ECOLE NORMALE SUPERIEURE DE LYON

Statistical Physics of Systems out of Equilibrium

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Thermal fluctuations and effective temperature in aging materials

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Outline

1) Phenomenological introduction to glasses

2) Aging, memory effects and history dependence

3) Thermal fluctuations and the Fluctuation Dissipation Relations during aging

4) The electrical thermal noise of two materials:
   a) a polymer after a quench
   b) colloidal glass during the sol-gel transition.

5) Comparisons of the experimental results with those of other experiments and of models of aging.

6) The mechanical noise.

7) Conclusions

Phenomenological introduction to the physics of glasses and to physical aging

What is a glass ?

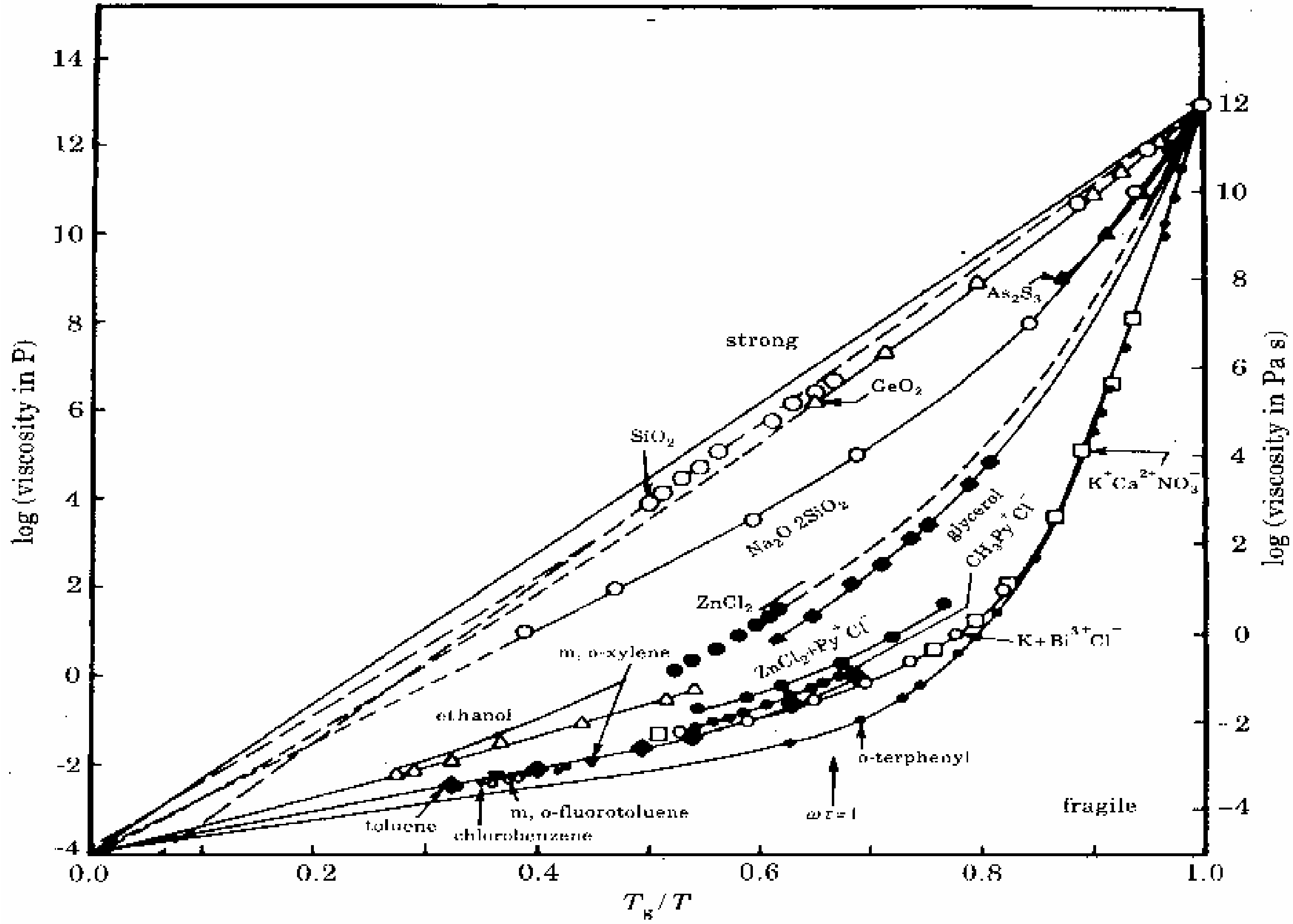
Type of glasses

Structural glasses

Magnetic glasses

Colloids

Viscosity as a function of Tg/T



- Tg is the glass transition temperature
- At Tg the viscosity is about 10^{12} Pa s
- For T>Tg the Young modulus falls down of several orders of magnitude

Mechanical measurements

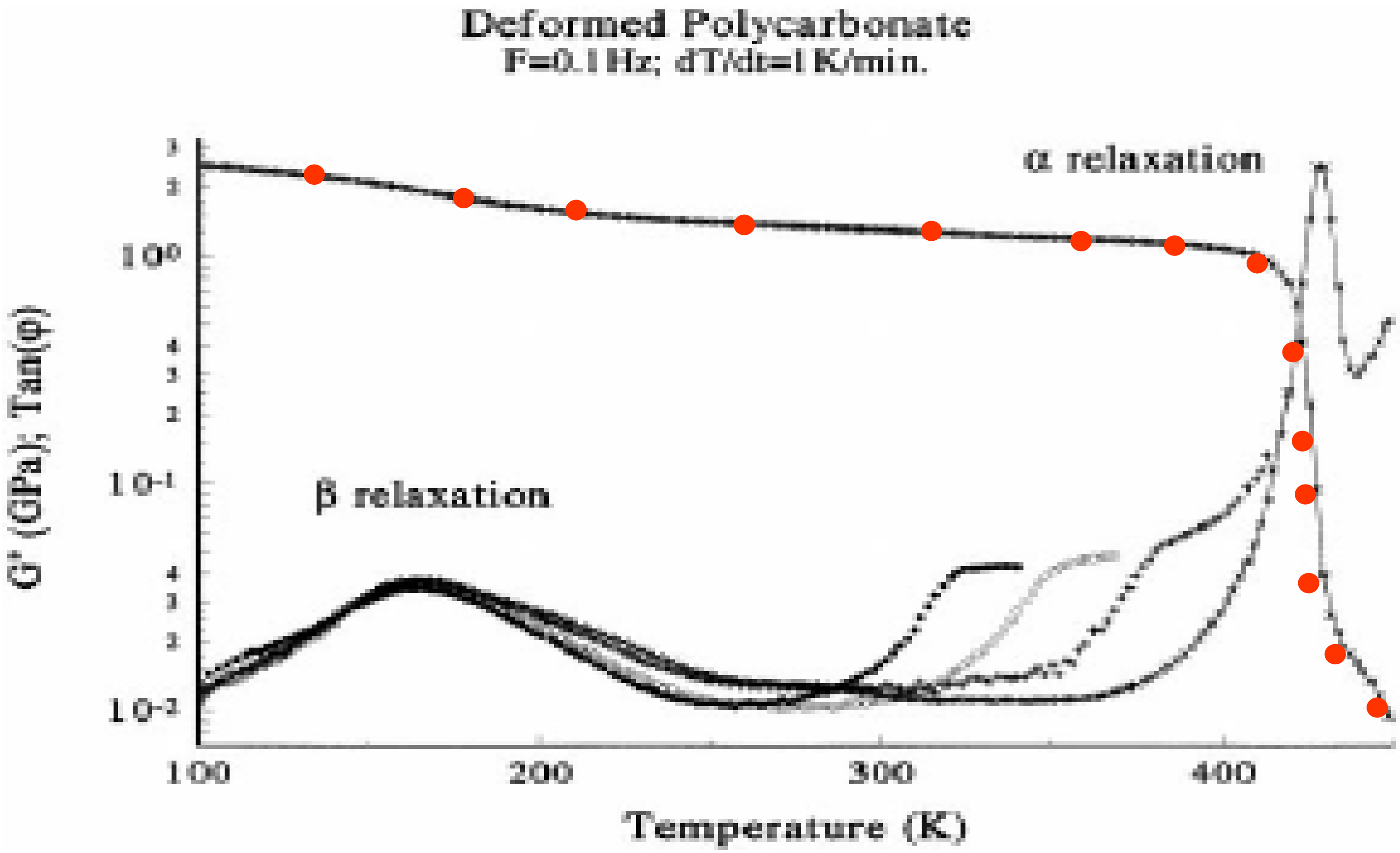


Fig. 3. Evolution of $\tan(\Phi) = G''/G'$ with temperature for successive heating runs for deformed polycarbonate (applied deformation close to 50%, in compression at ambient temperature). (●) first scan up to 339 K; (○) second scan up to 368 K; (+) third scan up to 413 K; (×) last scan up to 448 K, similar to undeformed sample. Between two successive heating runs, the sample is cooled at 6 K/min down to 100 K.

Dielectric measurements

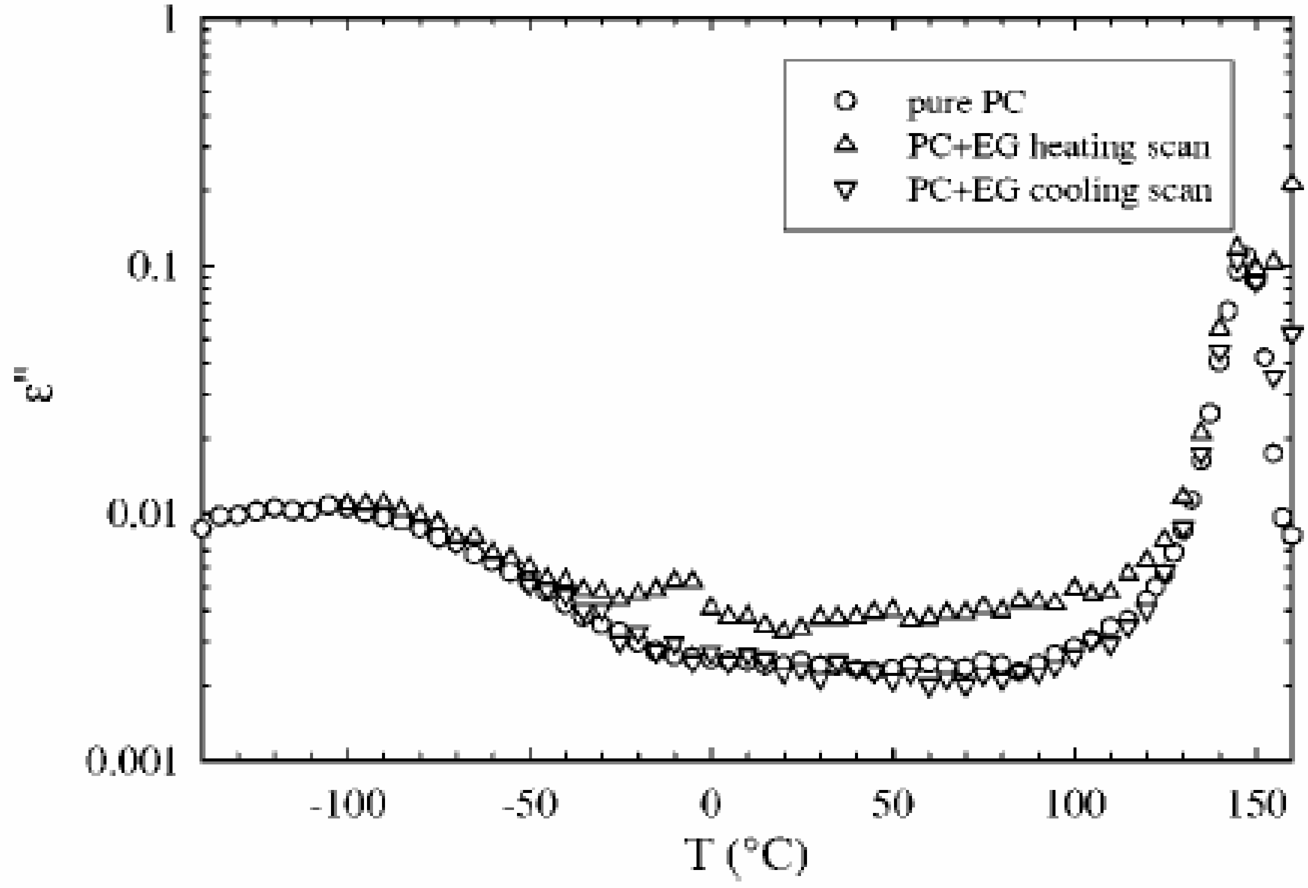


FIG. 4. Dielectric loss vs temperature at 1.2 Hz for pure PC and PC-EG systems during heating and cooling.

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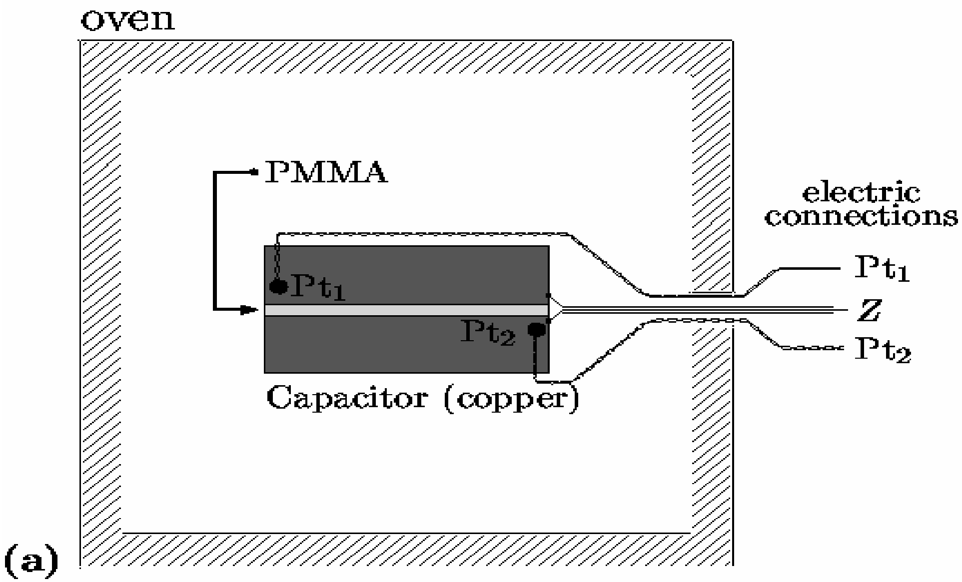
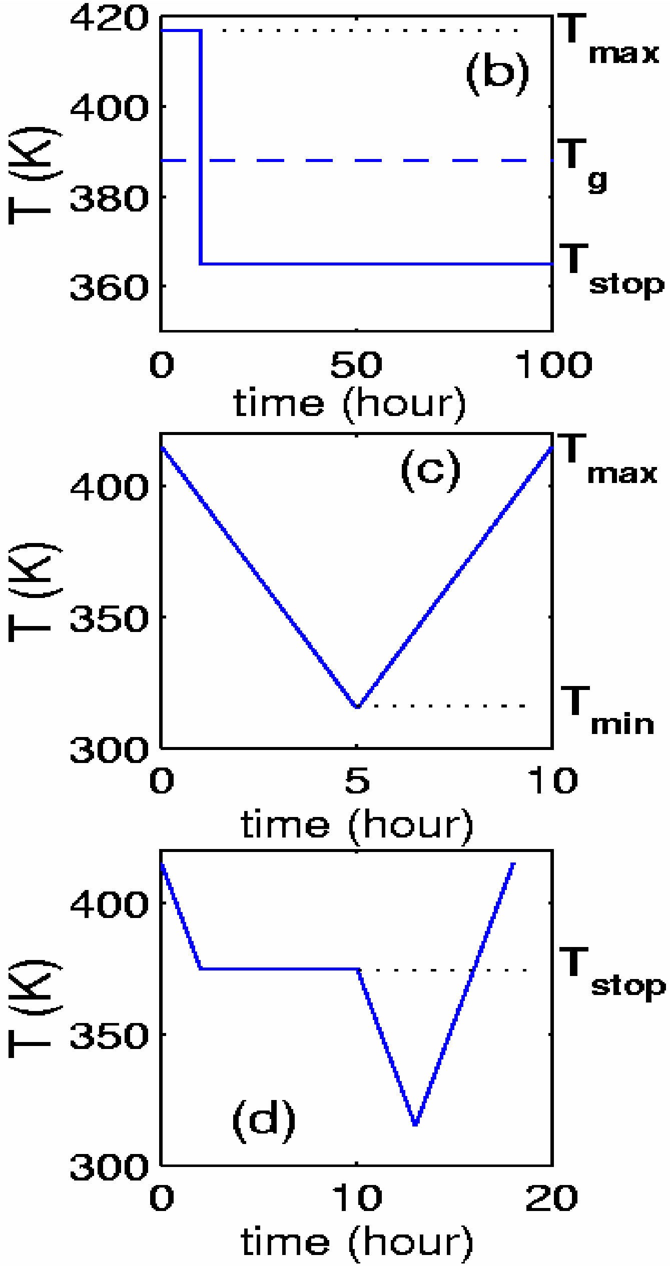
Aging and Memory effect in a polymer

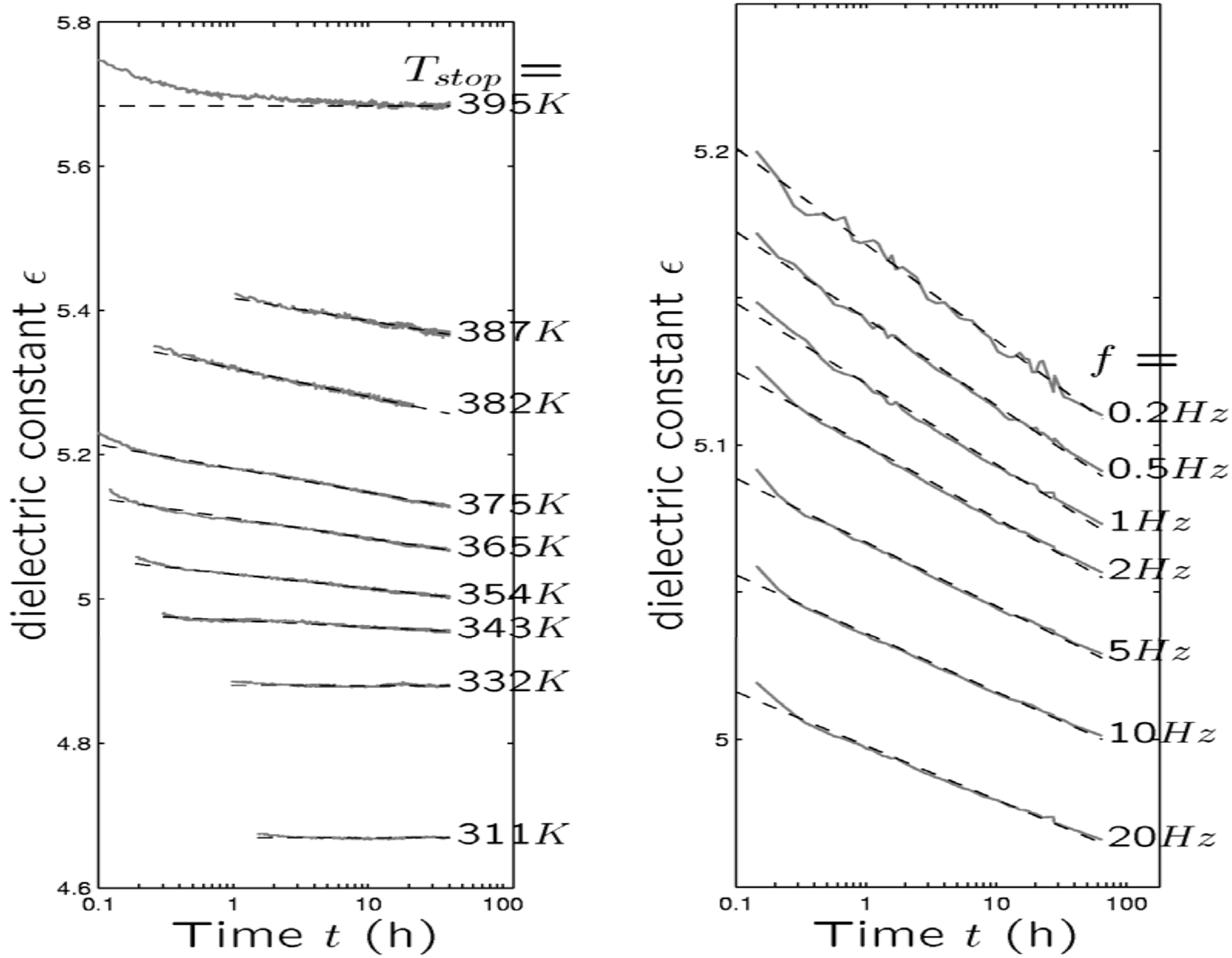
Experimental set-up



Typical thermal cycles applied to the sample



Aging of PMMA (T_g= 388K)



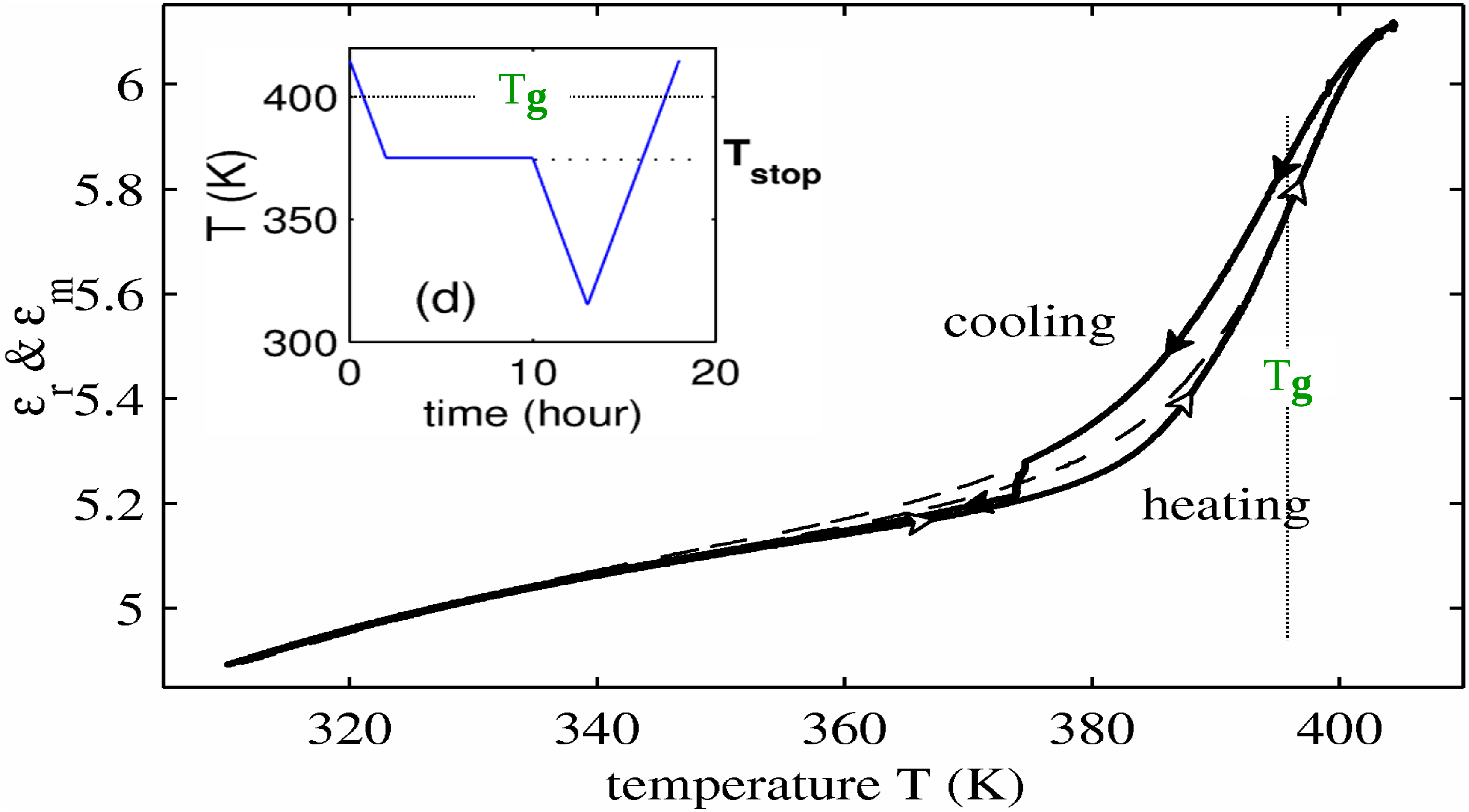
Dependence on t of ϵ after a quench.

(a) Aging measured at $f = 1Hz$ after a quench at various T_{stop}.

(b) Aging measured after a quench at $T_{stop} = 365K$ at various f.

Memory effect in PMMA

Evolution of ε at f=0.1Hz as a function of T

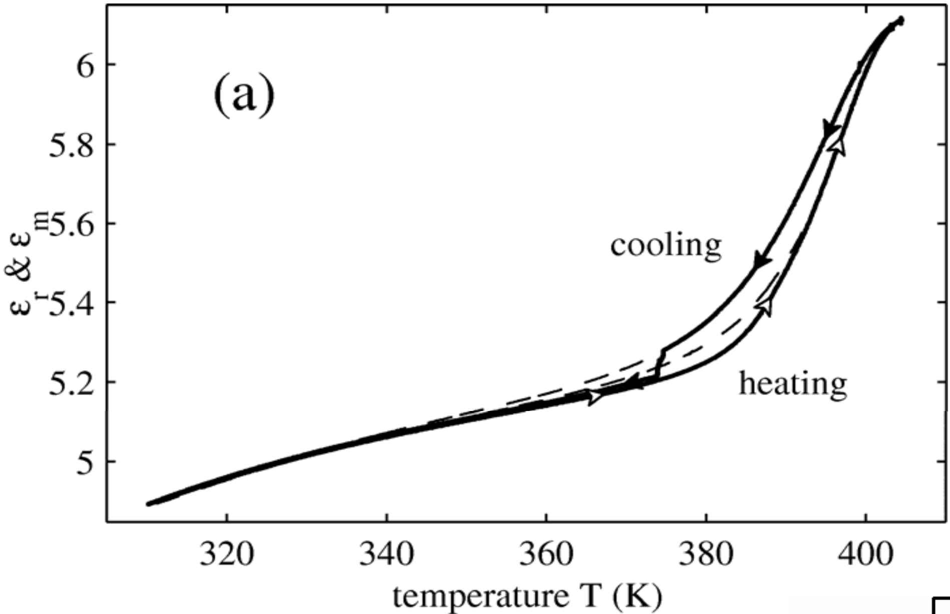


ϵ_r = dielectric constant measured with continuous ramp, - - - -

ϵ_m = dielectric c onstant measured with a cooling stop, ——

Memory effect in PMMA

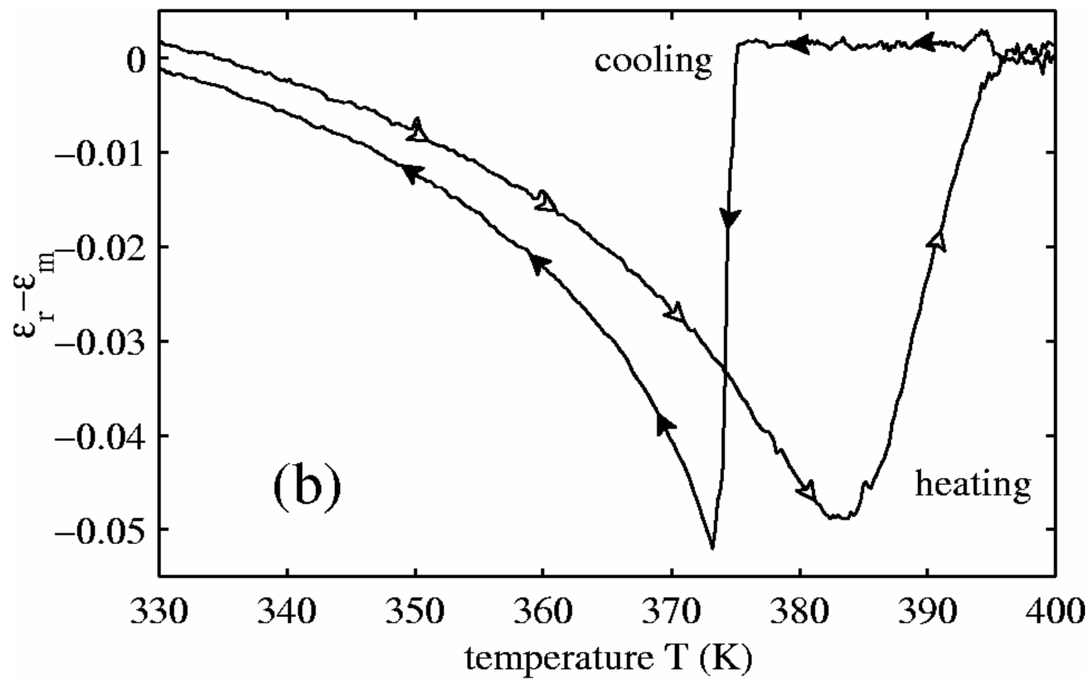
Evolution of ε at f=0.1Hz as a function of T



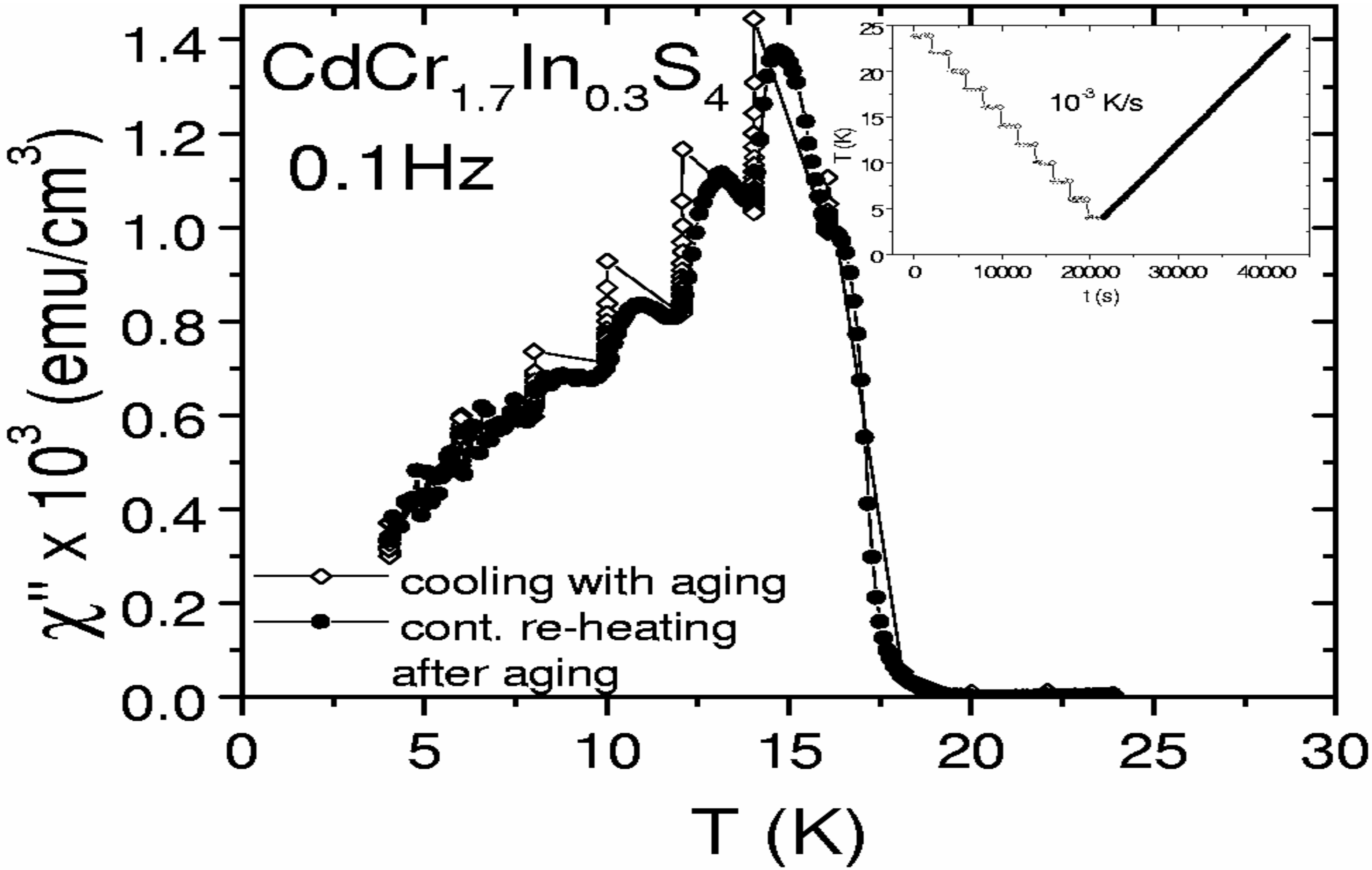
ϵ_r - - - - -

ϵ_m ———

$\epsilon_r - \epsilon_m$



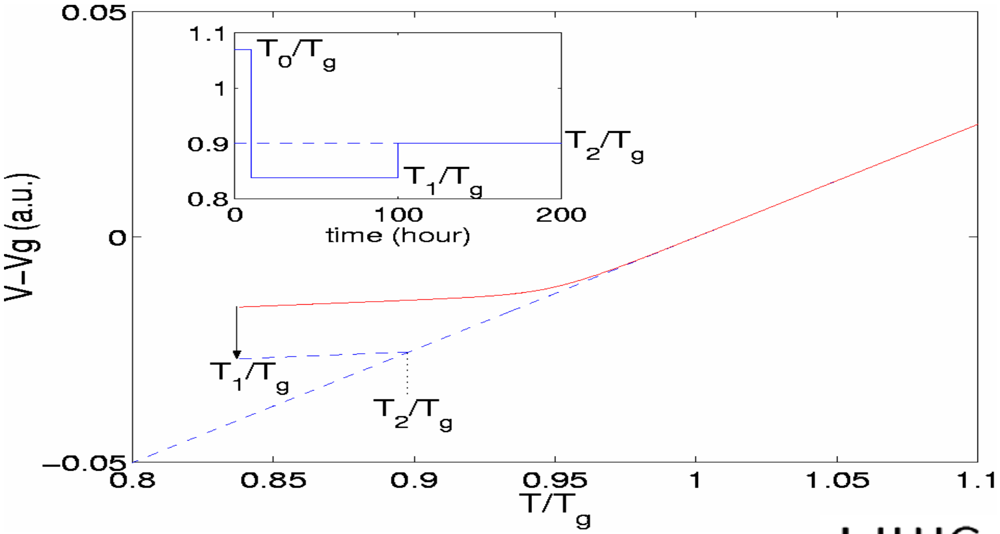
Memory effect in spin glasses



From:

V. Dupuis, E. Vincent, J.P. Bouchaud, J. Hammann, A.Ito, H. Aruga Katori, ***Aging, rejuvenation and memory effects in Ising and Heisenberg spin glasses***, Phys. Rev B 64 (17),174204,(2001). Also in cond-mat/0104399

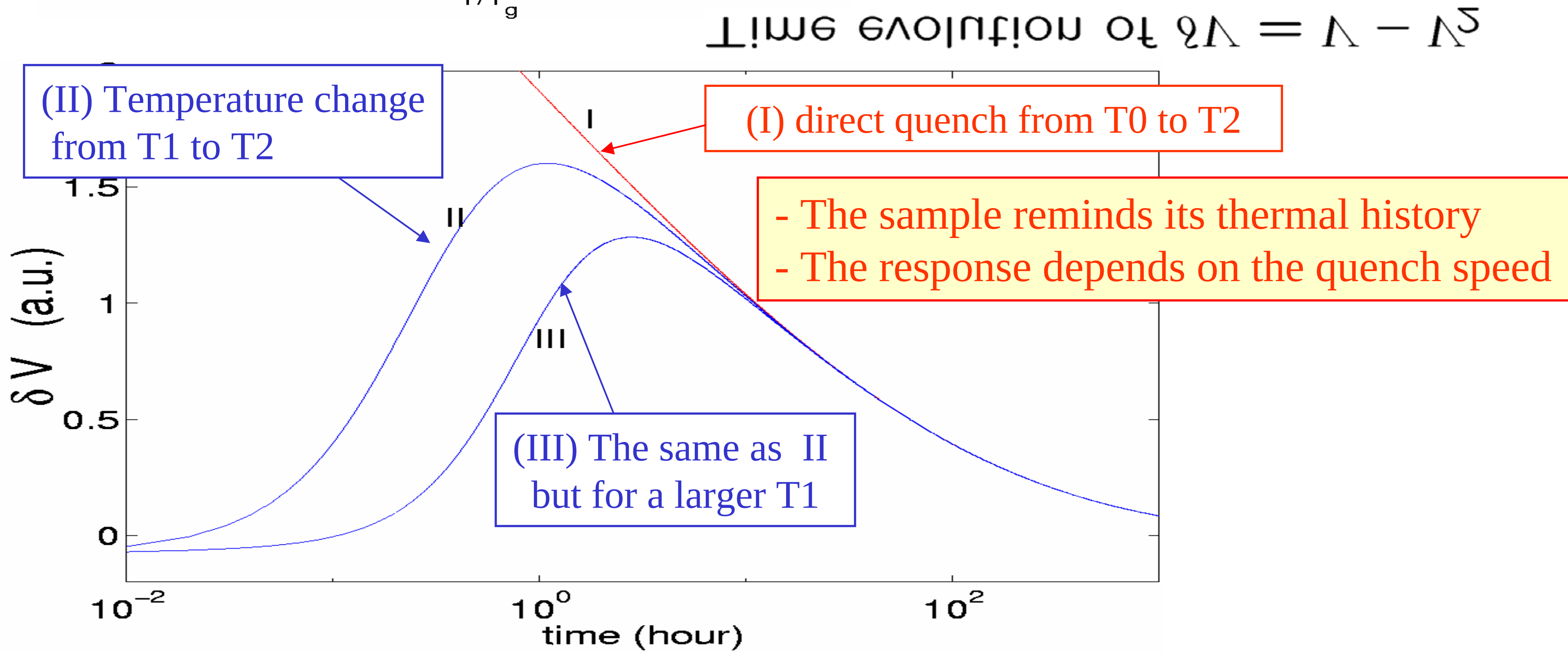
Kovacs Effect



Measure of the Volume

Fast quench

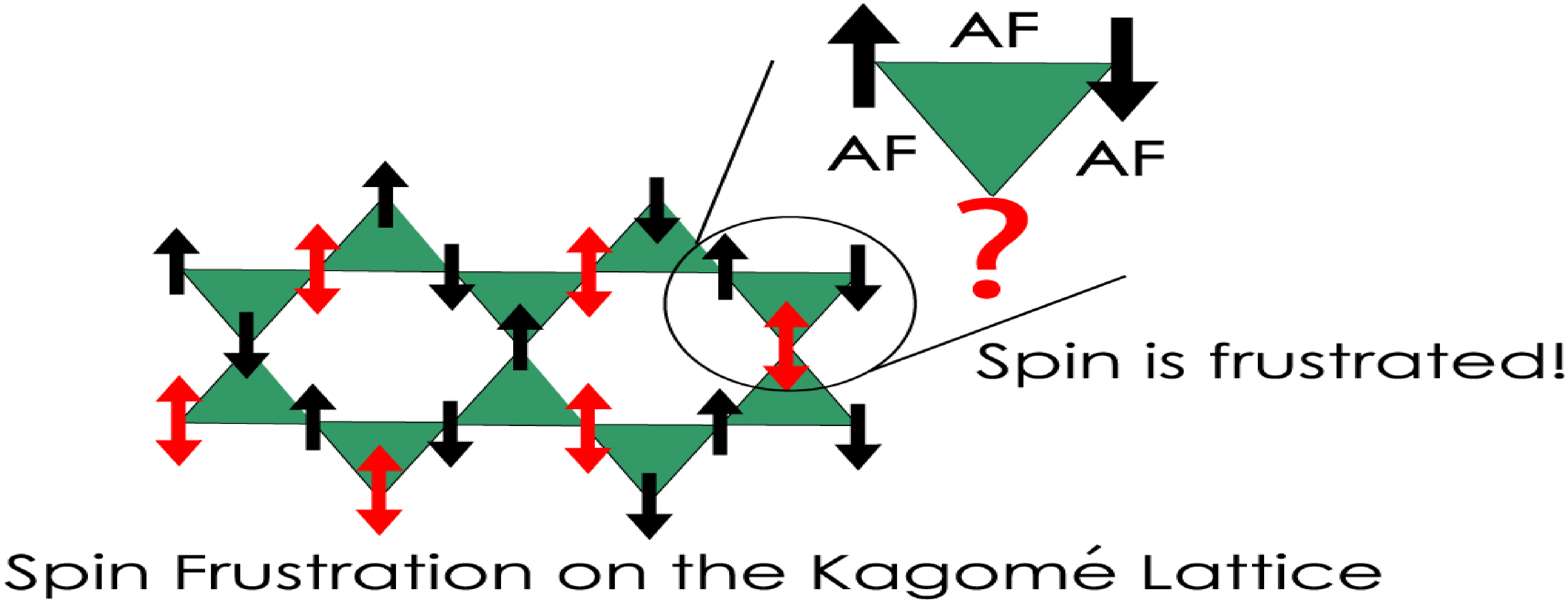
Slow ramp



What kind of models can be used ?

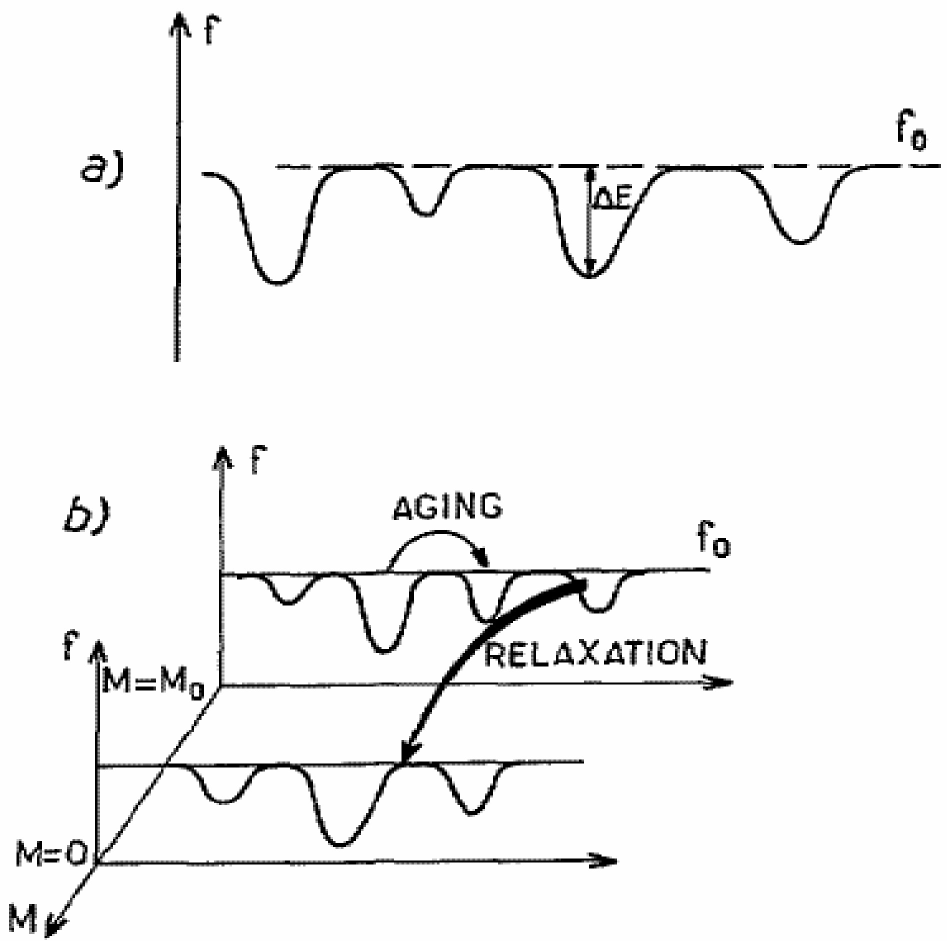
Important concept

Frustation



Energy landscape

Bouchaud trap model



Memory effects and trap model

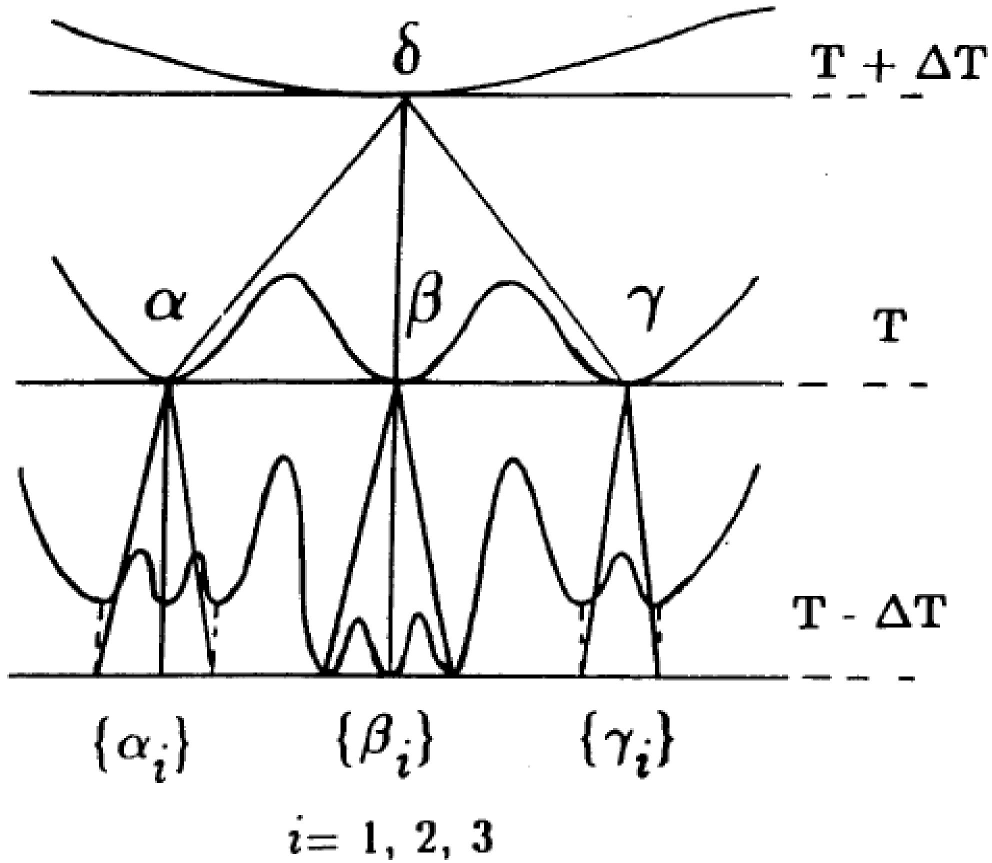


Fig. 6. Schematic picture of the hierarchical structure of the metastable states as a function of temperature.

Aging in glassy materials

Aging has been often characterized by studing the response functions of the systems

Smart experimental procedures, based

either on multiple cycles of cooling, heating and waiting times

or on the modulation of the applied external fields

have shown the existence of spectacular effects of aging in glassy materials, such as

rejuvenation and memory.

These studies have been extremely useful to fix several important constraints for the phenomenological models of aging.

Question: is the analysis of fluctuations useful ?

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FLUCTUACTION DISSIPATION THEOREM

in thermodynamic equilibrium

V and q are two conjugate variables

$$R(\omega) = \frac{\delta V(\omega)}{\delta q(\omega)}$$ is the response function

The thermal fluctuation spectrum $S(\omega) = <|V(\omega)|^2>$ is

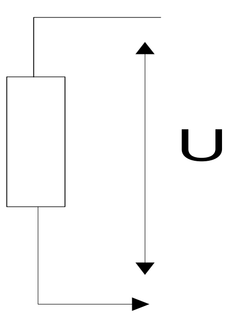
$$S(\omega) = \frac{4\,K\,T}{\omega}\; Im\{R(\omega)\}$$

Typical examples are :

(U,q)

Nyquist

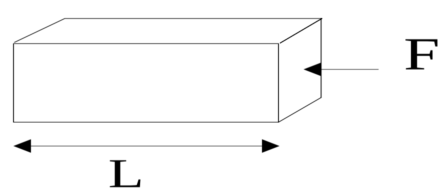
$$<|U^2(\omega)|> = 4\,K\,T\,Ro$$



(L,F)

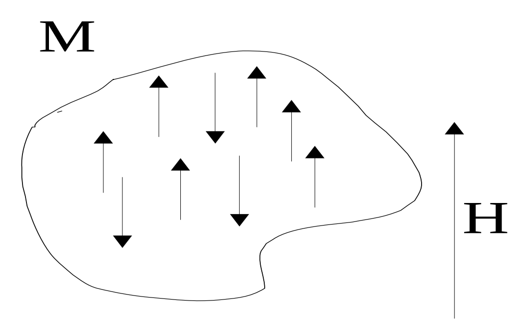
Density fluctuations

$$<|\delta L^2(\omega)|> \sim \frac{4\,K\,T}{\omega\; E''}$$



(M,h)

$$< M^2 > \sim KT\,\chi_m''$$



Fluctuation Dissipation Relation (FDR)

(Cugliandolo,Kurchan 1992.)

in a weakly out of equilibrium system

In a glass at $T < T_G$ the physical properties of the material depend on the aging time t_w after the temperature quench. Thus FDR takes the following form:

$$S(\omega, t_w) = \frac{4\ K_B\ T_{eff}(\omega, t_w)}{\omega}\ Im\{R_{Vq}(\omega, t_w)\}$$

FDR can be used to define an effective temperature of the system

$$T_{eff}(\omega, t_w) = \frac{S(\omega, t_w)\ \omega}{4\ K_B\ \ Im\{R_{Vq}(\omega, t_w)\}}$$

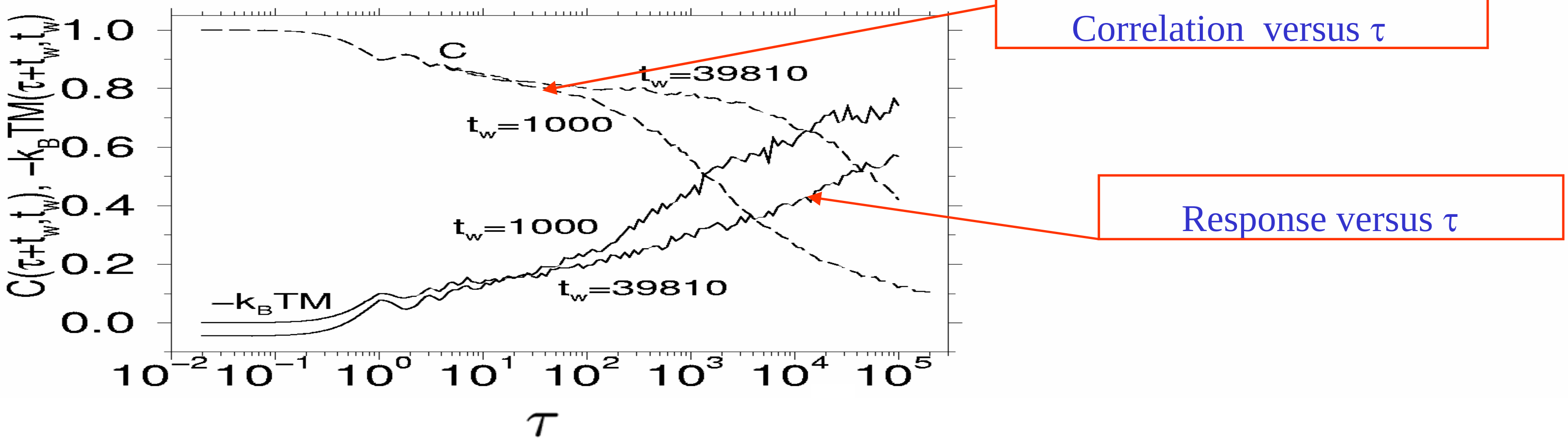
At equilibrium $T_{eff}(\omega, t_w) = T$

In terms of correlation function FDR takes the form

$$-C(t, t_w) + C(t_w, t_w) = K_B\ T_{eff}(t, t_w)\ R(t, t_w)$$

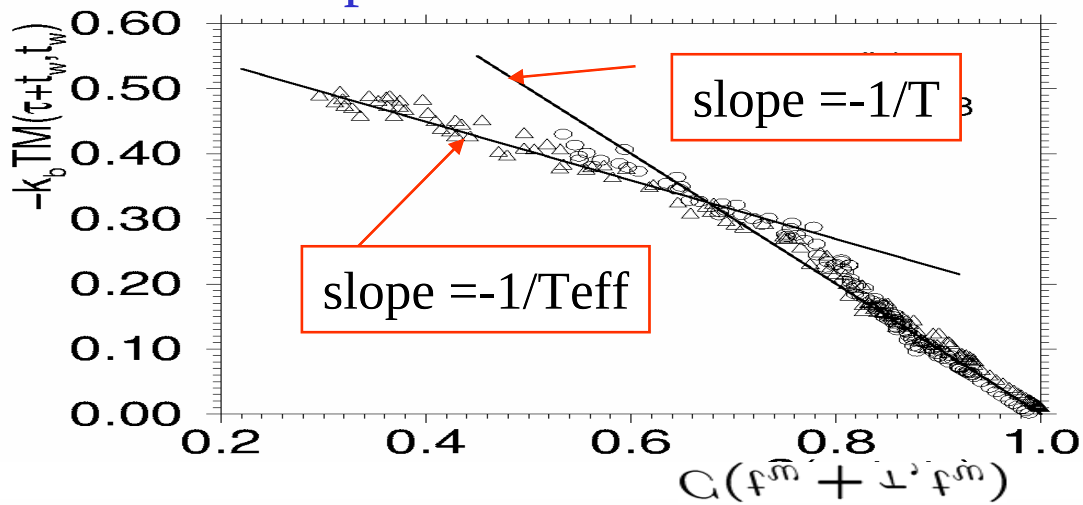
where $C(t, t_w)$ is the correlation function and $R(t, t_w)$ the integrated response

KOB , BARRAT, Fluctuation dissipation ratio in an aging Lennard-Jones glass, Europhys. Lett. 46, 637 (1999)



$$-C(t_w+\tau,t_w)+C(t_w,t_w) = K_B\,T_{eff}(t_w+\tau,t_w)\;M(t_w+\tau,t_w)$$

Response versus correlation



Experimental study of fluctuations

Why is interesting to study fluctuations and FDR in experiments?

I) The violation of FDT is model dependent.

II) Does it depend on the material ?

III) What is the statistics of the signal?

IV) Are fluctuations Gaussian or not ?

V) Is the effective temperature independent on the observables ?

VI) What are the properties of the Brownian motion of a particle inside a non equilibrium bath ?

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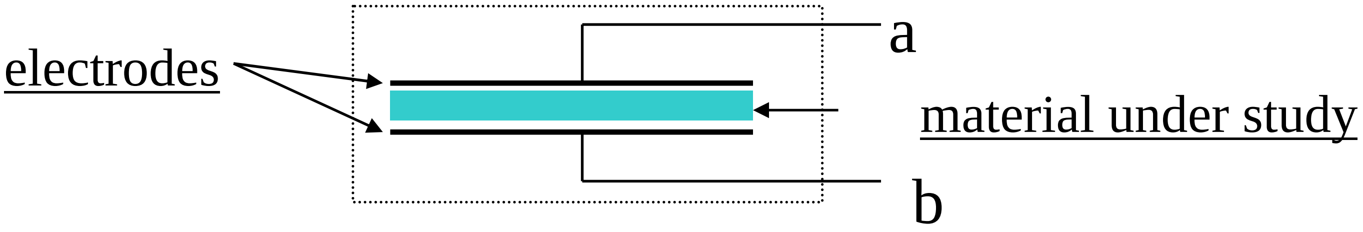
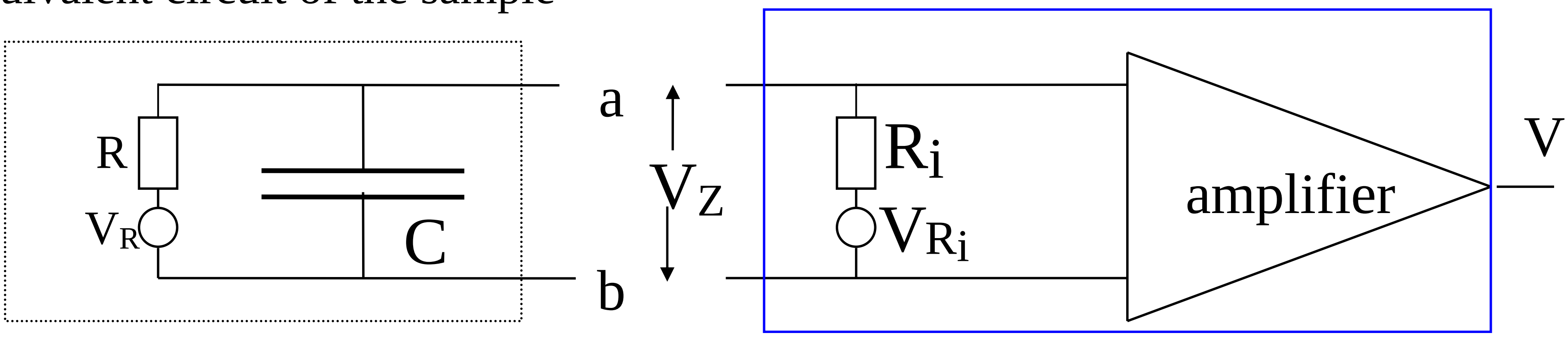
Dielectric measurements



Equivalent circuit of the sample



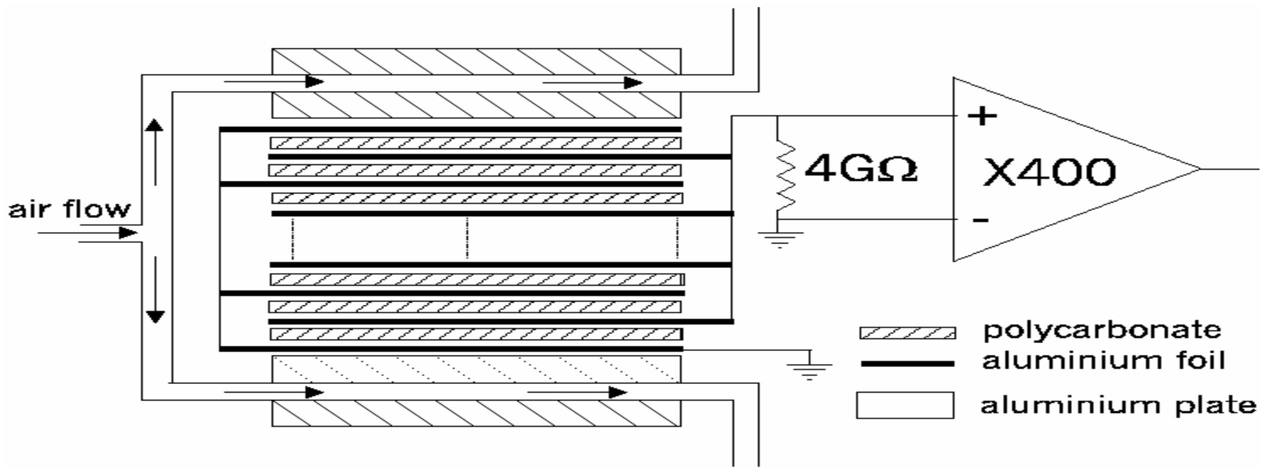
$V_R(\omega) = 4\ K_B\ T_{eff}\ R$,is the thermal noise voltage of R

The sample impedance is: $Z(t_w,\omega) = \dfrac{R}{(1 + i\omega\ R\ C)} = \dfrac{1}{i\omega(C'\ +\ i\ C'')}$

The corresponding noise spectrum S_z of V_Z is:

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

Dielectric Measurement on polycarbonate



Experimental set-up

Electrical features for noise measurements

Input voltage noise 5nV/ $Hz^{1/2}$ for f > 2Hz

Input current noise 1fA / $Hz^{1/2}$

Dielectric properties are measured by a precise current amplifier.

Temperature stability 0.1 %

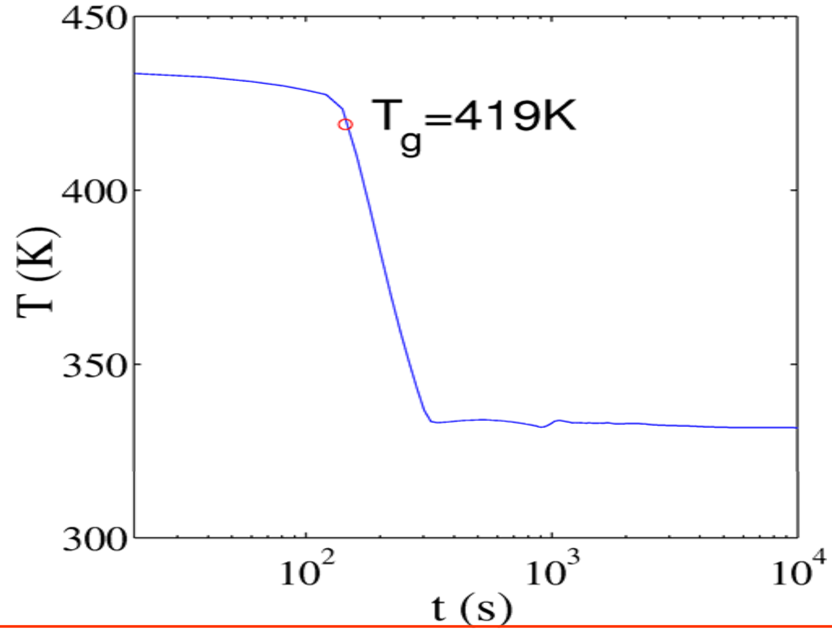
Max cooling rate -1K/s

Experimental procedure

a) The sample is heated at Ts=440K=1.05 Tg and quenched at a temperature T_f<Tg.

Typical temperature quench

Fast rate 1K/s
Slow rate 0.06 K/s



b) The aging time t_w is defined as the time spent at T< Tg

c) At T_f we measure FDR and the noise statistics.

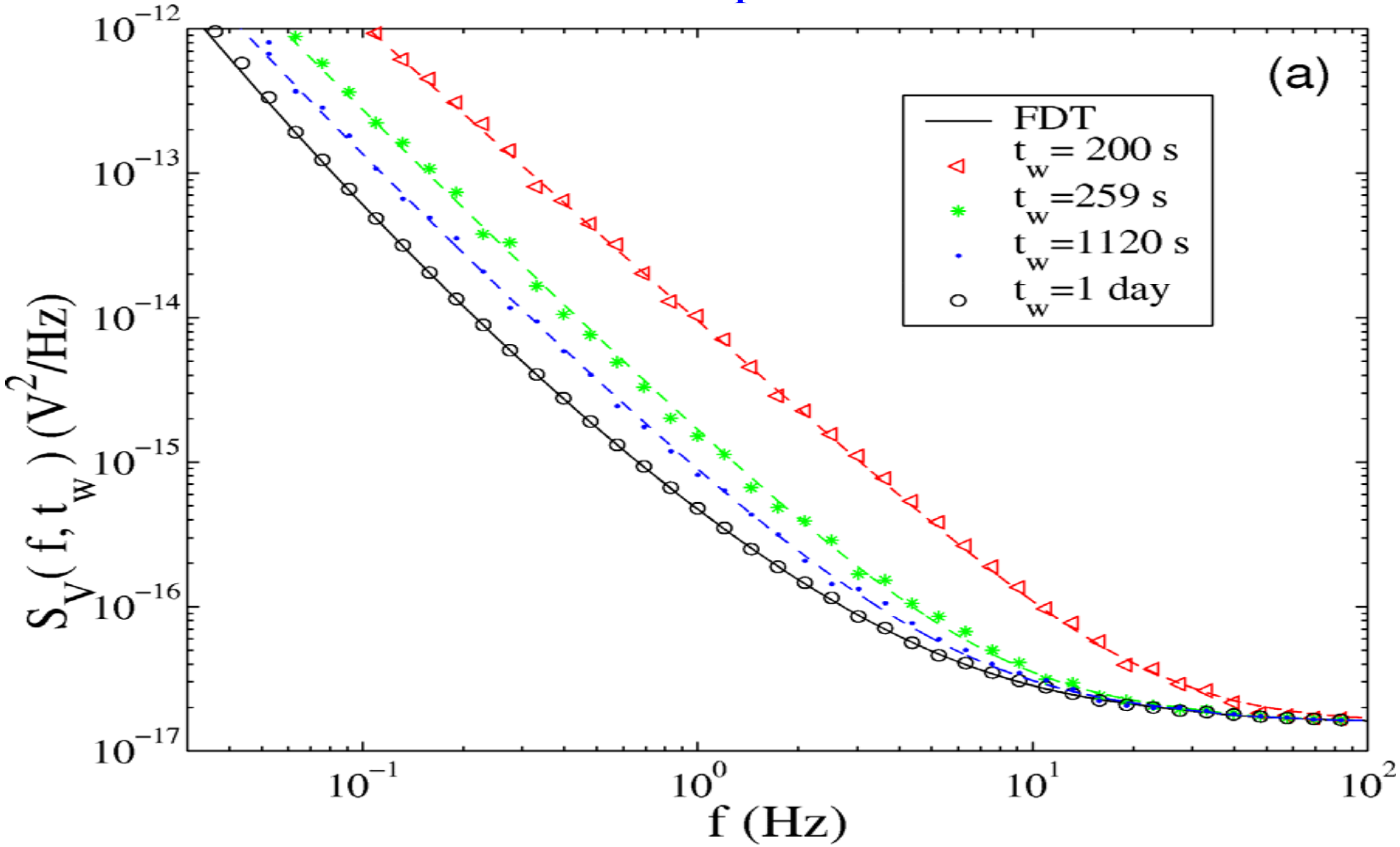
d) This experimental procedure is repeated several times for the same T_f

Measure at $T_f = 0.79T_g$

Fast quench at 1K/s

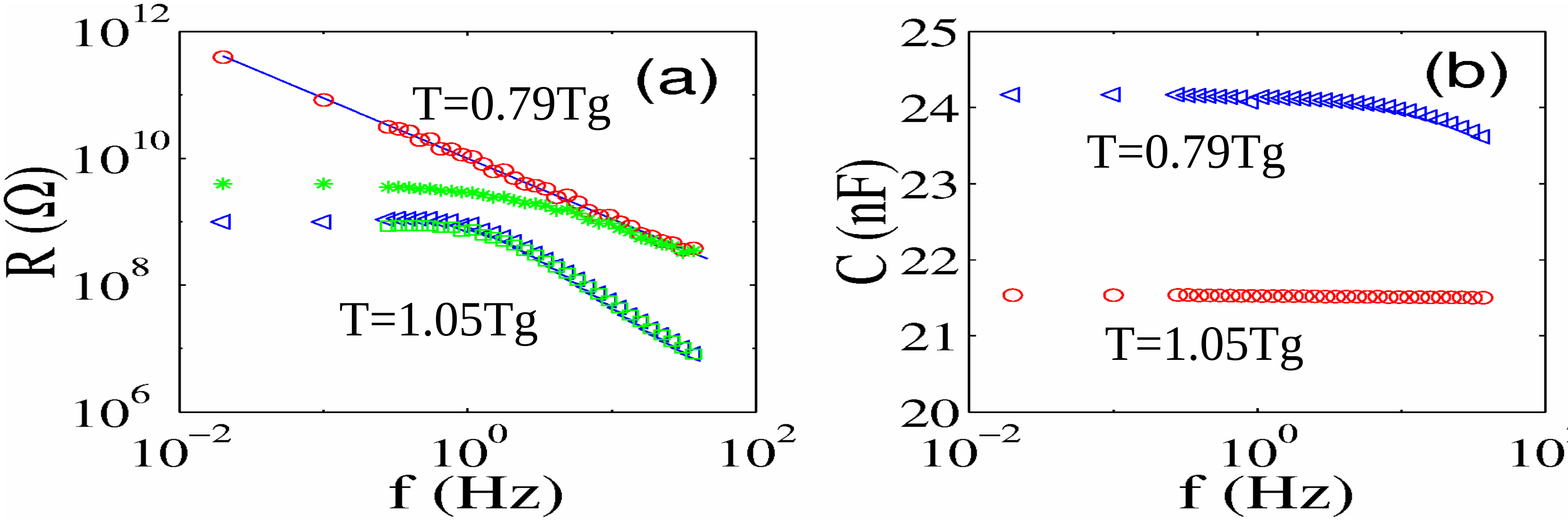
- Sample is heated at T_s=1.05
- Rapidly quenched (~2min) at T_f =0.79 Tg.
- The aging time t_w is defined as the time spent at T< Tg.

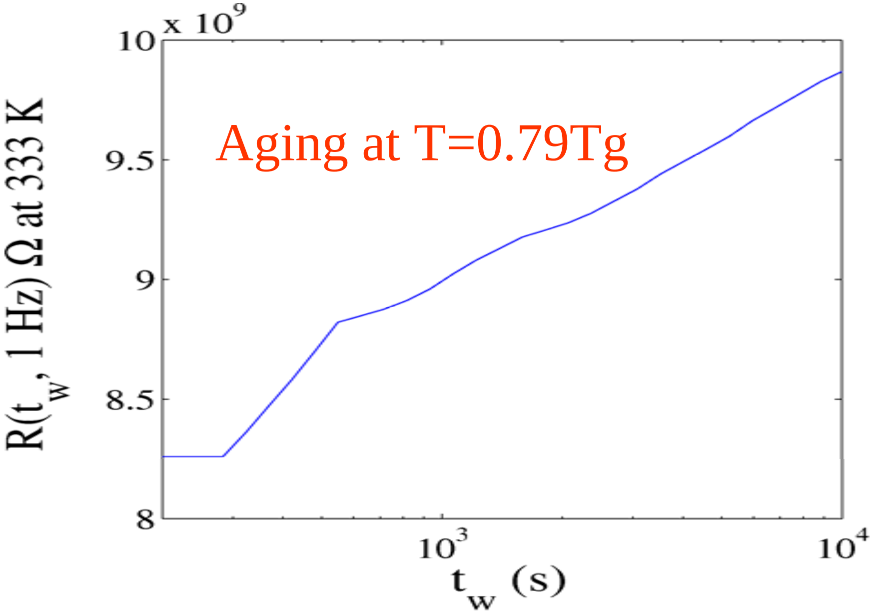
Noise spectra



Electrical response of the sample

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

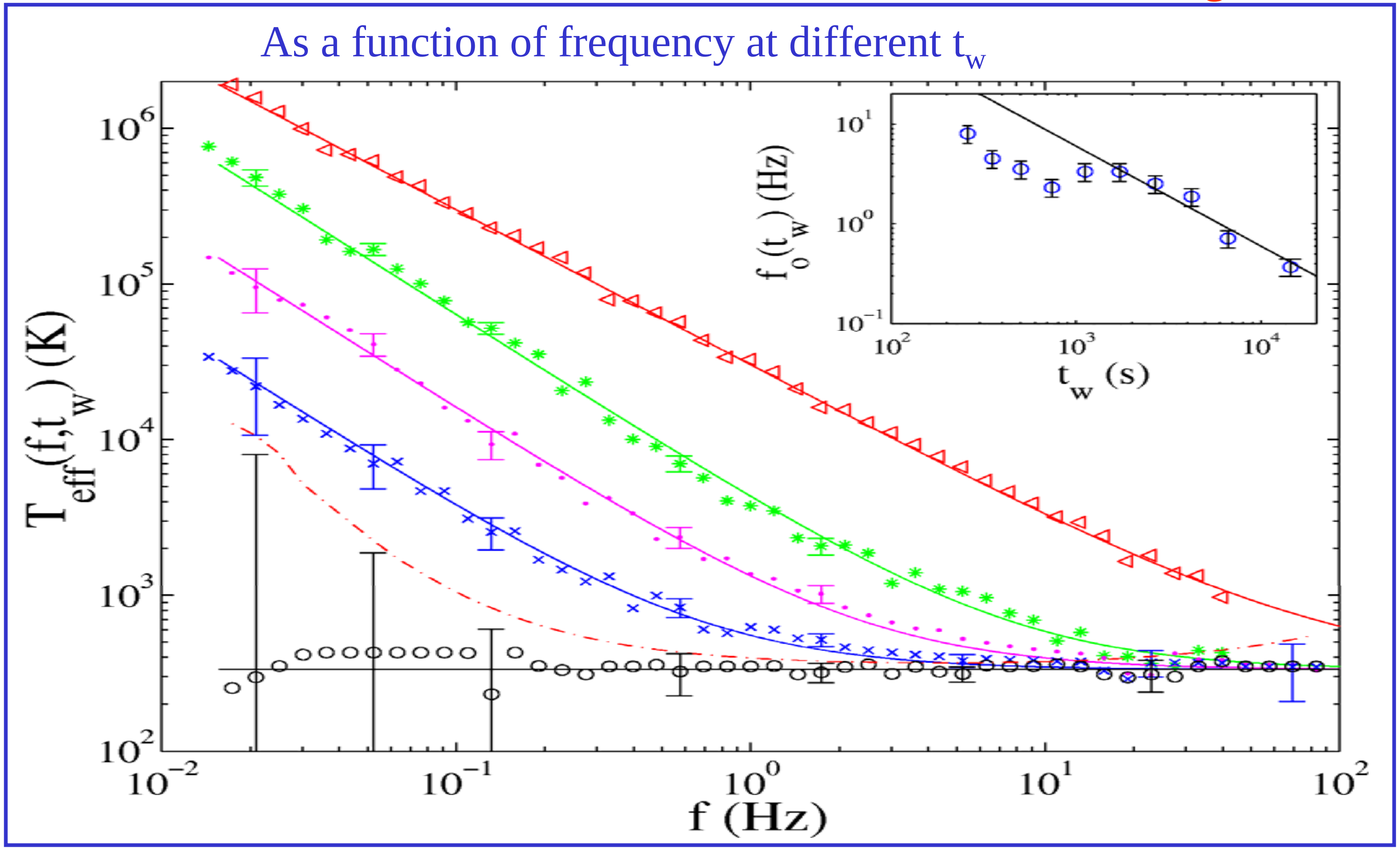




$$R = 10^{10}(1 \pm 0.05)\ f^{-1.05\pm0.01}\ \Omega$$

$$C = (21.5 \pm 0.05) nF$$

Effective temperature at $T_f = 0.79T_g$



A good fit of T_{eff} for $t_w > 200s$ is

$$T_{eff}(f,t_w) = T_f \; [\; 1 \; + \; (\frac{f}{f_o(t_w)})^{-1.1} \;]$$

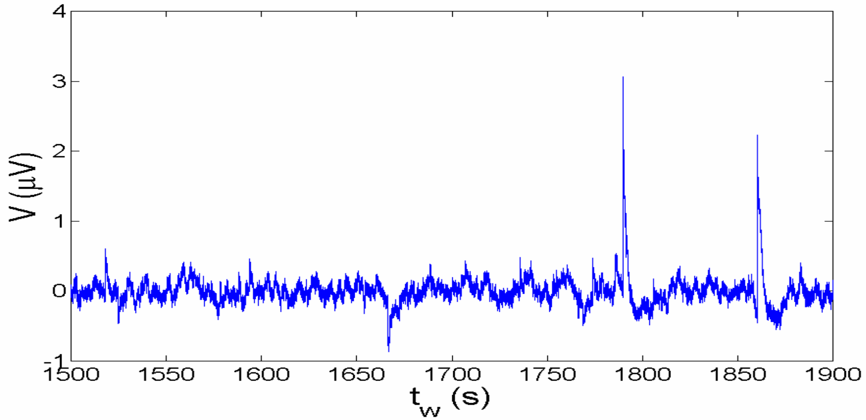
at $t_w < 2000$, $f_o(t_w)$ is not a simple power law of t_w.

$T_{eff}(f,t_w)$ are self similar

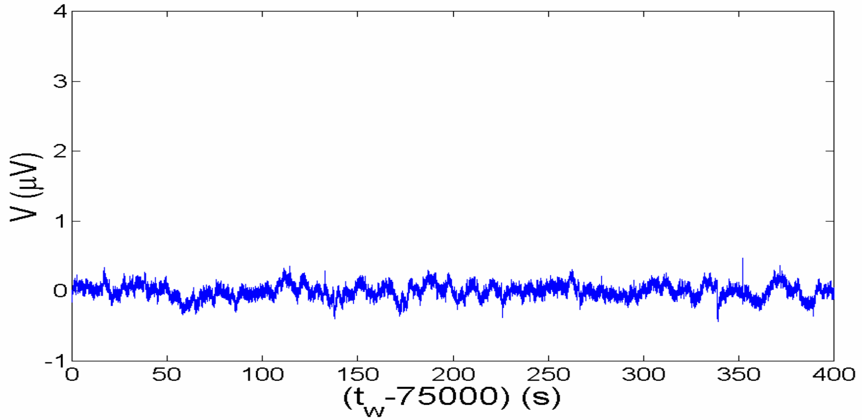
Polycarbonate polarisation noise

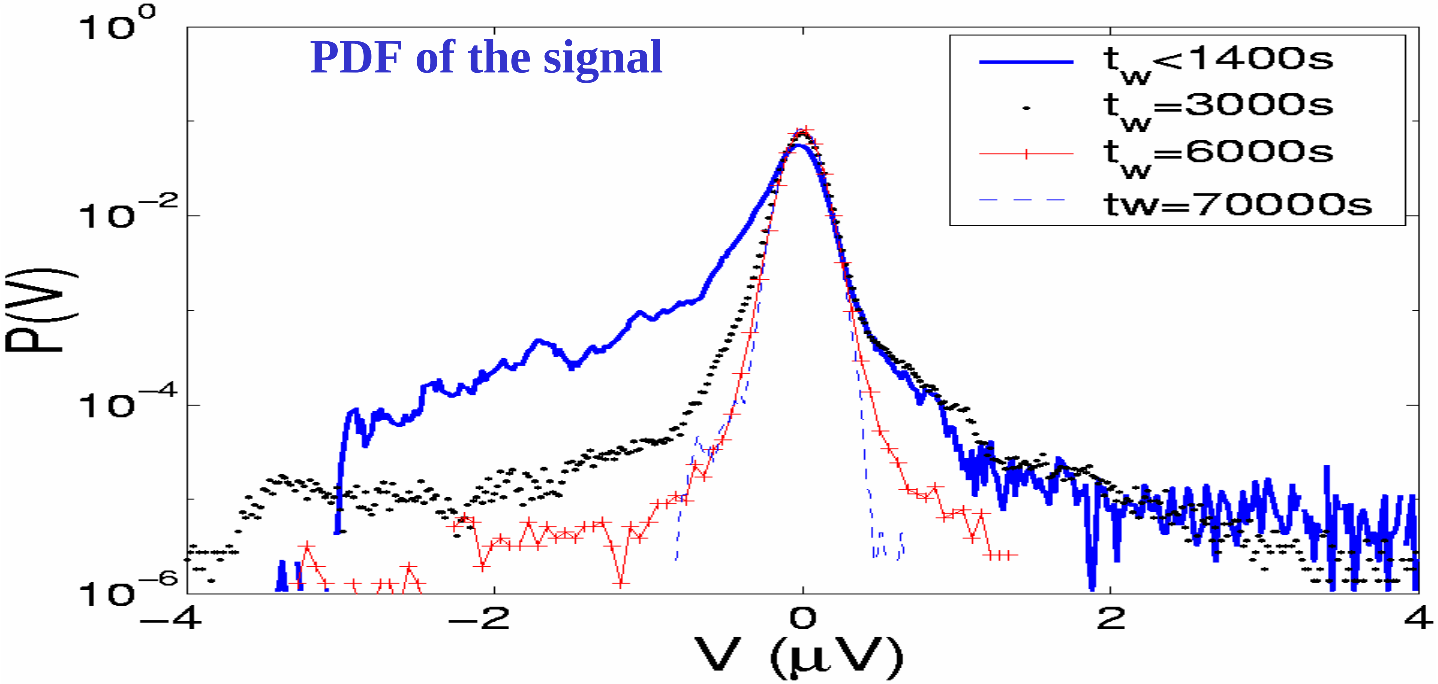
Noise signals as a function of time at $T_f = 0.79 T_g$

1500 s after the quench



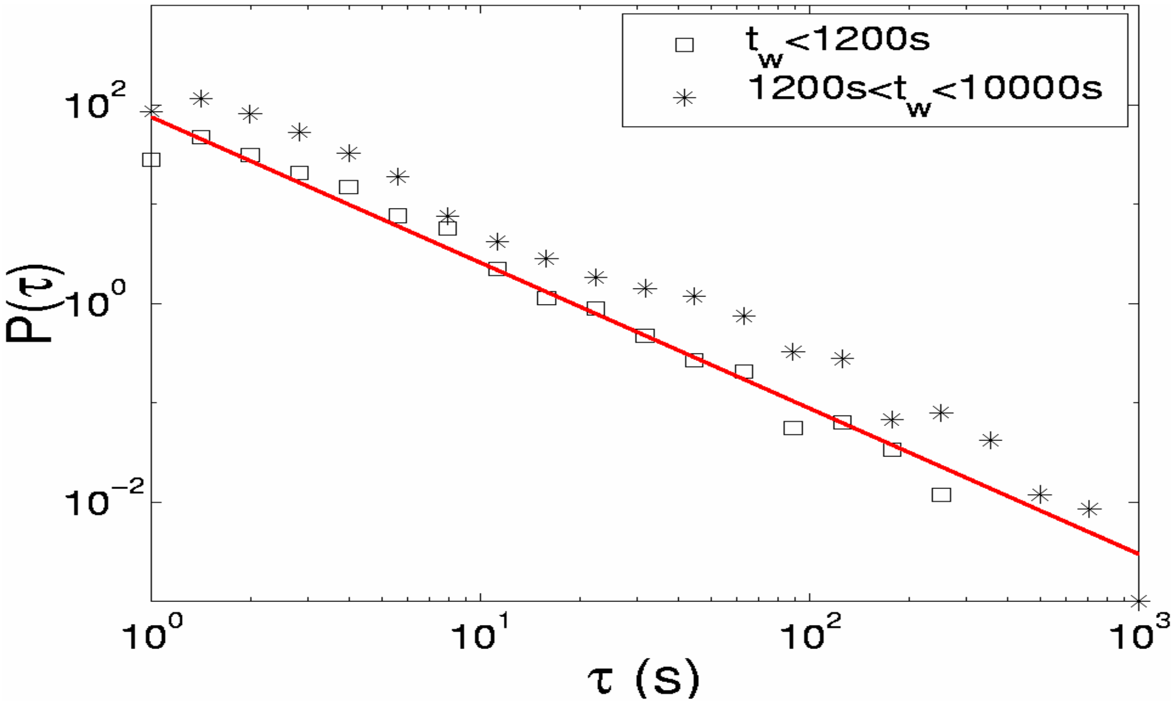
75000 s after the quench





When FDT is violated the fluctuations are not gaussian

PDF of the time τ between two pulses



$$P(\tau) \propto \tau^{-1.46}$$

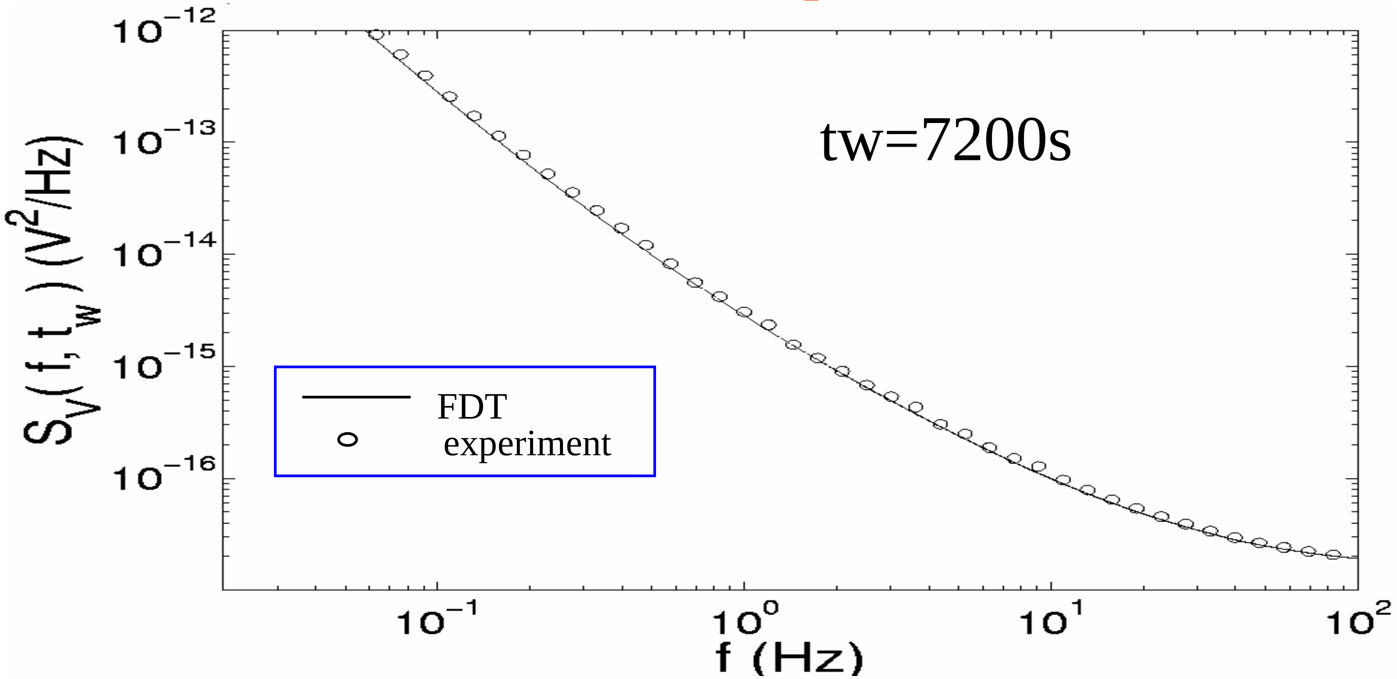
at $T/T_g = 0.79$

For the trap model of aging

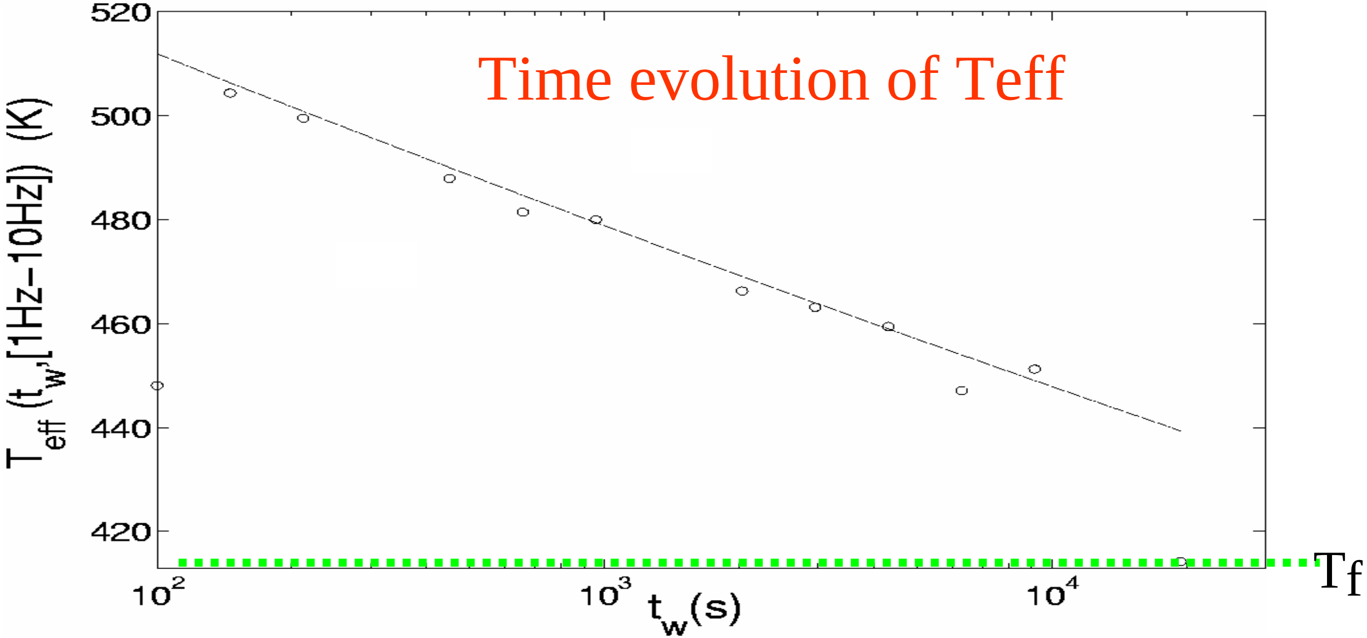
$$P(\tau) = \frac{\mu\ \tau_o^{\mu}}{\tau^{1+\mu}}$$

where $\mu = \frac{T}{T_g}$ and τ_o is a characteristic time scale

Measure at $T_f = 0.98 T_g$, slow quench

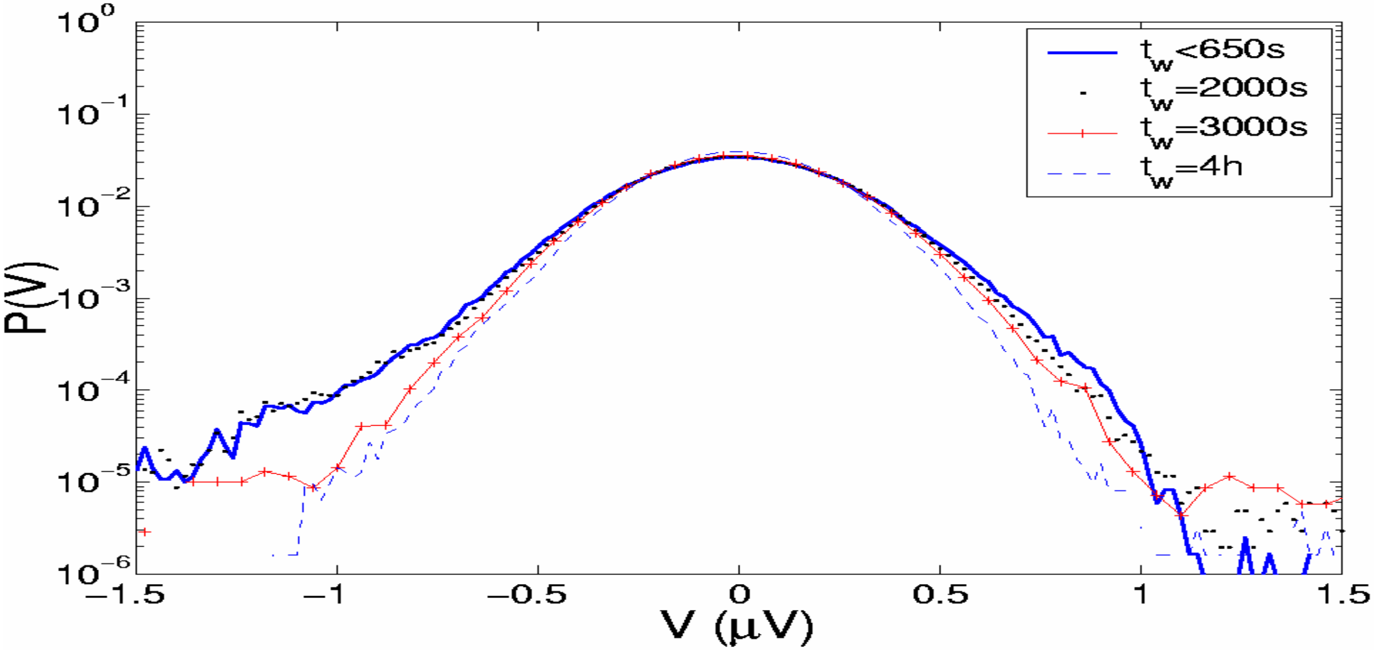


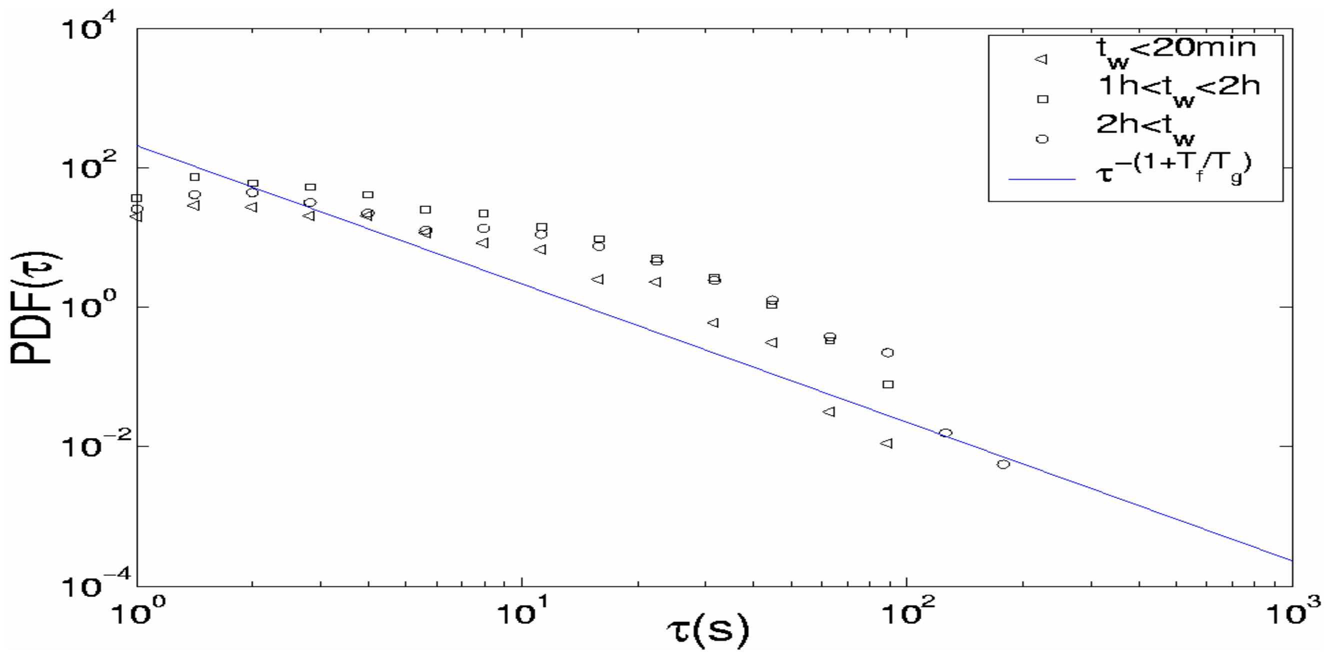
Noise spectra



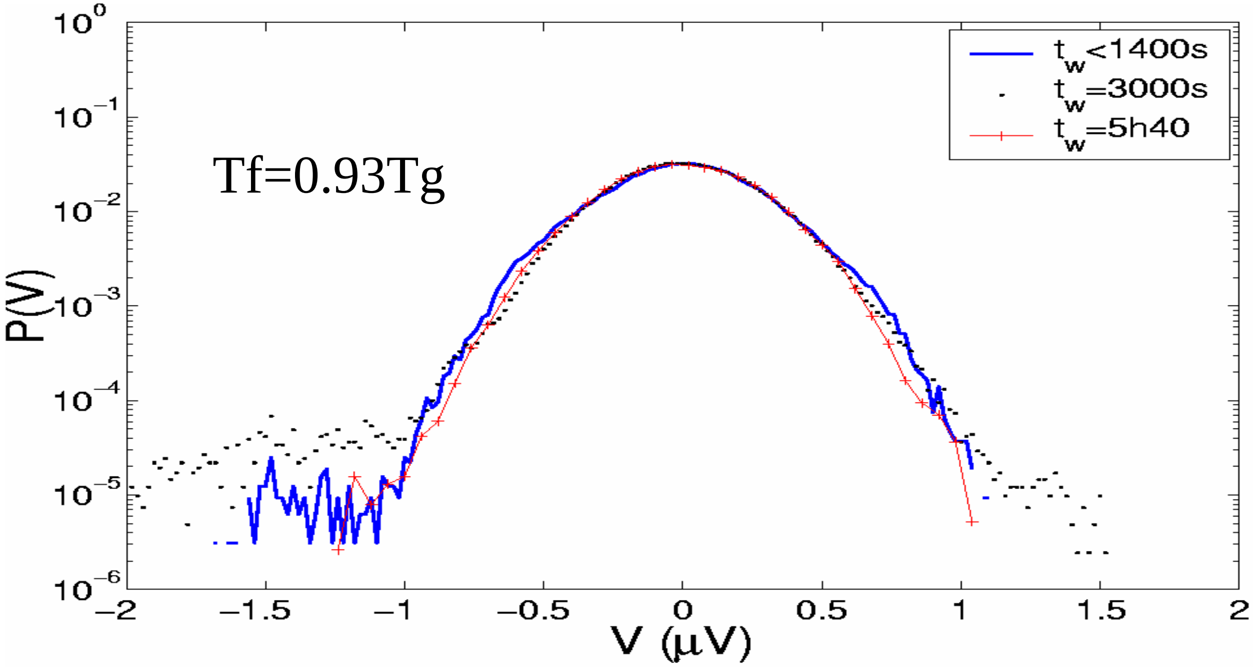
PDF after a slow quench

$T_f = 0.98\ T_g$

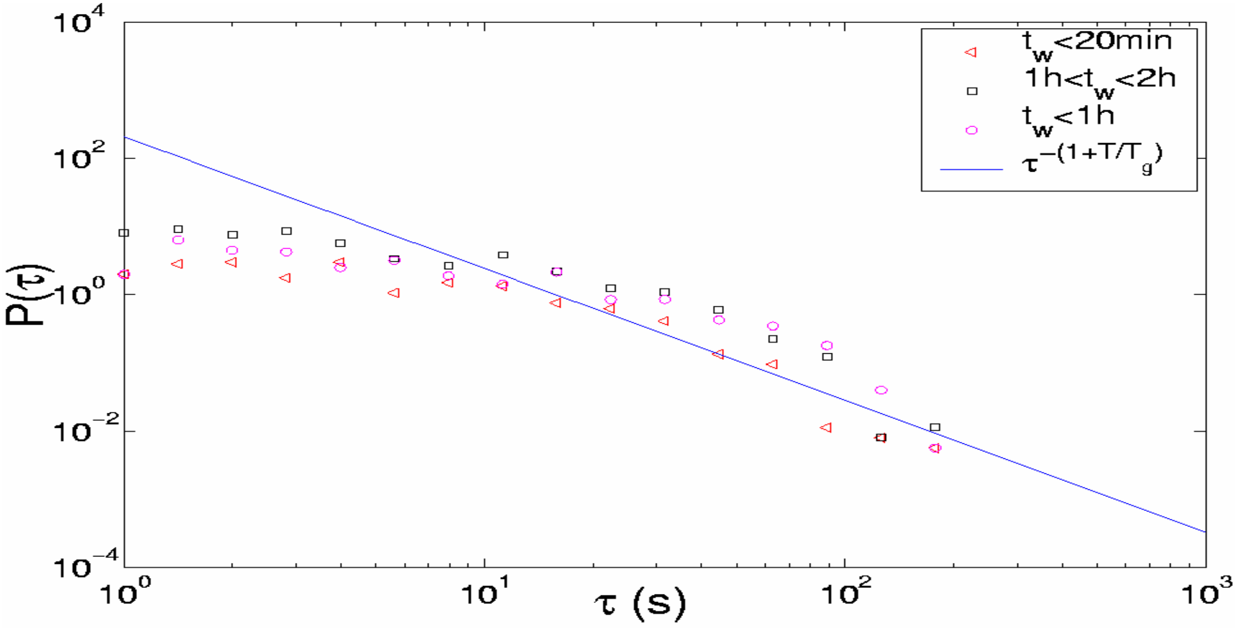


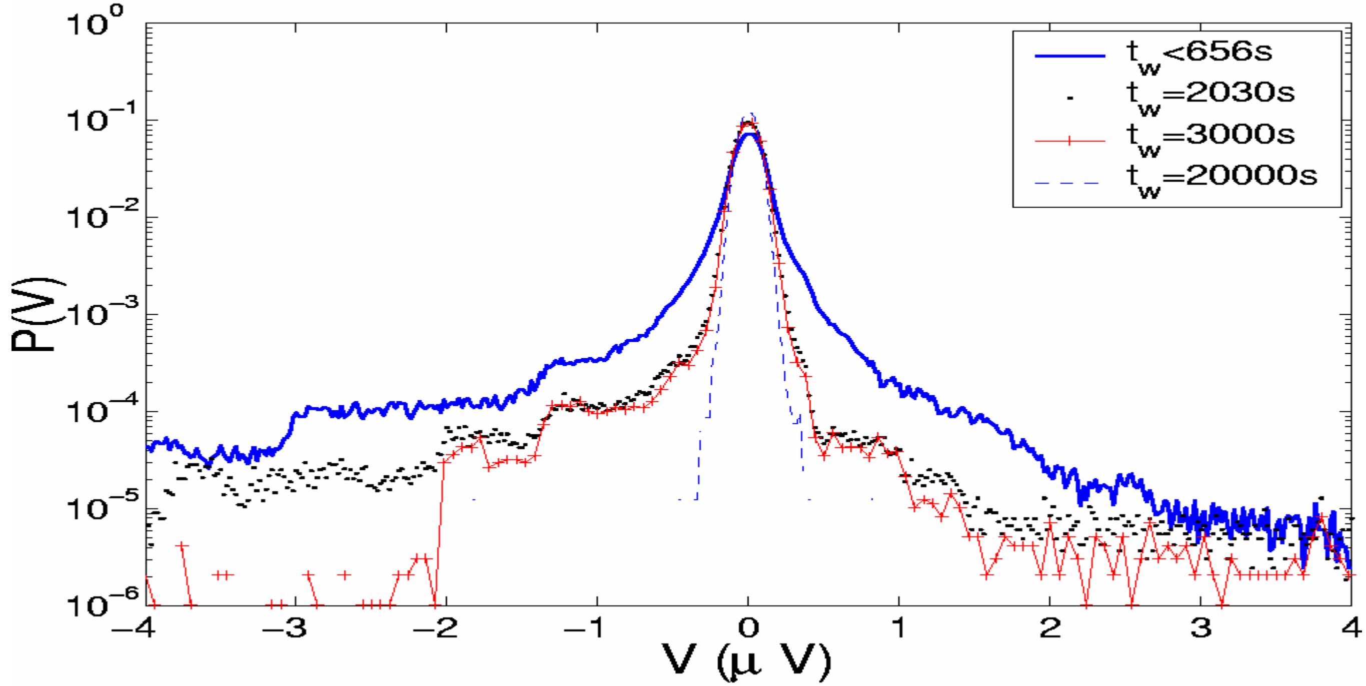


Measure at $T_f = 0.93T_g$



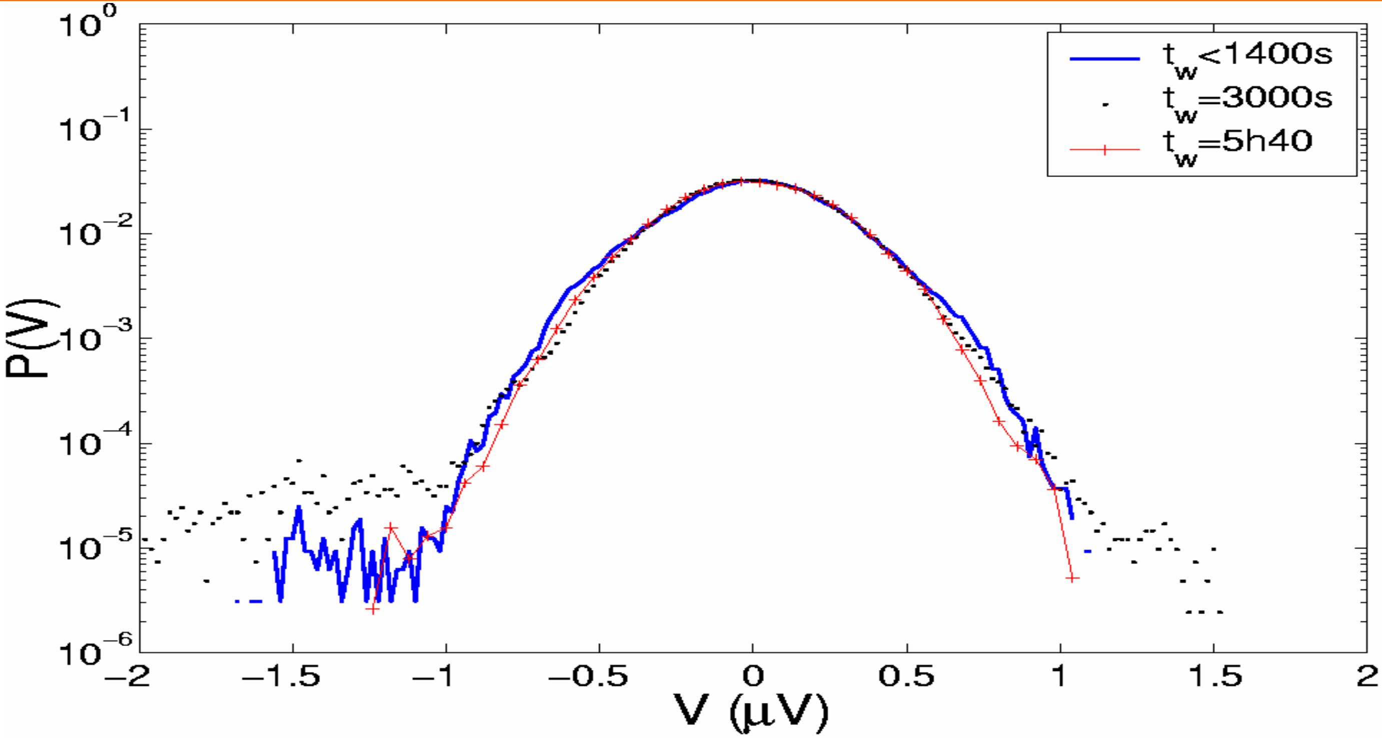
Slow quench at 0.06K/s





PDF at $T_f = 0.93T_g$

fast quench



PDF at $T_f = 0.93T_g$

slow quench

Summary of the results

- Dielectric measurements in a polymer show a violation of the FDT.
- The effective temperature (after a very fast quench) is huge at small t_w
- The amplitude and the persistence time of the violation are decreasing functions of frequency.
- The maximum frequency where the violation is observed scales as $1/t_w$
- The strong violation is produced by a very intermittent dynamics.
- The statistics of the signal is highly non Gaussian
- The statistics of the time between two peaks is similar to the one assumed by the trap model
- The intermittency depends on the quenching rate

Such a behavior is also observed in dielectric noise of a colloidal glass

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Other systems presenting intermittency

Local measurements of polymer dielectric properties using an AFM.

E. Vidal Russel, N. E. Israeloff, Nature 408, 695 (2000).

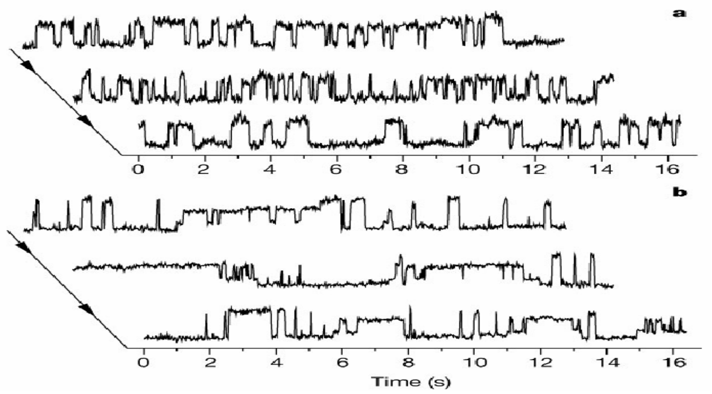


Figure 4. Time series of polarization. Two 50 s series showing random telegraph switching (RTS) noise. **a**, At 299 K, the rate of switching between two levels appears modulated. **b**, An example of a four-state switching at 300K is shown.

Velocity fluctuations of a particle in a colloidal gel present non Gaussian statistics and are intermittent

Weeks et al. Phys.Rev.Lett.89,95704(2002)

Time Resolved Correlation in Diffusing Wave Spectroscopy has shown a strong intermittency in the slow relaxation dynamics of a colloidal gel

Cipelletti et al., J.of Phys.: Cond. Matt.

Interpretation of intermittency

- Huge T_{eff} have been observed in numerical simulation of domain growth systems.

A. Barrat PRE 57 (1998) 3629

- Intermittency could be an indication of an activated process in a complex landascape

For example:

- Trap model predicts non trivial violation of FDT associated to an intermittent dynamics.
- The system evolves in deeper and deeper valleys
- The dynamics is fundamentally intermittent because either nothing moves or there is a jump between two traps.

- Heat exchange process between an aging system and the thermal bath may be intermittent. (A. Crisanti, F. Ritort, cond-mat/0307554)

Time statistics

- The dependence on the quenching rate is probably related to the fact that: *'far from equilibrium the system explores regions of the potential energy landscape distinct from that explored in thermal equilibrium'*

S. Mossa, F. Sciortino, cond-mat/0305526

E.M. Bertin, J.-P. Bouchaud, J.-M. Drouffe, C.Godreche cond-mat/0306089

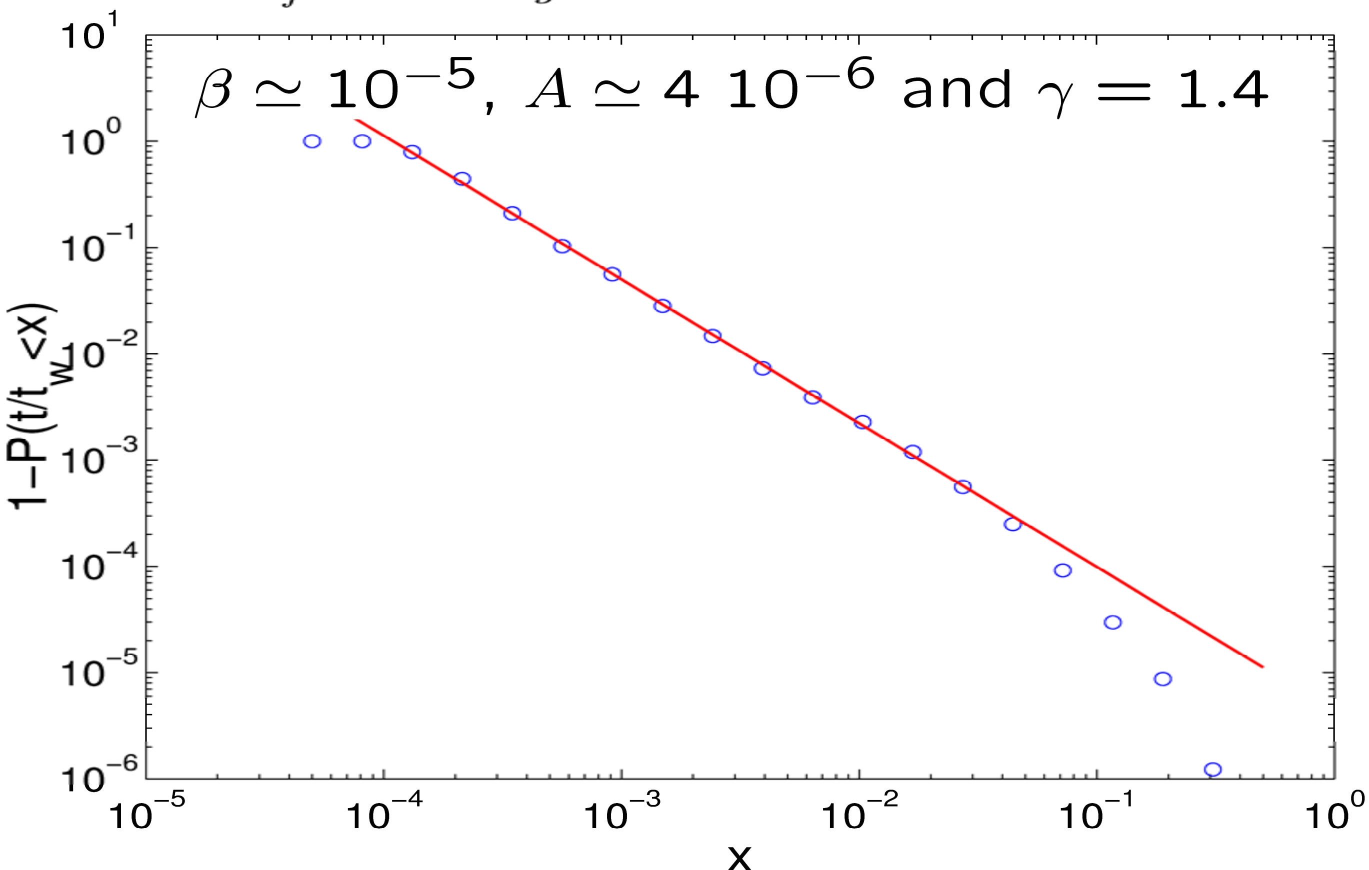
Comparisons between different models.

Statistics of $\frac{\tau}{t_w}$

$$P(\frac{\tau}{t_w} < X) = 1 - A\ (\beta + X)^{-\gamma}$$

for the Sibani's model $A = \beta = 1$ and $\gamma = 2.3$ independently of T_f.

Experimental result at $T_f = 0.79 T_g$



Time distributions

Experimental results:

- The PDF of the time between events is a power law:

$$\Psi(\tau, t_w) \propto \tau^{-\mu(t_w)}$$

Trap model of ref. : J.P.Bouchaud, J.Phys.,2, 1705,(1992).

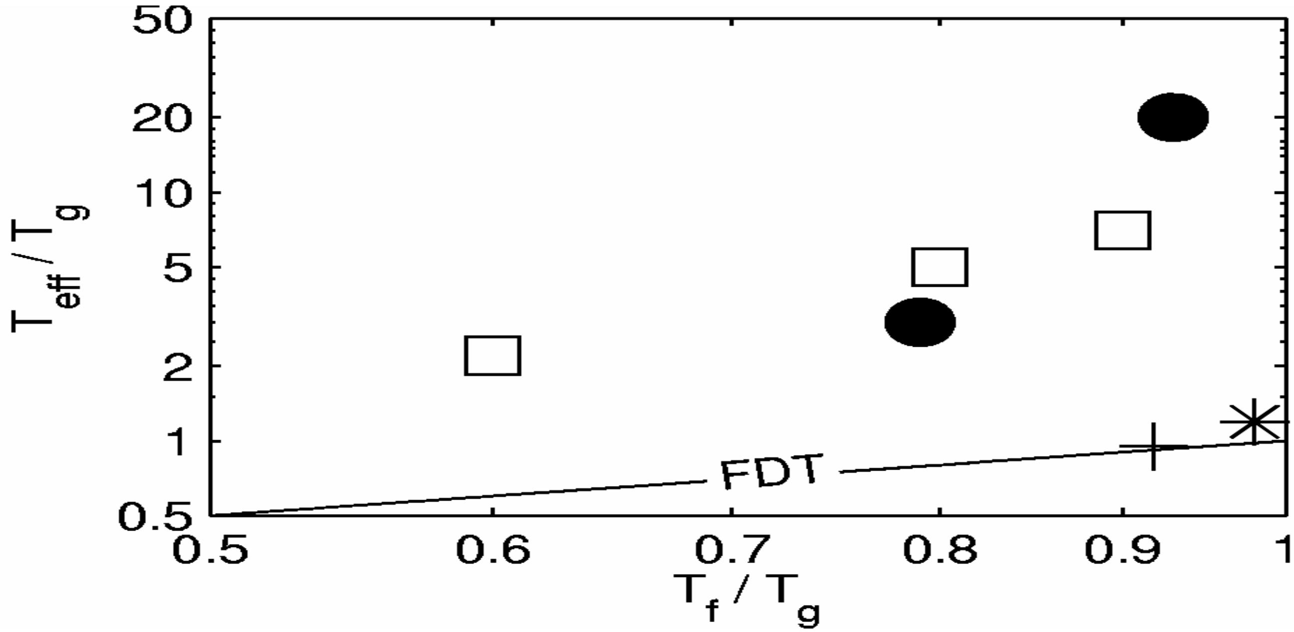
- The probability of finding $\frac{\tau}{t} < X$ is compatible with

$$P(\frac{\tau}{t} < X) = 1 - A\ (\beta + X)^{-\gamma}$$

- The probability of finding small τ decreases with t_w

Trap model of ref.: P. Sibani, J. Dell, Europhys. Lett. 64, 8, (2003)

T_{eff} in other experiments



$\frac{T_{eff}}{T_g}$ as a function of $\frac{T_f}{T_g}$ in different experiments

Normalized cooling rate: $$Q = \frac{\partial T}{\partial t}\frac{1}{T_g}$$

(□) spin glass ($q = q_{min}$, fast quench $Q = 0.5\ min^{-1}$

(•) polycarbonate ($f = 7Hz$, fast quench $Q = 0.12\ min^{-1}$)

(∗) polycarbonate ($f = 7Hz$, slow quench, $Q = 0.009\ min^{-1}$)

(+) glycerol ($f = 7Hz$ slow quench, $Q = 0.012\ min^{-1}$)

Outline

1) Phenomenological introduction to glasses

2) Aging, memory effects and history dependence

3) Thermal fluctuations and the Fluctuation Dissipation Relations during aging

4) The electrical thermal noise of two materials:
   a) a polymer after a quench
   b) a colloidal glass during the sol-gel transition.

Question:

Have the fluctuations of different observables,the same behaviour ?

6) The mechanical noise.

7) Conclusions

Conclusions

- Dielectric measurements show a non trivial violation of FDT during aging, in two very different materials
- The origing of the huge violation is a strongly intermittent dynamics.
- The intermittency depends on the quenching rate
- The dependence on the observables of the fluctuations is unclear. It is not the same for the two materials.
- High order statistics are certainly useful to understand the dynamics of these systems.
- Several models show a qualitative agreement with these observations.

L. Buisson, S. Ciliberto, Physica D 204, 1 (2005).
L. Buisson, S. Ciliberto and A. Garcimartin, Europhysics Letters , Vol.63, 603 (2003).
L. Bellon and S. Ciliberto, Physica D 168, 325 (2002)

Brownian motion in a colloidal glass out of equilibrium

Pierre Jop

Sergio Ciliberto

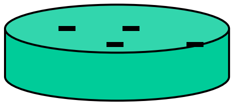
Artem Petrosyan

ENS Lyon

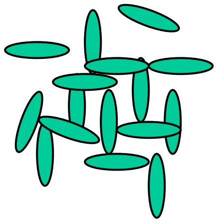
Laponite

Colloidal Suspension :

discs: d=25 nm, h=1 nm



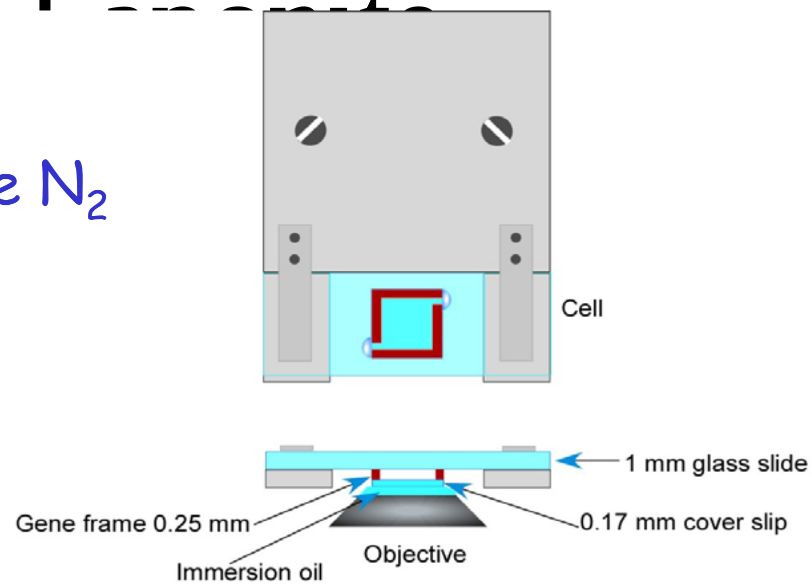
Fluid -> gel/colloidal glass



Fluid-Colloidal glass transition in a few hours

Debye length≈ 5 à 30 nm

Échantillons de



Préparés sous atmosphère contrôlée N_2

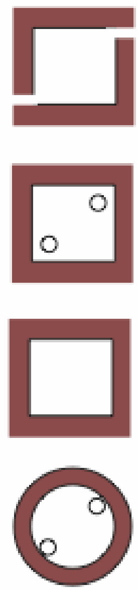
Φ_m = 1.2 à 3 wt% dans l'eau

pH = 10

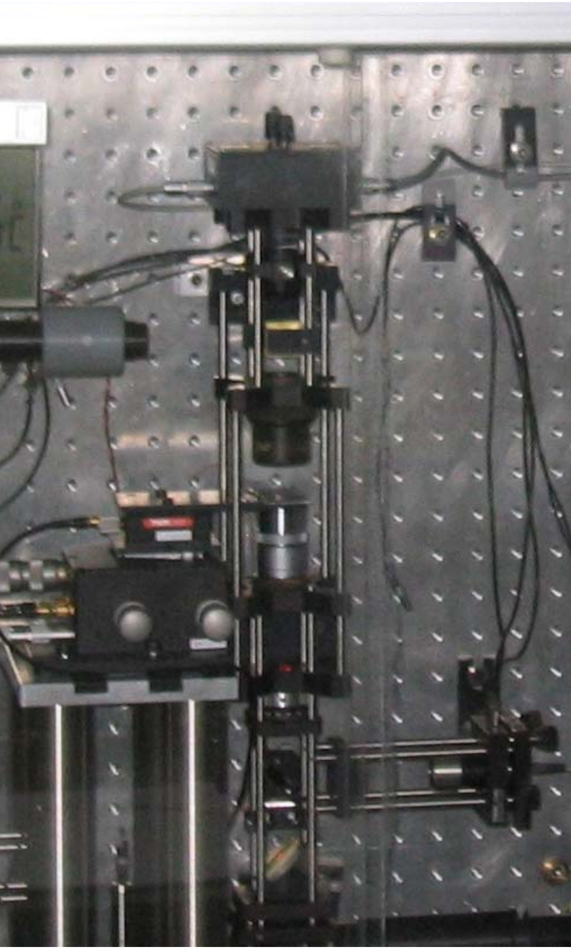
Force ionique : I de 10^{-4} à 5 10^{-3} M

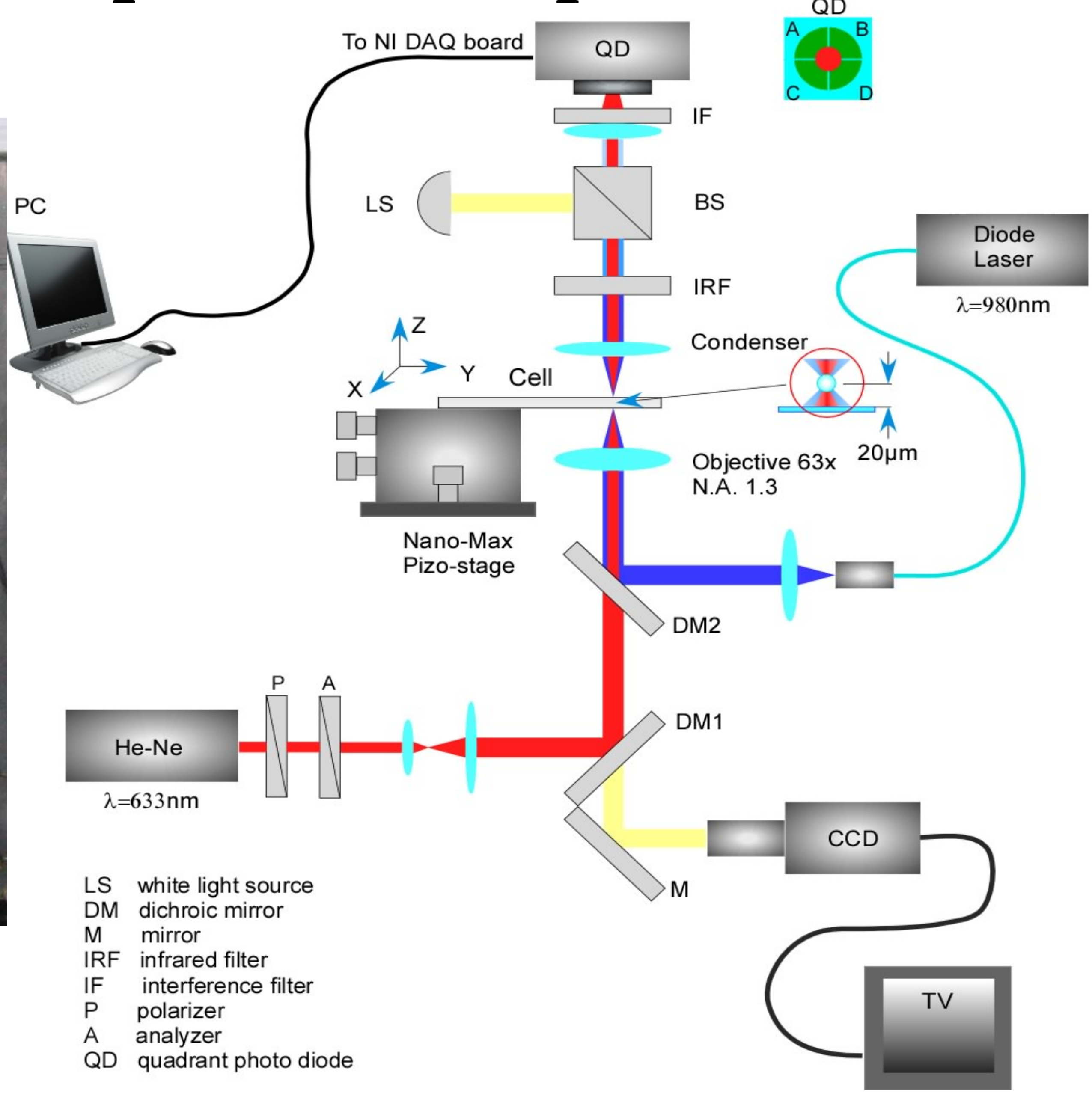
Filtrée (0.45 µm) pour briser les agrégats

Introduction de billes de verre dispersées par ultrasons



Optical set-up





Measure of the T_{eff}

Hp:
The global potential (colloid+laser) is harmonic

Equipartition holds out of equilibrium

$C_i = K_{Laponite} + K_i$ and $< \Delta x^2 >= \frac{K_B\ T}{C_i}$

K_i is the trap stiffness

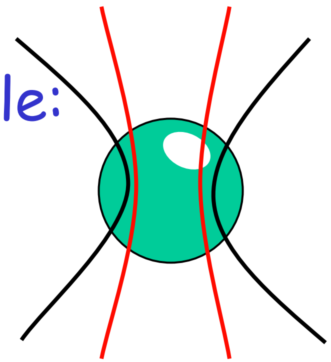
Measure of the fluctuations for 2 intensities

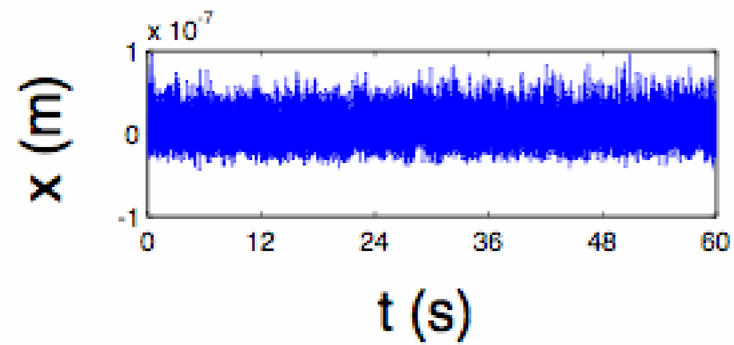
$$K_B\ T_{eff} = (K_2 - K_1)\frac{<\Delta x_1^2><\Delta x_2^2>}{(<\Delta x_1^2>-<\Delta x_2^2>)}$$

$$K_{Laponite} = \frac{(K_1<\Delta x_1^2>-K_2<\Delta x_2^2>)}{(<\Delta x_1^2>-<\Delta x_2^2>)}$$

Position signals

Brownien particle:
Glass sphere
d=1 μm



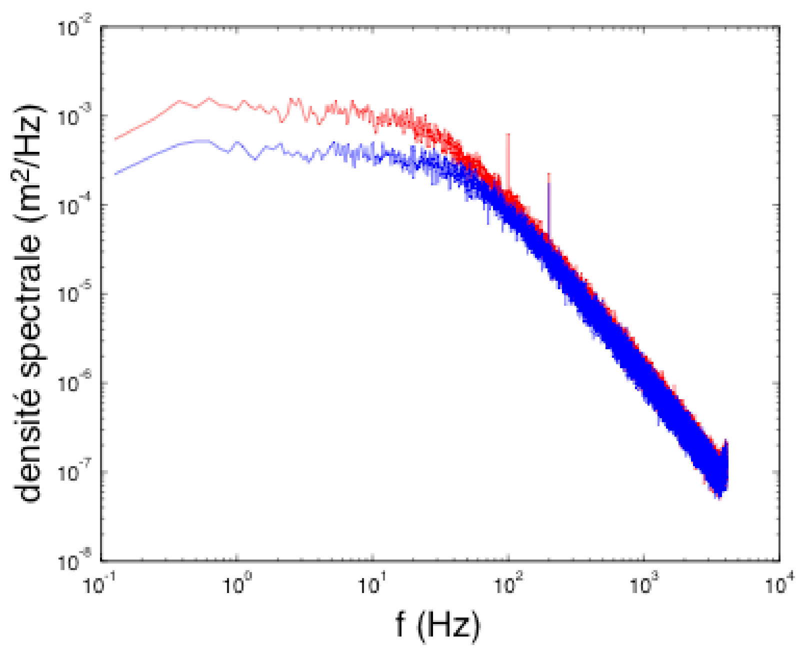


Acquistion frequency
8 kHz

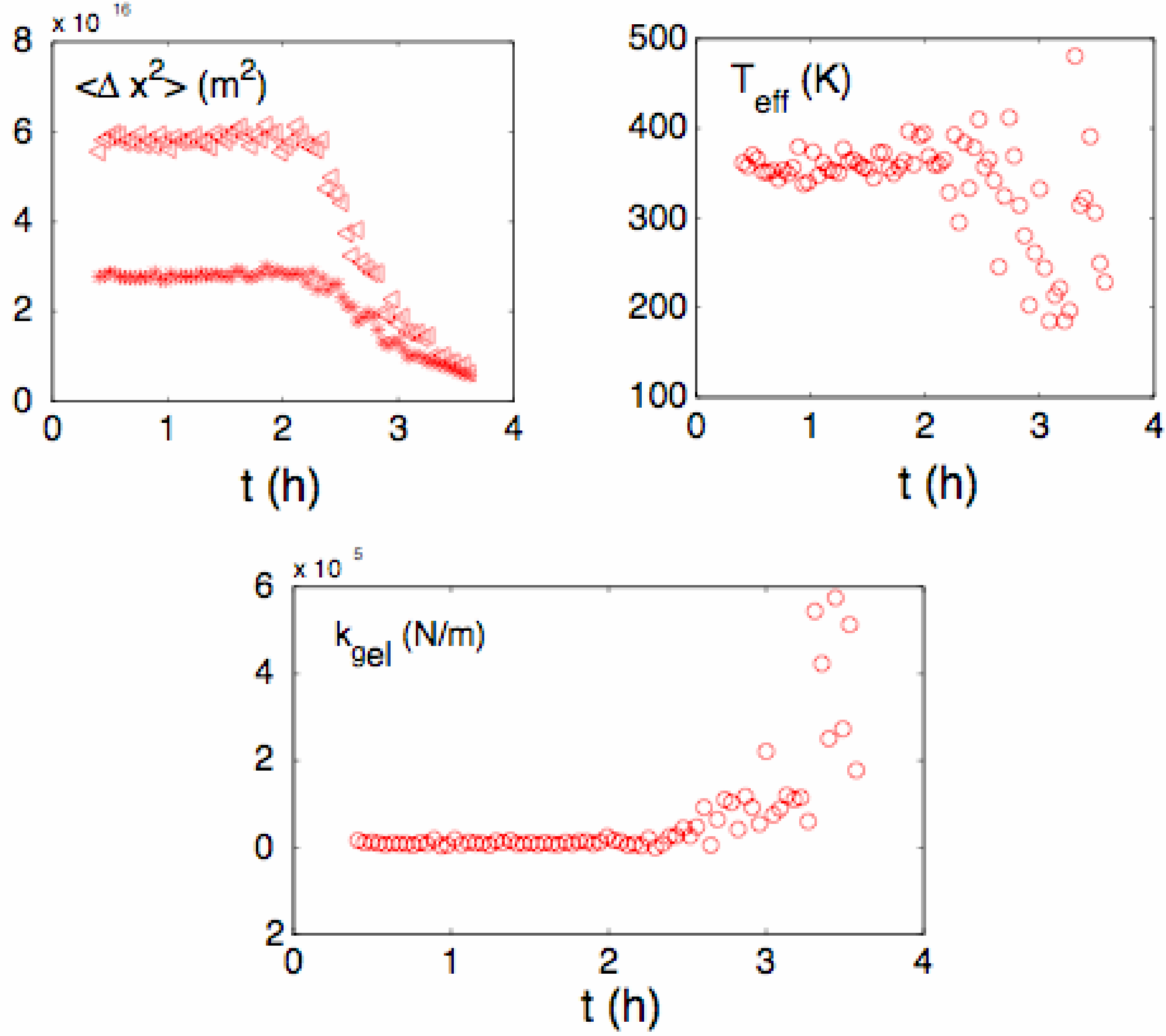
Constant power measurement
1min

k_1=7.47 pN/μm

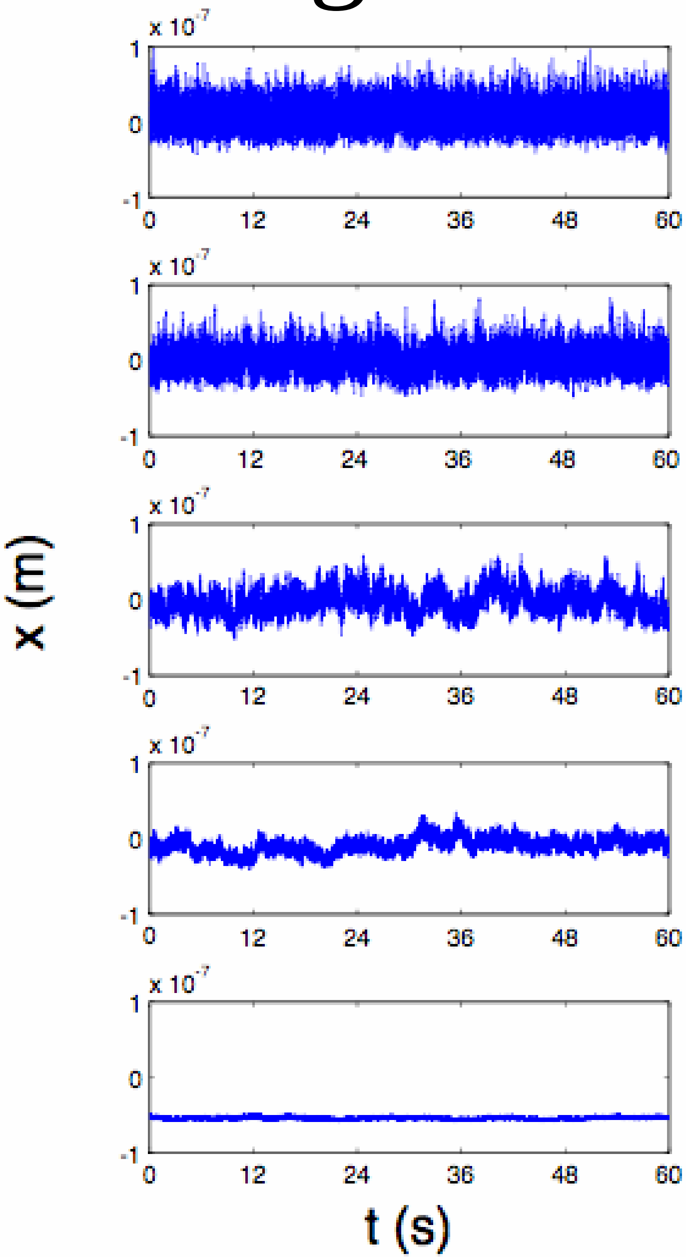
k_2=16.7 pN/μm



Experimental Results



Signal evolution



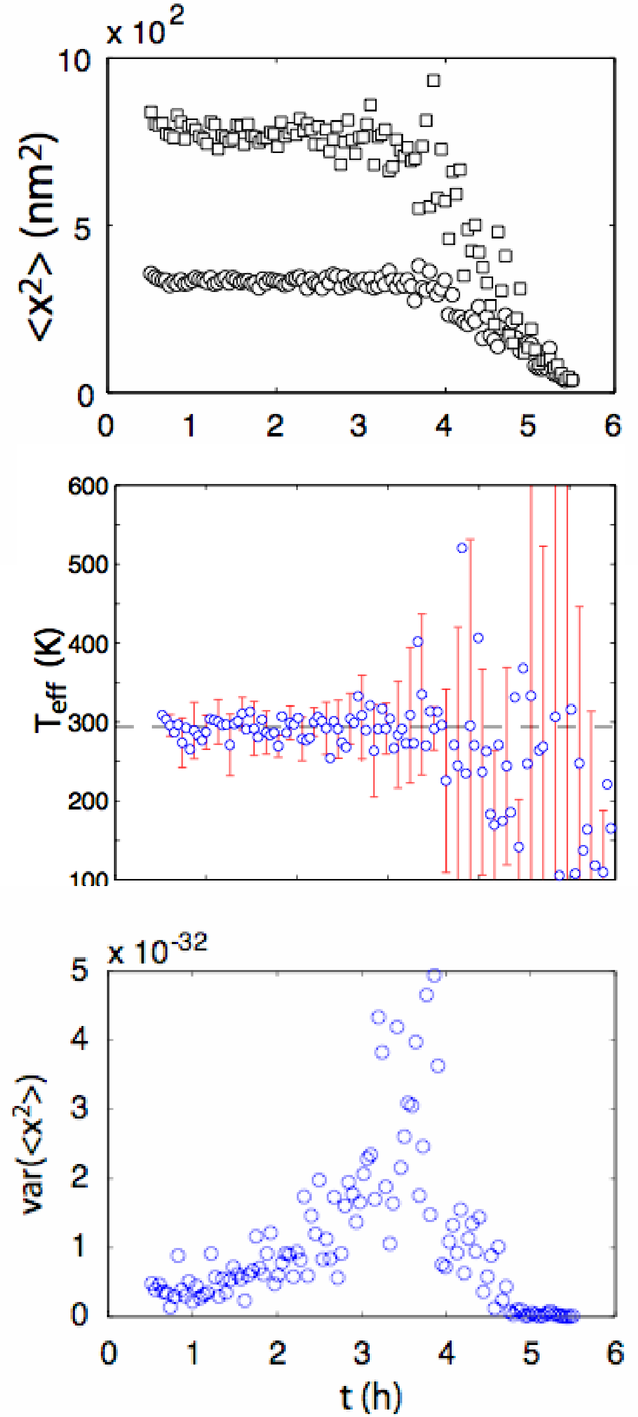
t = 30 min

t = 1h50 min

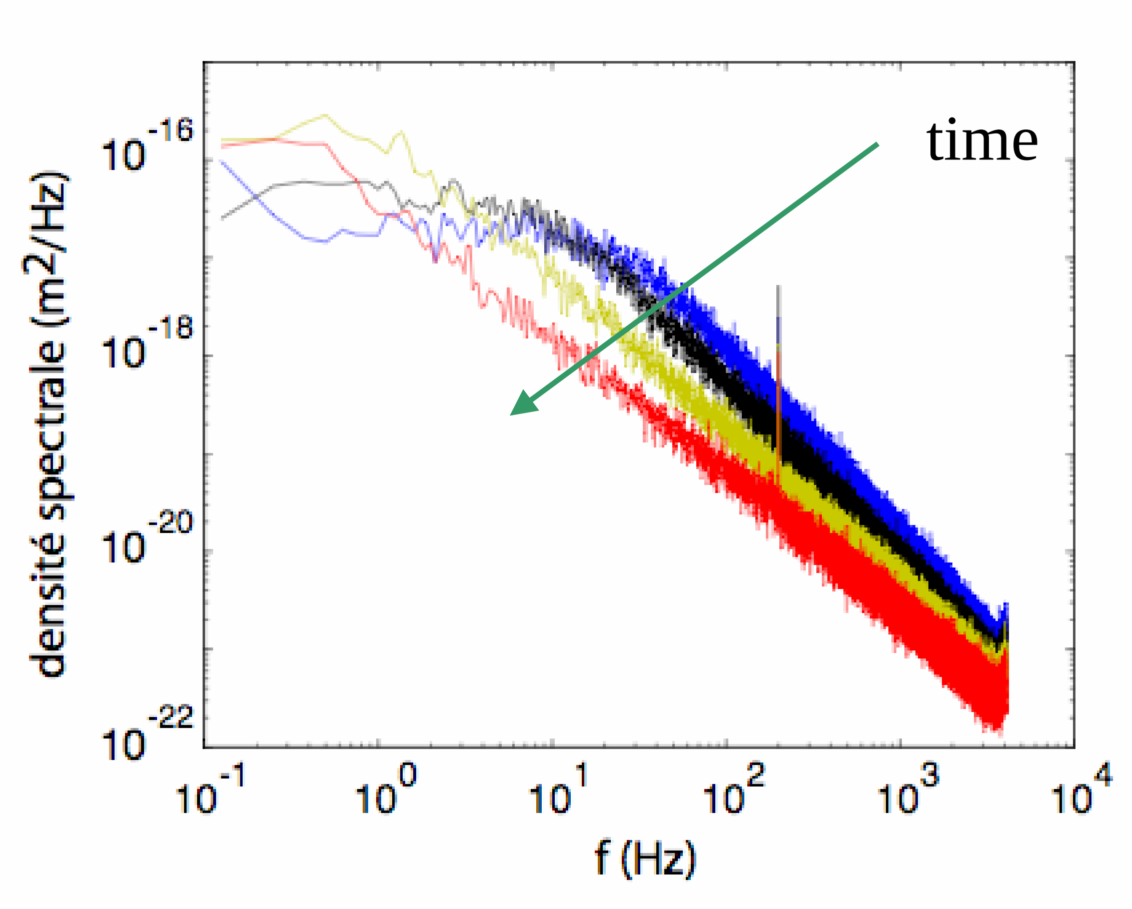
t = 3h10 min

t = 4h30 min

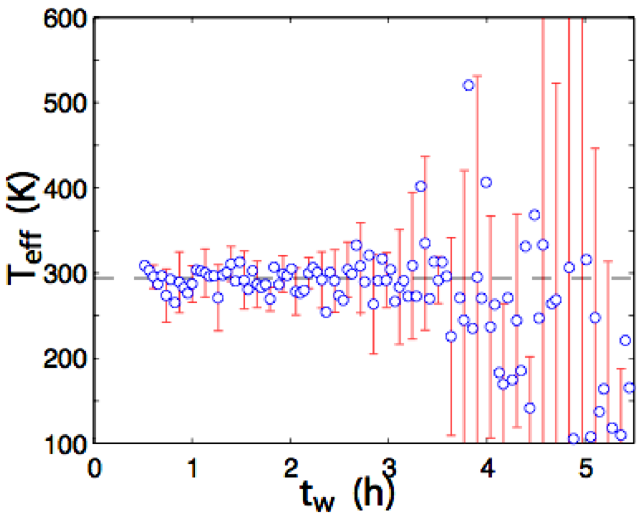
t = 5h30 min

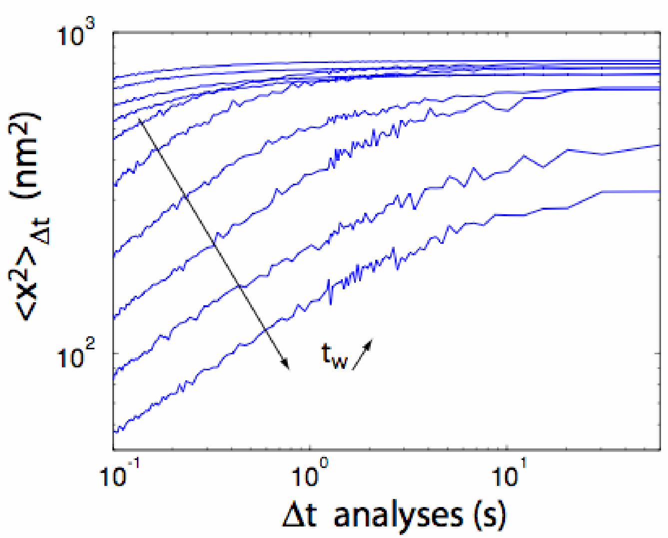


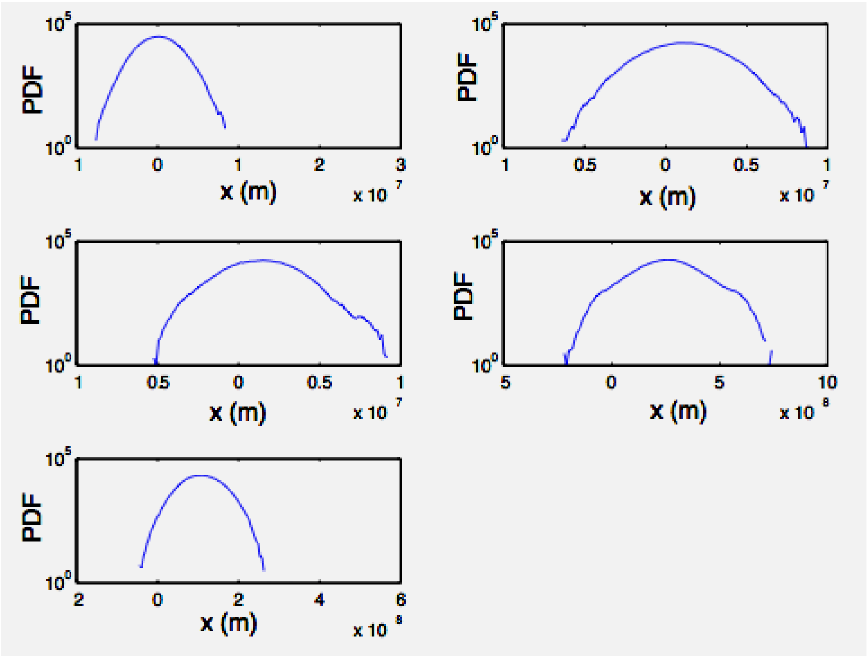
Spectra as a function of time



Limits of the method

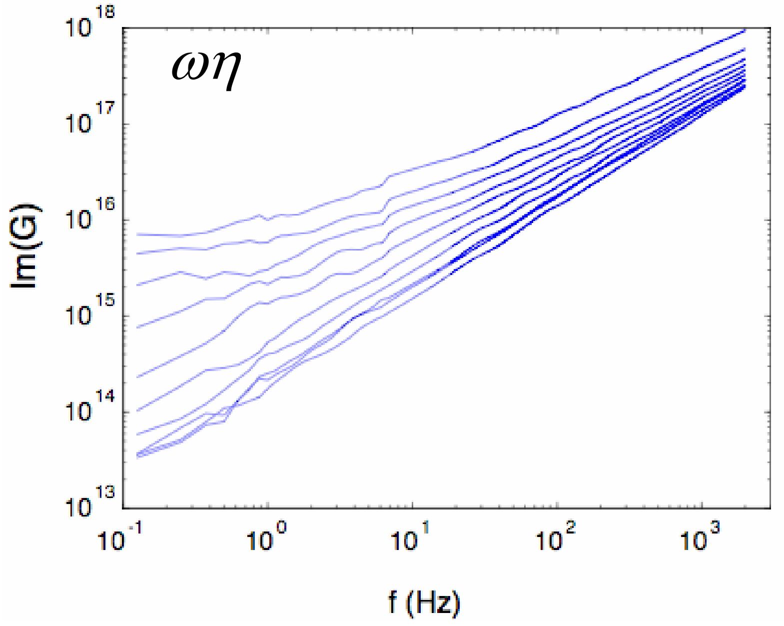






Kramers-Kronig

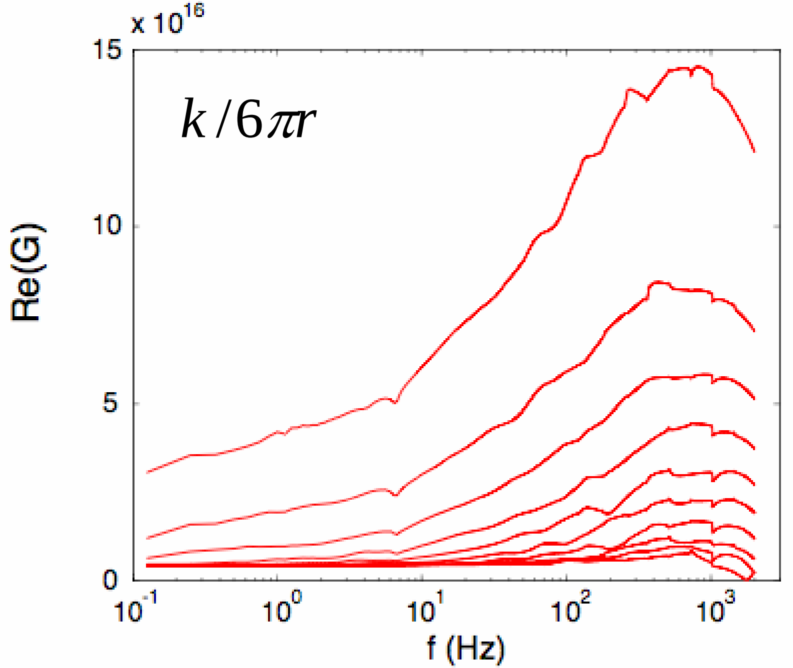
$$S(\omega, t_w) = \frac{4\ K_B\ T_{eff}}{\omega}\ Im\{\alpha(\omega, t_w)\}$$



Hp: : the effective temperature is the same for all the modes

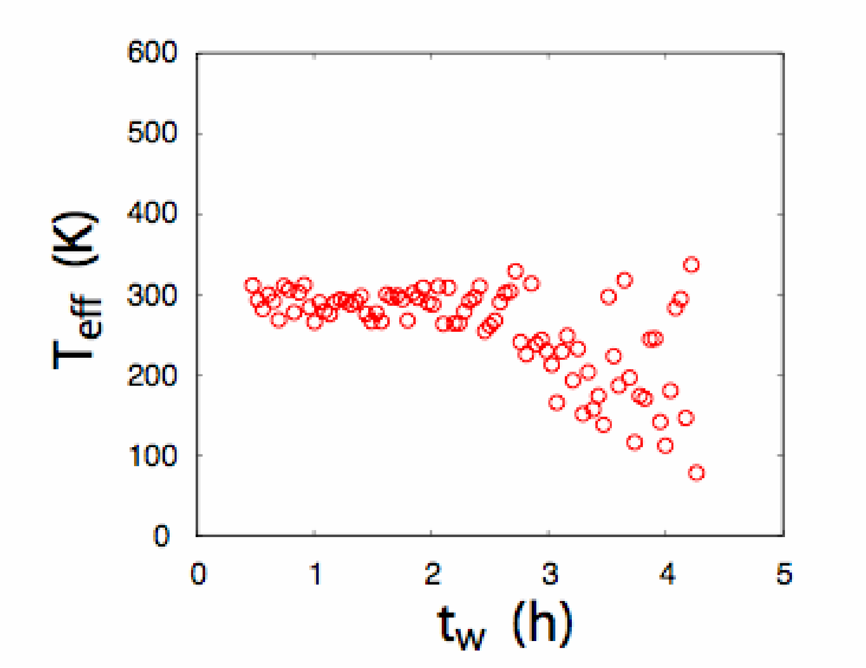
$$\alpha'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\xi \alpha''(\xi)}{\xi^2 - \omega^2} d\xi$$

$$\alpha(\omega) = \frac{1}{6\pi r G(\omega)}$$

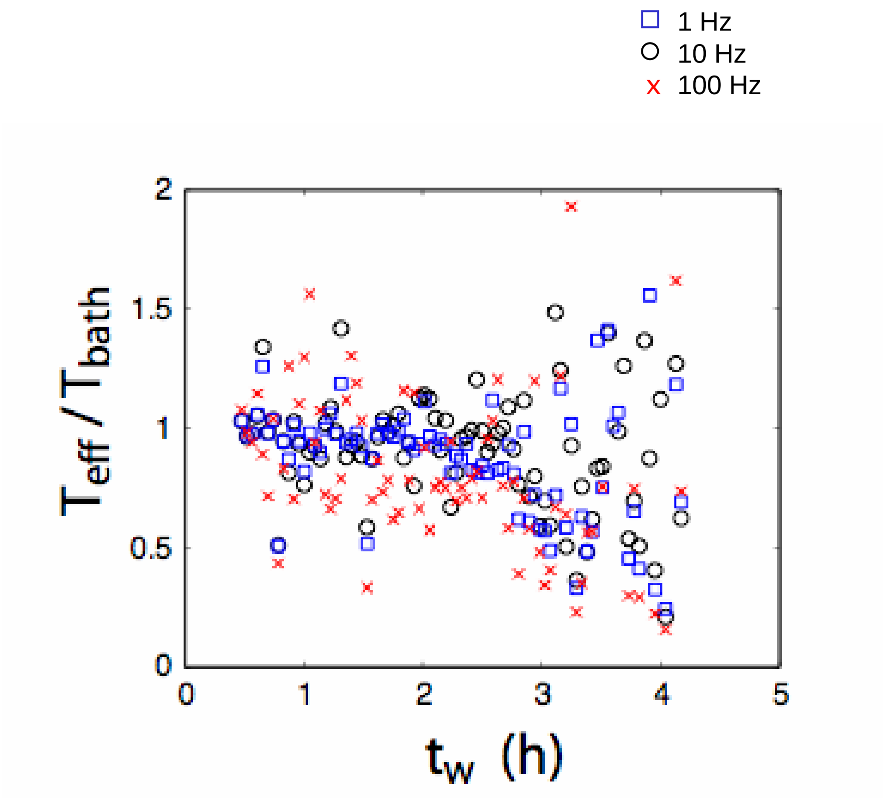


$$T_{eff} G' / T_{bath} = k / 6\pi r$$

Comperison of the results

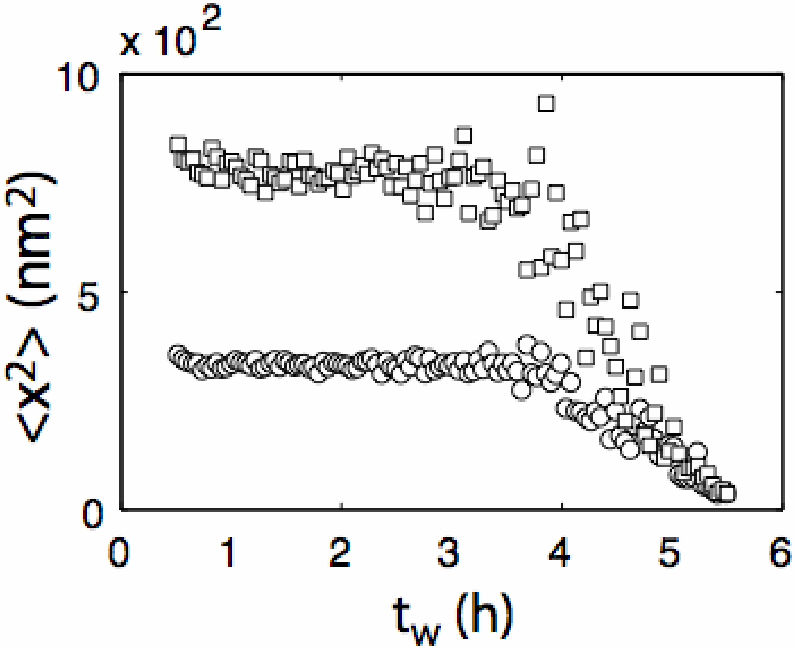


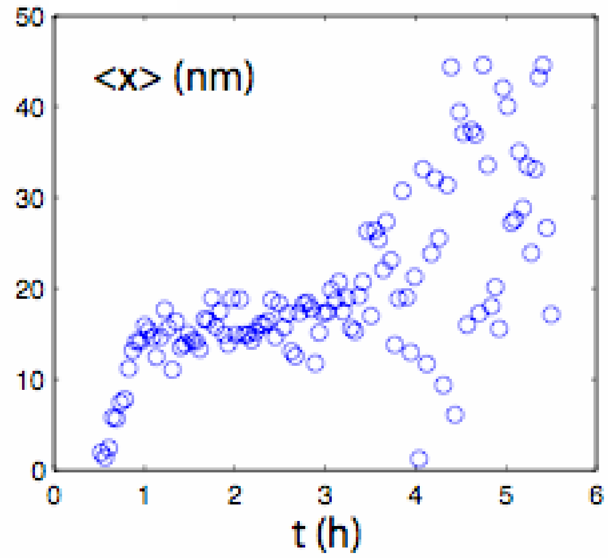
« Variance »



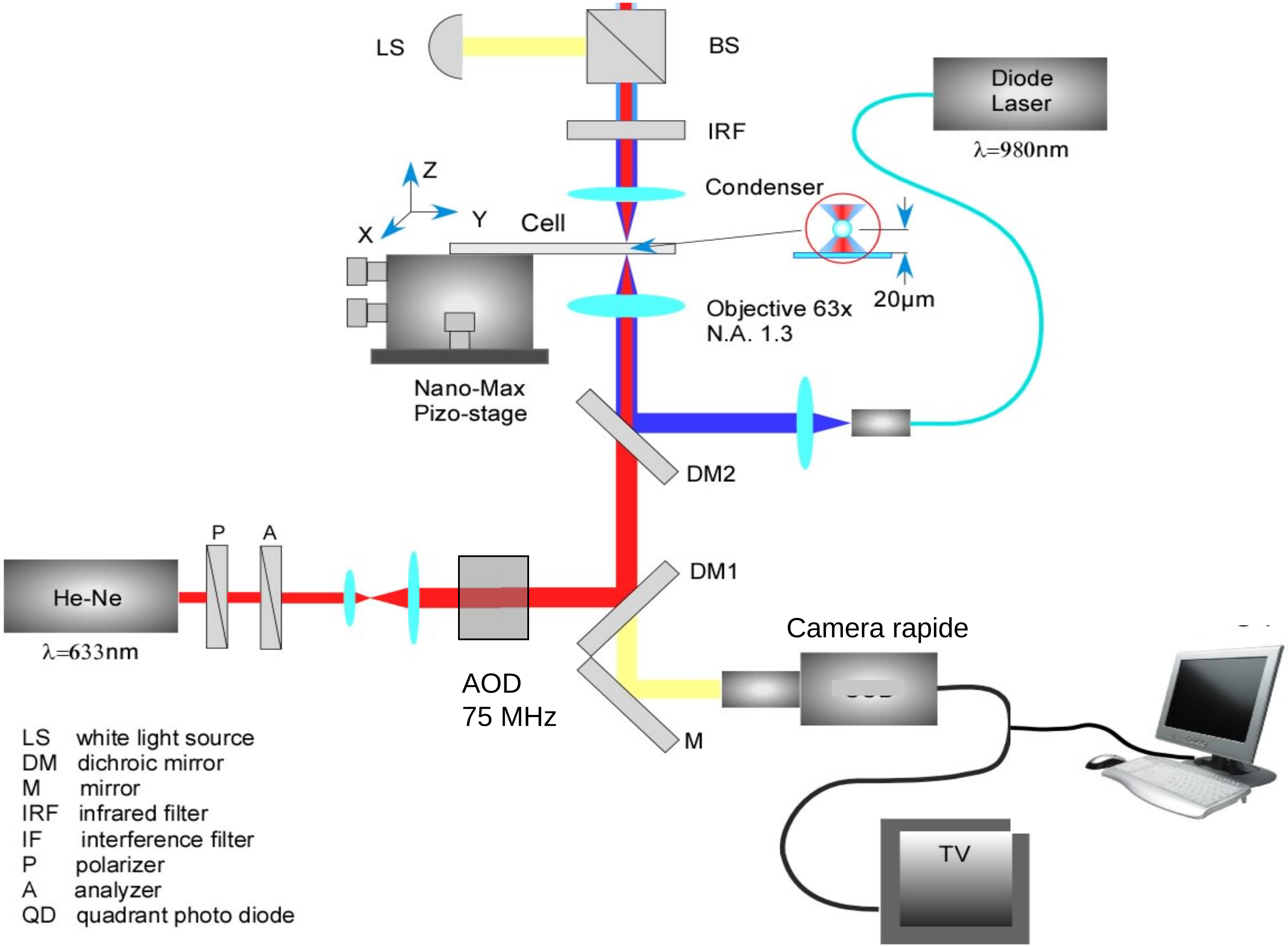
« Kramers »

Dérive aux temps longs

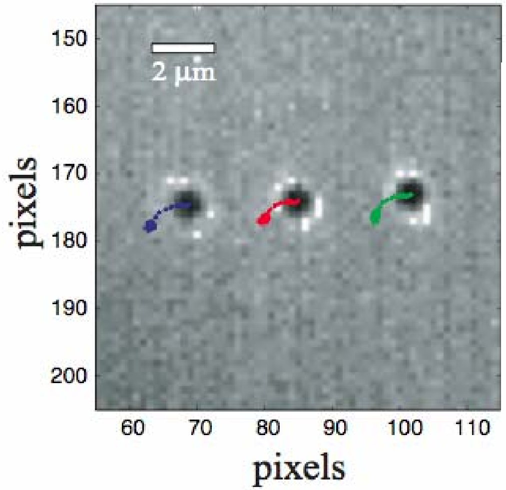


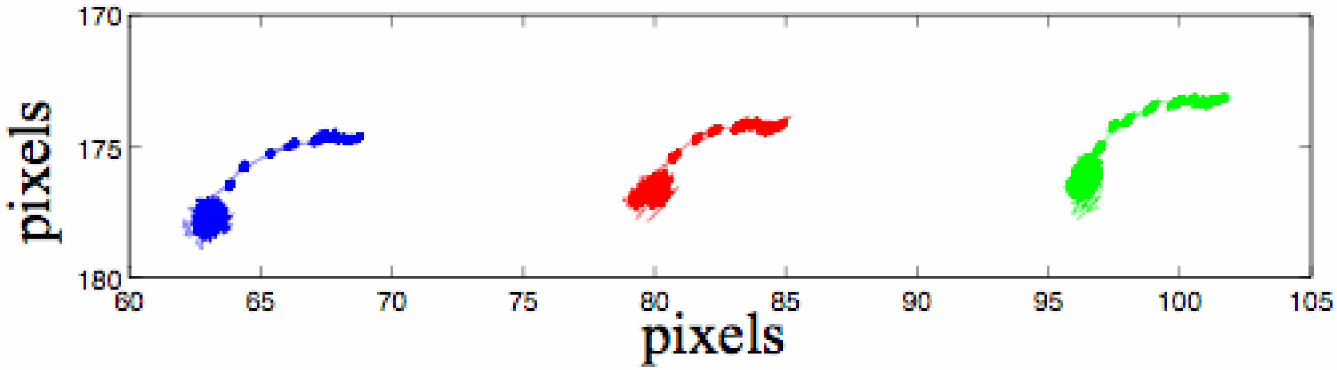


Multiple traps

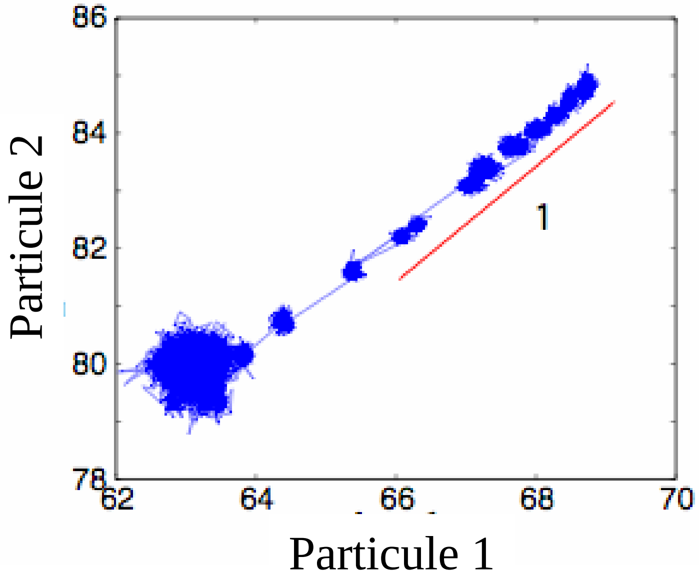


Collective motion

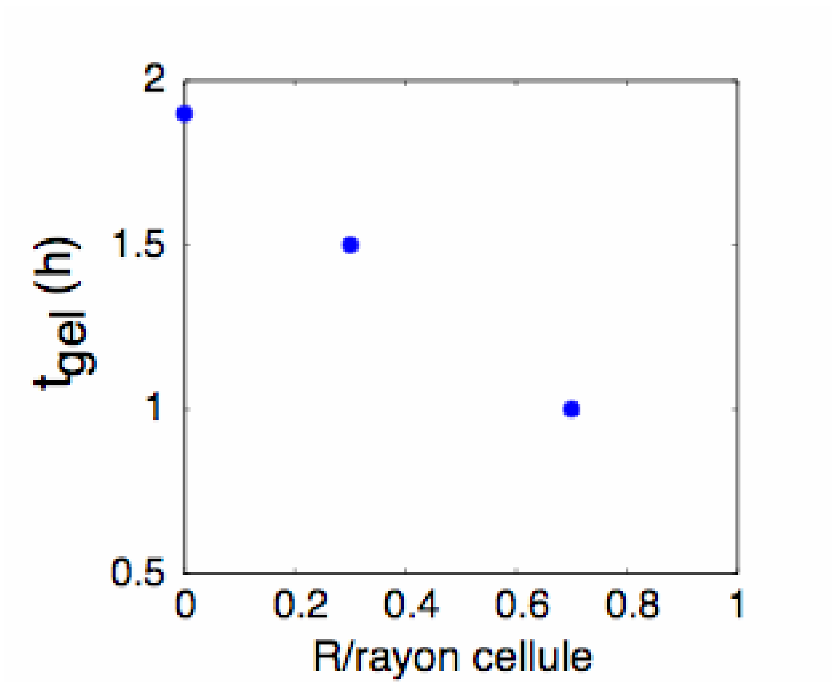


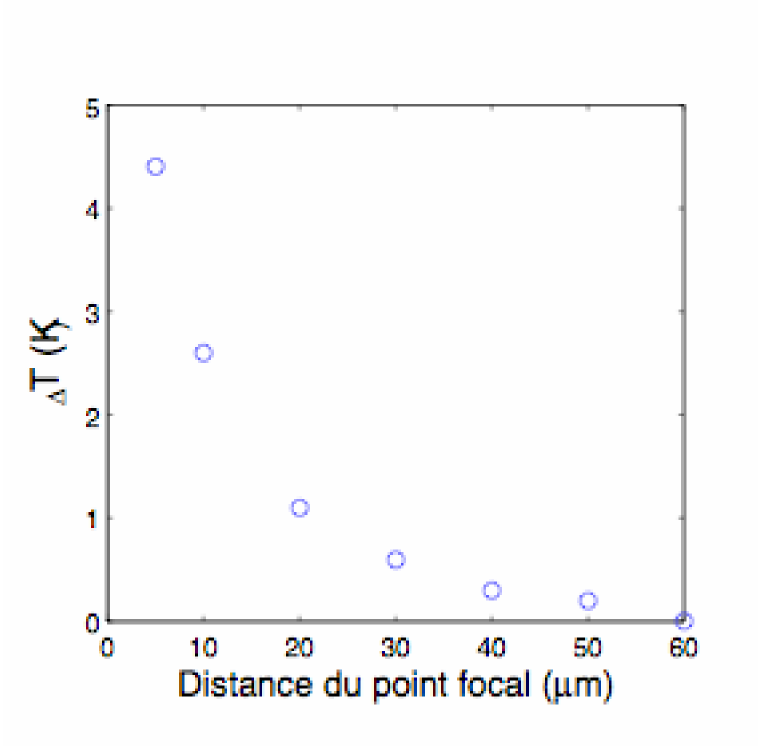


Large scale correlation



Influence des paramètres





Forme et fabrication des échantillons
Raideurs du piège optique
Taille des billes
Concentration de Laponite

→ Teff = T° bain

Conclusions

- The effective temperature is equal to that of the bath
- Large fluctuations of the variance appear near the solidification time.

- There is a collective slow motion at very large scale

Measurements of fluctuations during de sol-gel transition in a colloidal glass

For a gel the physical properties change as a function of the time after the preparation. We measure the electric properties of Laponite (synthetic clay consisting of discoid charged particles).

Laponite is well characterized by means of light scattering experiments. Its behavior turns out to be very close to that of a glass.

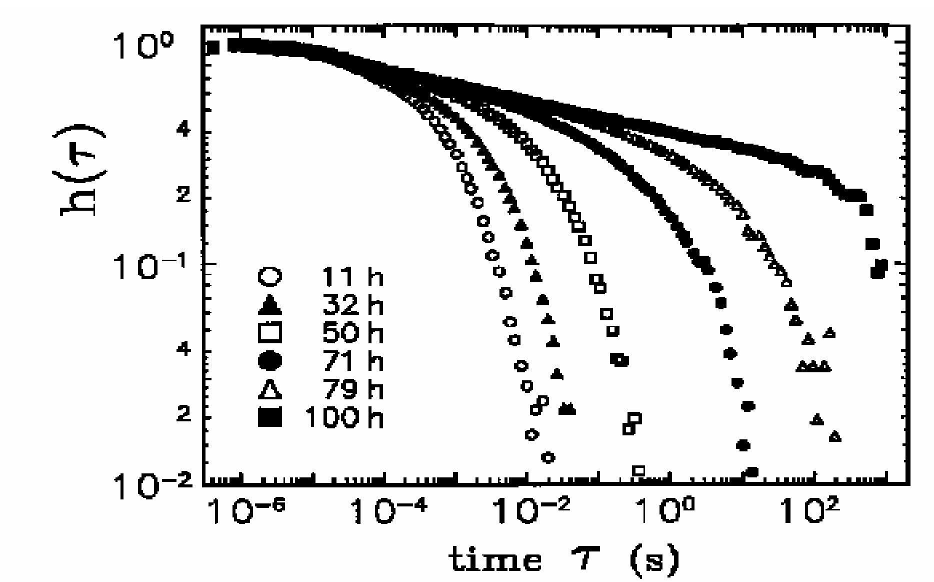
Preparation

-The Laponite solution is prepared in a clean N_2 atmosphere
-Laponite particles are dissolved at a concentration C in pure water under stirring
- The solution is then filtered.

The speed of the sol-gel transition is controlled by the concenteration C

C has been varied between 2.5% and 3% mass fraction

Aging of Laponite

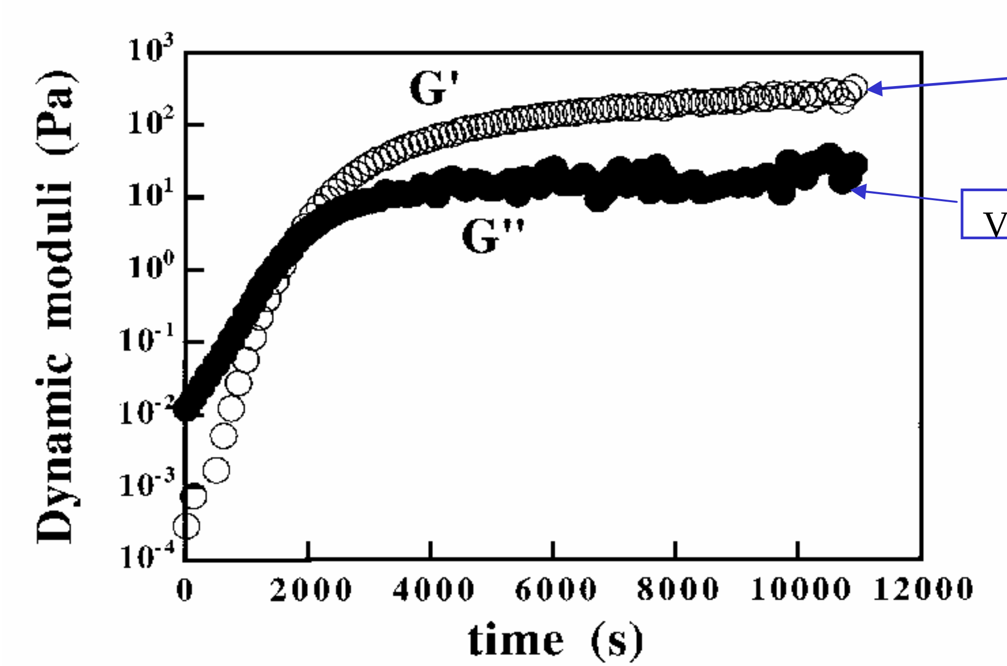


Dynamic light Scattering Experiment

(Density Fluctuations)

M. Kroon et al. ,
Phys. Rev. E 54, 6541–6550 (1996)

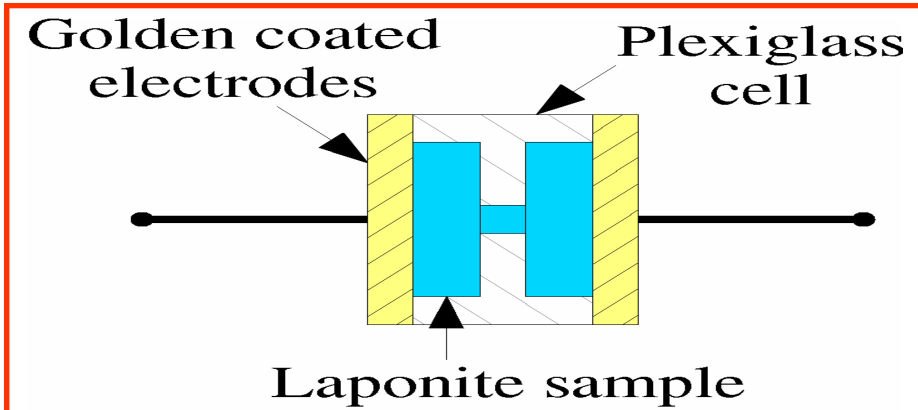
Typical intensity correlation functions at different t_w after the preparation of the sol



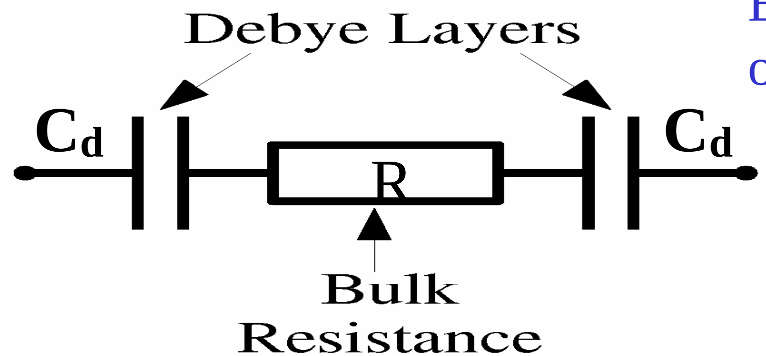
Elastic properties

D.Bonn et al.,
Europhysics Lett. 45, 52 (1998).

Experimental set up



The cell



Equivalent electrical circuit of the cell, of impedance:

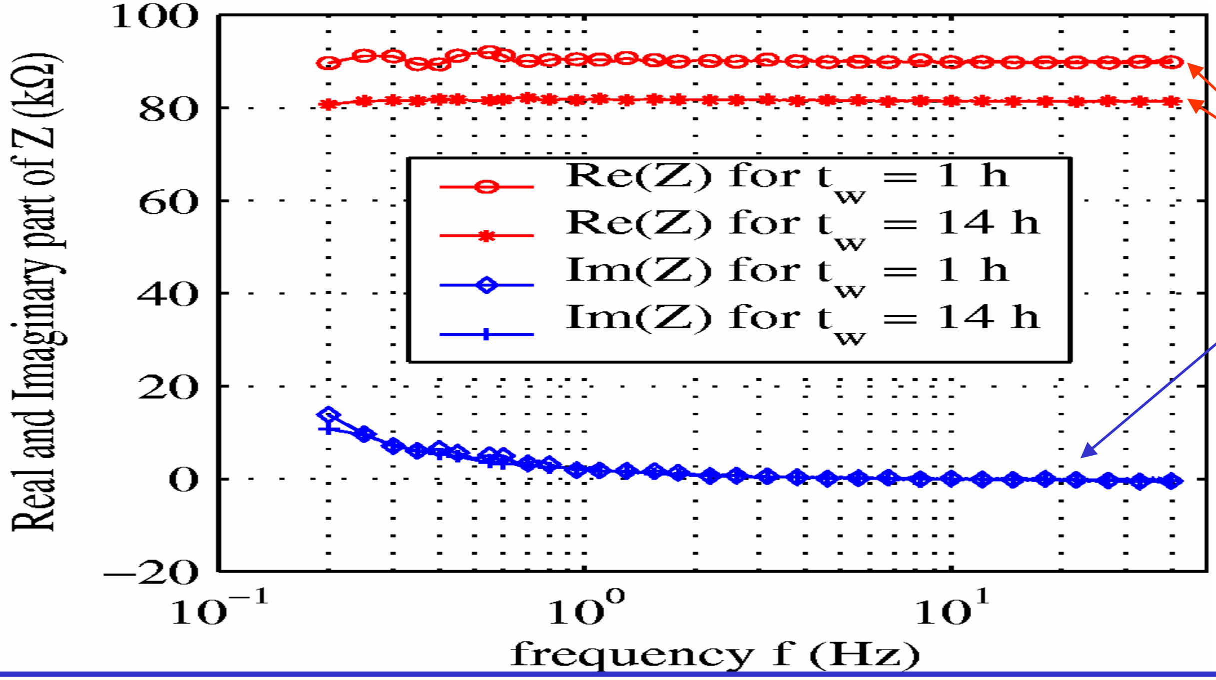
$$Z_c = R - \frac{i}{2\ \pi\ f\ C_d}$$

$$\text{For } f >> \frac{1}{2\ \pi\ R\ C_d} \quad \Rightarrow Z_c \simeq R$$

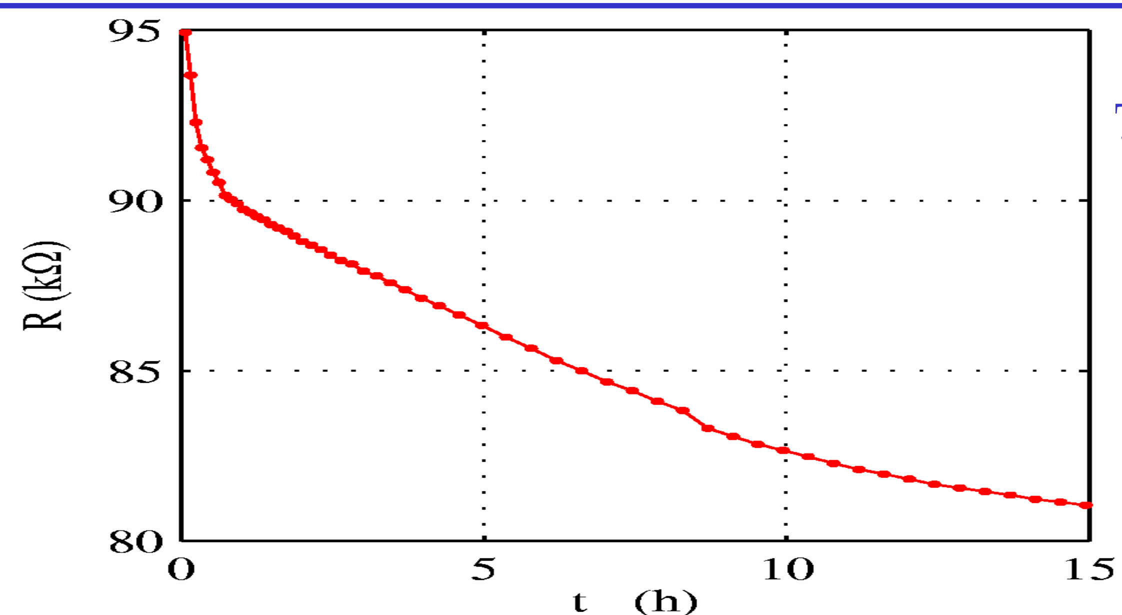
and the noise spectrum at equilibrium is:

$$S(f) = 4 K_B\ T\ R$$

Electrical response function of Laponite at C=2.5%

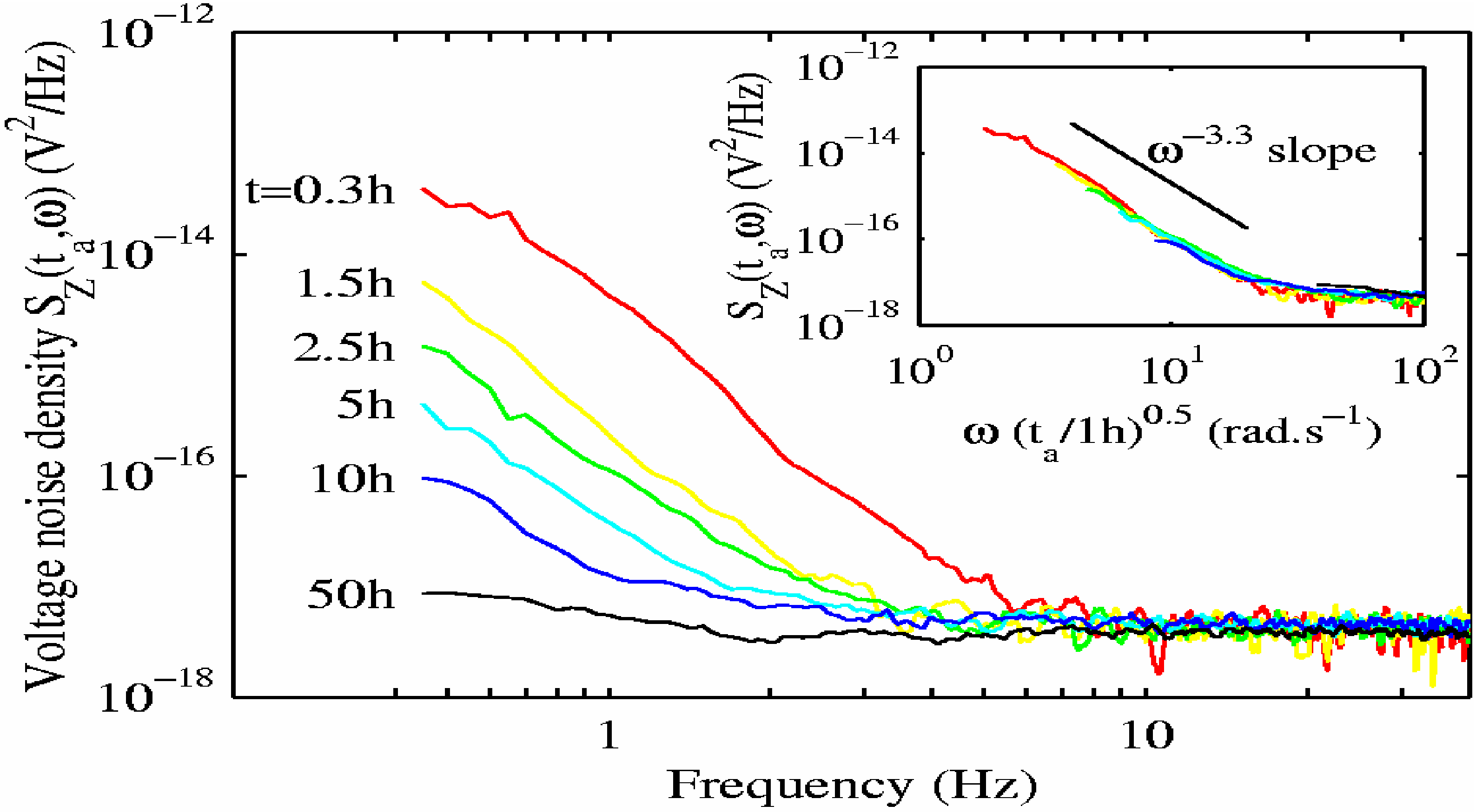


Real and imaginary part of Zc versus frequency at two different t_W



Time evolution of the bulk resistance

Noise spectrum of Laponite at 2.5%



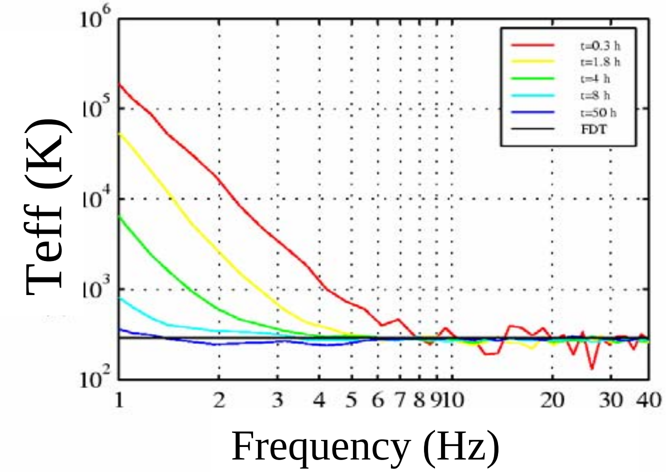
The strong increase of S_Z for low frequencies is well fitted by:

$$\omega^{-3.3\pm0.4}$$

Good rescaling of the spectra for: $\omega t_a^{1/2}$

Effective temperature of Laponite

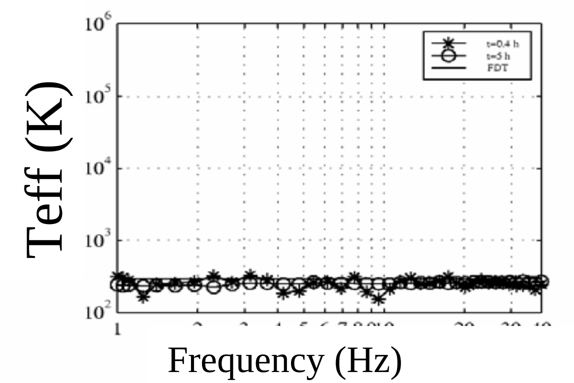
$$T_{eff}(t_a,\omega) = \frac{\pi S_Z(t_a,\omega)}{2k_B Re\left[Z(t_a,\omega)\right]}$$



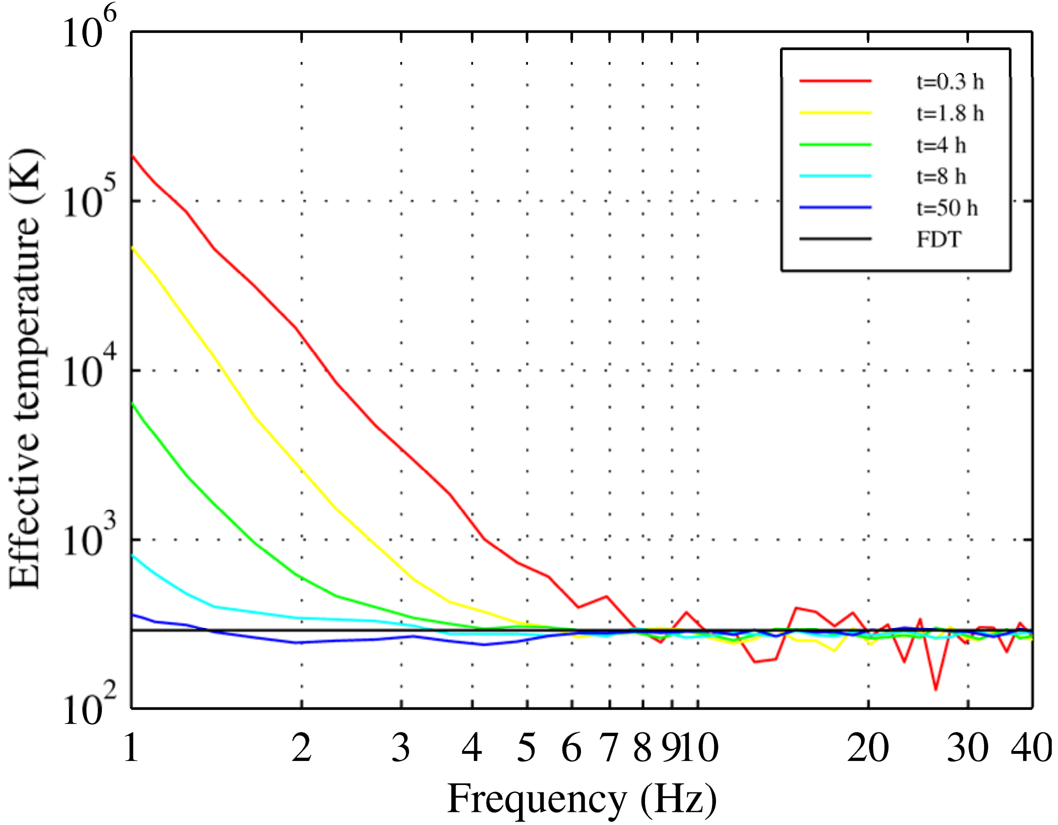
Large violation of the fluctuation dissipation relation for electrical properties of Laponite

Solution test : $NaOH$ at $10^{-3}\ mol.l^{-1}$

Test



No violation is observed in this case

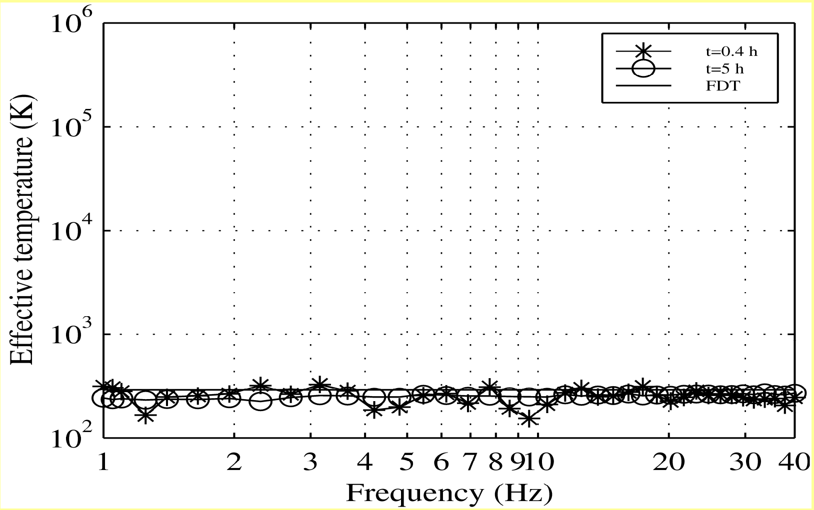


Effective temperature of Laponite

Large violation of FDT for the electrical properties of Laponite

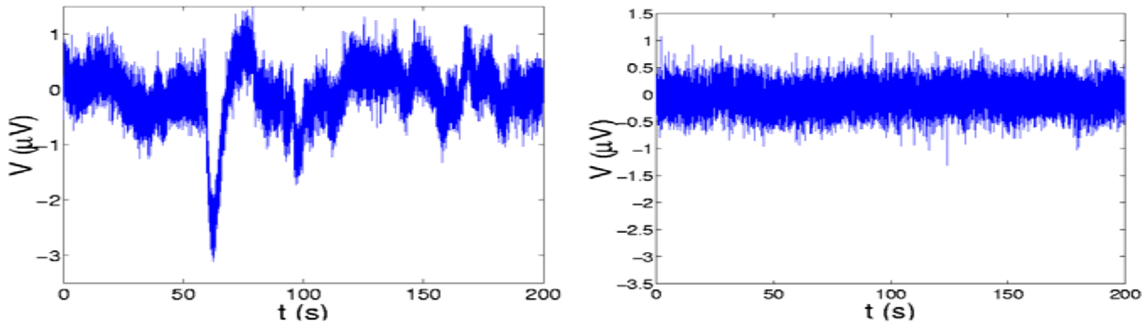
Solution test: $NaOH$ at 10^{-3} $mol.l^{-1}$

No violation is observed in this case



Signal of Laponite at C=2.5%

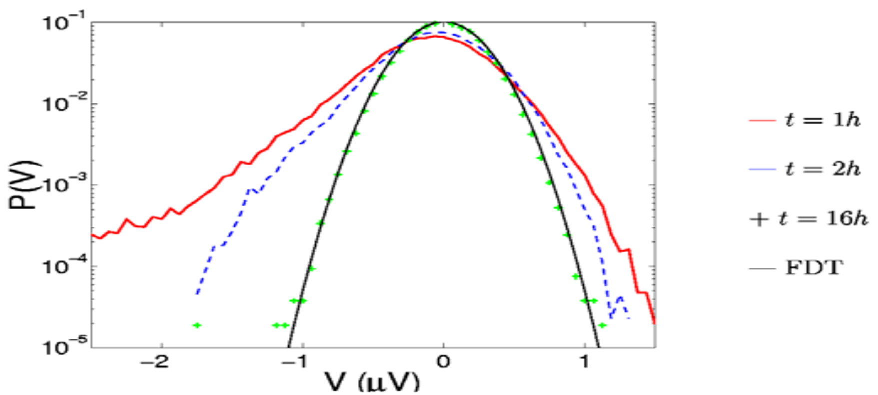
Signal as function of time



1 hour after preparation

16 hour after preparation.

PDF of the signals

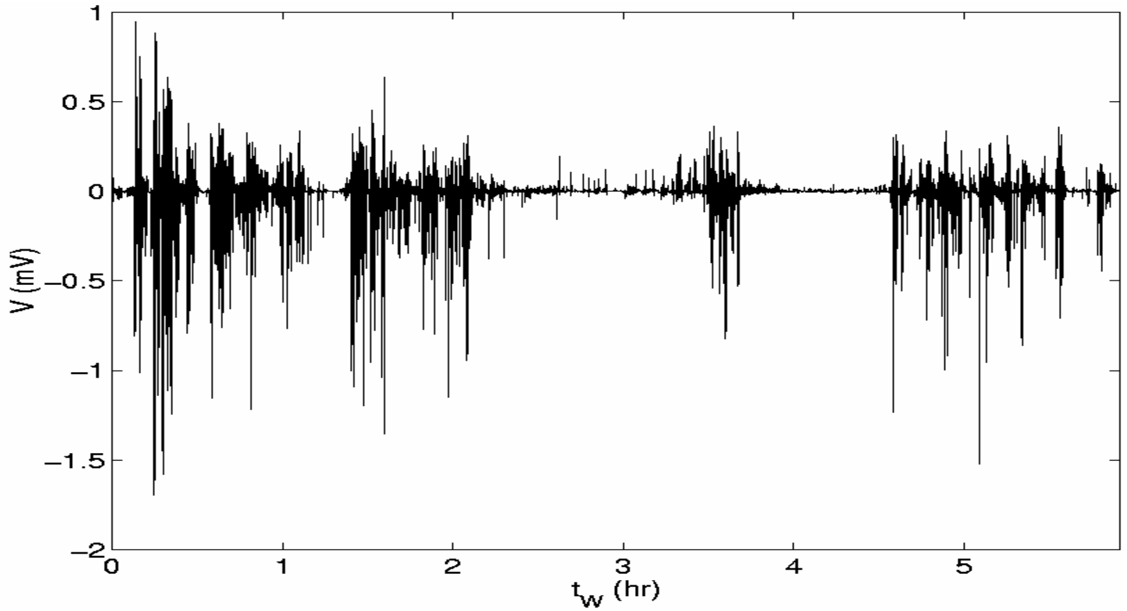


When FDT is violated the fluctuations are not Gaussian

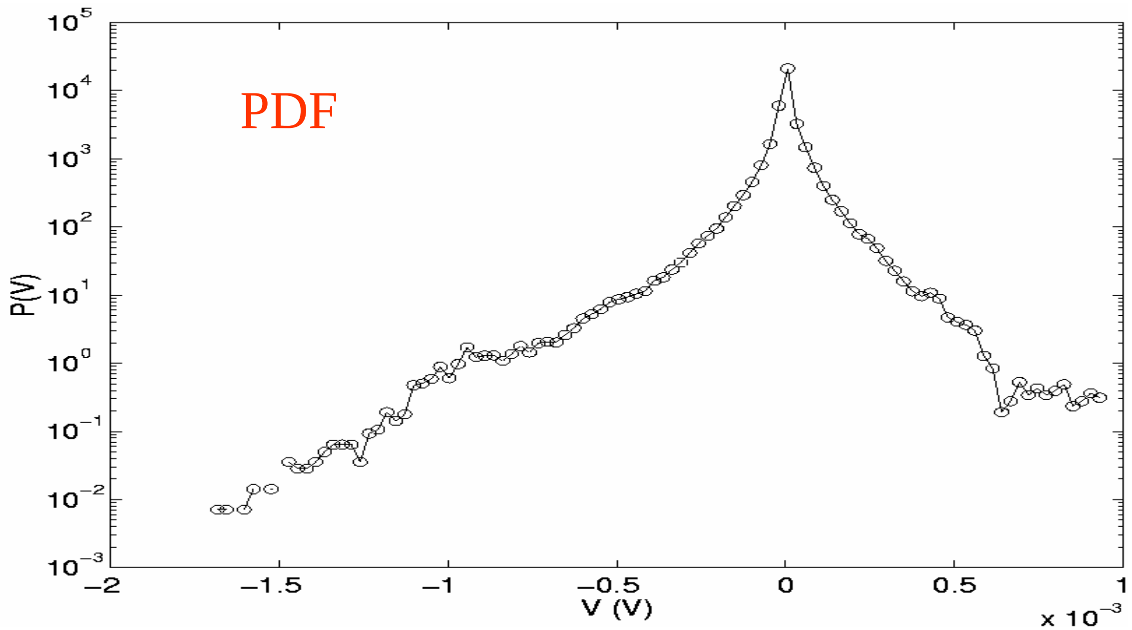
Buisson, Bellon, Ciliberto, J. of Phys.: Cond Mat. 2003

Signal of Laponite at C=3.5%

(a)



(b)



Intermittency increases with concentration, which is equivalent to the quench rate