Santa Barbara 16 April 2003

On the Violation of the Fluctuation-Dissipation Theorem During Aging Processes

(experimentalist point of view)

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Outline

I) Aging and motivation for new experiments

II) Use of the fluctuation dissipation relation to define an effective temperature for a weakly out of equilibrium system, such as an aging glass.
(Cugliandolo, Kurchan, 1993)

III) Measure of the fluctuation dissipation relation in the electric properties of

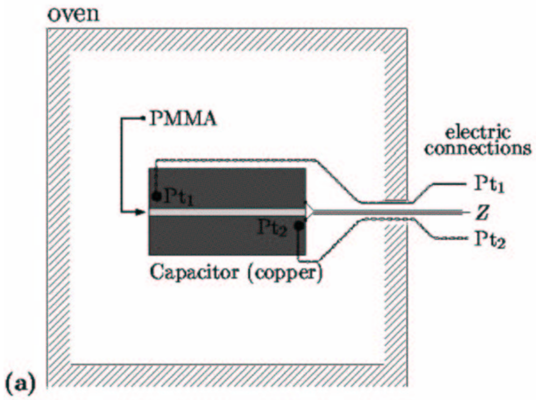
a) A colloidal glass during the transition from a fluid like sol to a solid-like material.
b) A polymer after a quench

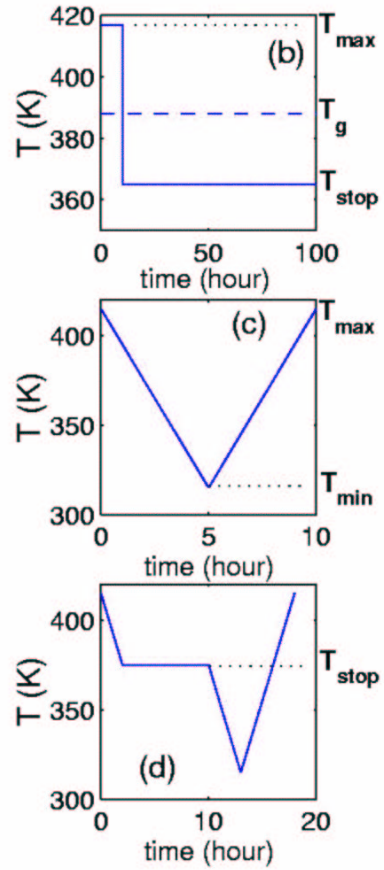
IV) Models of aging and other systems.

V) Measure of the fluctuation dissipation relations in the mechanical properties of a colloidal glass

VI) Conclusions

Aging and Memory effect in a polymer



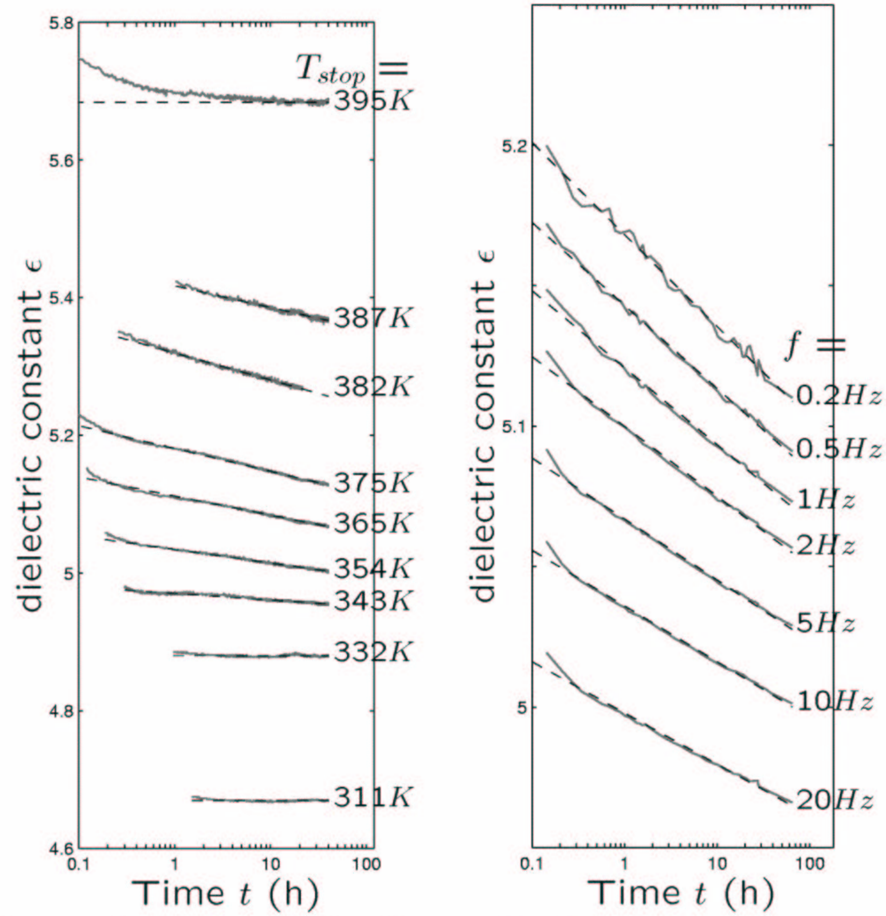


(a) **Experimental set-up for PMMA**. PMMA is the dielectric of a capacitor whose vacuum capacitance is $C_0 = 230pF$.

$\epsilon = \epsilon' + \ i \ \epsilon''$ is the PMMA dielectric constant.

(b-d) **Typical thermal cycles applied to the sample**

Aging of PMMA



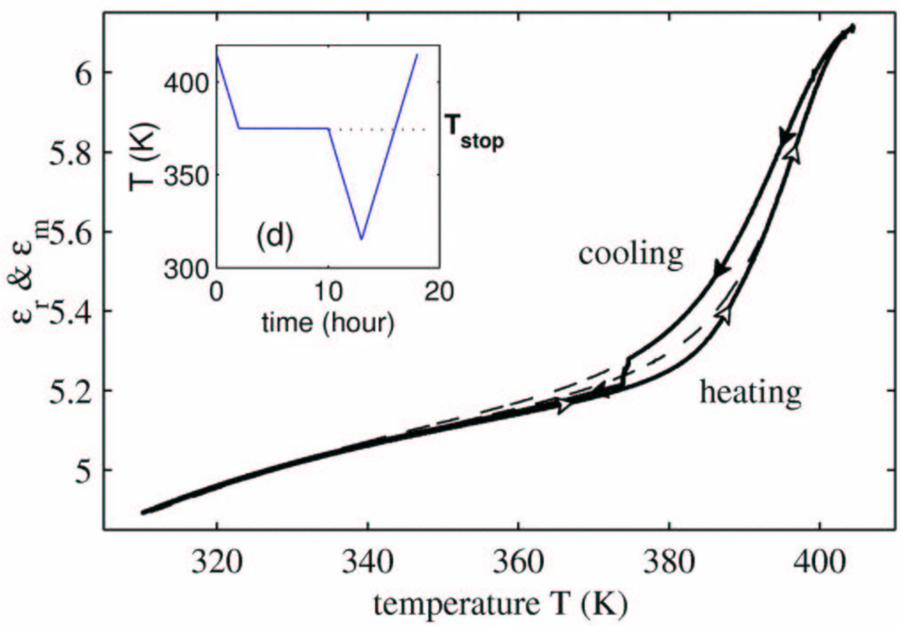
Dependence on t of ϵ after a quench.

(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



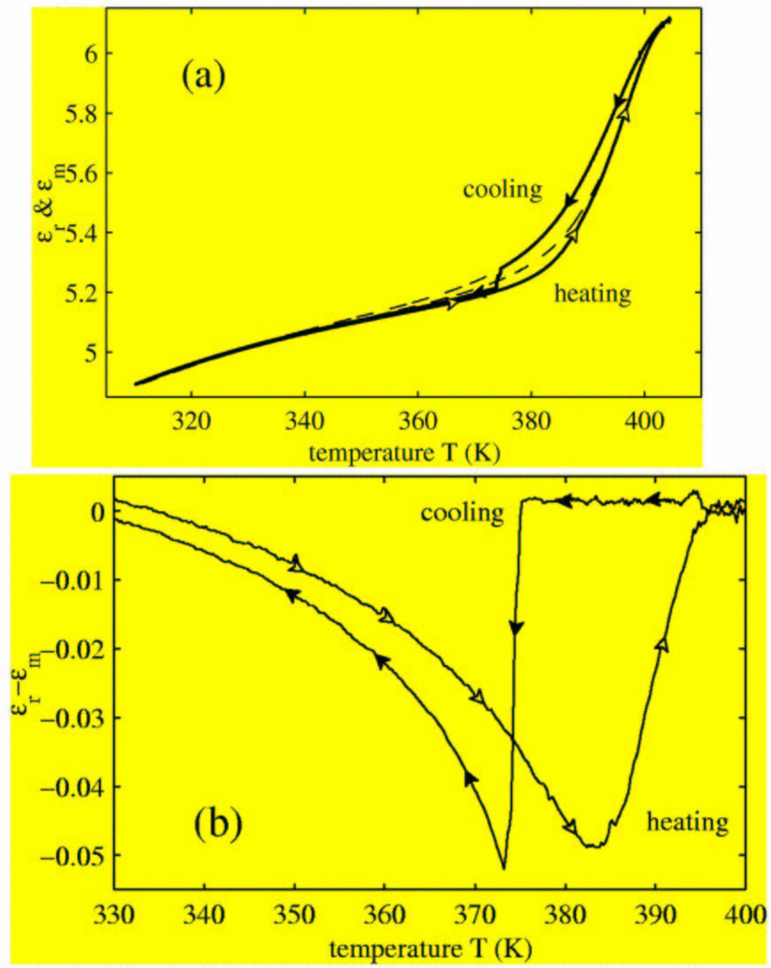
- - - Reference curve

—— Curve with a cooling stop

ϵ_r = dielectric constant measured without a cooling stop

ϵ_m = dielectric constant measured with a cooling stop

Memory effect in PMMA



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

ϵ_r = dielectric constant measured without a cooling stop

ϵ_m = dielectric constant measured with a cooling stop

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 constrains for the phenomenological models of aging.

Question: is the analysis of fluctuations useful ?

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FLUCTUACTION DISSIPATION THEOREM
in thermodynamic equilibrium

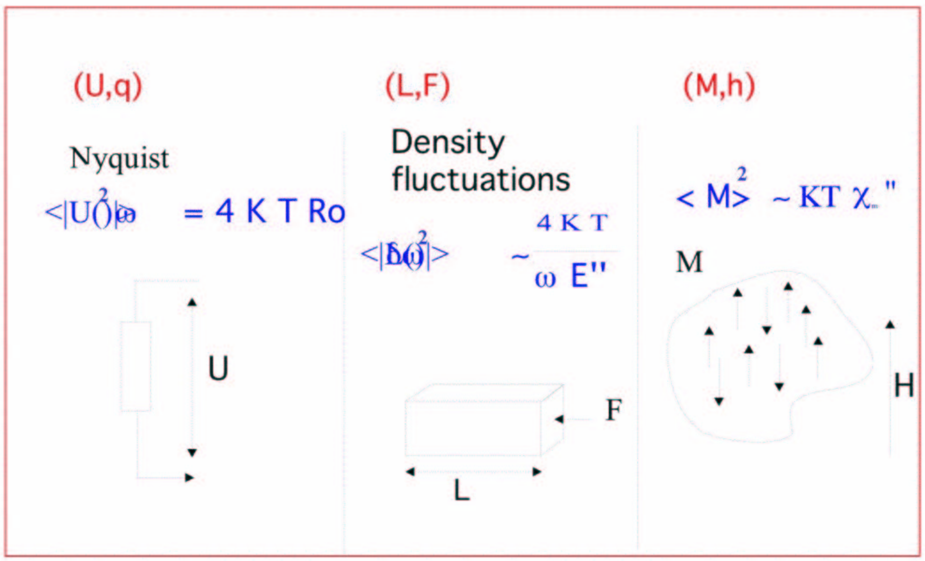
V and q are two conjugate variables in the system Hamiltonian

$$R(\omega) = \frac{\delta V(\omega)}{\delta q(\omega)}$$ 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 exemples are:



Fluctuation Dissipation Relation (FDR)

in a weakly out of equilibrium system
(Cugliandolo,Kurchan 1992.)

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

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

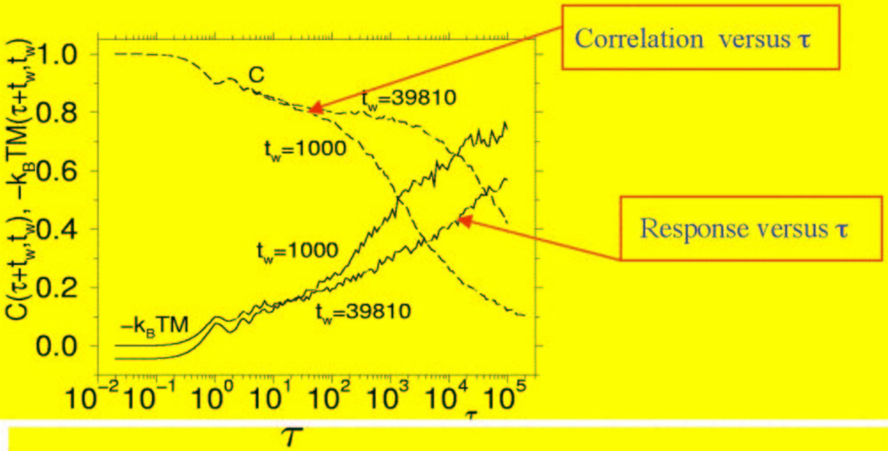
At equilibrium $T_{eff}(\omega, t_w) = T$

In terms of correlation function FDR takes the form

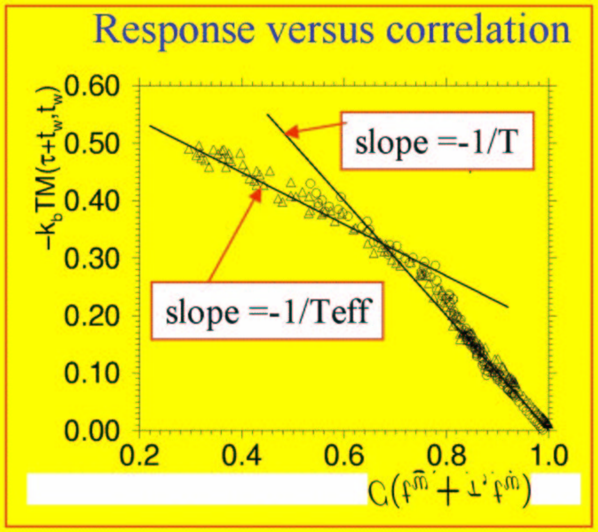
$$-C(t, t_w) + C(t_w, t_w) = K_B\ T_{eff}(t, t_w)\ R(t, t_w)$$

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)



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



FDR in out of equilibrium system

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

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

Theoretical background:

- -1983 Sompolinsky
- -1987 Hoenberg and Shraiman
- -1992 Cugliandolo and Kurchan, Parisi, Barrat, Bouchaud, Mezard, Berthier………..

Experiments

- -1970 xray scattering on PMMA
- -1999 Grigera et al., super-cooled liquid (single frequency measurements).
- -2001 Bellon et al., sol-gel transition
- -2002 Herisson et al., spin-glass
- -2002 Buisson et al, polymer

Why is interesting to study FDR in experiments ?

I) The violation of FDT is model dependent

II) Several questions can be asked:

II-a) What is the statistics of the signal ? Are the fluctuations Gaussian or not ?

II-b) Is the effective temperature independent of the couple of variables ?

X-ray experiments

Intensity $I(0)$ of scattered x-rays at small angles is related to the density fluctuations $\delta\rho$:

$$\frac{<\delta\rho^2>}{\rho^2} \propto I(o)$$

From FDT

$$<\delta\rho^2> \ = \ \frac{K_B \ T \ \rho^2 \chi_T}{V}$$

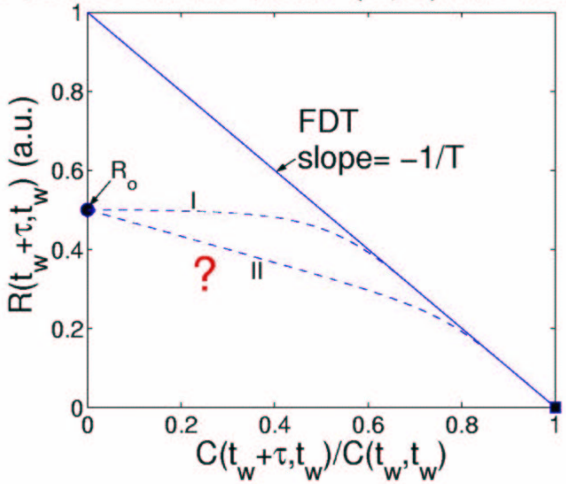
where χ_T is the isothermal compressibility.

Weandorf and Fisher found a violation between 2.5 and 5 of this expression for various polymers.

Comparison with theory:

$$-C(t_w+\tau,t_w)+C(t_w,t_w)=K_B \ T \ R(t_w+\tau,t_w)$$

only two points on the plane (C,R) are available



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c) Noise signals statistics and models of aging.

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Measurements of FDT during the sol-gel transition

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

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

Laponite chemical and physical properties

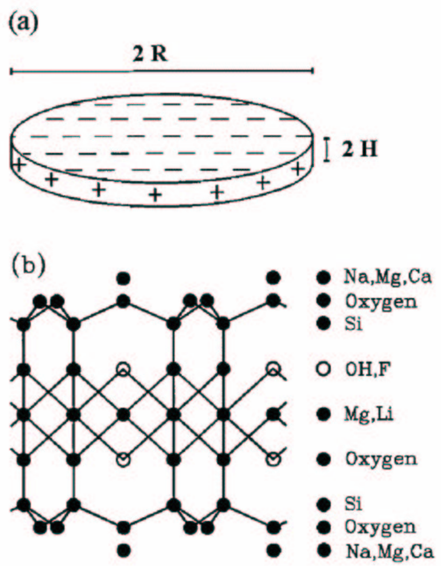


FIG. 1. (a) The disklike shape of the primary Laponite RD particle, and (b) the structure of the primary Laponite particle, as seen from aside (facing the rim). The surface charge distribution as shown in (a) results from the dissolving of surface attached ions (Na, Ca, Mg) into the surrounding liquid. The distribution is fixed due to the crystalline structure of the particle. The legend on the right in (b) displays the elements present in this structure in a horizontal fashion.

Preparation

-The Laponite solution is prepared in a clean N_2 atmosphere

-Laponite particles are dissolved at a concentration of 2.5 % mass fraction in pure water under vigorous stirring

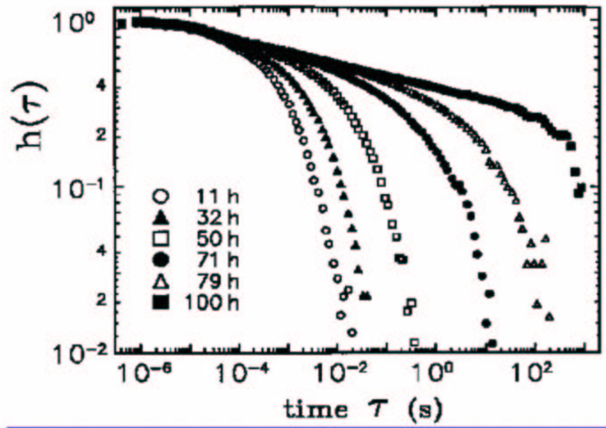
- The solution is then filtered.

Aging of Laponite

Dynamic light Scattering Experiment

(Density Fluctuations)

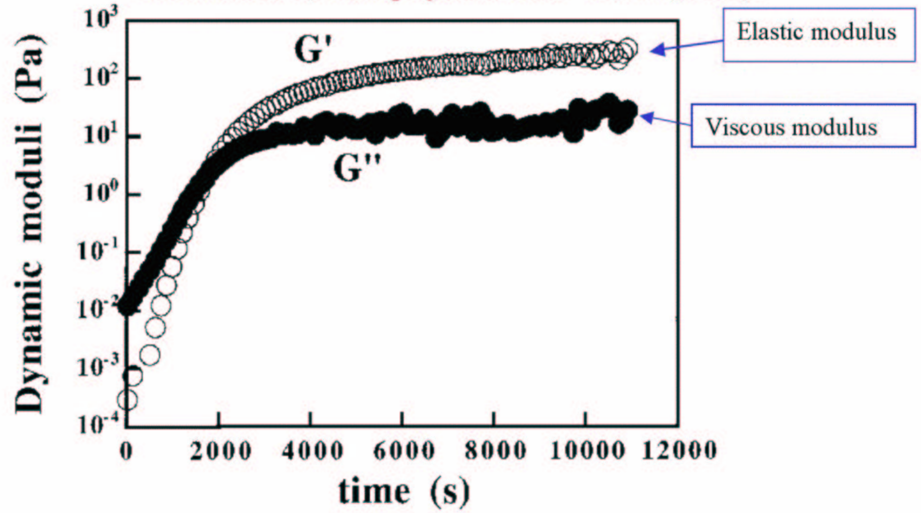
M. Kroon et al. , Phys. Rev. E 54, 6541–6550 (1996)



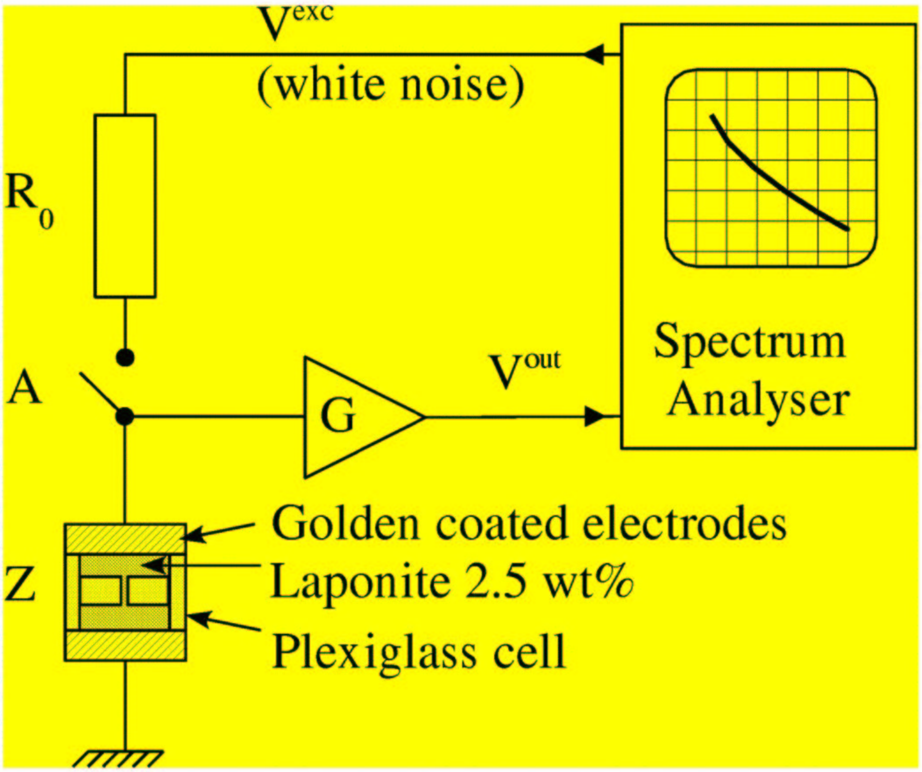
Typical intensity correlation functions at different t_w after the preparation of the sol

Elastic properties

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



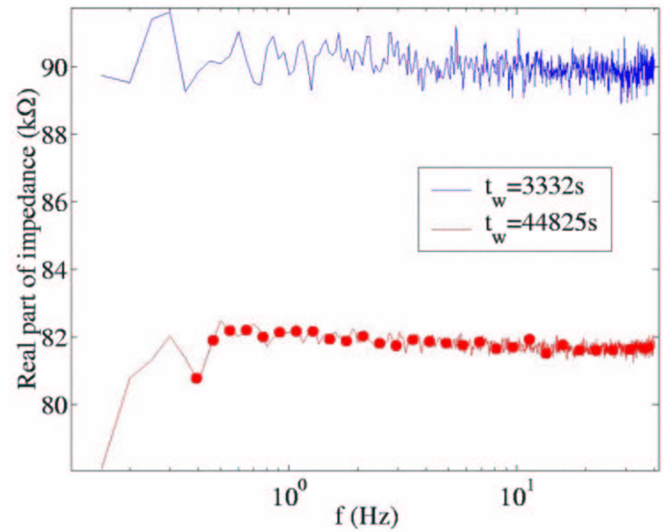
Experimental set up



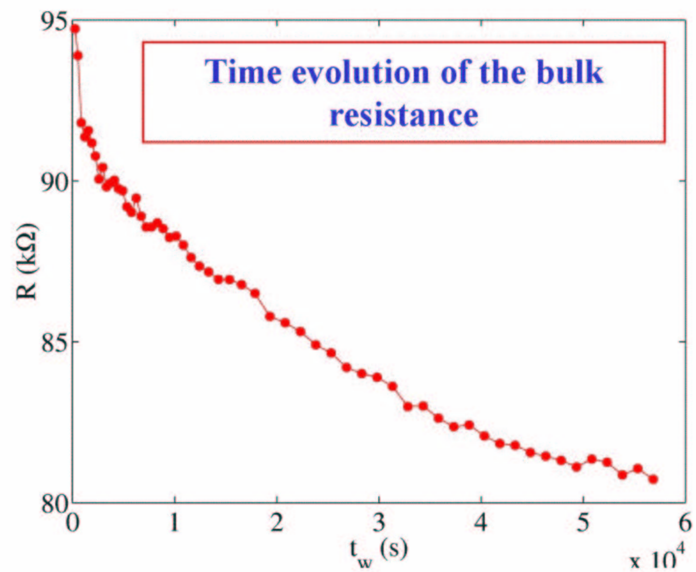
equivalent circuit

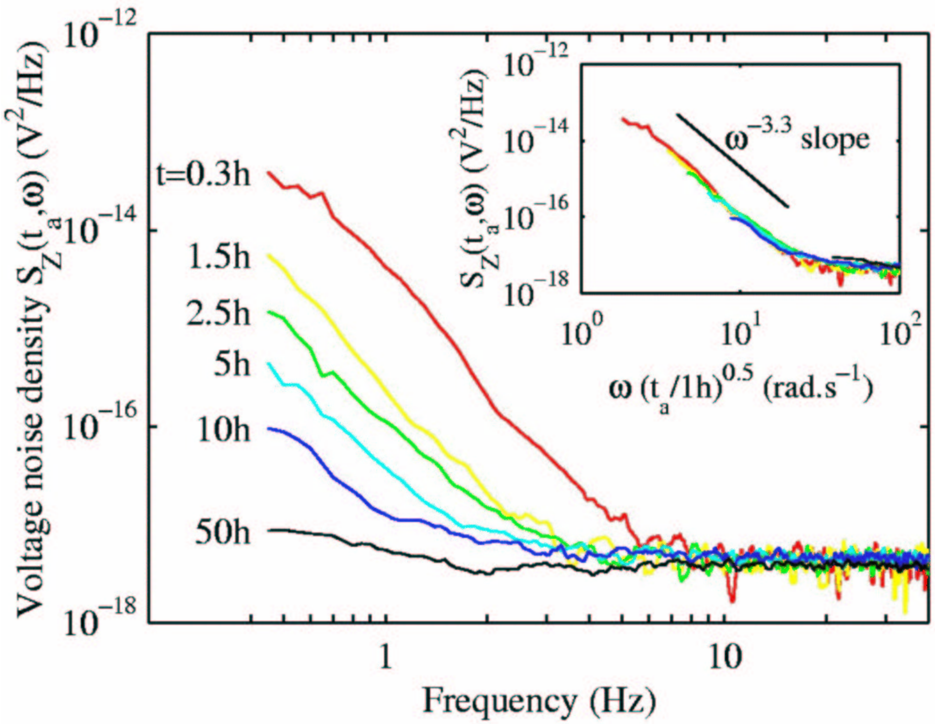
R = gel bulk resistance
Zd= impedance of the Debye layer (capacitance Cd//Rd)

Electrical response function of Laponite



Bulk resistance versus frequency at two different times





Voltage noise density of one sample for different aging times.

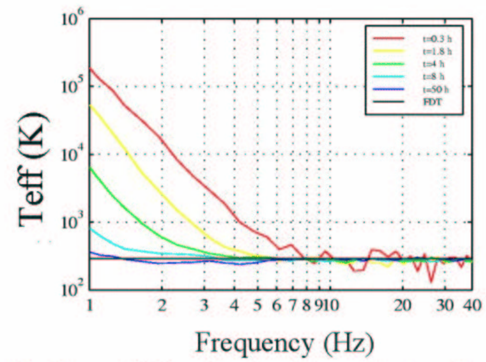
The strong increase of S_Z for low frequencies is quite well fitted by a power law:

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

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

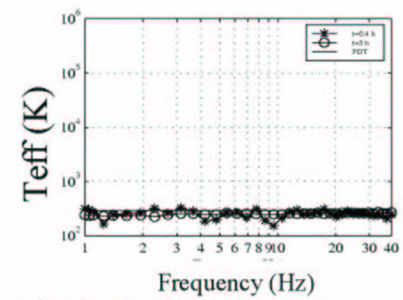
Effective temperature of Laponite

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



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

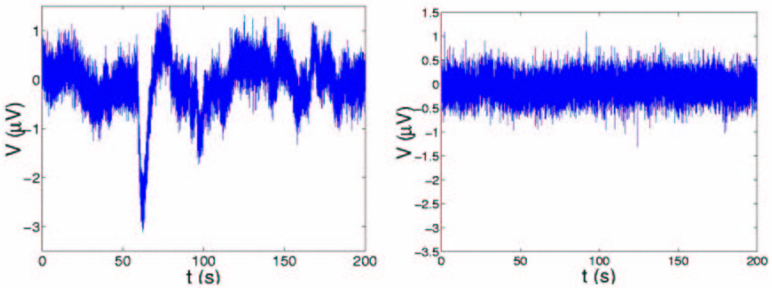
Solution test : $NaOH$ at 10^{-3} $mol.l^{-1}$



No violation is observed in this case

Signals in Laponite electric measurements

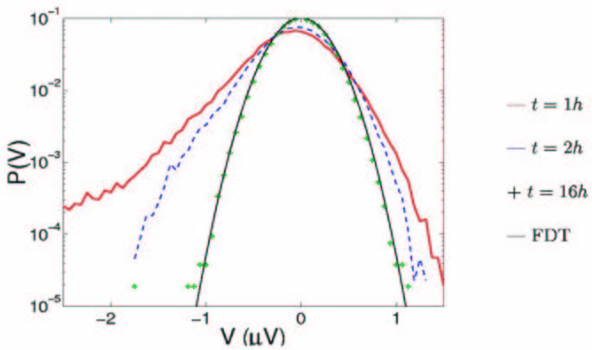
Signal as function of time



1 hour after preparation

16 hour after preparation.

PDF of the signals



When FDT is violated the fluctuations are not Gaussian

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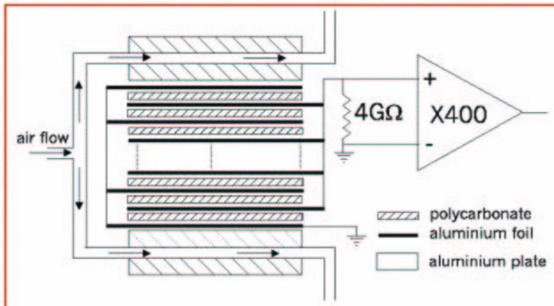
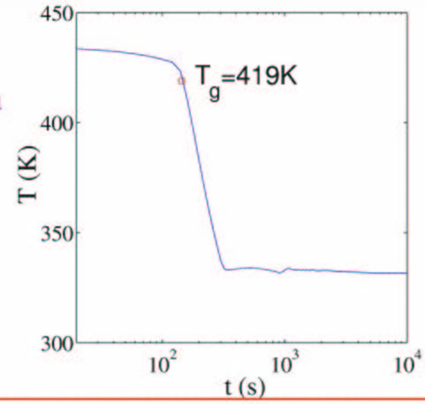
Dielectric Measurement on polycarbonate



Experimental set-up

Typical temperature quench



Electrical features for noise measurements
Input voltage noise 5nV/ $Hz^{1/2}$ for f > 2Hz
Input current noise 1fA / $Hz^{1/2}$

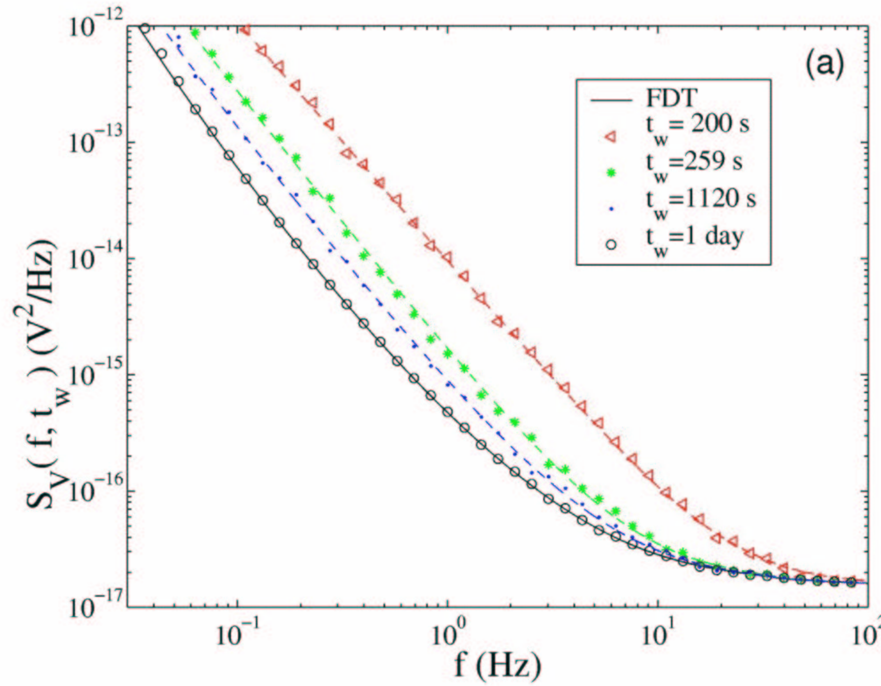
Dielectric properties are measured by a Novocontrol Dielectric Analyzer

Temperature stability 0.1 %
Max cooling rate -1K/s

Measure of dielectric noise and response in polycarbonate (Tg=419K)

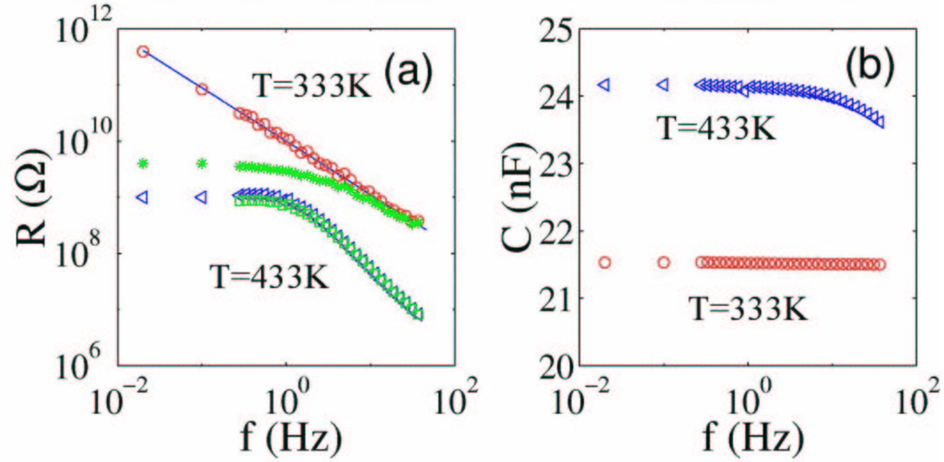
Sample is heated at 433K and rapidly quenched in ~1 mn at T_f=333K. The aging time t_w is defined as the time spent at T< Tg.
This experimental procedure is repeated several times to reduce statistical noise

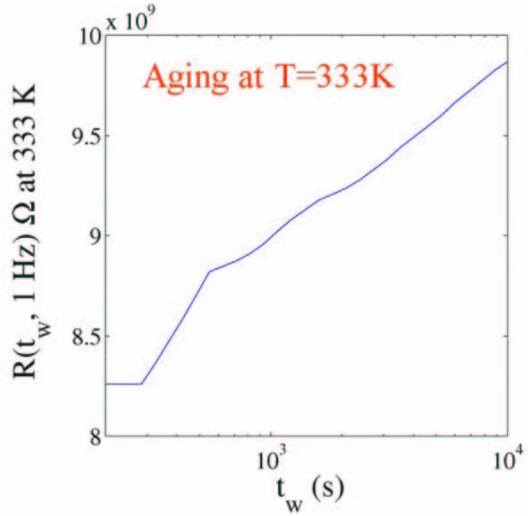
Noise spectra



Electrical response of the sample

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





Polycarbonate impedance

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

The corresponding noise spectrum of C is

$$S_Z(t_w,f) = 4\ K_B\ T_{eff}(\omega,t_w)\ Real[Z(t_w,\omega)] = \frac{4\ K_B\ T_{eff}(\omega,t_w)\ R}{1+(\omega\ R\ C)^2}$$

Taking into account the input resistance $R_i = 4G\Omega$ of the amplifier, the noise spectrum at the amplifier input is :

$$S_V(f,t_w) = \frac{4\ K_B\ R\ R_i\ [\ T_{eff}(\omega,t_w)\ R_i +\ T\ R]}{(R+R_i)^2+(\omega\ R\ R_i\ C)^2} + \boxed{+\frac{S_\xi(f)\ (R\ R_i)^2}{(R+R_i)^2+(\omega\ R\ R_i\ C)^2} + S_\eta(f)}$$

Amplifier noise contribution

where

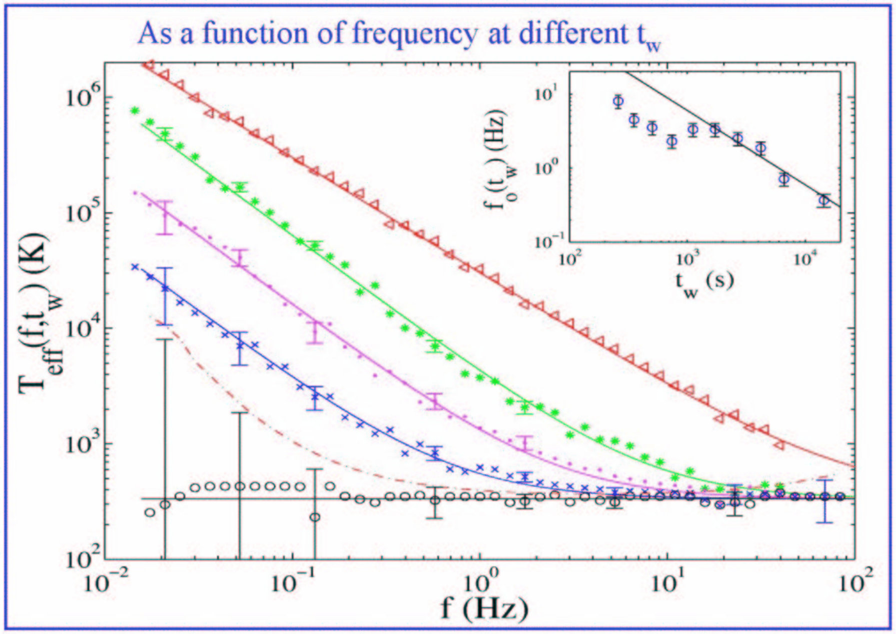
$S_\eta(f)$= voltage noise spectral density of the amplifier.

$S_\xi(f)$= current noise spectral density of the amplifier.

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

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

Effective temperature during aging of polycarbonate



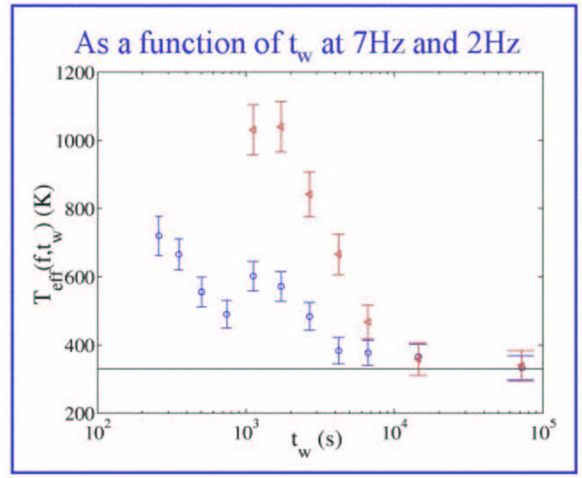
A good fit of T_{eff} for $t_w > 200s$ is

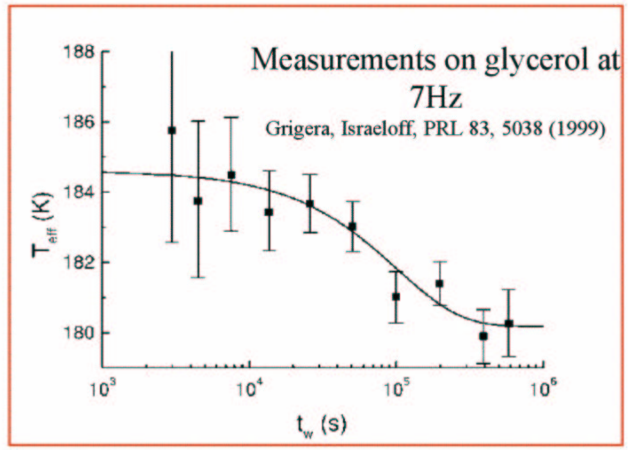
$$T_{eff}(f, t_w) = T_f \; [\; 1 \; + \; (\frac{f}{f_o(t_w)})^{-1.1} \;]$$

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

Effective temperature during aging of polycarbonate



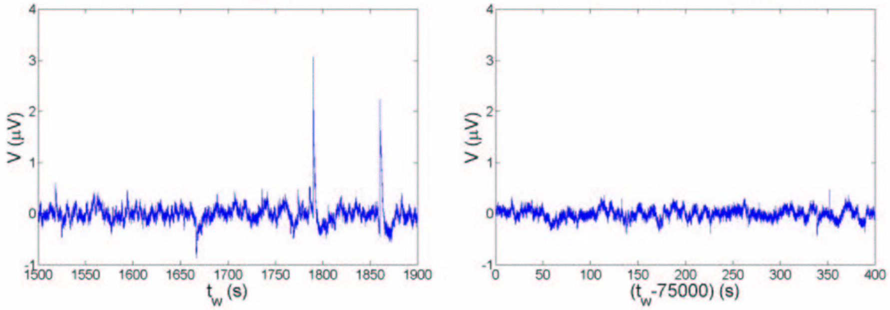


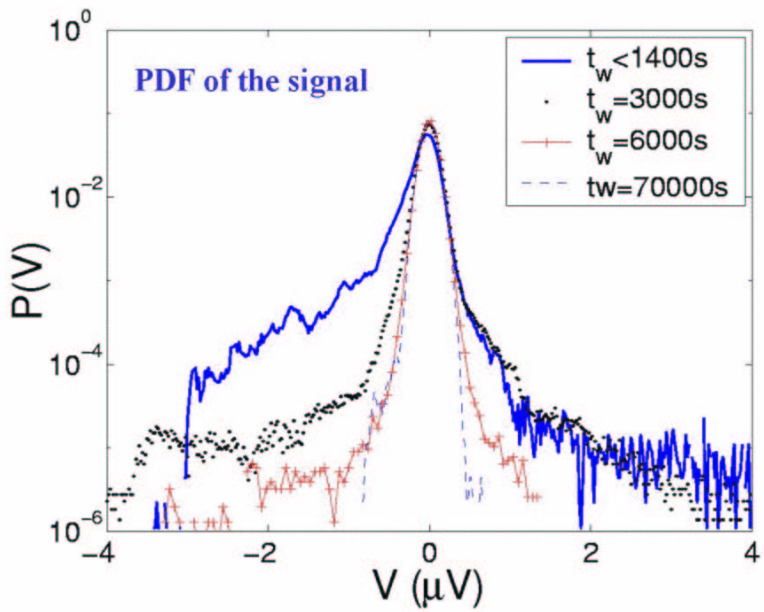
at $t_w = 1000s$
In our experiment $(T_{eff} - T_f)/(T_g - T_f) \simeq 2.4$
In glycerol $(T_{eff} - T_f)/(T_g - T_f) \simeq 1$

Polycarbonate polarisation noise

Noise signals as a function of time

1500 s after the quench 75000 s after the quench

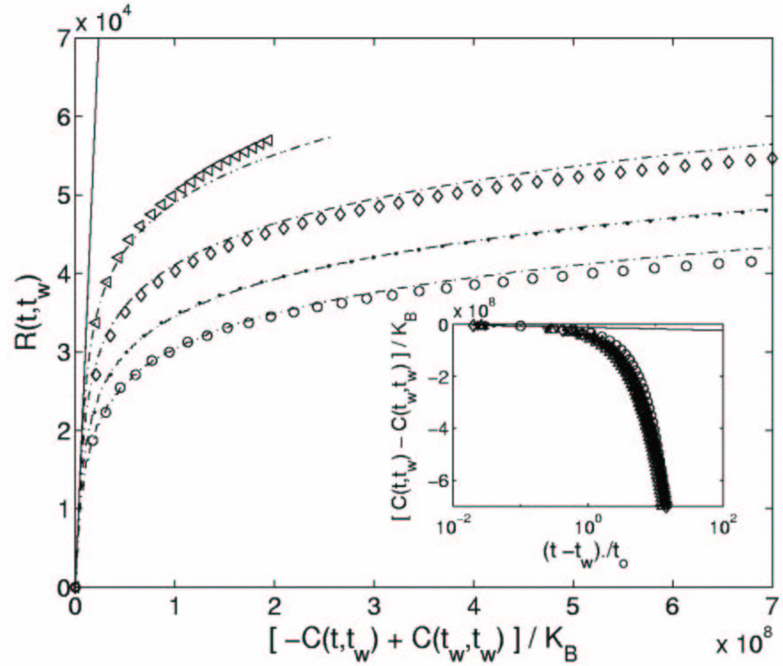




When FDT is violated the fluctuations are not gaussian

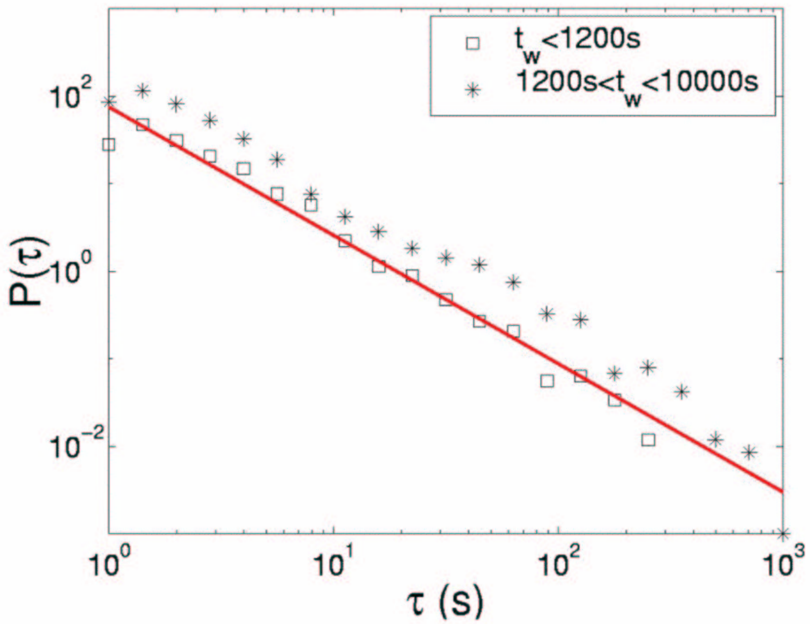
Response versus correlation

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



$(\circ)\ tw = 256s,\ (\bullet) t_w = 353s,$
$(\Diamond) t_w = 4200s,\ (\triangleleft) t_w = 6542s$

PDF of the time τ between two pulses



$P(\tau) \propto \tau^{-1.46}$ at $T/T_g = 0.8$

The trap model for aging predicts that

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

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

Summary of the results

- Dielectric measurments in a gel (during the sol gel-transition) and in a polymer (after a quench) show a strong violation of the FDT.
- The effective temperature is huge at small t_w
- The amplitude and the persistence time of the violation are decreasing functions of frequency.
- The violation is observed even for $\omega t_w >> 1$. It may last for more than 3h for f>1Hz.
- The strong violation is produced by a very intermittent dynamics.
- The statistics of the signal is highly non Gaussian

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Interpretation

- 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:
  - The 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.

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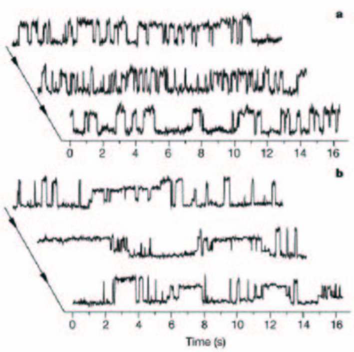
question: are there other experiments presenting such an intermittent dynamics ?

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, Proceedings, Pisa 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.

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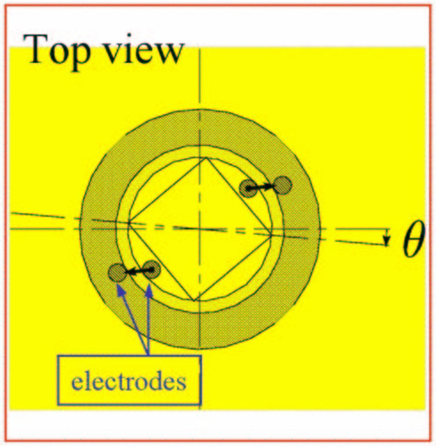
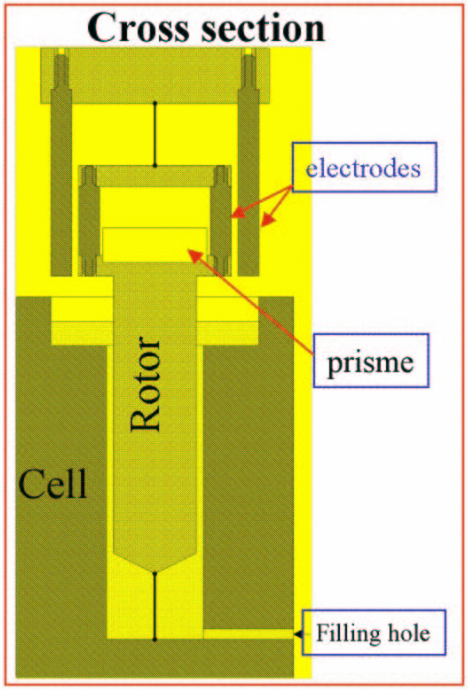
Rheological Measurements on Laponite

Question: Has the effective temperature, defined using a different couple of variables, the same behaviour ?

Rheometer

(RSI, September 2002)





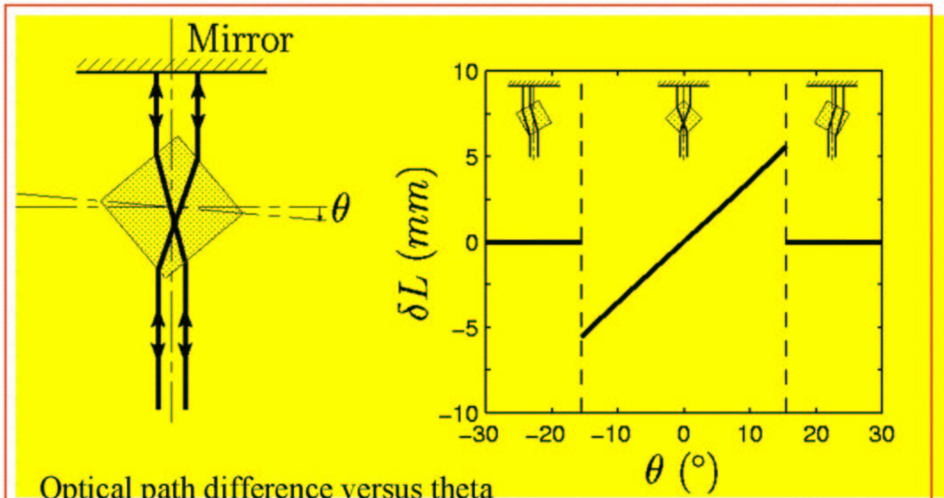
$\Gamma_{ext} =$ Torque on the rotor $= B\ \delta v^2$

δv voltage between electrodes

Rheometer performances:

sensitivity: $10^{-10} rad/\sqrt{Hz}$ equivalent to

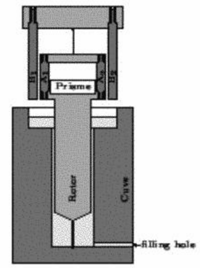
$$10^{-13} N \cdot m/\sqrt{Hz}$$

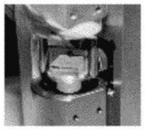


Optical path difference versus theta

Rheological properties of Laponite

Rheometer





Rheometer performances :
sensitivity : $10^{-10} rad/\sqrt{Hz}$ equivalent to $10^{-13} N \cdot m/\sqrt{Hz}$
The response is :

$$\chi_{\theta\Gamma_{ext}} = \frac{\delta\theta}{\Gamma_{ext}}$$

where

$$\frac{1}{\chi_{\theta\Gamma_{ext}}} = (k - J\omega^2) - i\alpha\eta\omega$$

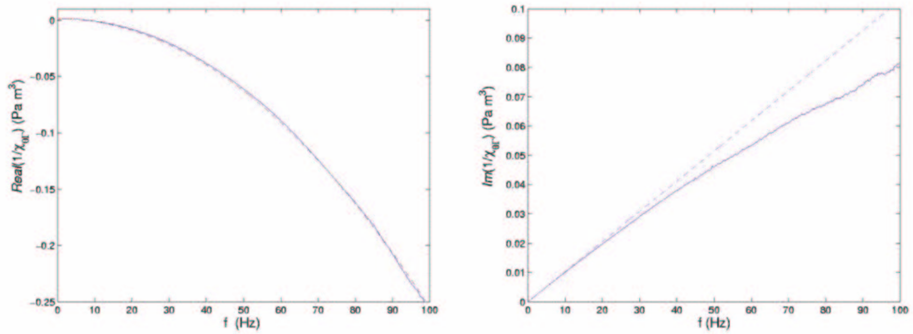
η fluid viscosity
J moment of inertia
α geometric factor

In this case the fluctuation dissipation relation is :

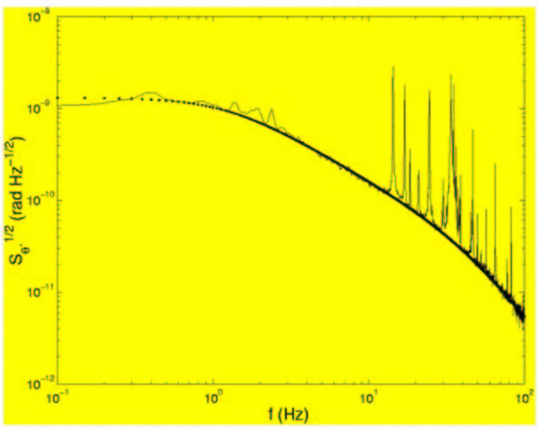
$$S_\theta = \frac{4K_BT}{\omega} Im(\chi_{\theta\Gamma_{ext}})$$

Test with a silicon oil $\eta = 2.2 Pa/s$

Response of the rheometer to a torque with a white spectrum $\Gamma_{ext} \simeq 10^{-10} N \cdot m/\sqrt{Hz}$



Spectrum of the thermal fluctuations of θ

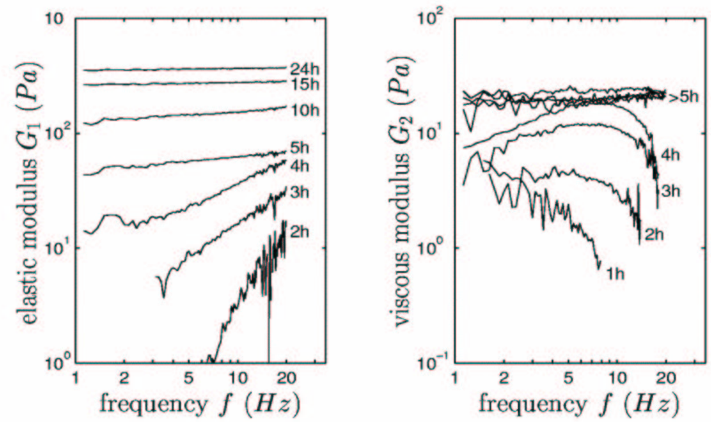


FDT..............

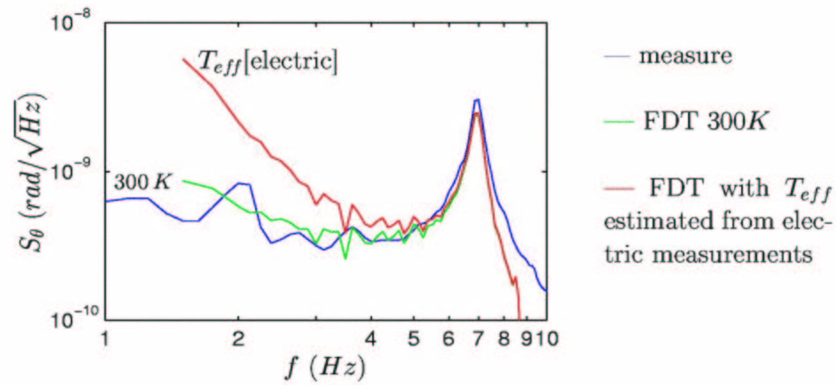
The fluctuation dissipation relation can be checked

Laponite at 2.5% mass concentration in water

Viscoelastic properties as a function of time



Spectrum of the thermal fluctuations of θ



No detectable violation of FDT in rheological measurements

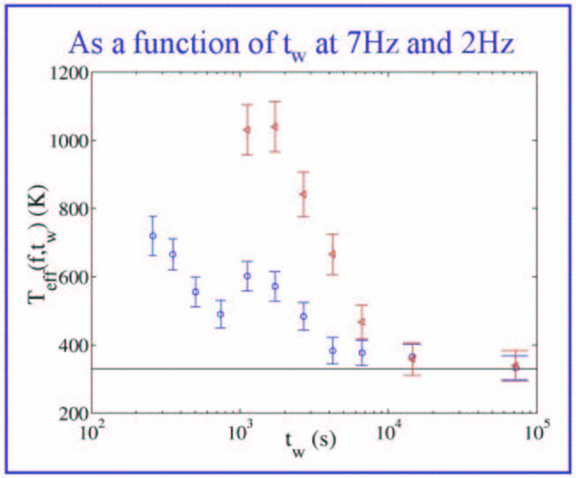
Conclusions

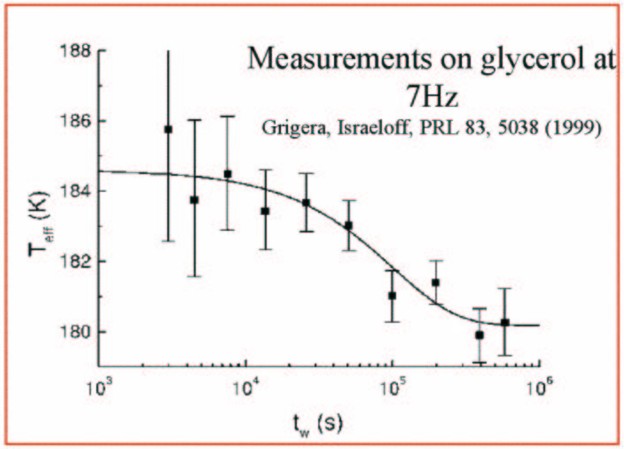
- Dielectric measurements show a non trivial violation of FDT during aging.
- The dynamics is strongly intermittent
- The effective temperature does not seem to be the same for different couples of variables (in Laponite). Much work is needed to understand this important point.
- High order statistics are certainly useful to understand the dynamics of these systems

Useful transparencies

Supercooled fluids and polymers (dielectric measurements)

Effective temperature during aging of polycarbonate





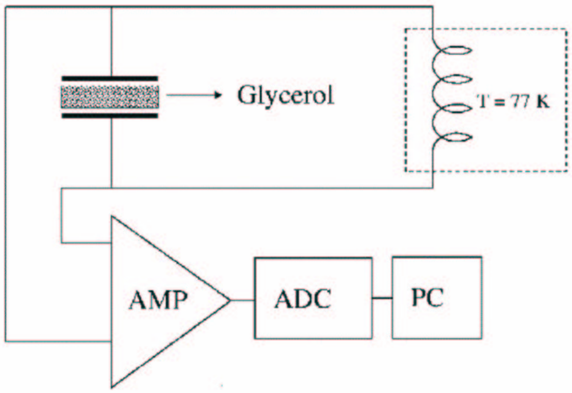
at $t_w = 1000s$

In our experiment $(T_{eff} - T_f)/(T_g - T_f) \simeq 2.4$

In glycerol $(T_{eff} - T_f)/(T_g - T_f) \simeq 1$

Measurement on Glycerol

Grigera, Israeloff, PRL 83, 5038 (1999)



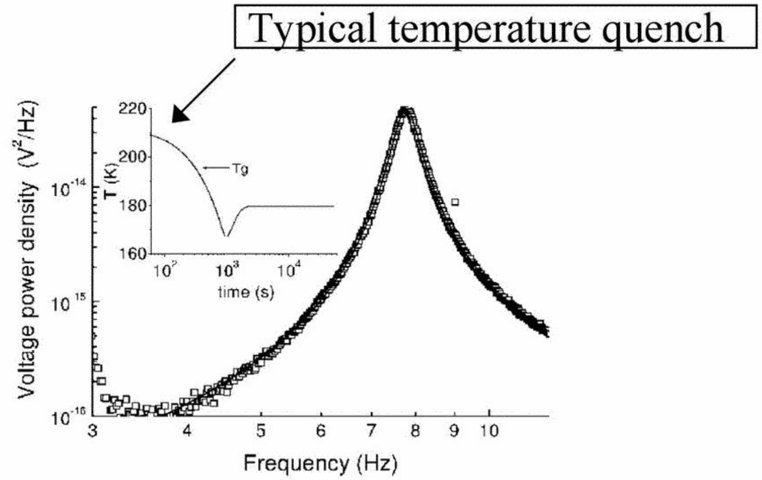
Experimental set-up

Resonant circuit with C=C'-iC" and L=L'+iL"

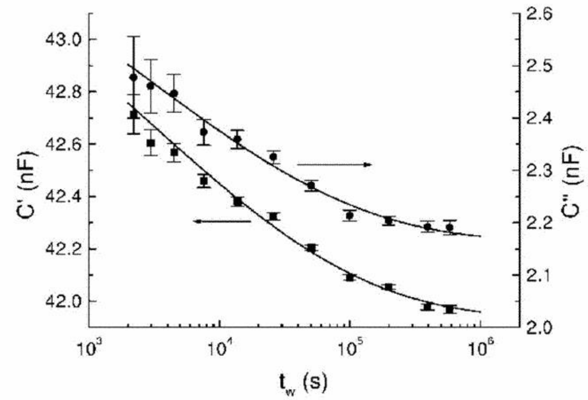
The noise spectrum is:

$$S_V(\omega) = \frac{2k_B}{\pi}\,\frac{-\omega^3 T_{\rm eff}(\omega_0, t_w)\,|L|^2 C'' - \omega T_0 L''}{1 - 2\omega^2(L'C' - L''C'') + \omega^4 |L|^2 |C|^2},$$

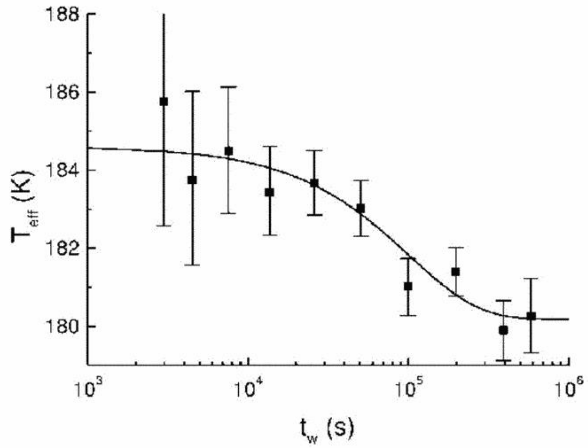
Noise spectrum near resonance



Response at 7Hz as a function of time



T_{eff} measured at 7Hz as a function of time



Local Measurements

Figure 1. Heterogeneous scenario. **a**, The imaginary component of the dielectric susceptibility, ε'', is assumed to arise from a superposition of Debye peaks. In a mesoscopic sample (**b**), the individual Debye peaks become apparent as spectral features, particularly in the high-frequency tail of the α –peak. In the thermal noise spectrum (**c**) the Debye peaks appear as Lorentzians, which also produce spectral features.

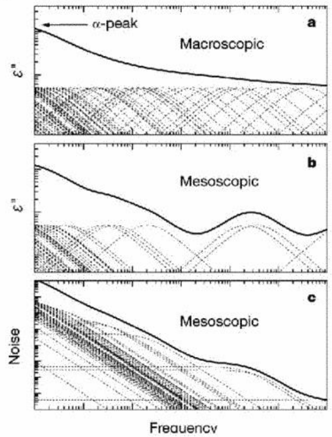


Figure 2. Noise spectra for PVAc at T 299 K. **a**, The AFM measurement setup. **b**, Successive polarization noise spectra (vs. frequency) show the appearance and subsequent disappearance of a spectral feature. Each spectrum is a 1-hour average with the relative starting time indicated. The dashed line shows a Lorentzian spectrum.

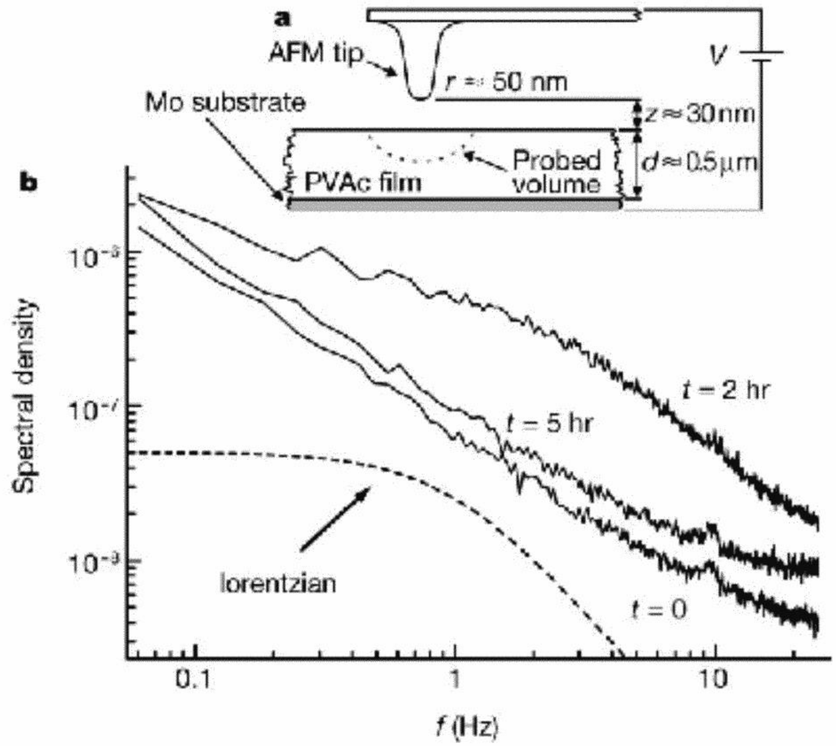


Figure 3. Lifetime of heterogeneities. The autocorrelation function of the local power spectral exponent[15] is shown for three temperatures with exponential fits and characteristic times. Inset: Heterogeneity lifetime and α–relaxation time[14] are plotted vs. inverse temperature.

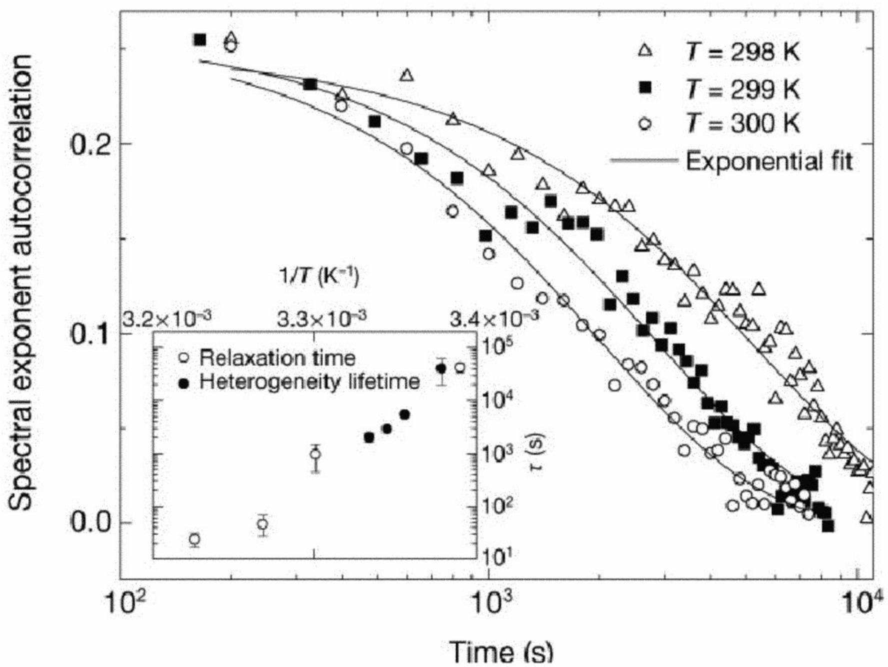


Figure 4. Time series of polarization. Two 50 s series showing random telegraph switching (RTS) noise. **a**, At 299 K, the rate of switching between two levels appears modulated. **b**, An example of a four-state switching at 300K is shown.

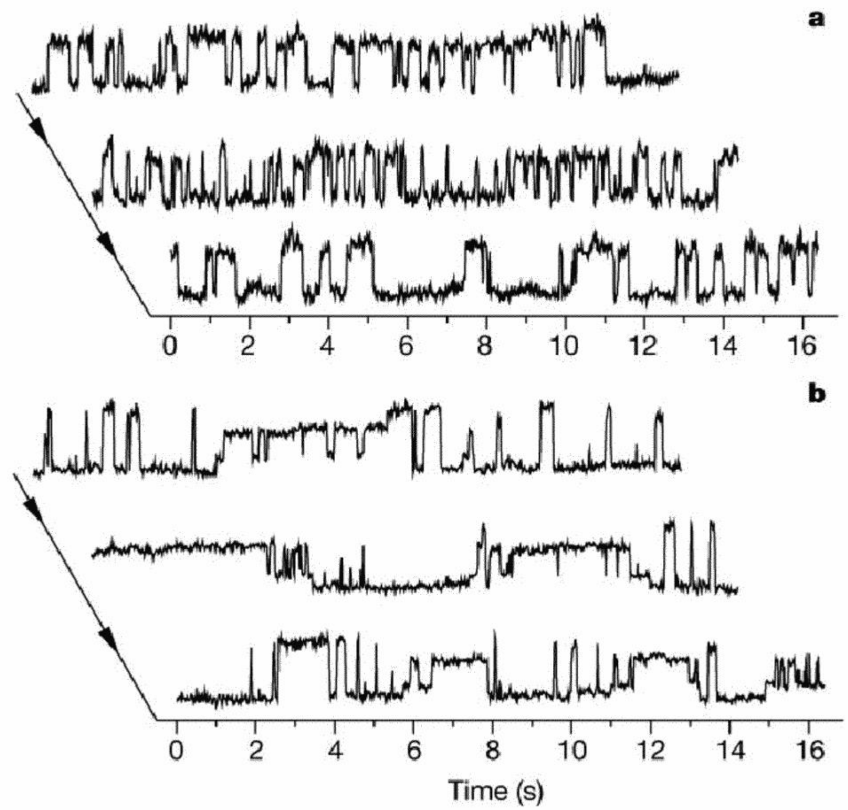
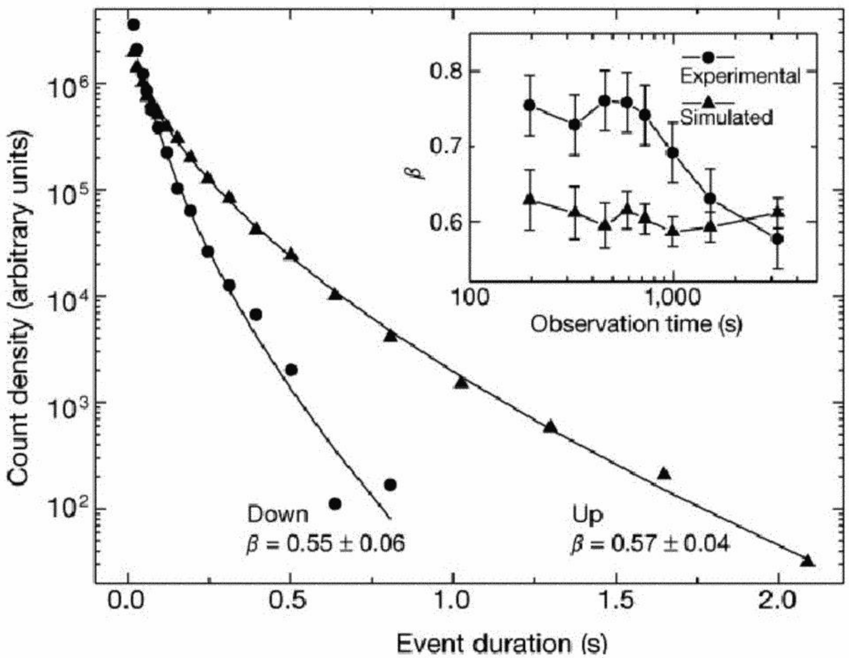
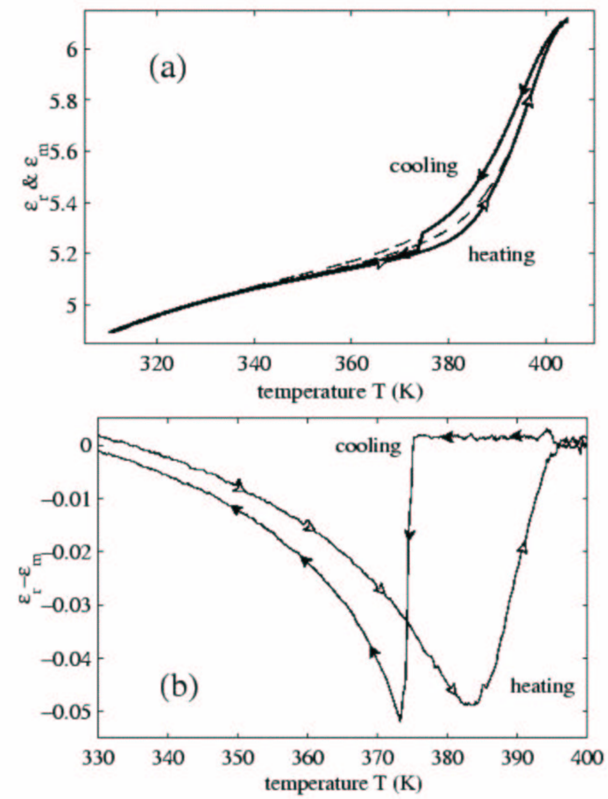


Figure 5. Individual cluster kinetics. Histograms of event durations for upper and lower states of a long-lived two-state RTS observed for 3200 s at 299 K are shown (points) with stretched exponential fit (solid line). An exponential would appear as a straight-line on this plot. The fit parameters are indicated. Inset: Average stretching exponent vs. observation time for the up-state data and a simulated intrinsic stretched-exponential RTS.



MEMORY EFFECT IN PMMA



Evolution of ϵ at $\nu = 0.1Hz$ as a function of T.

ϵ_r is the measured dielectric constant without a cooling stop

ϵ_m is the measured dielectric constant with a cooling stop

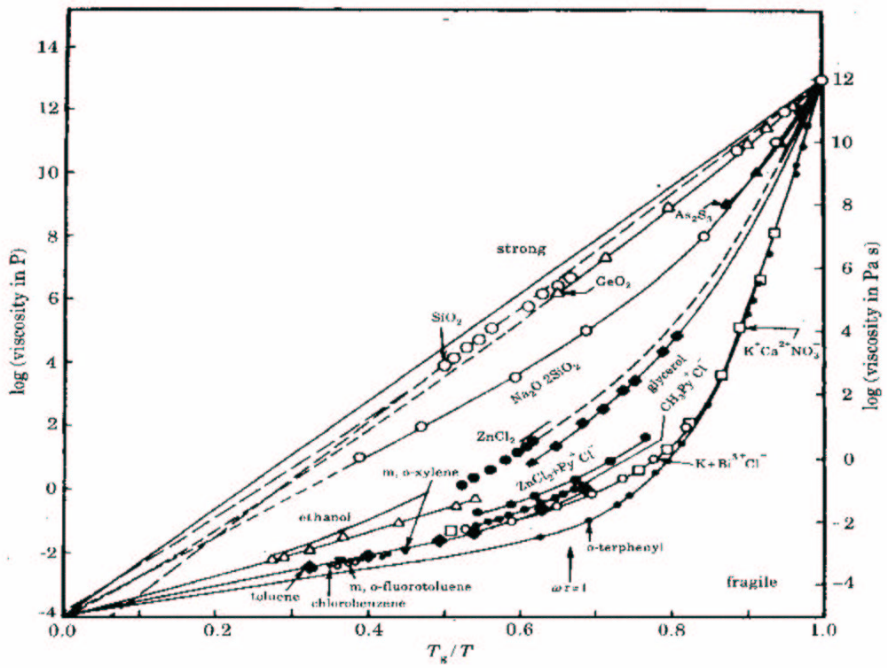
Interpretation

These results seem to indicate that memory and rejuvenation phenomena in the aging process may be described :

I) By models based on a hierarchical free energy landscape, whose barriers grow when temperature is lowered (Bouchaud, Vincent)

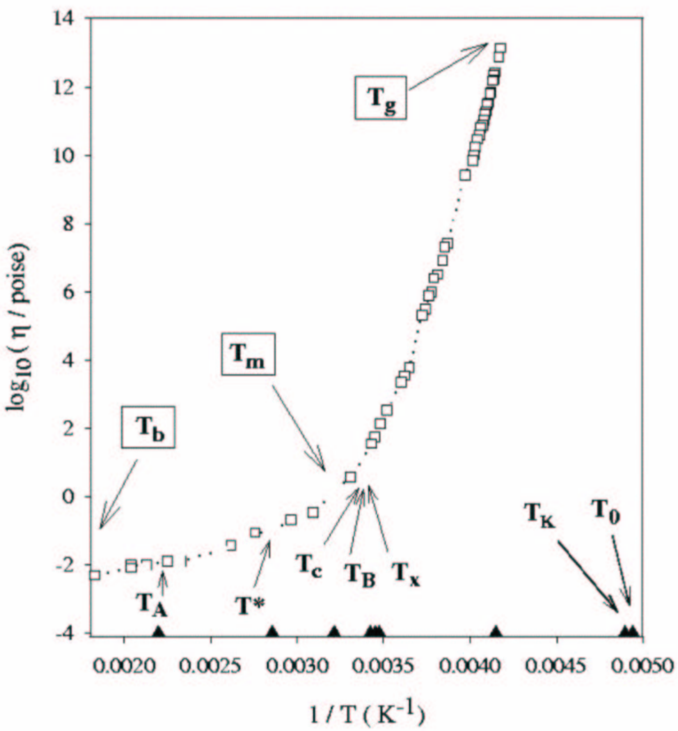
II) By models based on a slow domain growth and domain walls reconformations in the pinning field created by disorder (Bouchaud)

Viscosity as a function of Tg/T



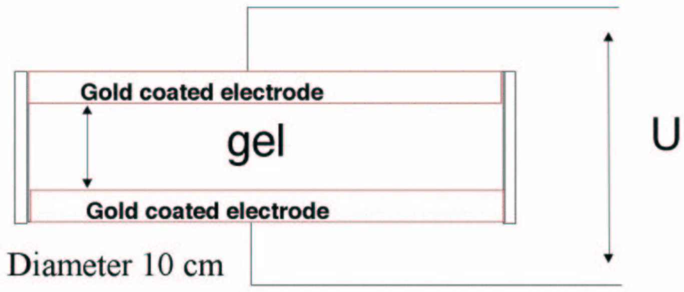
GLASS TRANSITION

Viscosity



Dielectric measurement at very low frequencies in Laponite

Experimental set up



Problems

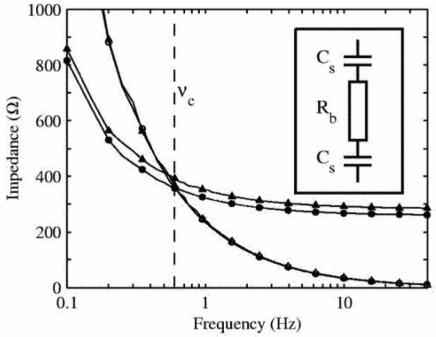
- **Glass transition temperature not well defined**
- **Formation of the Debye layers on the electrodes**

equivalent circuit

R = gel bulk resistance
Zd= impedance of the Debye layer (capacitance Cd//Rd)

Electrical response function of Laponite at 2.5% mass concentration in water

a) Frequency dependence of a sample impedance for 2 different aging times



$t_a = 0.3h$
real part (▲)
imaginary part (△)

$t_a = 24h$
real part (●)
imaginary part (○)

b) Time evolution of the bulk resistance