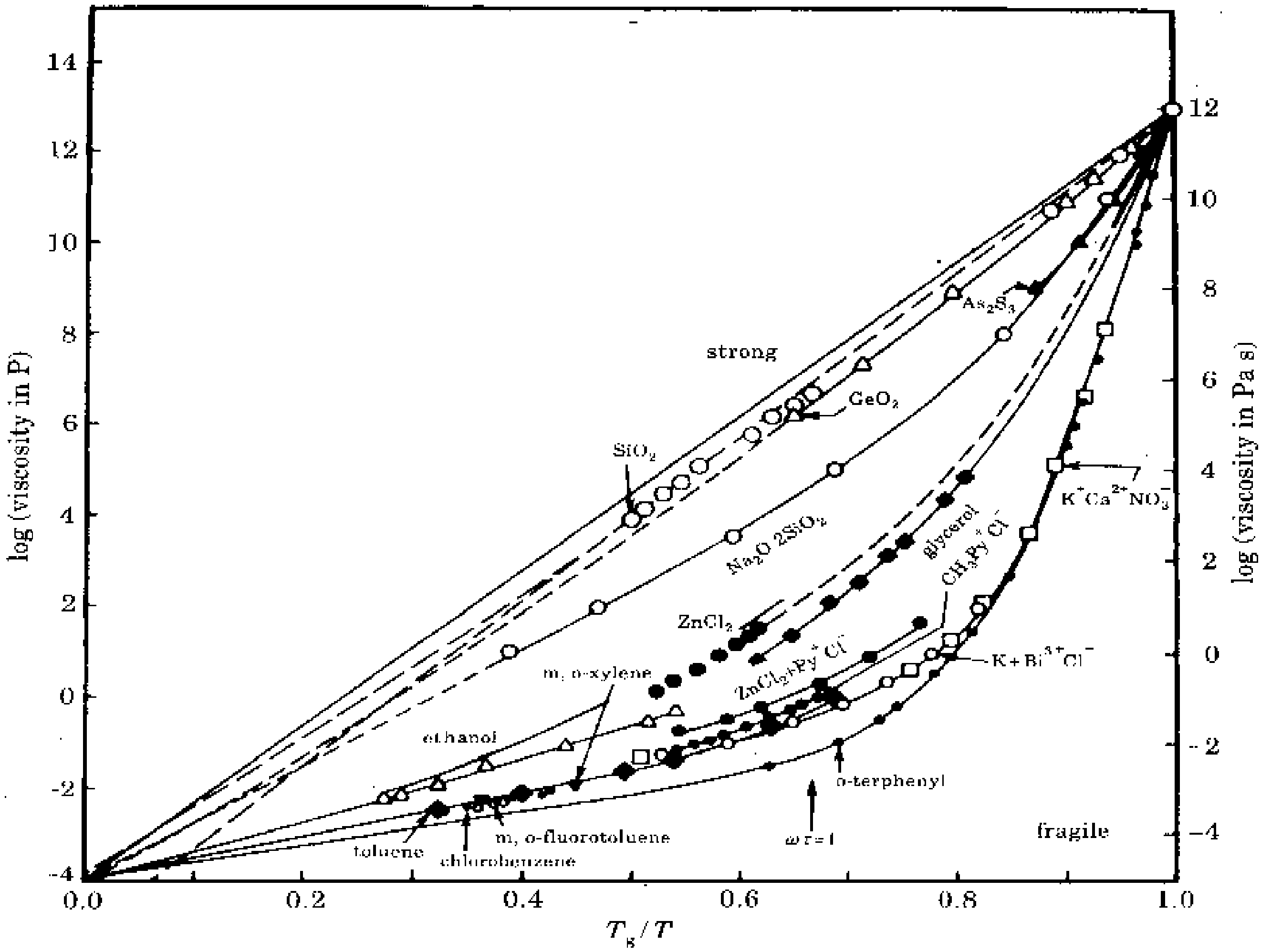
Viscosity as a function of Tg/T



- 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

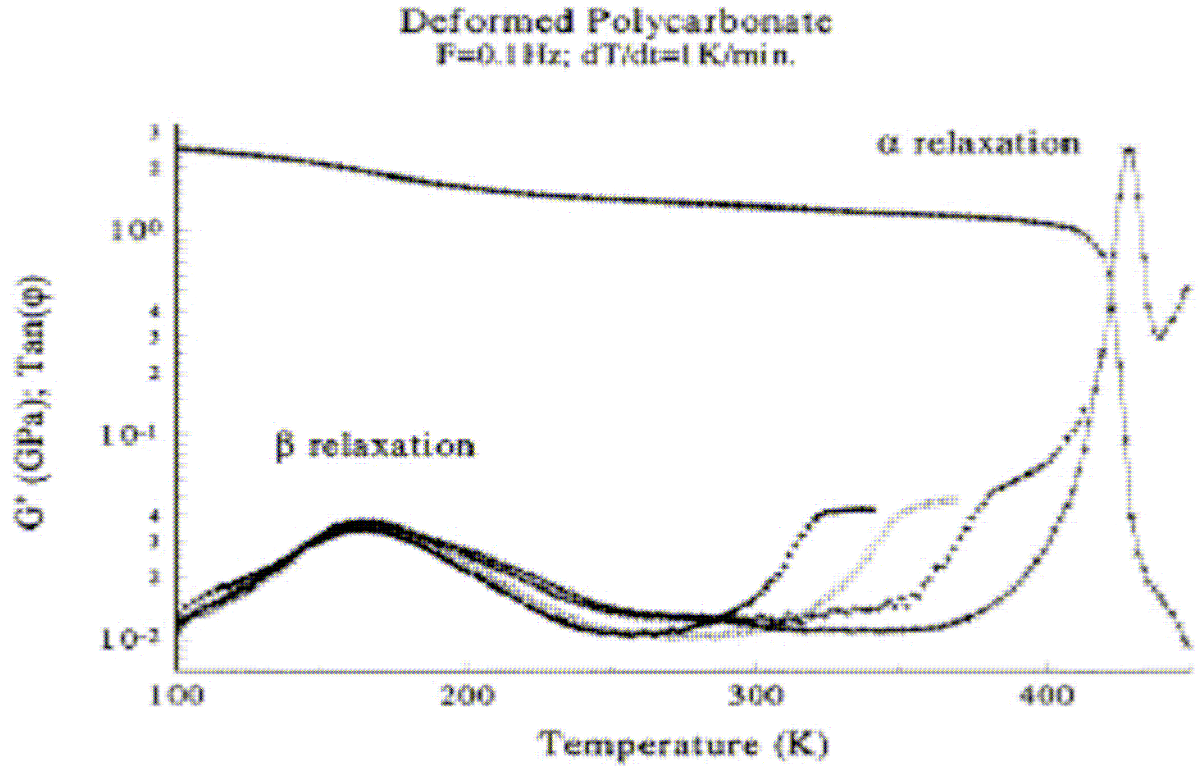


Fig. 3. Evolution of $\tan(\Phi) = G''/G'$ with temperature for successive heating runs for deformed polycarbonate (applied deformation close to 50%, in compression at ambient temperature). (●) first scan up to 339 K; (○) second scan up to 368 K; (+) third scan up to 413 K; (×) last scan up to 448 K,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

Dielectric measurements

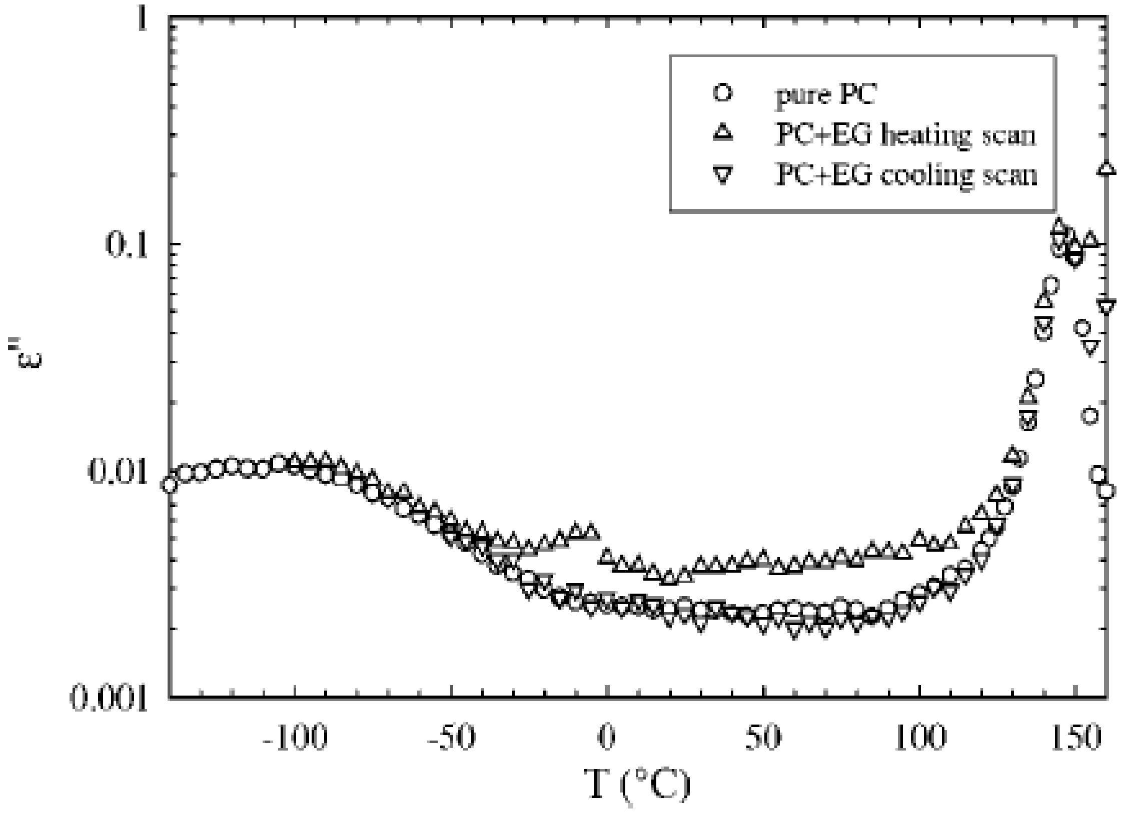
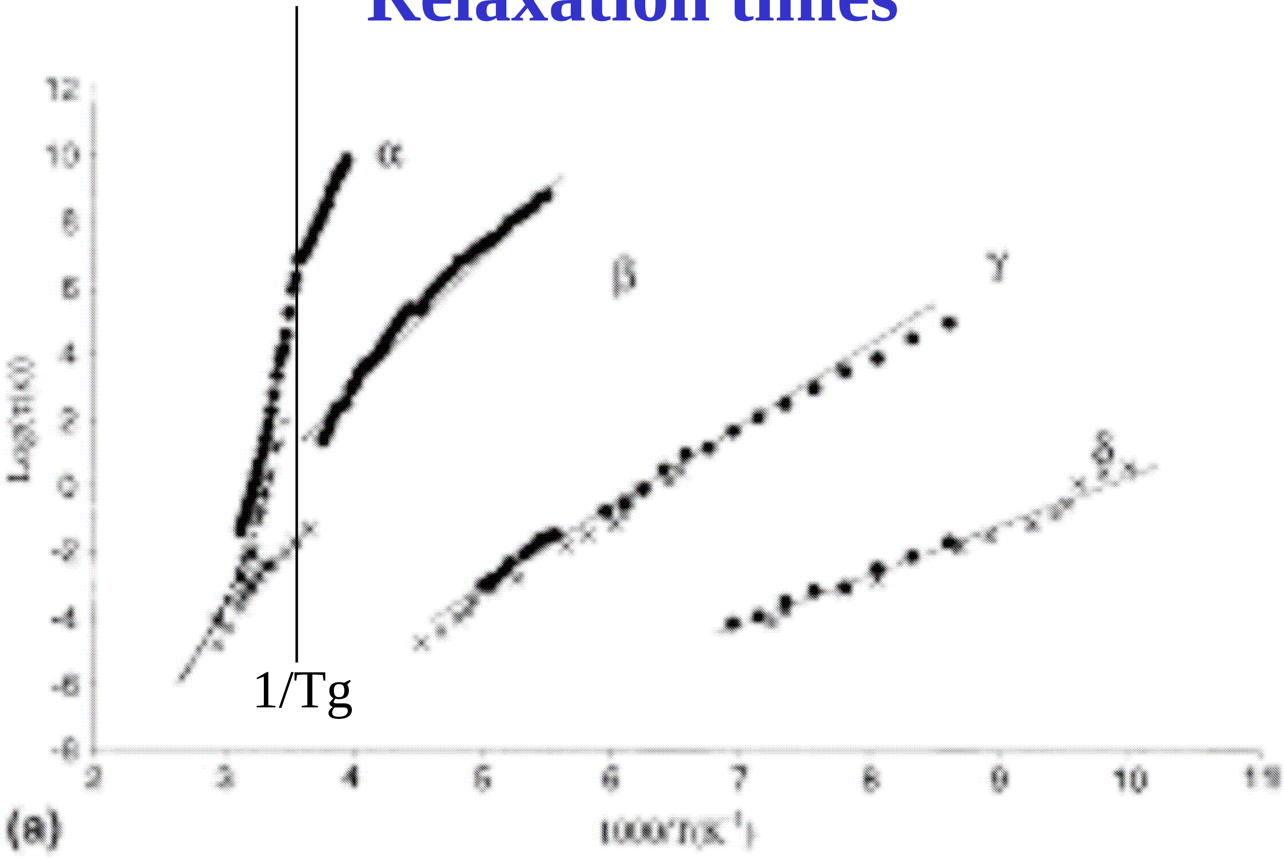


FIG. 4. Dielectric loss vs temperature at 1.2 Hz for pure PC and PC-EG systems during heating and cooling.

Relaxation times



Vogel-Fulcher-Tamman law for T>Tg

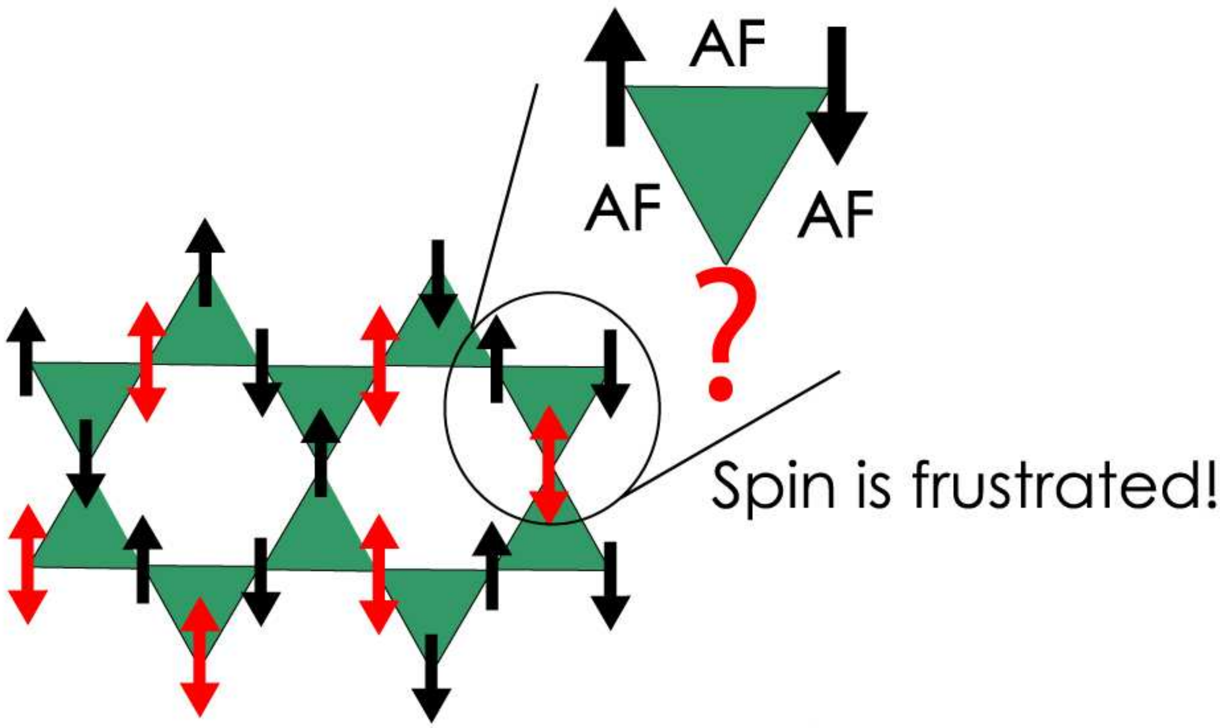
$$\tau = \tau_o \ \exp\left(\frac{B}{T - To}\right)$$

where To<Tg

Type of glasses

- Structural glasses
- Magnetic glasses
- Colloids

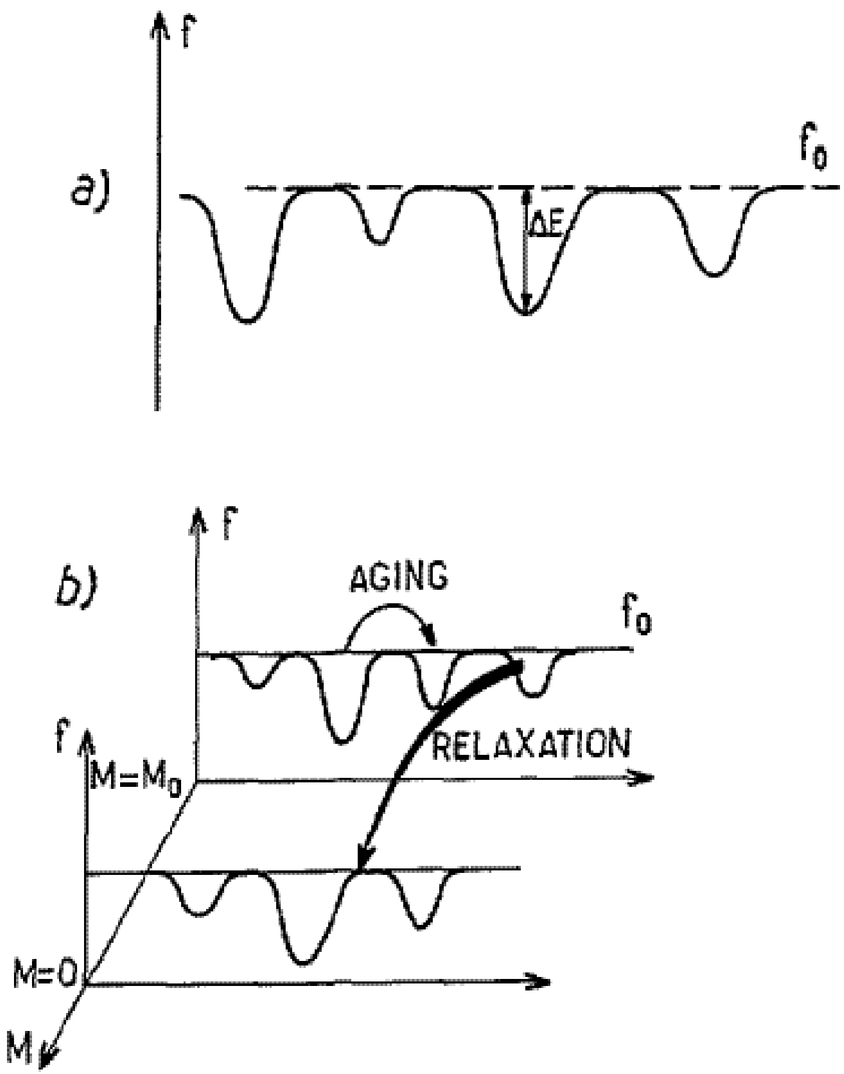
Frustation



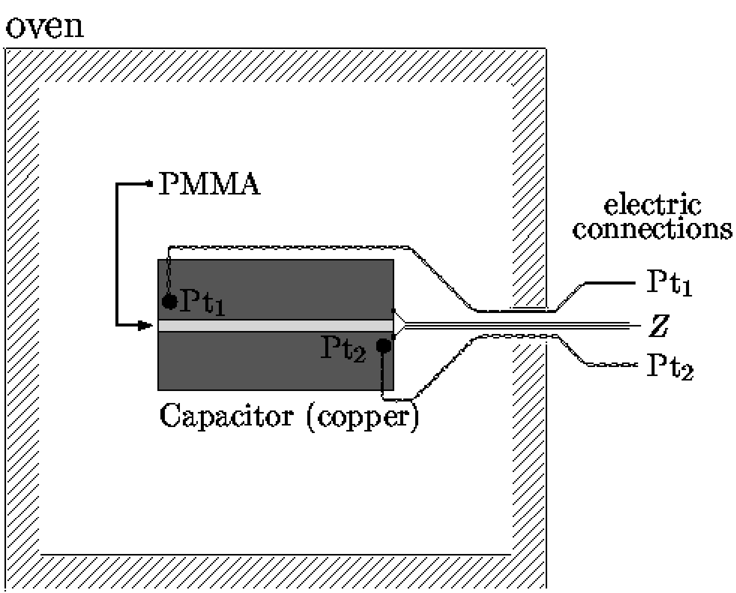
Spin Frustration on the Kagomé Lattice

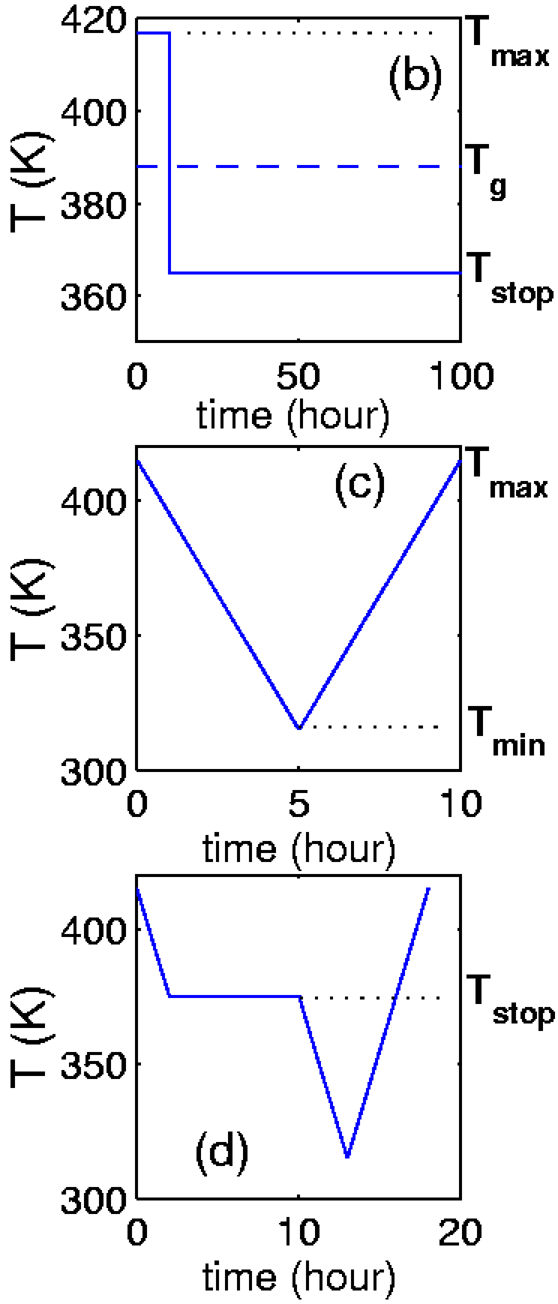
Energy landscape

Bouchaud trap model



Aging and Memory effect in a polymer

(a) 

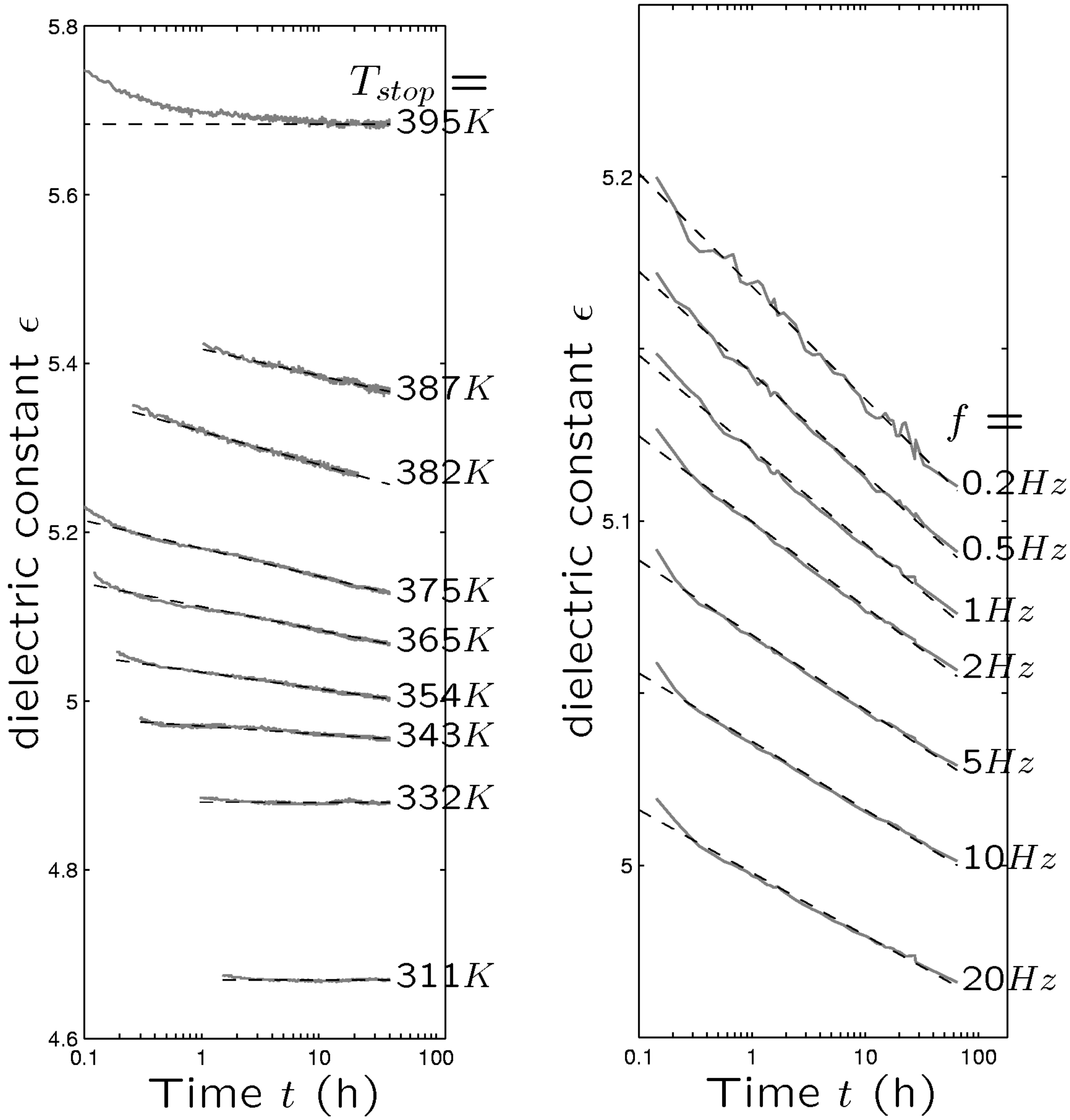


(a) **Experimental set-up for PMMA**. PMMA is the dielectric of a capacitor whose vacuum capacitance is $C_0 = 230pF$.

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

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

Aging of PMMA (T_g= 388K)



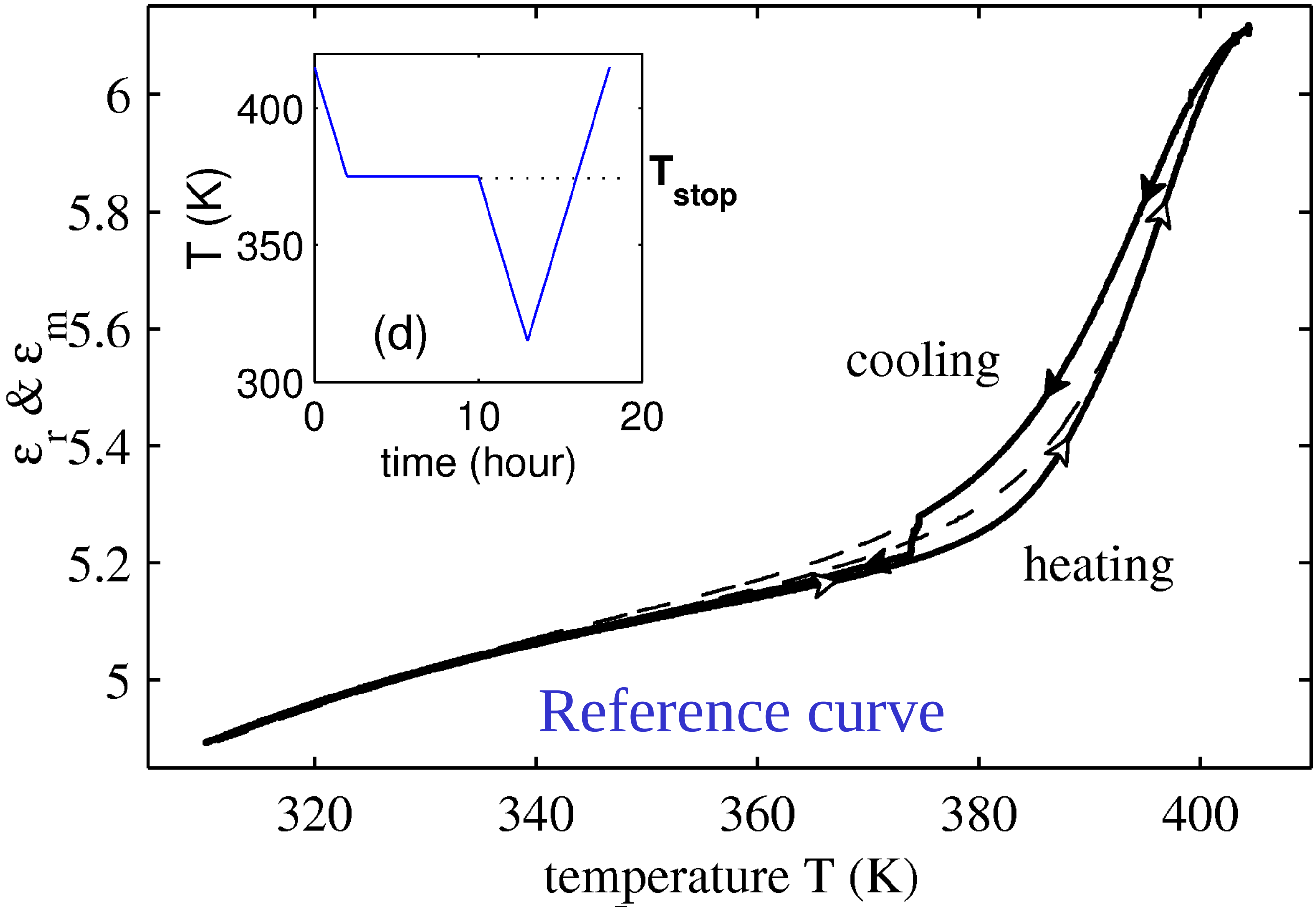
Dependence on t of ϵ after a quench.

(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



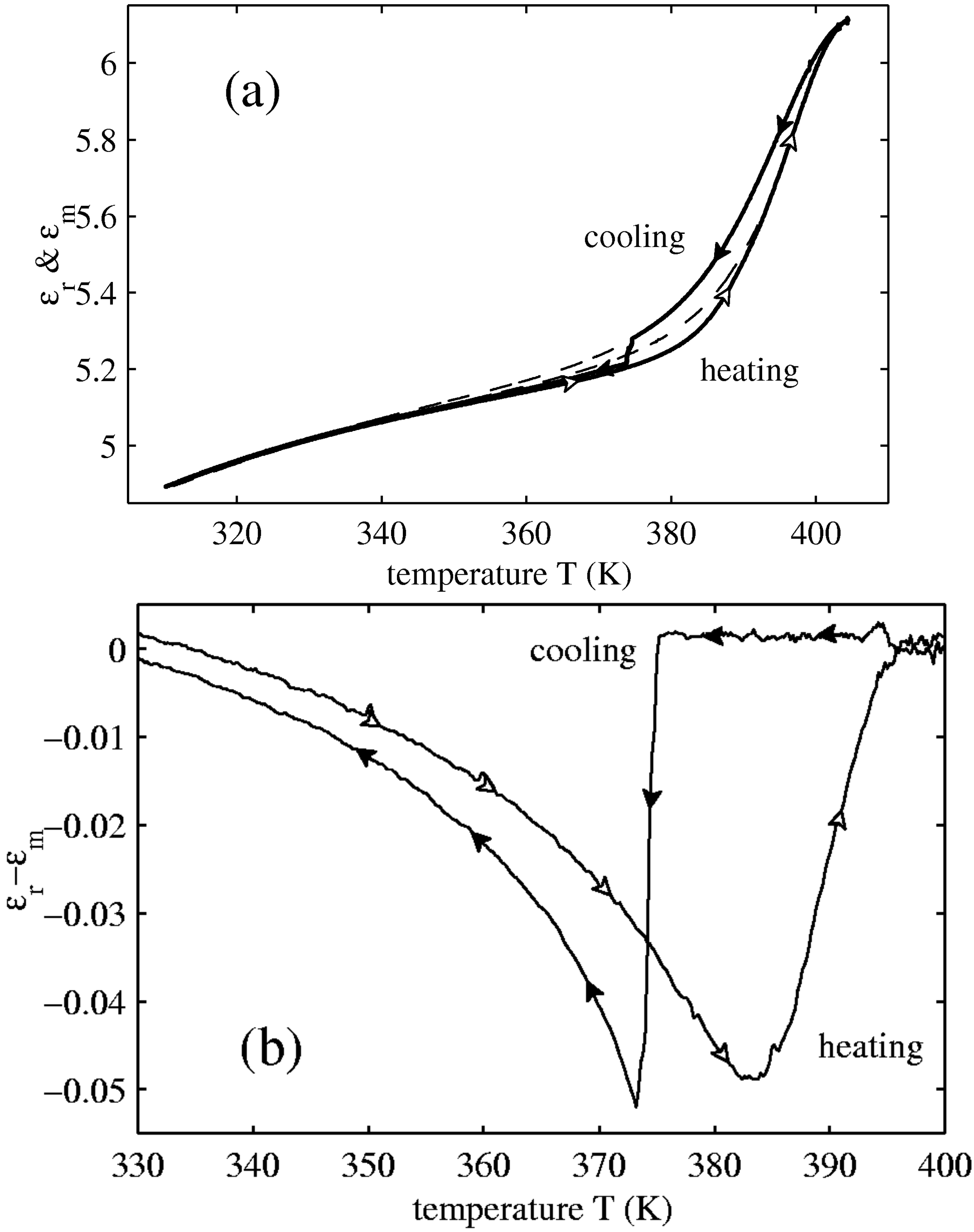
- - - Reference curve

—— Curve with a cooling stop

ϵ_r = dielectric constant measured with continuous ramp

ϵ_m = dielectric constant measured with a cooling stop

Memory effect in PMMA

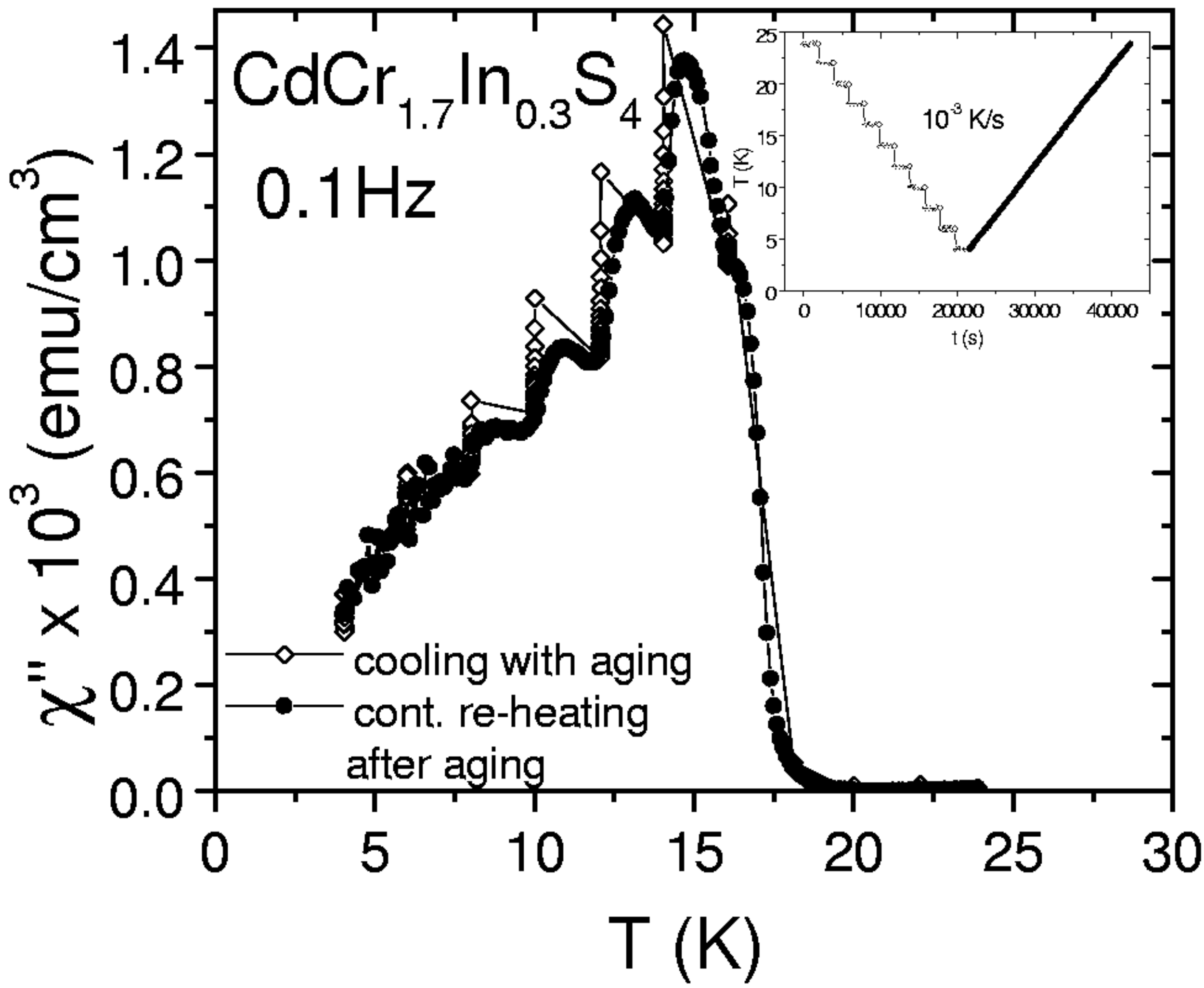


Evolution of ε at f=0.1Hz as a function of T

ϵ_r = dielectric constant measured without a cooling stop

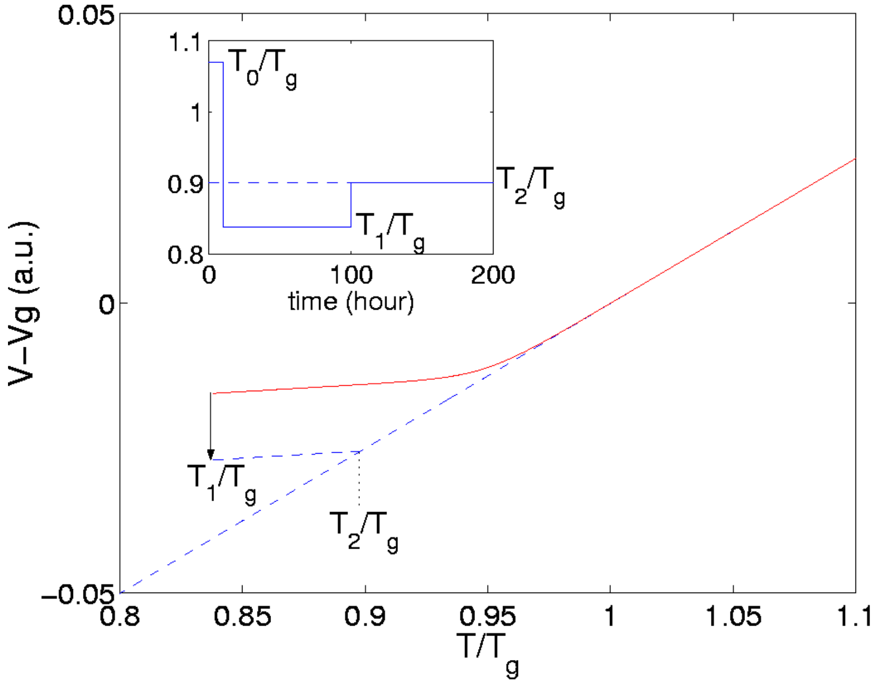
ϵ_m = dielectric constant measured with a cooling stop

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

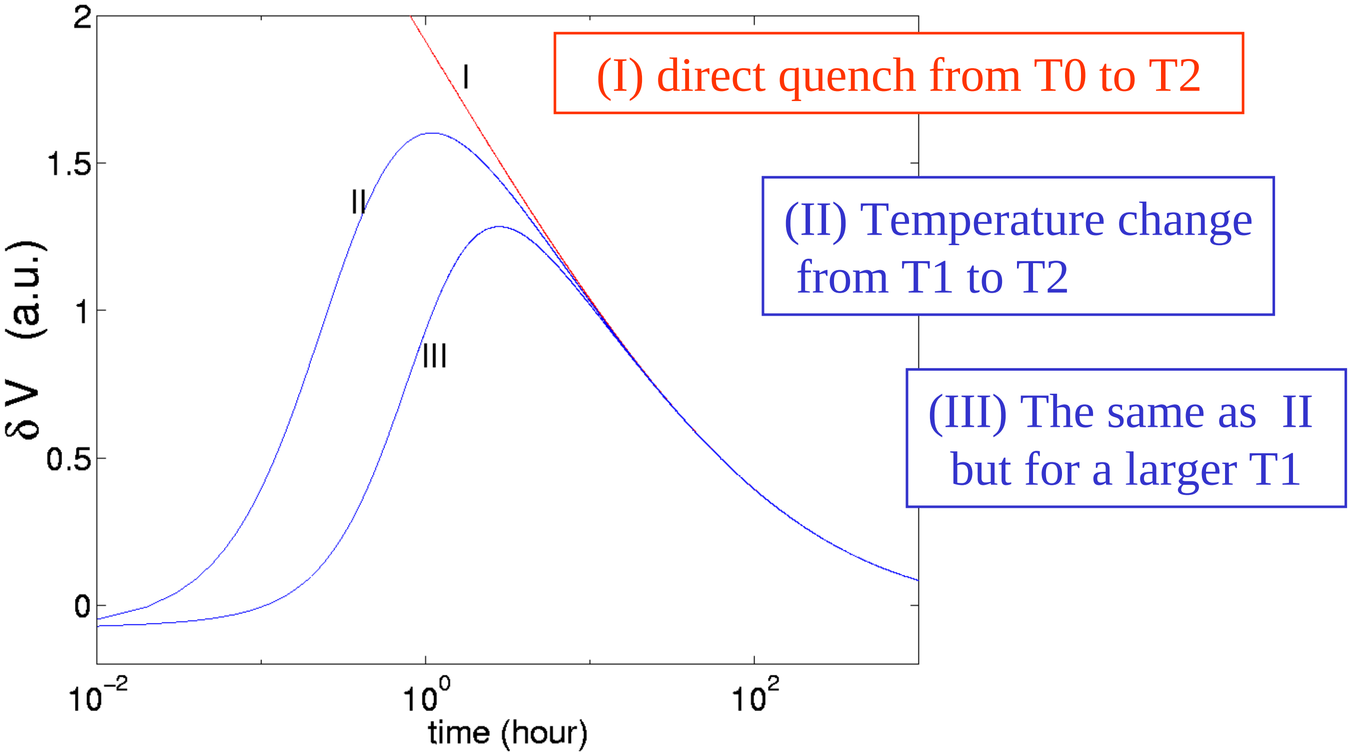


Measure of the Volume

Fast quench

Slow ramp

Time evolution of $\delta V = V - V_2$



- The sample reminds its thermal history
- The response of the system depends on the quench speed

Memory effects and trap model

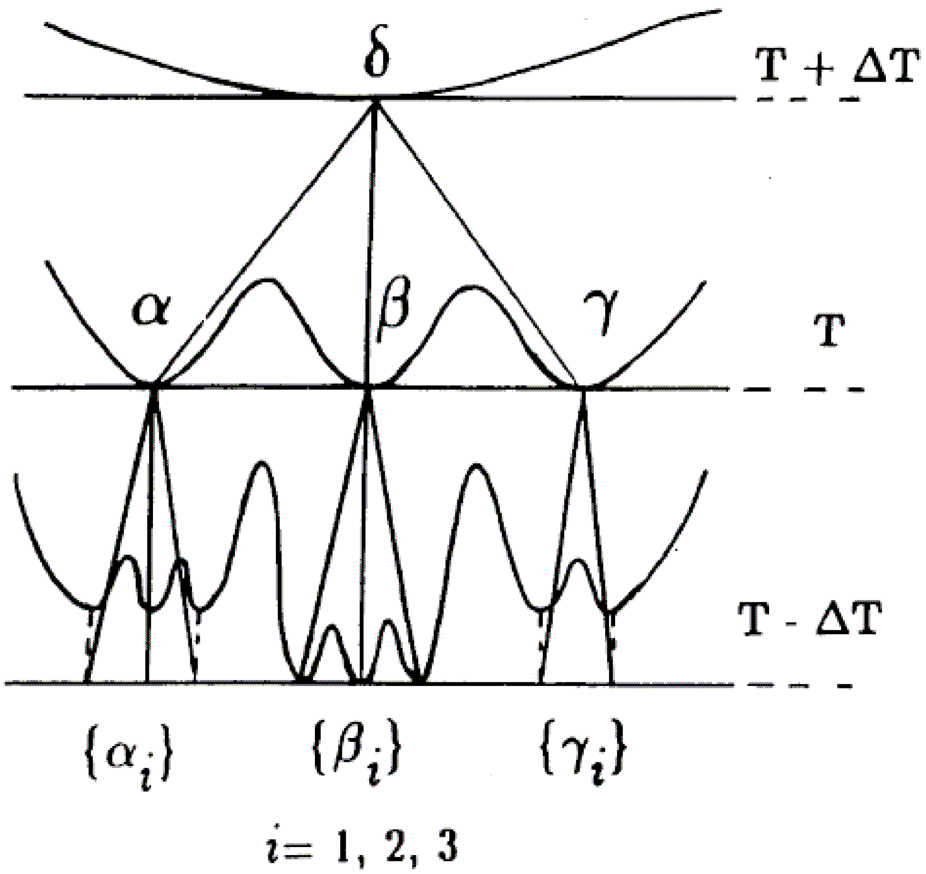


Fig. 6. Schematic picture of the hierarchical structure of the metastable states as a function of temperature.

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 ?

Outline

1) Thermal fluctuations and the Fluctuation Dissipation Relations during aging

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

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

4) The mechanical noise.

5) Conclusions

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

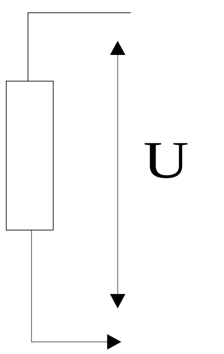
$$S(\omega) = \frac{4\,K\,T}{\omega}\, Im\{R(\omega)\}$$

Typical examples are :

(U,q)

Nyquist

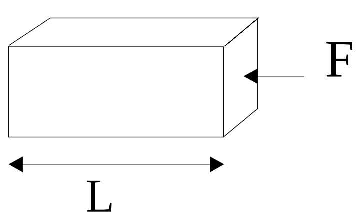
$$<|U^2(\omega)|> = 4\,K\,T\,Ro$$



(L,F)

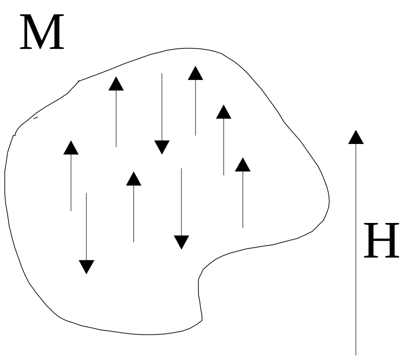
Density fluctuations

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



(M,h)

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



Fluctuation Dissipation Relation (FDR)

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

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

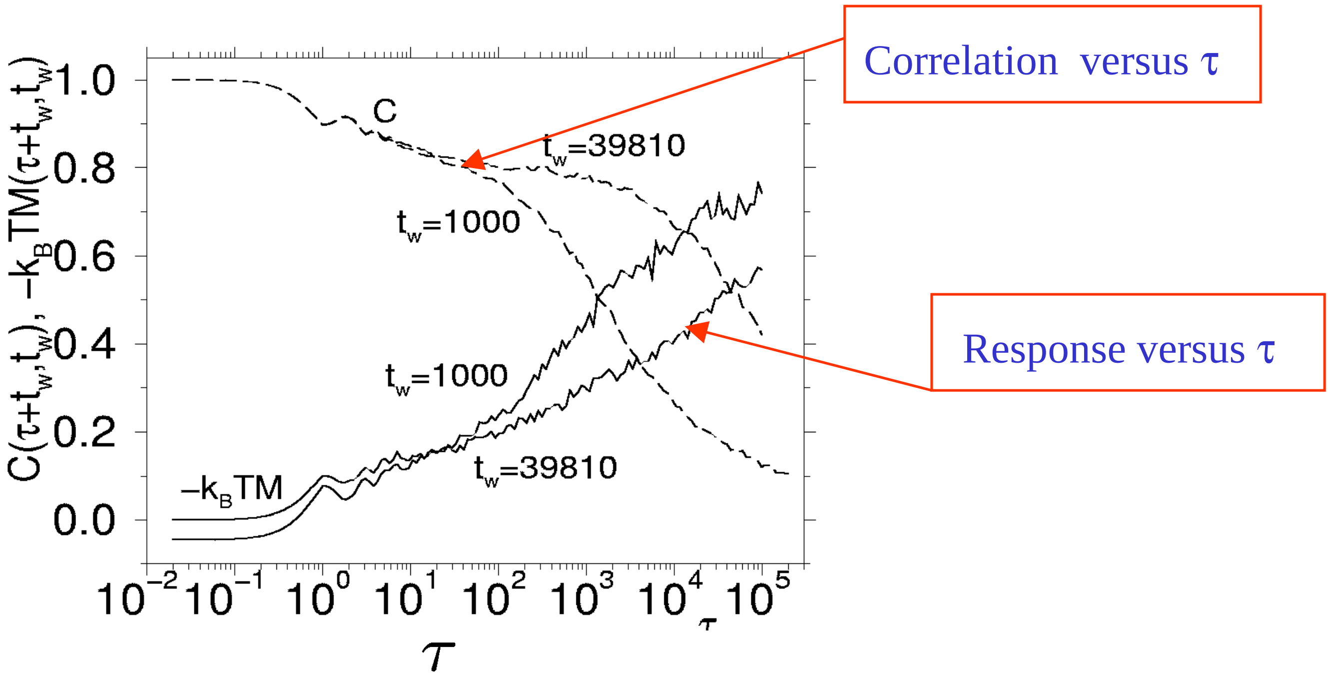
At equilibrium $T_{eff}(\omega, t_w) = T$

In terms of correlation function FDR takes the form

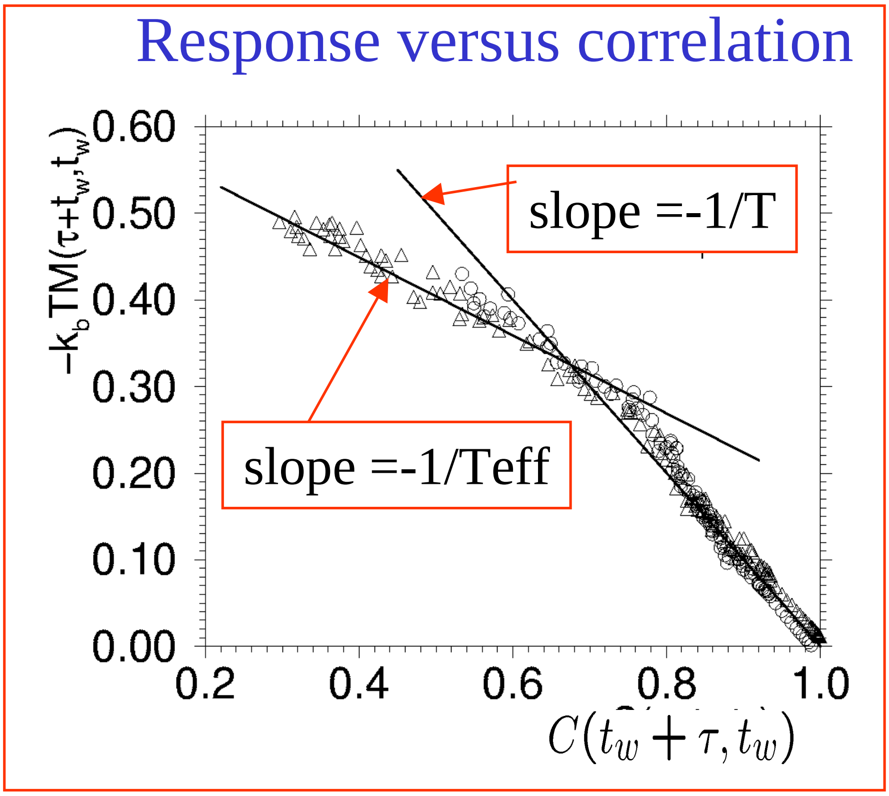
$$-C(t, t_w) + C(t_w, t_w) = K_B\ T_{eff}(t, t_w)\ R(t, t_w)$$

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

1) This definition of temperature seems to be appropriate for several systems.
Cugliandolo, Kurchan, Peliti (1997), Kob, Barrat (1999)
Berthier, Barrat (2002), Liu, Nagel (2002),
Sciortino(2002)………………..

2) The robustness of this definition of temperature has been questioned .
S. Fielding, P. Sollich, (2002), Perez-Madrid, Reguera, Rubi (2002).

Experiments

- 1970 x-ray scattering on PMMA (Weandorf and Fisher)
- 1999 Grigera, Israeloff, super-cooled liquid
- 2001 Bellon, Ciliberto, sol-gel transition
- 2002 Herisson and Ocio, spin-glass
- 2002 et 2005 Buisson, Ciliberto, polymer

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

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

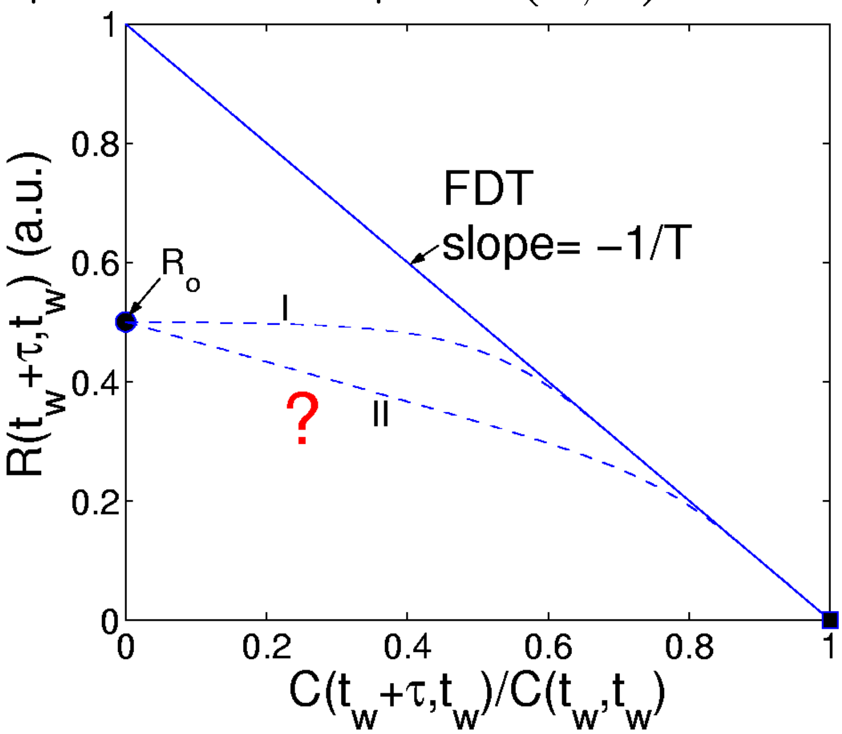
where χ_T is the isothermal compressibility.

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



Spin Glass experiment

Herisson and Ocio

Insulating spin glass $CdCr_{1.7}In_{0.3}S_4$

Tg=16K

Quench at 0.8Tg.

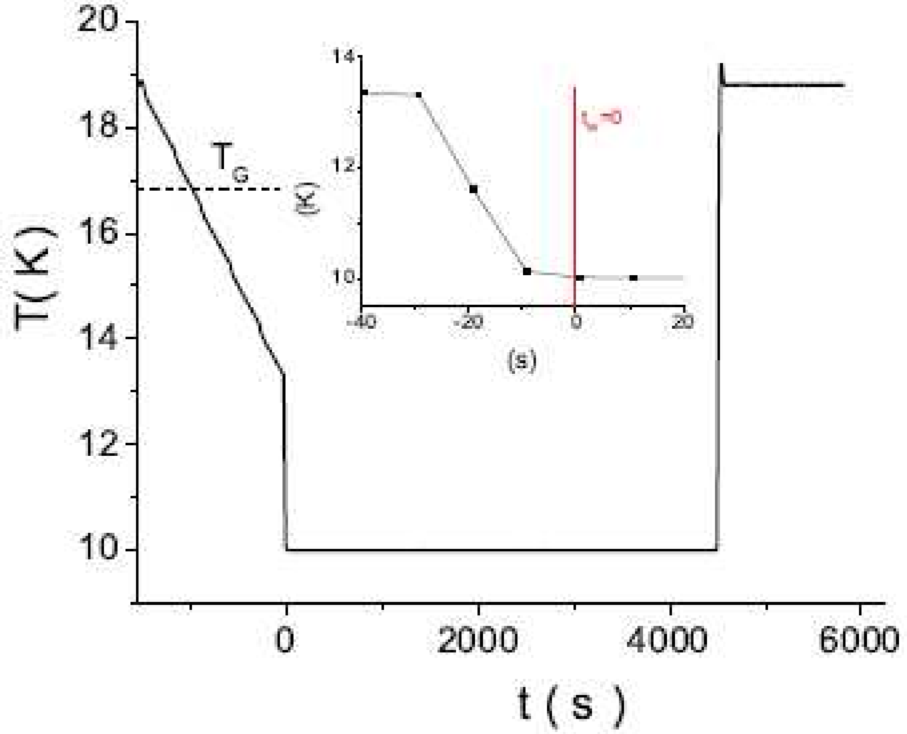


Fig. 4. A typical thermal history of the sample for a 4, 500 srecord at 10 K. In inset, detail on the crucial part, the last 3 K's cooling.

Spin Glass experiment

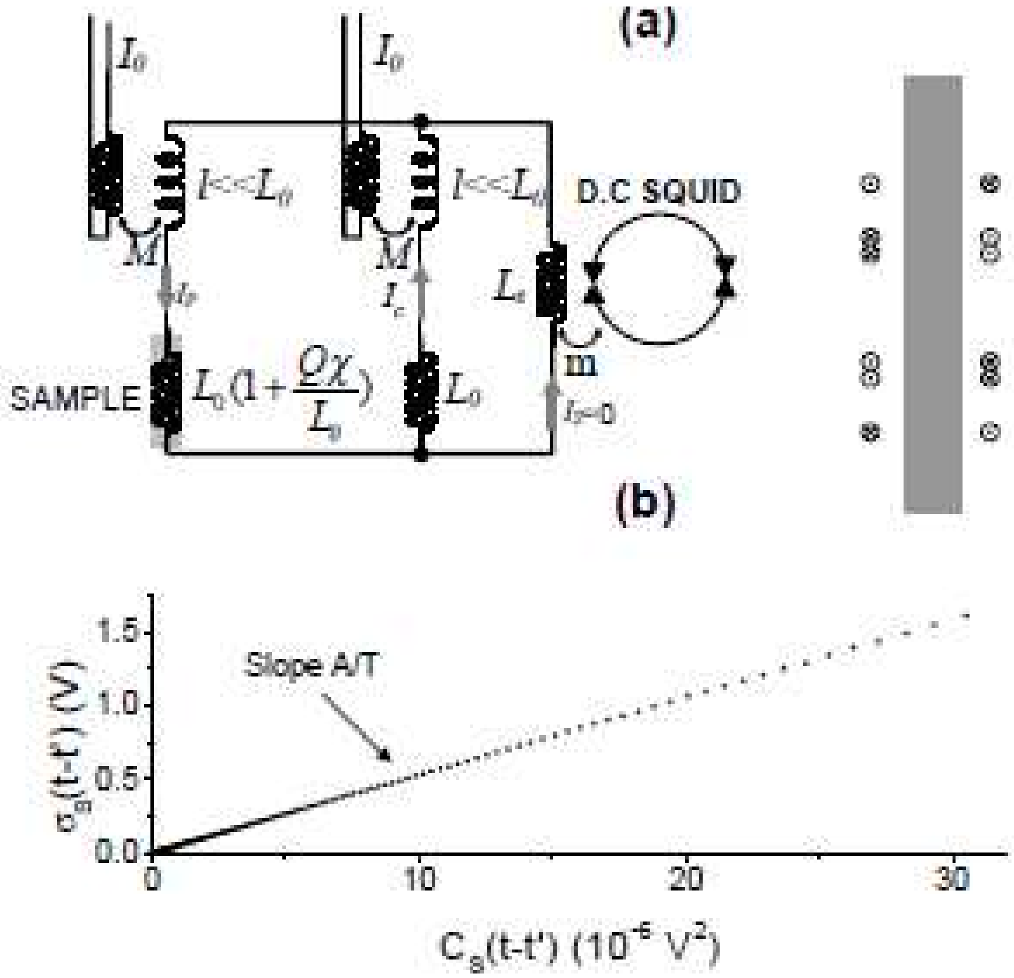


FIG. 1: a) Schematic of the detection circuit. The pick-up coil (right side), containing the cylindrical sample, is a third order gradiometer made of +3 -6 +6 -3 turns. b) Calibration is obtained by measuring relaxation versus correlation in a high conductivity copper sample at equilibrium at $4.2K$.

Spin Glass experiment

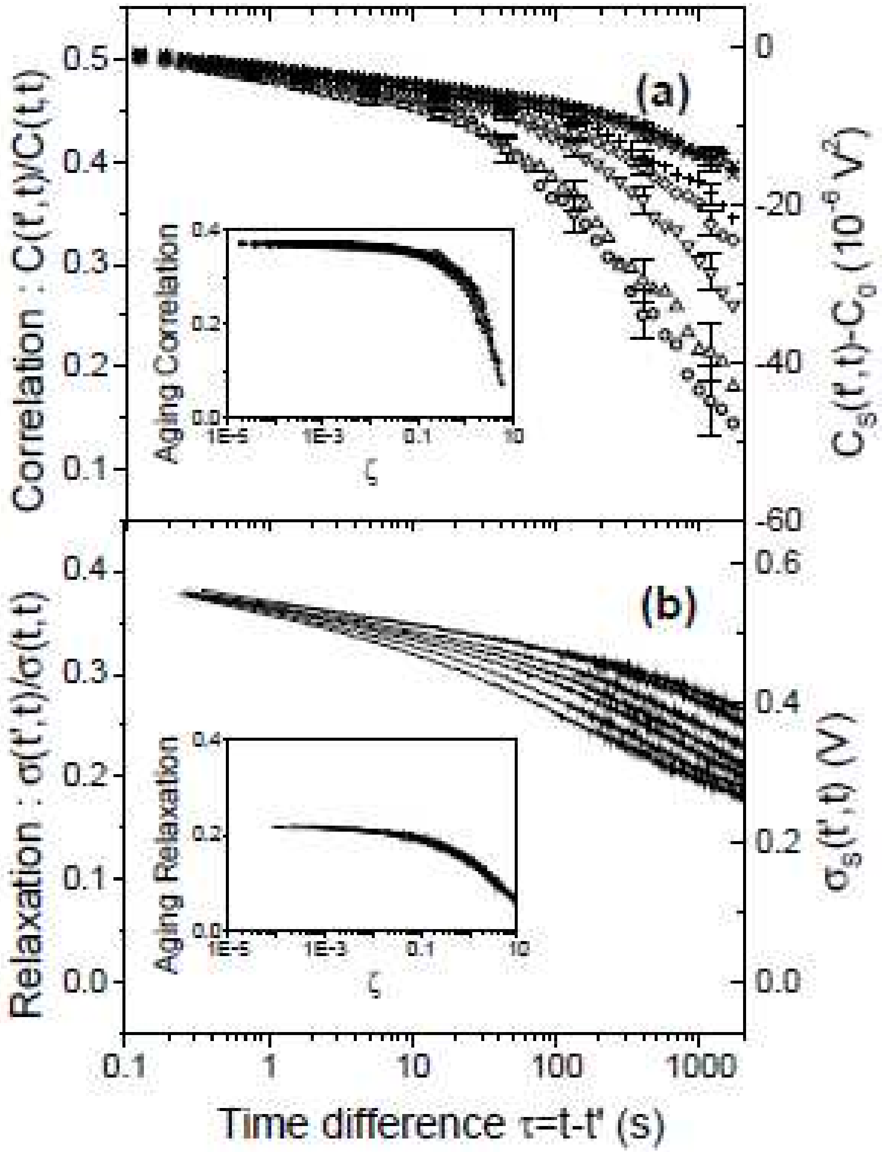


FIG. 2: Aging and scaling of (a) correlation (b) relaxation at $T = 0.8T_g$. Both are measured for waiting times $t' = 100$ ($\circ$), 200 ($\triangle$) , 500(∇), 1000($\diamond$), 2000 ($+$) , 5000($\times$), 10000($*$) seconds from bottom to top. Reported error-bars on correlation have a length of two standard-deviation, corresponding to averages over records. In insets, scaling of the aging parts versus $\zeta = (t^{1-\mu} - t'^{1-\mu})/(1-\mu)$, using $\mu = 0.87$. The stationary parts are found to obey a power-law decrease with an exponent $\alpha = 0.05$.

Spin Glass experiment

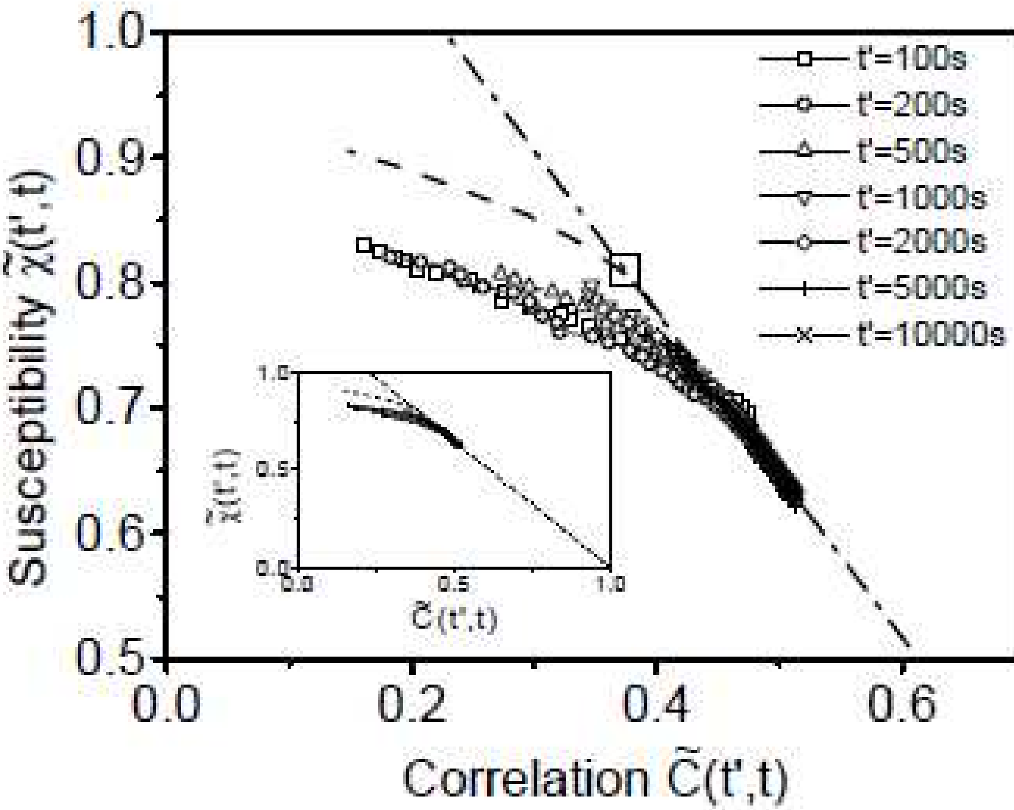


FIG. 3: FD-plot. Relaxation measurements are plotted versus correlation functions for each t'. The dot-dashed line (FDT line) is calculated for $T = 0.8Tg = 13.3K$, from the calibration obtained with the copper sample. The dashed line represents the scaling extrapolation for $t' \to \infty$. The branching point with the FDT line, corresponds to $\tilde{C} = q_{EA}$ (square symbol, with size giving the error range). In Inset, the same data in the whole range.