \tau} \dot{x}(t')(\gamma_t * \dot{x})(t, t_w) dt',$$

$$W_\tau = \int_{t_w}^{t_w + \tau} F \dot{x} dt$$

Q and W are fluctuating quantities which satisfy Fluctuation Theorem

For  $F=0$  then:

$$\Delta U_{\tau}(t_w) = Q_{\tau}(t_w)$$

$$\Delta U_{\tau}(t_w) = \frac{1}{2}k(x(t_w + \tau)^2 - x(t_w)^2) + \int_{t_w}^{t_w + \tau} \dot{x}(t)(K_t * x)(t, t_w) dt,$$

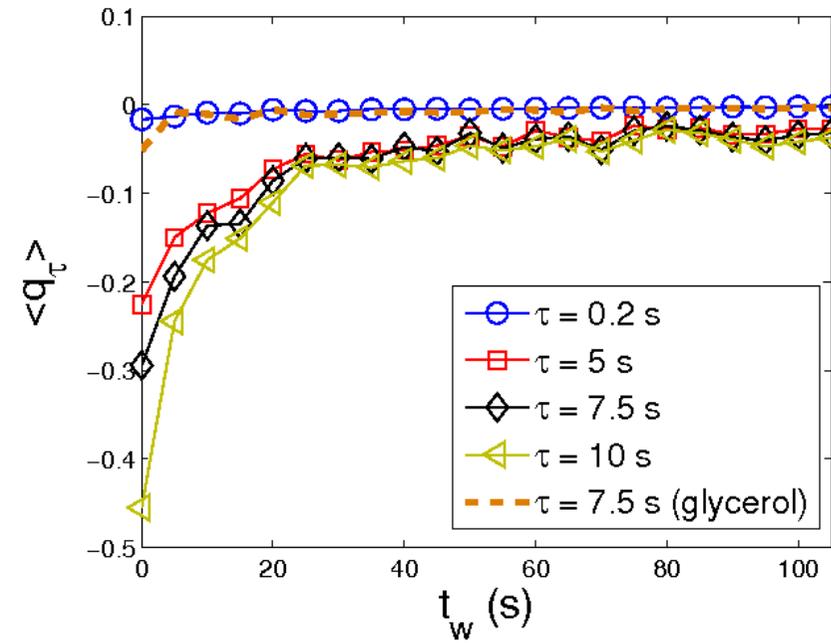
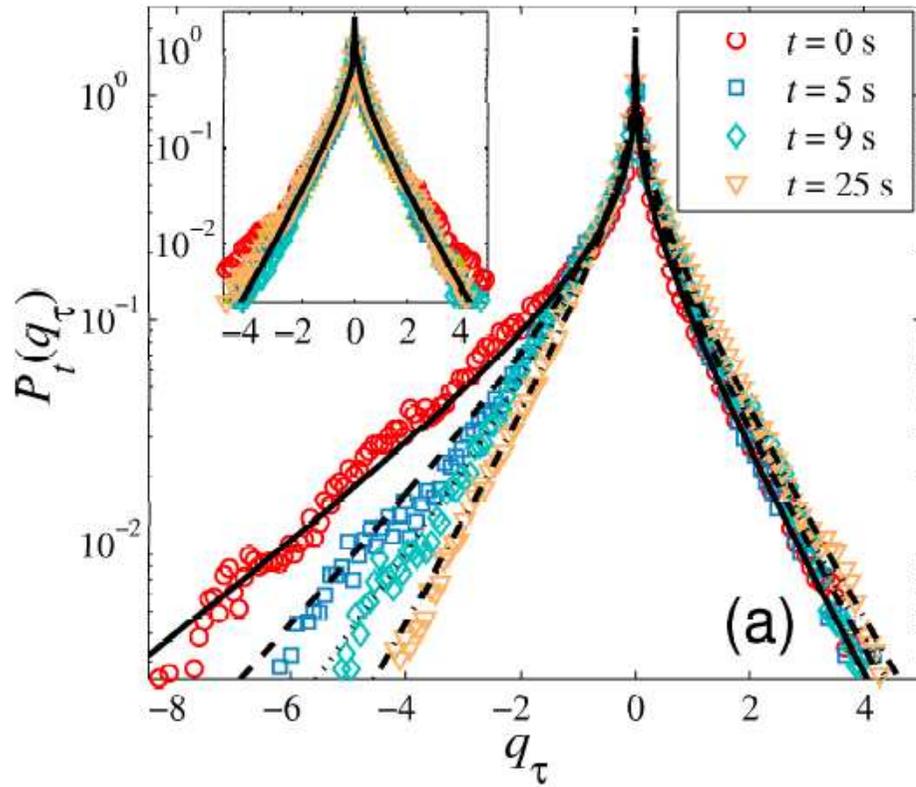
for  $t_w < 200s$

For  $t_w < 200s$ ,  $Q_{\tau}$  can be computed from  $\Delta U_{\tau}$ .

A. Crisanti and F. Ritort, Europhys. Lett. **66**, 253 (2004).

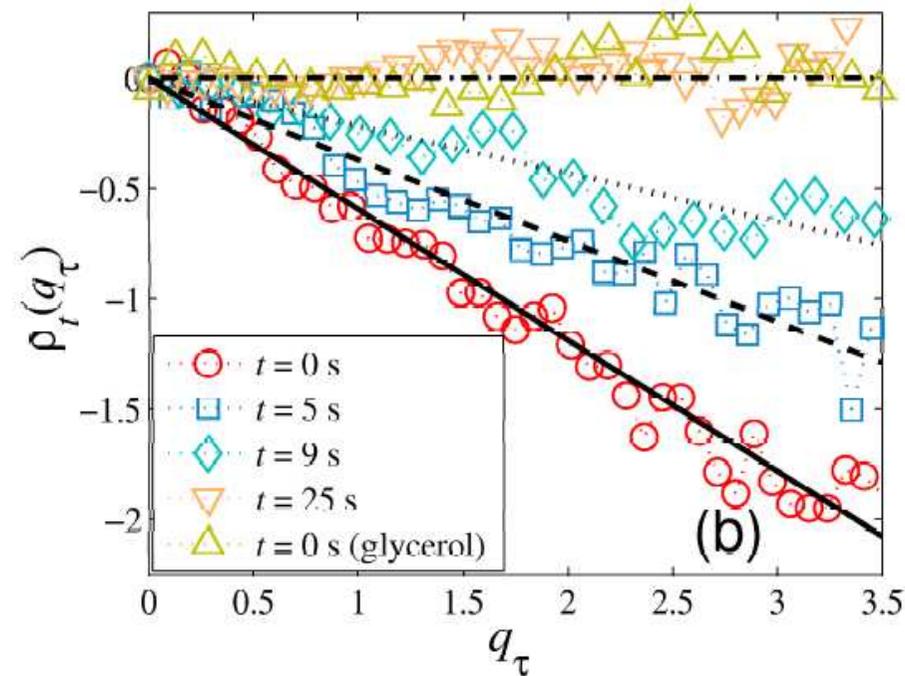
# Energy PDF

$$q_\tau = \frac{Q_\tau}{k_B T}$$



Mean heat

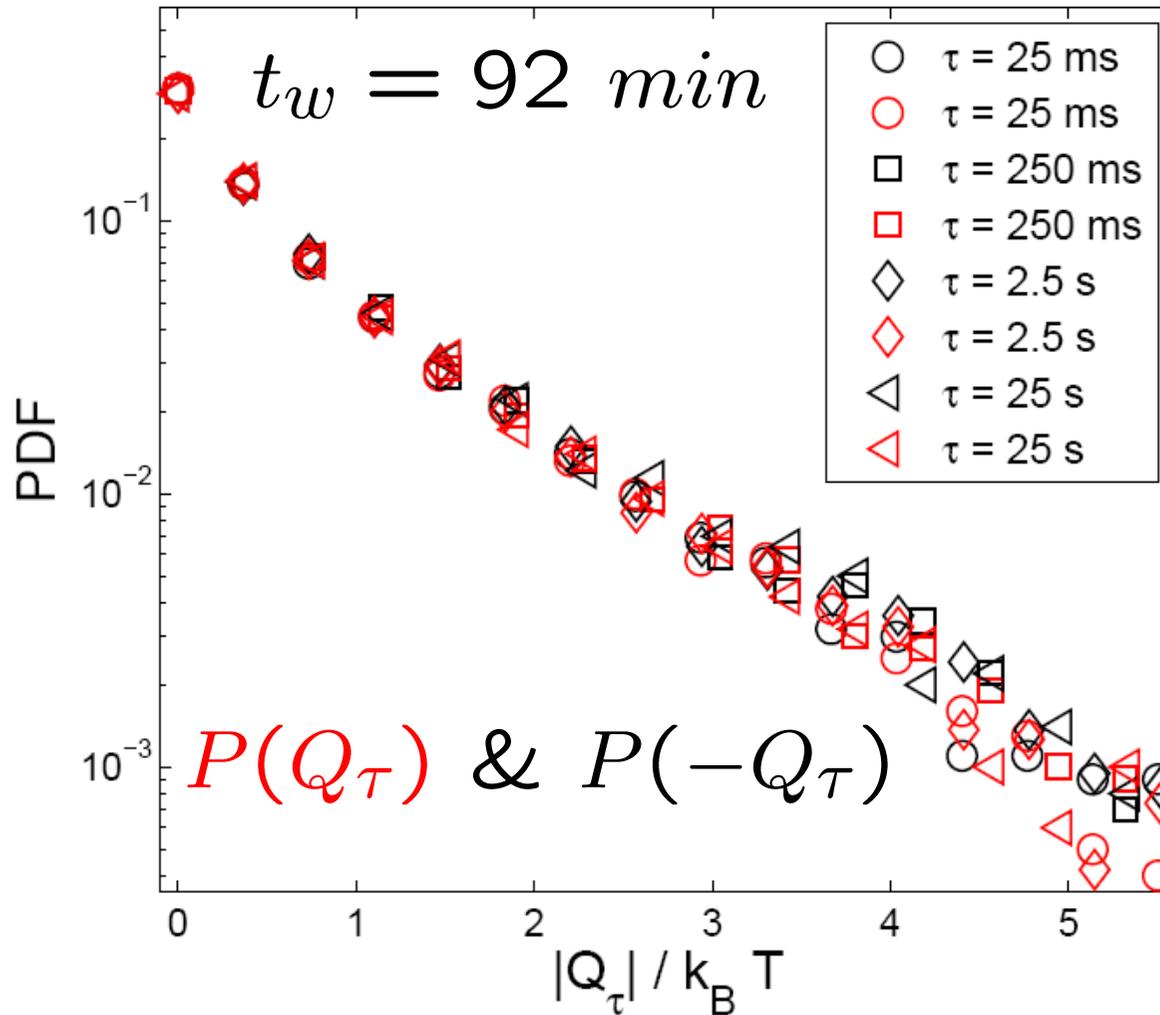
# Gelatine liquid-solid transition



$$\rho(q_\tau) = \log \frac{P(q_\tau)}{P(-q_\tau)}$$

$$\rho(q_\tau) = -\left(\frac{1}{T_{eff}(t+\tau)} - \frac{1}{T_{eff}(t)}\right)T q_\tau$$

# Heat Fluctuations for Laponite



$P(Q_\tau) = P(-Q_\tau)$   
for  $t_w \leq 350 \text{ min}$   
and  $T_{eff} = T$ .

# Conclusions on local heating of gelatine

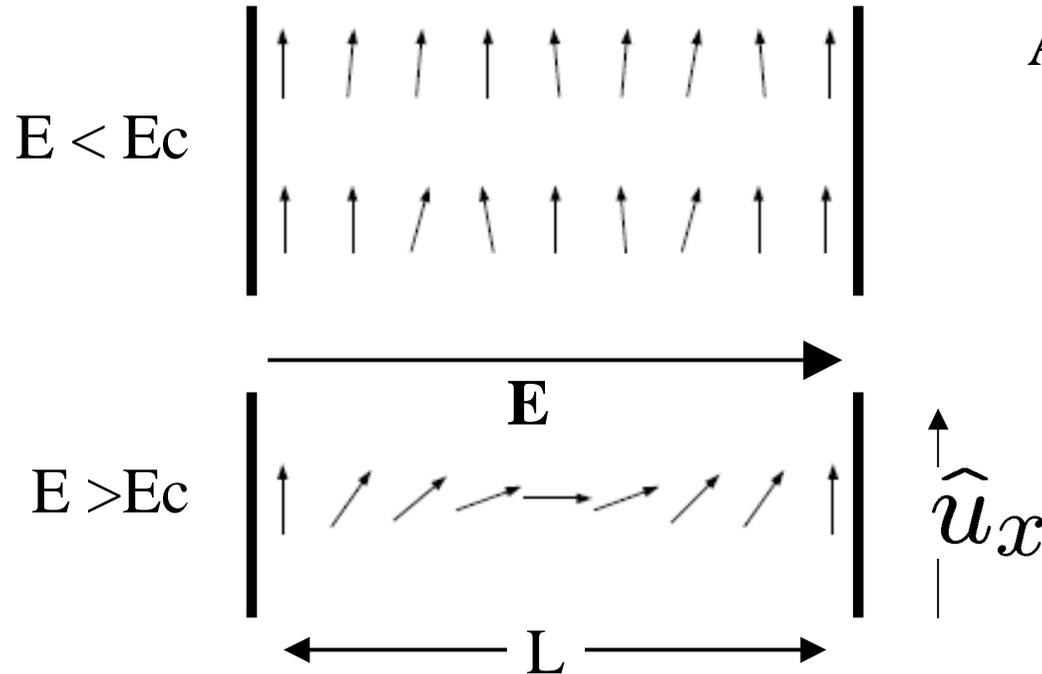
The liquid-solid transition is studied inside a drop of liquid

- a) Relaxation dynamics independent of the distance from the boundary of the drop
- b) The dynamics transfers heat towards the bath
- c) The FDT is violated
- d) The fluctuations of heat are asymmetric

# **Aging at the critical point**

## **Fréedericksz transition**

A. Caussarieu, S. Joubaud, B. Géraud, A. Petrosyan



A liquid crystal consists of elongated molecules

$\hat{n}$  is the director

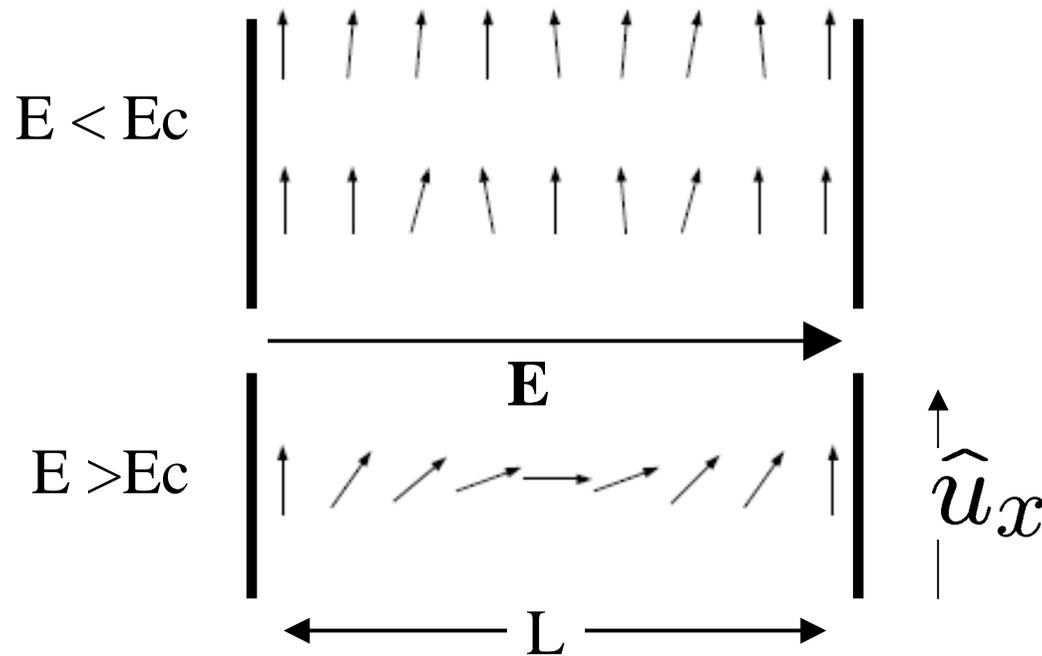
Surface treatment.  
Parallel anchored  
(planar allignement)

Competition between :

- Elastic energy  $\hat{n} // \hat{u}_x$
- Electrostatic energy  $\hat{n} // \vec{E}$

Control parameter :  
voltage difference  $U$

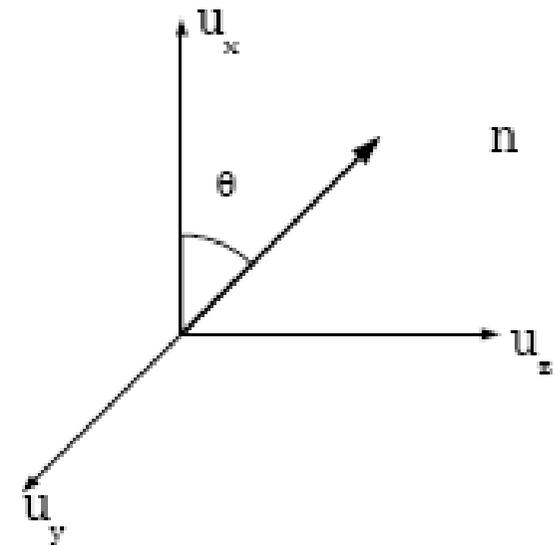
## Liquid Crystals and Fréedericksz transition (II)



$\hat{n}$  is the director

Control parameter :  
voltage difference  $U$

Solution of the form:  $\theta(z) = \theta_o(x, y) \sin\left(\frac{\pi z}{L}\right)$

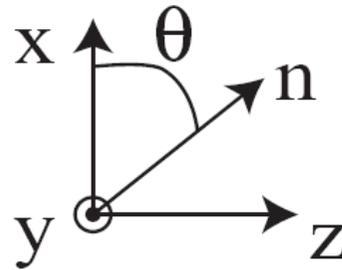


## Fréedericksz transition

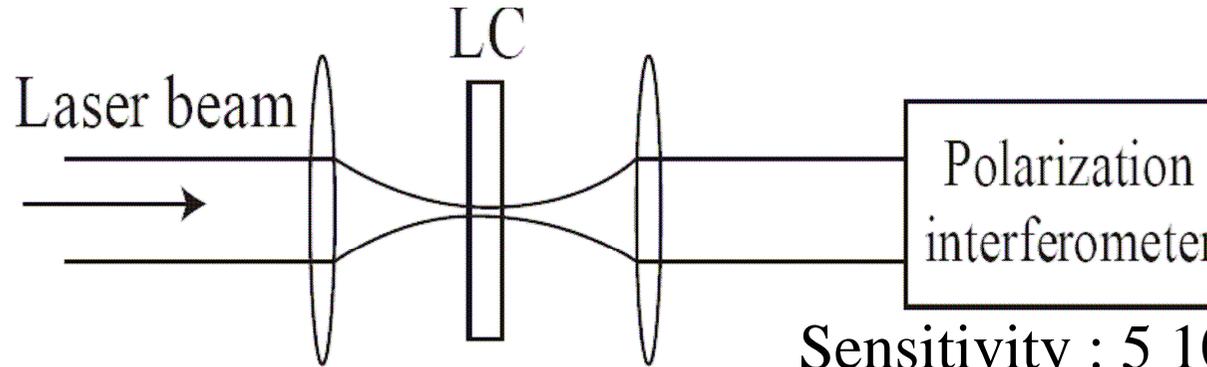
- The Fréederick transition is a second order phase transition
- The order parameter is  $\theta_0(x, y)$
- The control parameter is  $\epsilon = U^2/U_c^2 - 1$
- The relaxation time is  $\tau_{relax} = \tau_o/\epsilon$
- The correlation length  $\xi_r = \frac{L}{\pi\sqrt{\epsilon}}$

# Experimental set-up

$$E_0(\hat{x} + \hat{y})$$



$$E_0(\exp(i\Phi_x)\hat{x} + \exp(i\Phi_y)\hat{y})$$



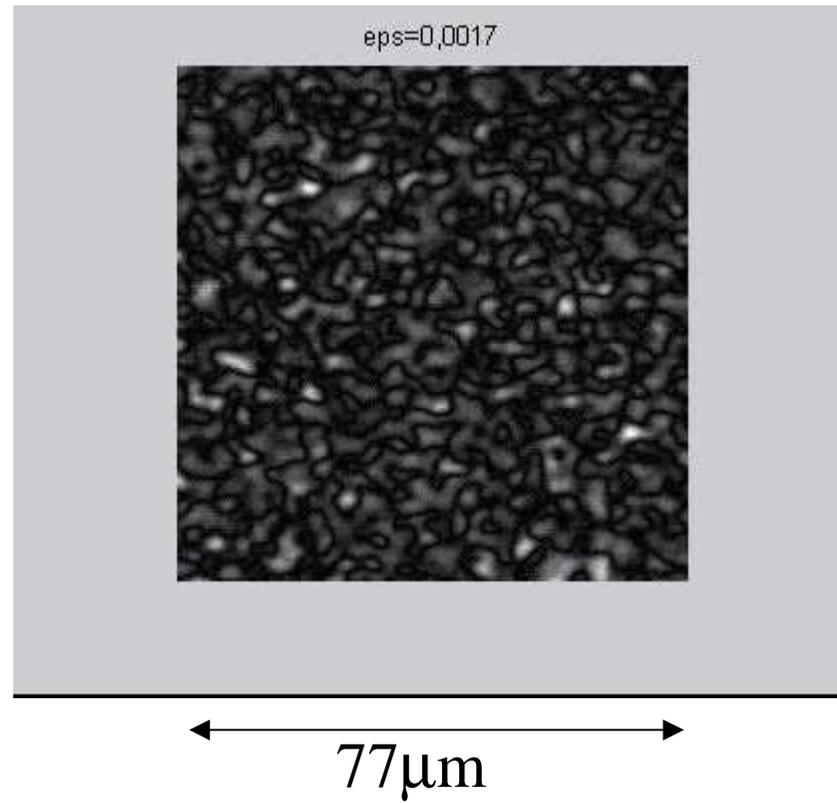
Sensitivity :  $5 \cdot 10^{-14} \text{ m/Hz}^{1/2}$

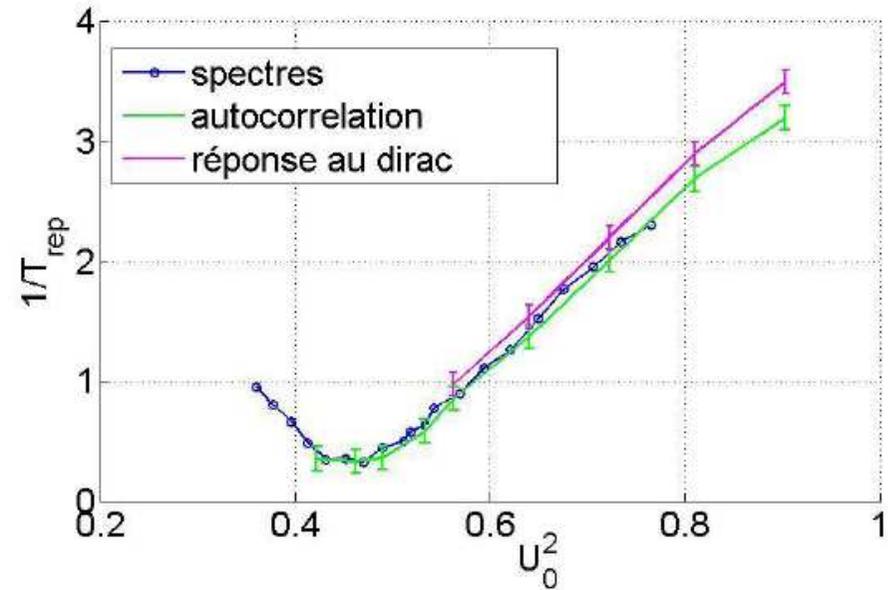
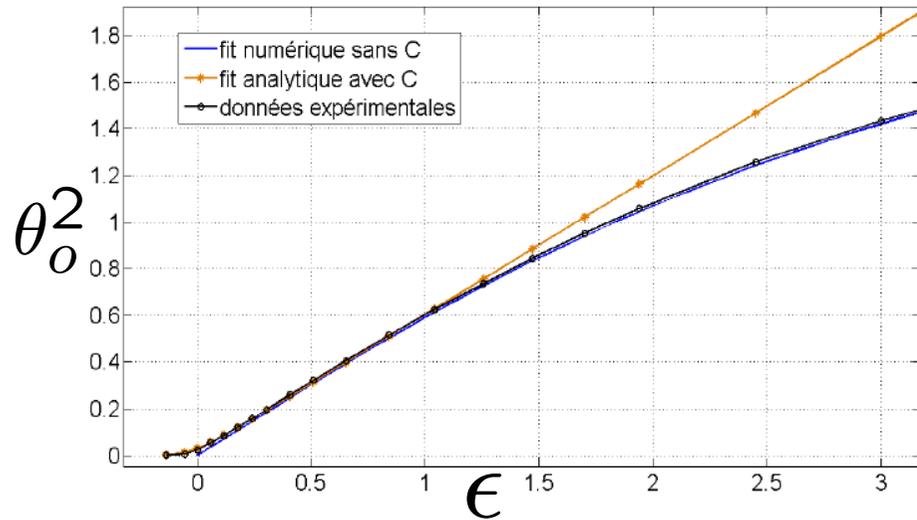
$$L=7\mu\text{m}$$

$$\zeta = \iint_A \theta_0^2 \frac{dx dy}{A}$$

A is the measuring area

# Space-time dynamics

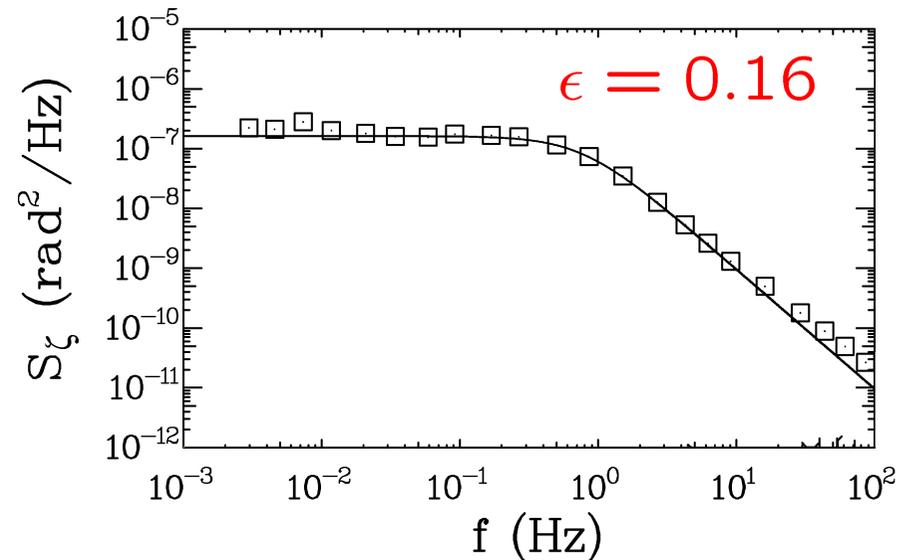


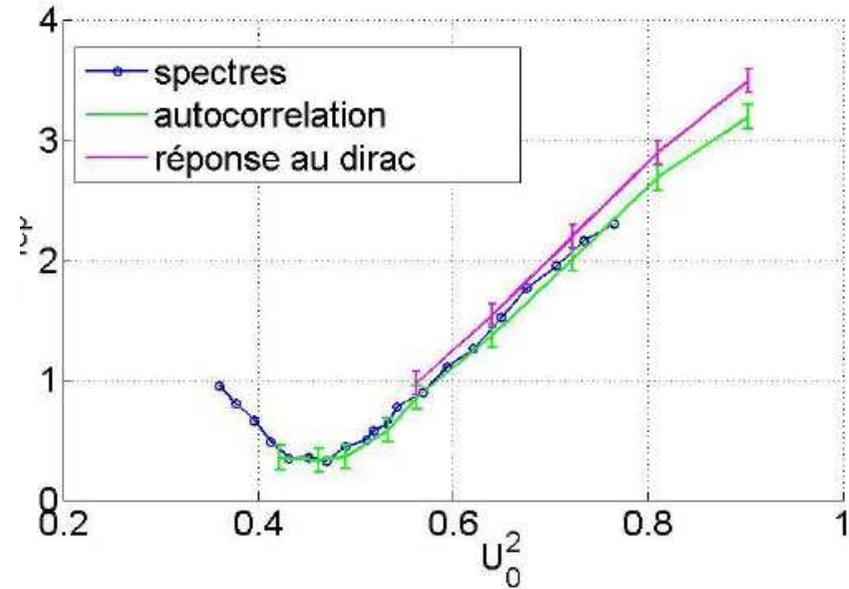
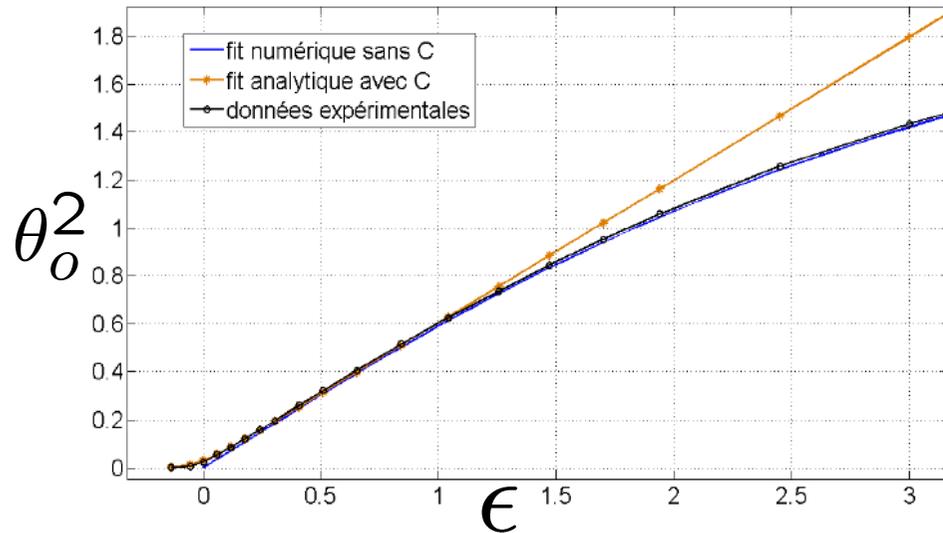


$$\tau_0 \dot{\theta}_0 = \epsilon \theta_0 - \alpha \theta_0^3$$

$$\tau_0 \delta \dot{\theta}_0 = -2\epsilon \delta \theta_0 + \eta(t)$$

$$\epsilon = \frac{U_0^2}{U_c^2} - 1$$

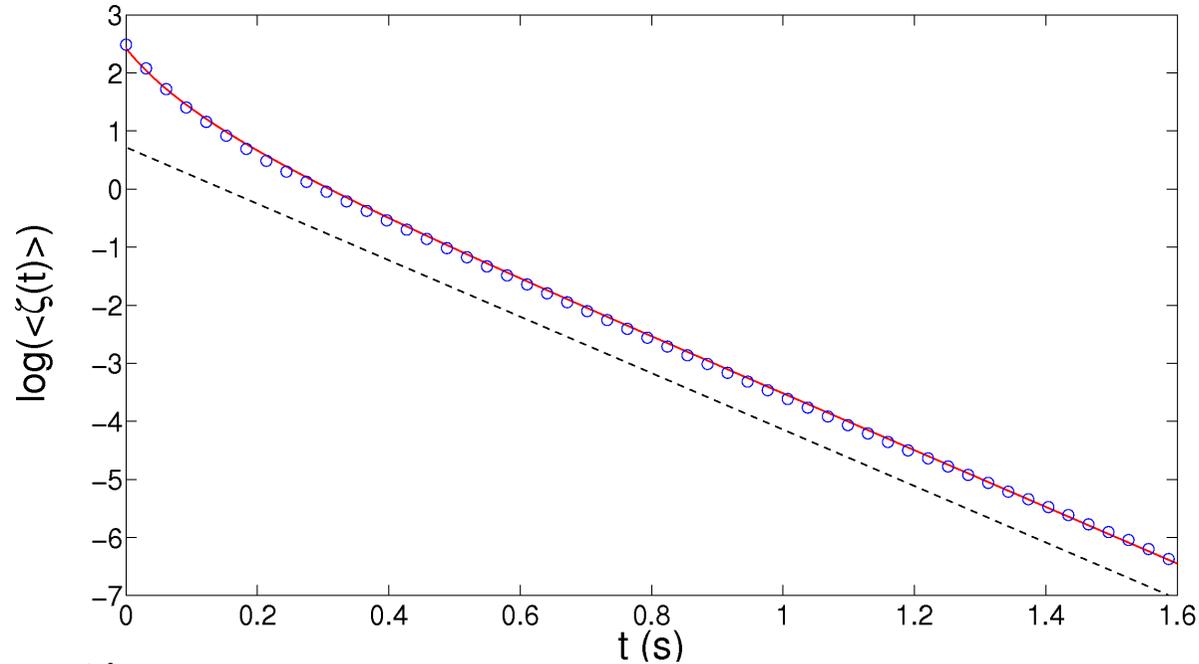




$$\tau_0 \dot{\theta}_0 = \epsilon \theta_0 - \alpha \theta_0^3 + C$$

# Time evolution after a quench in LC

from  $\epsilon_1 = 0.3$  to  $\epsilon_0 = 0.01$



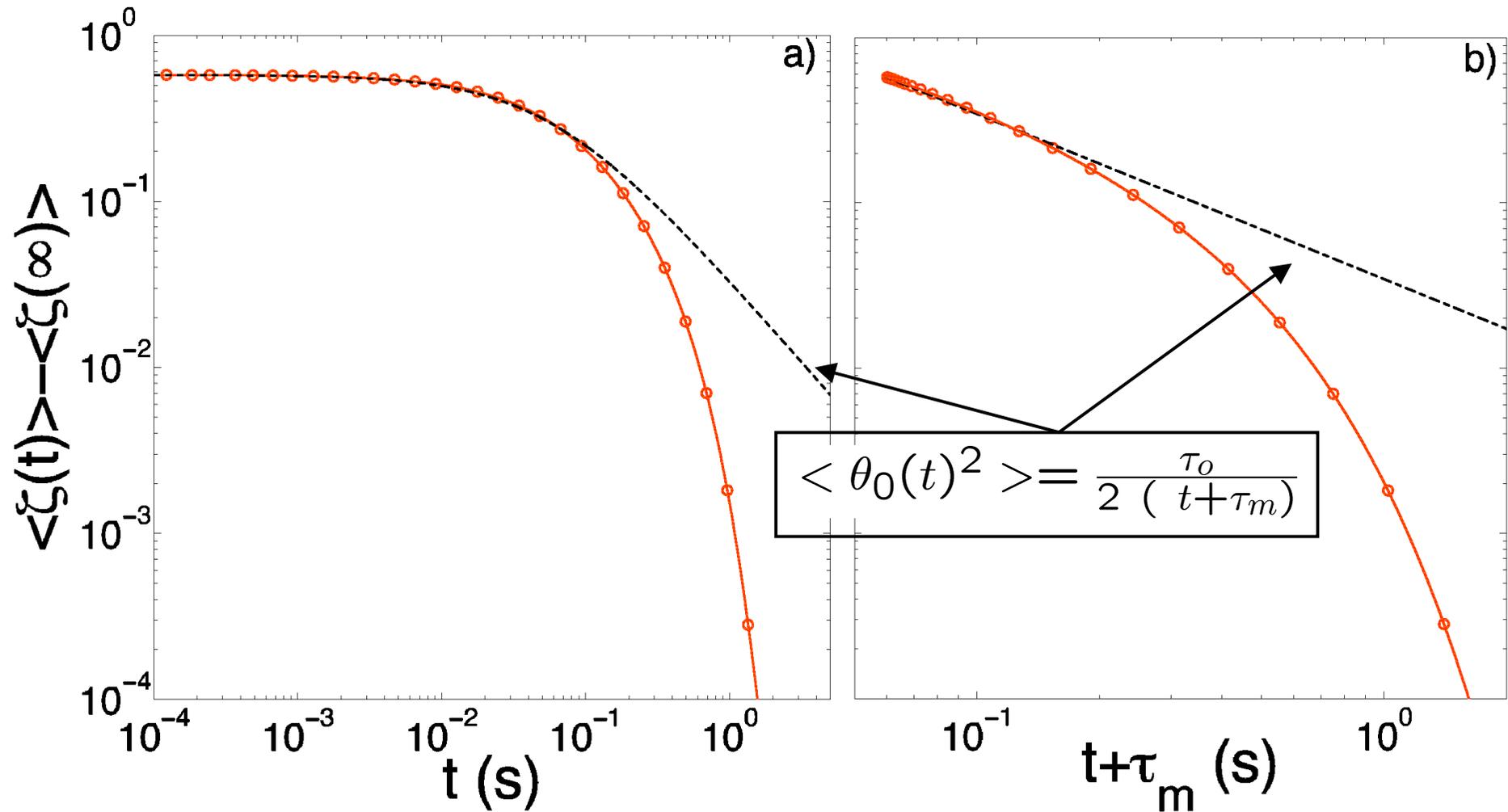
Fit function

$$\langle \zeta(t) \rangle = \frac{\langle \zeta(\infty) \rangle}{1 + \left( \frac{\langle \zeta(\infty) \rangle}{\langle \zeta(0) \rangle} - 1 \right) \exp\left(-\frac{2\epsilon_0 t}{\tau_0}\right)},$$

$$\text{with } \langle \zeta(\infty) \rangle = \frac{2\epsilon_0}{(2k + \epsilon_0 + 1)} \text{ and } \langle \zeta(0) \rangle = \frac{2\epsilon_1}{(2k + \epsilon_1 + 1)}$$

# Time evolution of $\zeta$ after a quench

Quench from  $\epsilon_1 \simeq 0.3$  to  $\epsilon_0 \simeq 0.01$   $\tau = \frac{\tau_0}{2\epsilon} \simeq 0.22s$



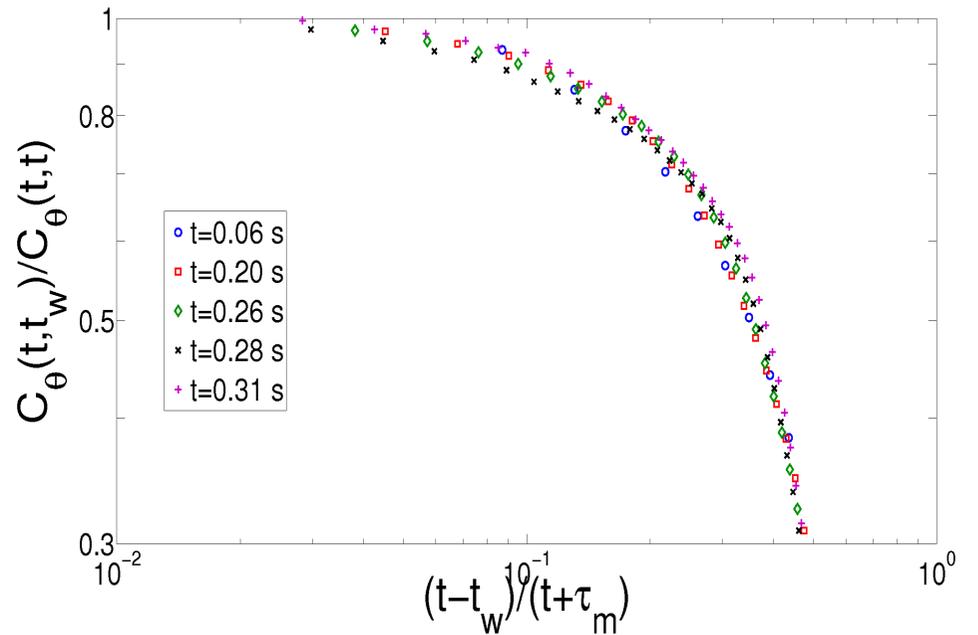
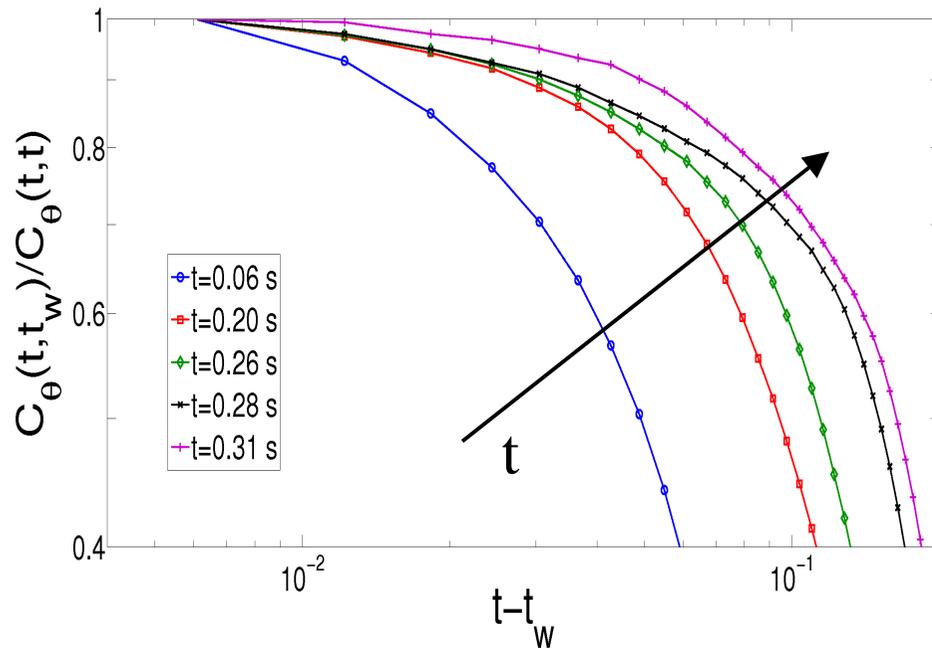
# Correlations

$$\zeta(t) = \theta_0(t)^2 = \psi_0^2(t) + 2\psi_0\delta\theta = \langle \zeta(t) \rangle + \delta\zeta(t)$$

$$\psi_0^2(t) = \langle \zeta(t) \rangle$$

$$C_\zeta(t, t_w) = \langle \delta\zeta(t)\delta\zeta(t_w) \rangle = 4\psi_0(t)\psi_0(t_w) C_\theta(t, t_w)$$

Master curve by rescaling  
 $(t - t_w) \rightarrow (t - t_w)/(t + \tau_m)$



## FDT in the LC experiment: the measure of the response function

$$\chi(t, t_w) = \frac{\langle \Delta\theta \rangle}{\Gamma_{ext}} = \int_{t_w}^t R(t, t') dt' \quad C_\theta(t, t_w) = \langle \delta\theta(t)\delta\theta(t_w) \rangle$$

**FDR**

$$\chi(t, t_w) = \frac{1}{k_B T_{eff}(t, t_w)} (C_\theta(t, t) - C_\theta(t, t_w))$$

In equilibrium

$$T = T_{eff}$$

Which is the appropriate external torque  $\Gamma_{ext}$  for the LC ?

$\Delta\theta$  is the response of  $\theta$  to  $\delta\epsilon$

$$\tau_0 \Delta\dot{\theta} = [\epsilon - 3 \alpha \theta_0(t)^2] \Delta\theta(t) + \delta\epsilon \theta_0(t)$$

$\Gamma_{ext}$

## FDT in the LC experiment:

$$\delta\theta = \frac{\delta\zeta(t)}{2\psi_0(t)}$$

$$\Gamma_{ext} = 4B\psi_0(t) \delta\epsilon$$

Experimental test of these results (JSTAT P01033, 2009) :

- 1) Out of equilibrium, using the Transient Fluctuation Theorem
- 2) FDT in equilibrium

**In equilibrium**  $\psi_0(t) = \psi_0(t_w) = \psi_0$

$$\chi(\tau) = \frac{\langle \Delta(\tau) \rangle}{\Gamma_{ext}} = \frac{\chi_{\zeta, \delta\epsilon}}{4B \psi_0^2}$$

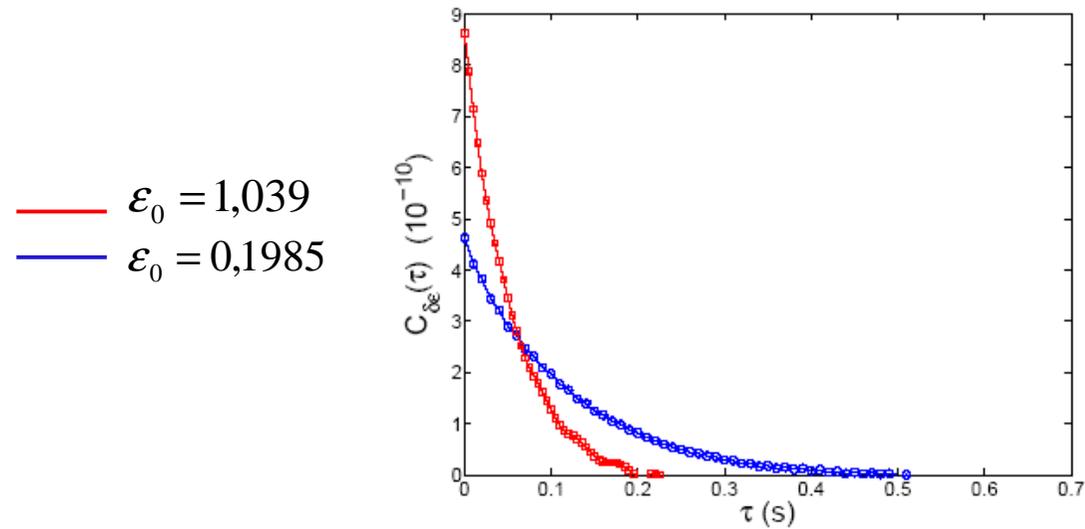
$$C_\zeta(t, t_w) = 4\psi_0^2 C_\theta(t, t_w)$$

and FDT

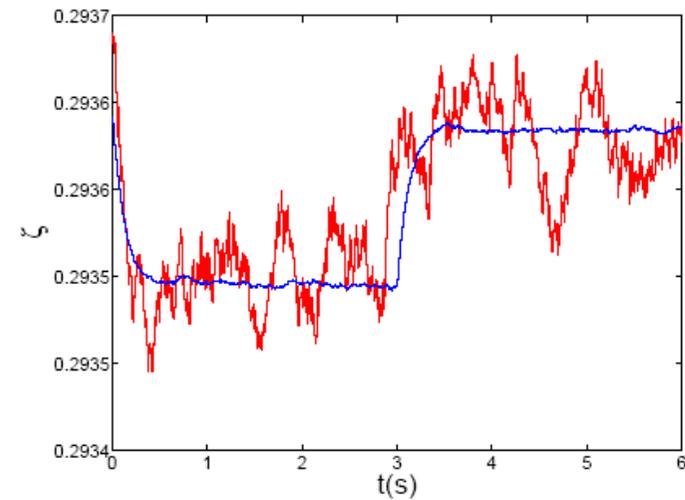
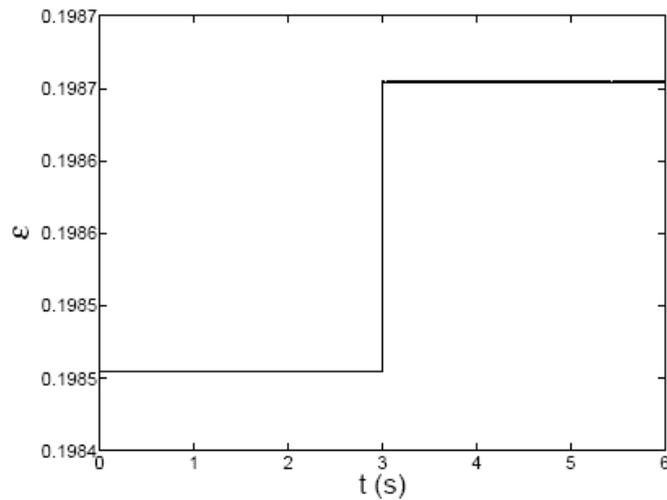
$$\frac{\chi_{\zeta, \delta\epsilon}}{B} = \frac{1}{k_B T} (C_\zeta(t, t) - C_\zeta(t, t_w))$$

with  $B = A\pi^2 K_1 / 4L$

# FDT in the LC experiment in equilibrium

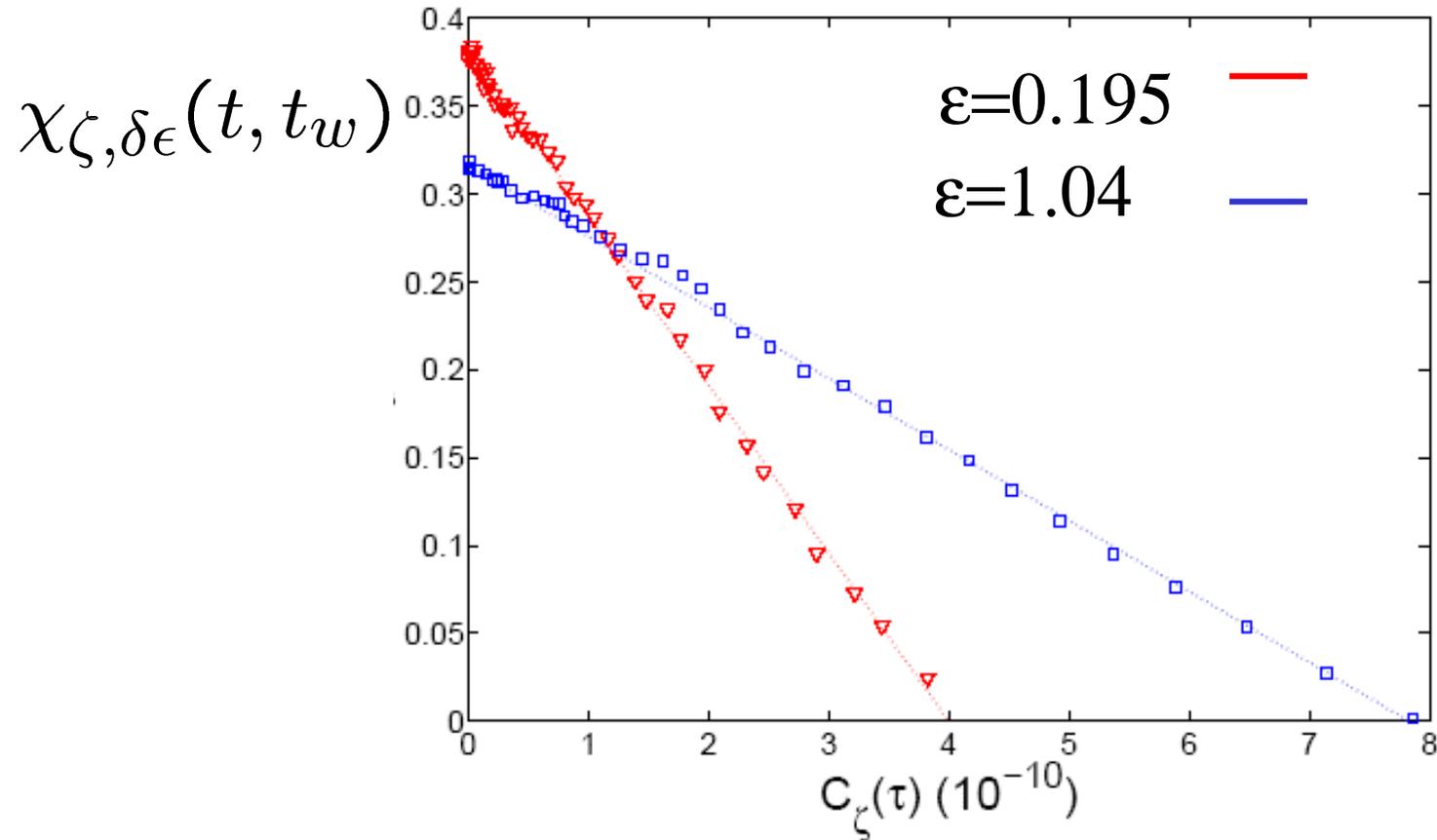


- response function



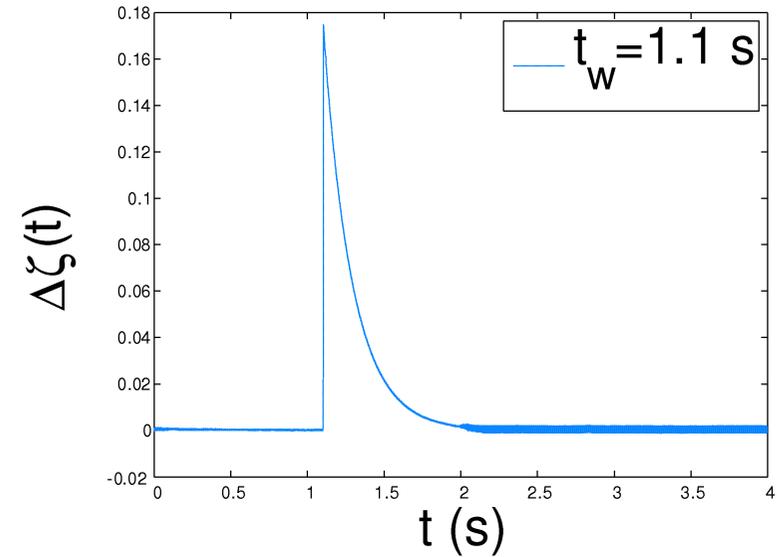
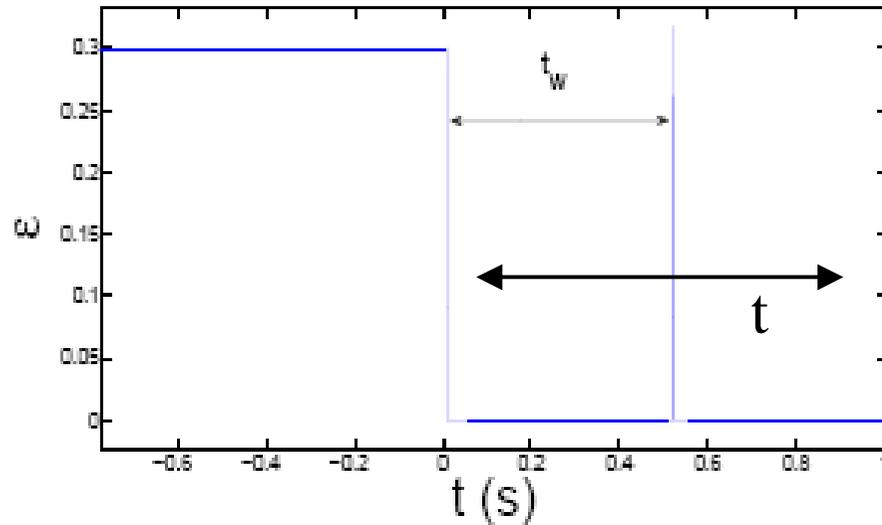
## FDT in the LC experiment in equilibrium

$$\frac{\chi_{\zeta, \delta\epsilon}}{B} = \frac{1}{k_B T} (C_{\zeta}(t, t) - C_{\zeta}(t, t_w)) \quad \text{with } B = \mathcal{A}\pi^2 K_1 / 4L$$



at  $\epsilon = 0.195$  ,  $\frac{B}{k_B T} = 8.4 \cdot 10^8$ ,  $\mathcal{A} = 2.4 \text{mm}^2$  and  $D_0 \simeq 1.8 \text{mm}$

# Response function during aging



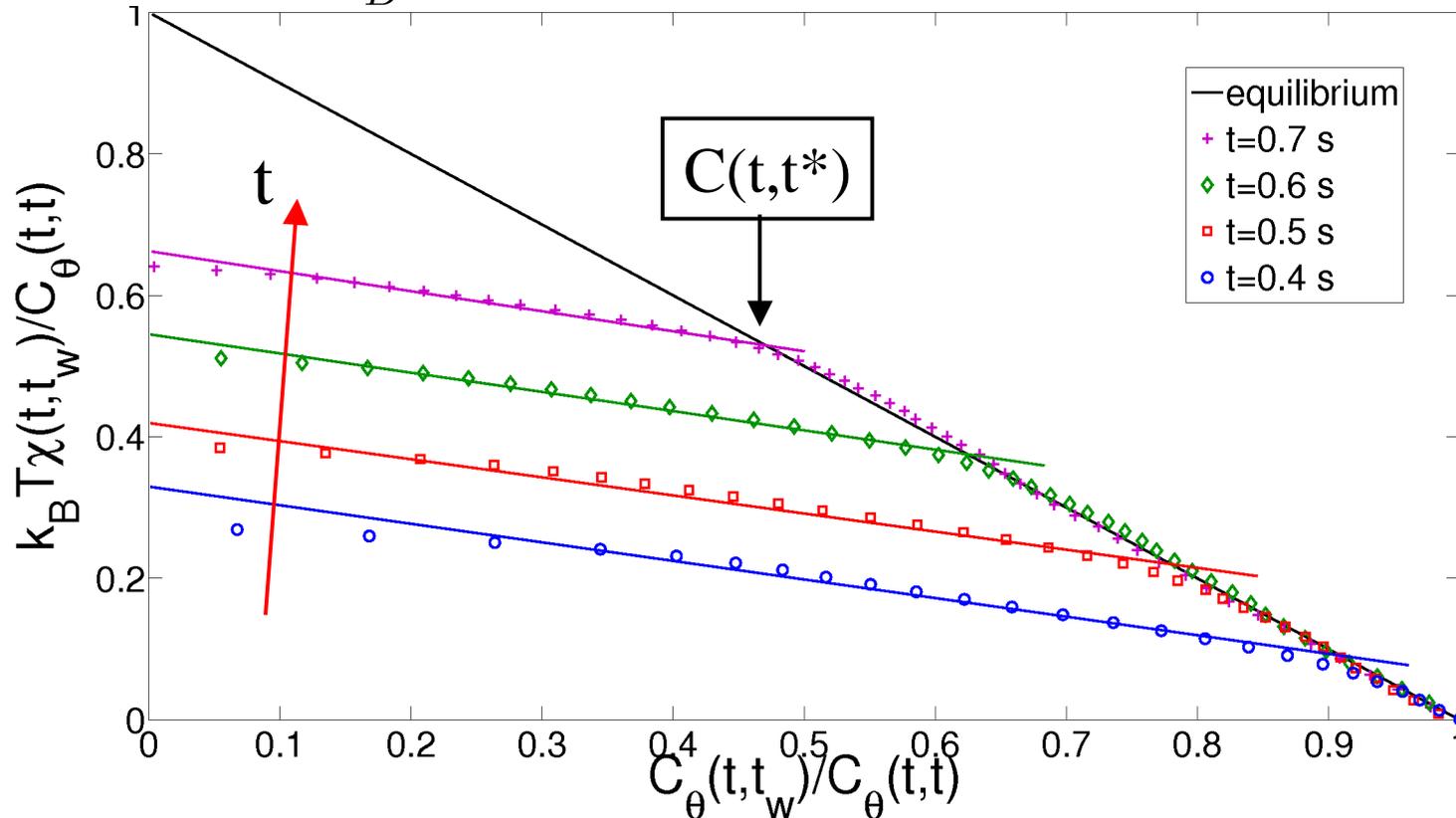
$$\Delta = \theta_0(t) - \psi_0(t) \quad \text{and} \quad \Delta = \frac{\zeta(t) - \psi_0(t)^2}{2\psi_0(t)} = \frac{\zeta(t) - \langle \zeta(t) \rangle}{2\psi_0(t)} = \frac{\Delta\zeta}{2\psi_0(t)}$$

$$R(t, t_w) = \frac{\langle \Delta(t) \rangle}{\Gamma_{ext}(t_w)} = \frac{R_{\zeta, \delta\epsilon}(t, t_w)}{4B \psi_0(t_w) \psi_0(t)}$$

$$\chi(t, t_w) = \frac{\langle \Delta(t) \rangle}{\Gamma_{ext}} = \int_{t_w}^t R(t, t') dt'$$

# FDT out of equilibrium: fixed $t$ as a function of $t_w$

$$\chi(t, t_w) = \frac{X(t, t_w)}{k_B T} (C_\theta(t, t) - C_\theta(t, t_w)) \quad \text{with } T_{eff} = \frac{T}{X(t, t_w)}$$



for  $C(t, t_w) > C(t, t^*)$ ,  $X = 1$  and  $T_{eff} = T$

for  $C(t, t_w) < C(t, t^*)$ ,  $X \simeq 0.33$  and  $T_{eff} \simeq 3T$

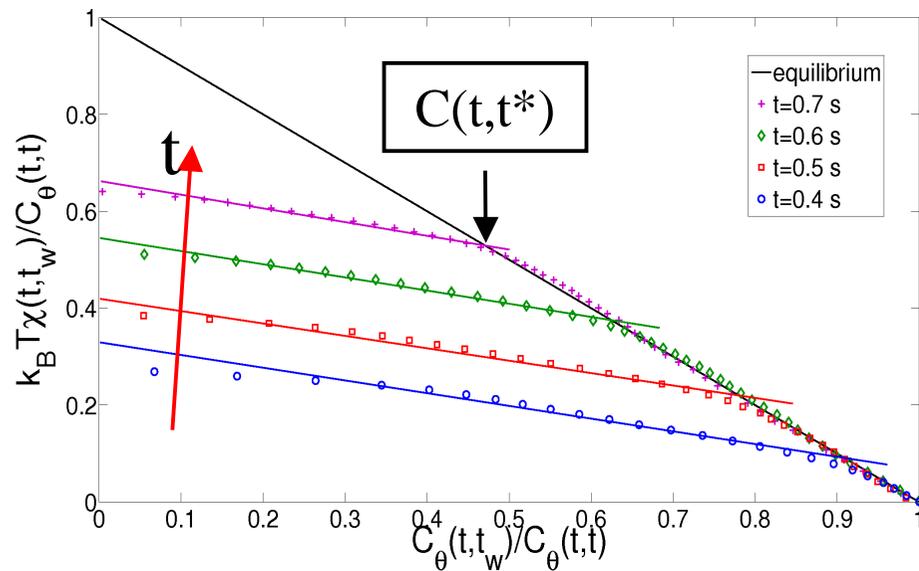
L. Cugliandolo, J. Kurchan, and L. Peliti, Phys. Rev. E 55, 3898 (1997).

D. Hérisson and M. Ocio, Phys. Rev. Lett. 88, 257202, (2002)

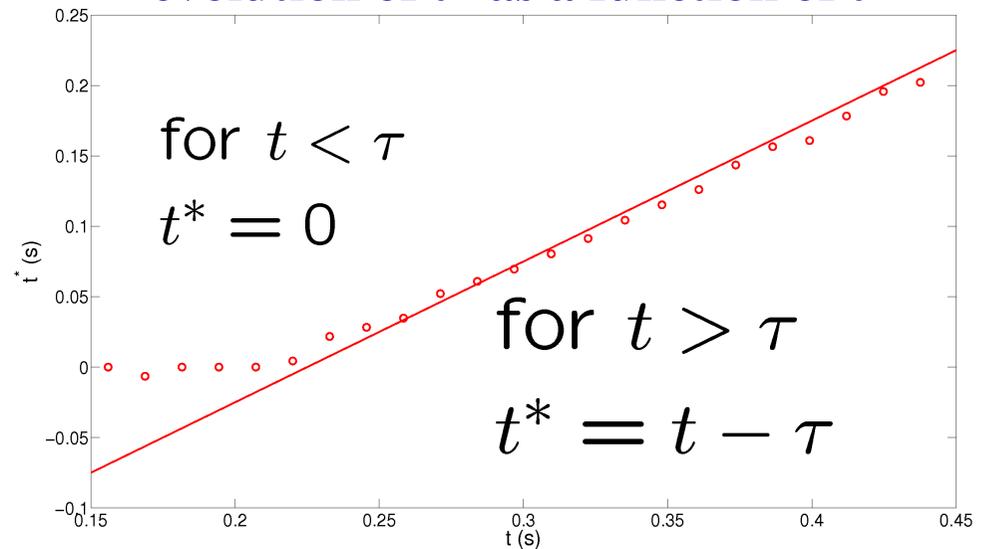
# FDT out of equilibrium: fixed $t$ as a function of $t_w$

for  $C(t, t_w) > C(t, t^*)$ ,  $X = 1$  and  $T_{eff} = T$

for  $C(t, t_w) < C(t, t^*)$ ,  $X \simeq 0.33$  and  $T_{eff} \simeq 3T$



## evolution of $t^*$ as a function of $t$



$\frac{t^*}{t} = 1 - \frac{\tau}{t}$  for  $t > \tau$  defines the length of the equilibrium interval with respect to the total time.

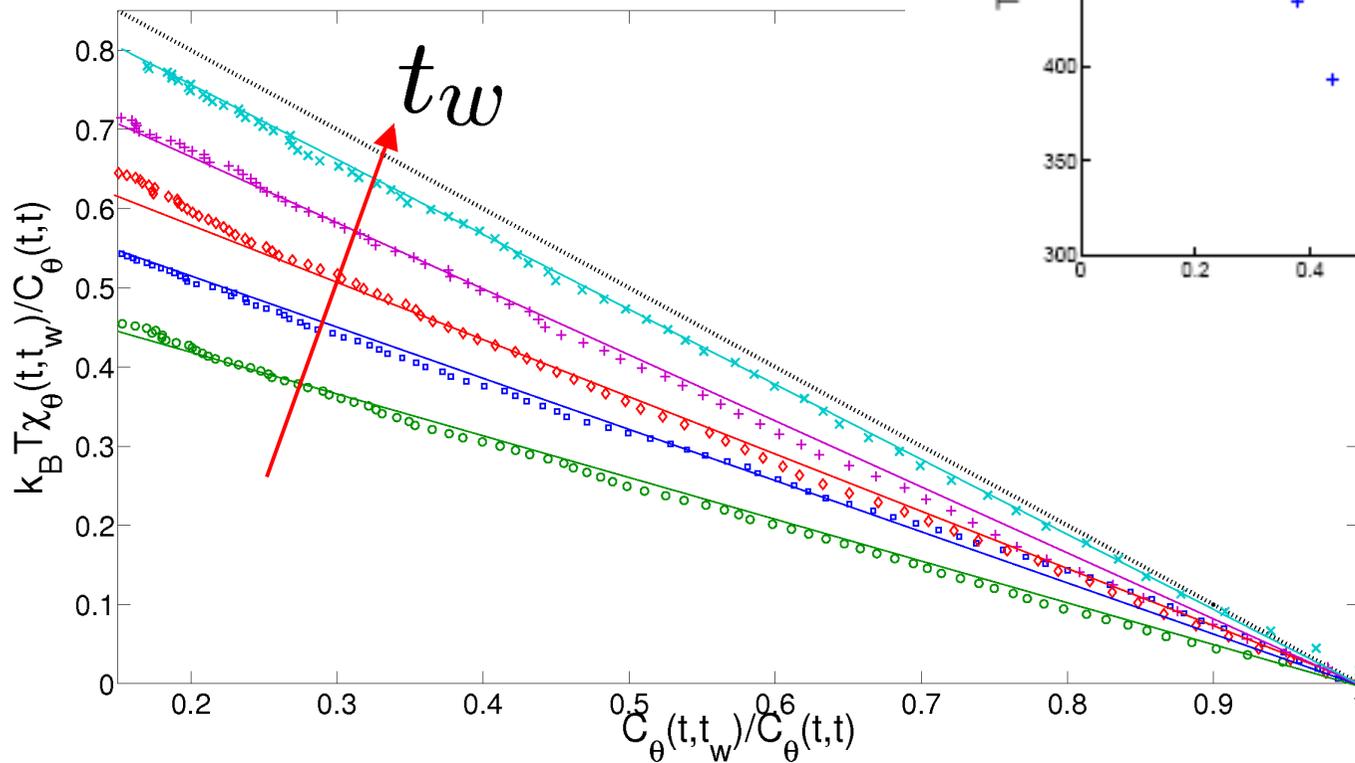
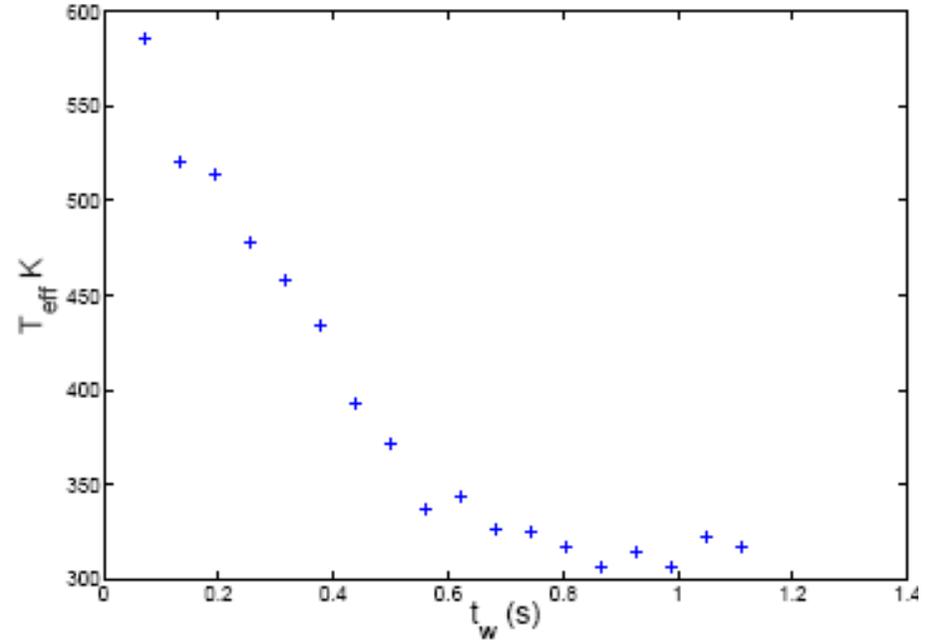
At  $\epsilon_0 = 0, \Rightarrow \tau = \infty$  : the equilibrium interval does not exist.

# FDT out of equilibrium: fixed $t_w$ as a function of $t$

$$\chi(t, t_w) = \frac{X(t, t_w)}{k_B T} (C_\theta(t, t) - C_\theta(t, t_w))$$

with  $T_{eff} = \frac{T}{X(t, t_w)}$

evolution of  $T_{eff}$  versus  $t_w$



## Conclusions on the quench at critical point

Using a liquid crystal driven by an electric field at the Fréedericksz transition we observe that :

- After a quench close to the critical point the system presents power law decay. A **rescaling similar to the one used in aging materials, produces a master curve of correlations**
- FDT is violated during the decay. The observed violation depends on the procedure used to define  $t$  and  $t_w$ .
- For the “good procedure” an asymptotic temperature can be defined, which is not the one computed from mean field.

# Perspectives

- Dependence on the observable
- Intermittency
- Confinement
- Space time dependence
- High order moments
- FDT violation versus aging of response

