Phénomènes de relaxation dans les verres

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Orléans University

Conditions Extrêmes des Matériaux : Haute Température et Irradiation

CEMHTI UPR 3079 CNRS

Ageing of glasses…?

Nuclear waste

household
refuse

Ageing of glasses

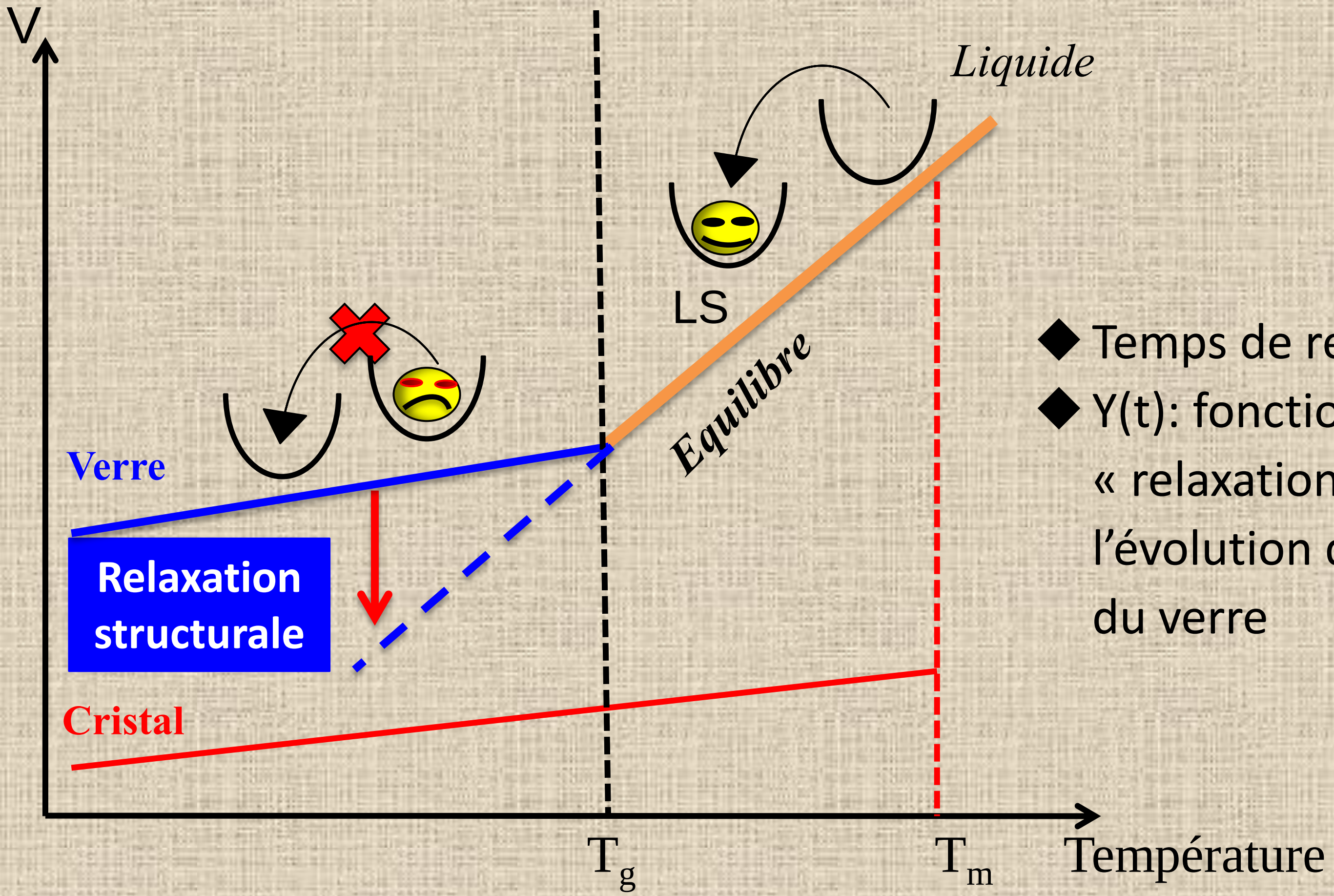
Chemical reasons

physical reasons

Le verre: équilibre ou hors équilibre…?

Le verre obtenu par refroidissement d'un liquide surfondu

Système hors-équilibre $\xrightarrow{T,\ P,\ t\ \ldots}$ **Equilibre**

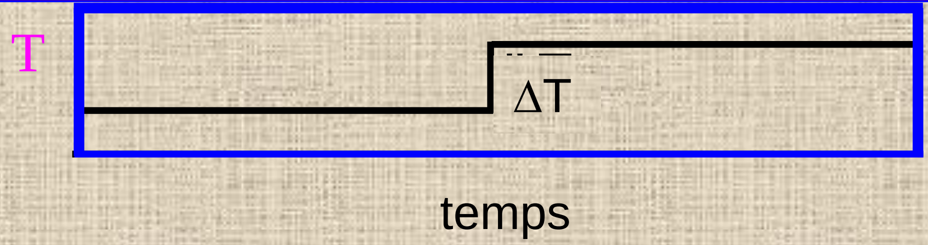


- ◆ Temps de relaxation τ
- ◆ Y(t): fonction dite de « relaxation » qui traduit l'évolution d'une propriété du verre

Outil de mesure
temps expérience τ_{exp}

Fonction de relaxation y(t)

sollicitation en température : expérience en temps

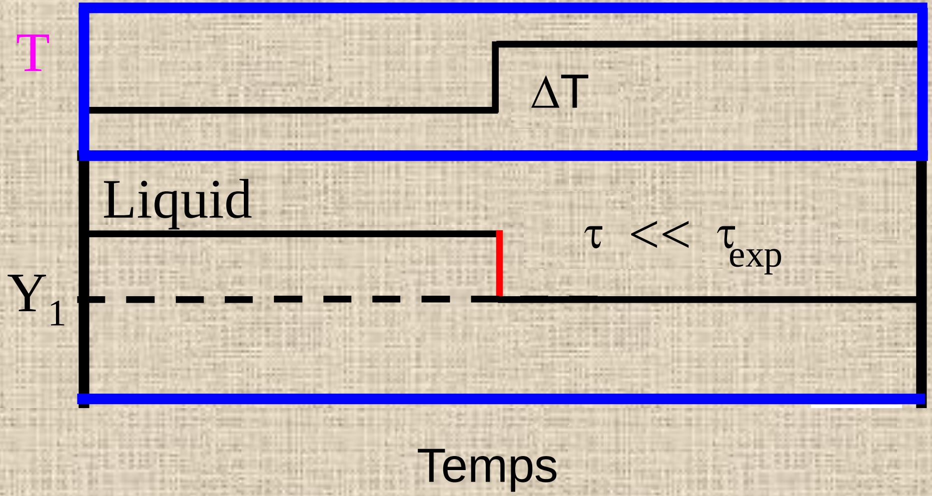


Outil de mesure

temps expérience τ_{exp} ⟺ **Fonction de relaxation y(t)**

sollicitation en température : expérience en temps

à l'état liquide ⟹



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Outil de mesure
temps expérience τ_{exp}

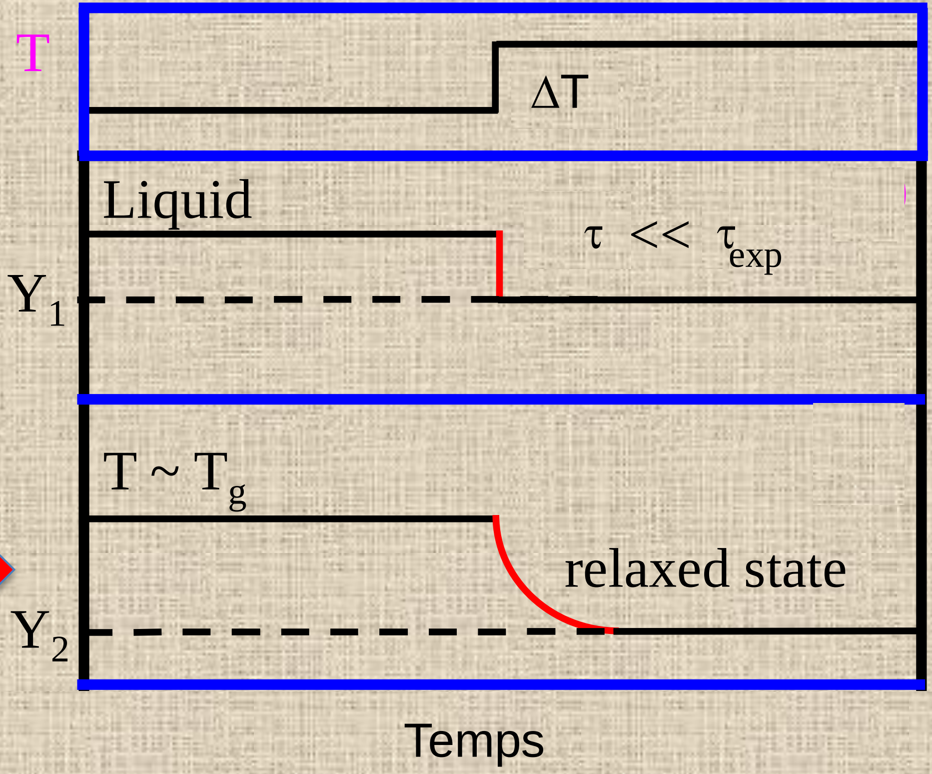
↔

Fonction de relaxation y(t)

sollicitation en température : expérience en temps

à l'état liquide

dans l'intervalle de Tg



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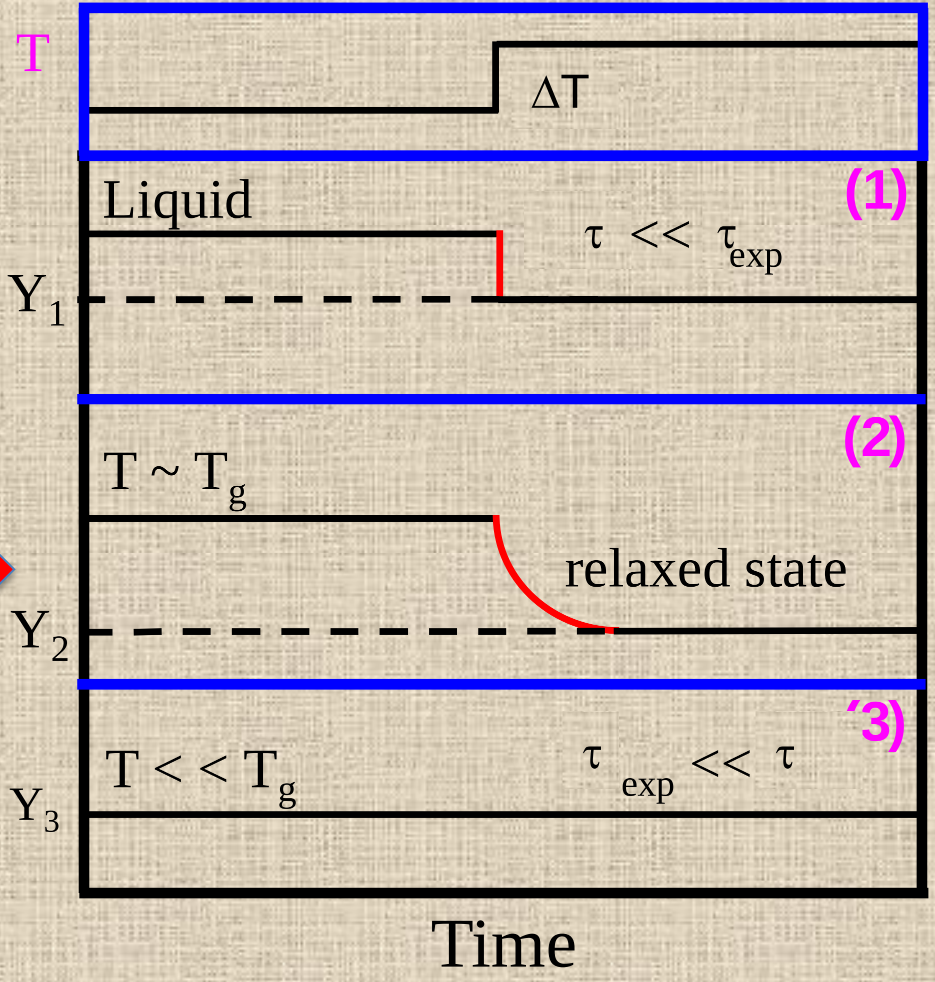
Outil de mesure
temps expérience τ_{exp}

Fonction de relaxation y(t)

sollicitation en température : expérience en temps



à l'état liquide

dans l'intervalle de Tg

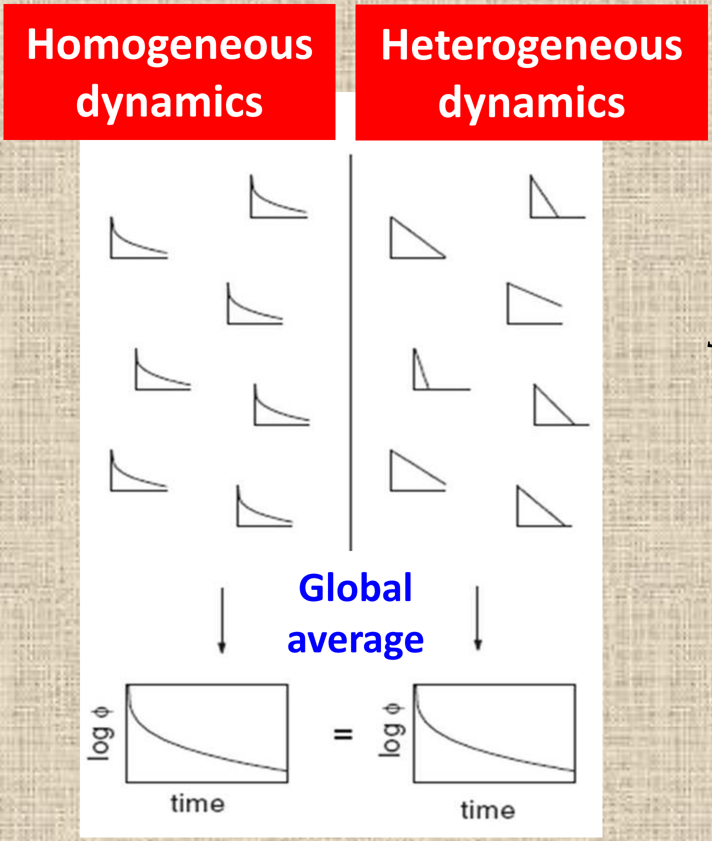
à la température ambiante

Heterogeneous dynamics relaxation

Polymers, molecular glasses…

Y(t)→ several relaxation processes

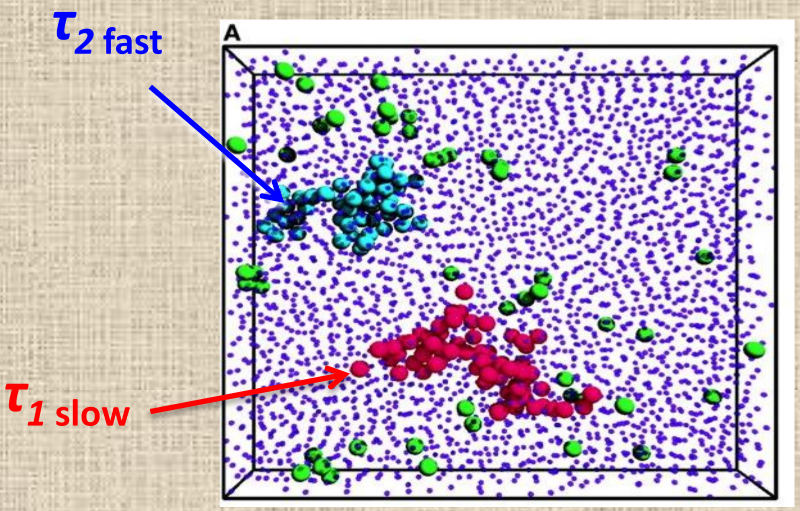
$$y(t) = \sum_{i=1}^{n} y_{0i} \exp\left(\frac{-t}{\tau_i}\right)$$


Homogeneous dynamics

Heterogeneous dynamics

Global average

Colloidal solution T<Tg



E.R. Weeks, Science (2000)

$$y(t) = y_0 - w \exp\left(\frac{-t}{\tau}\right)^{\beta}$$

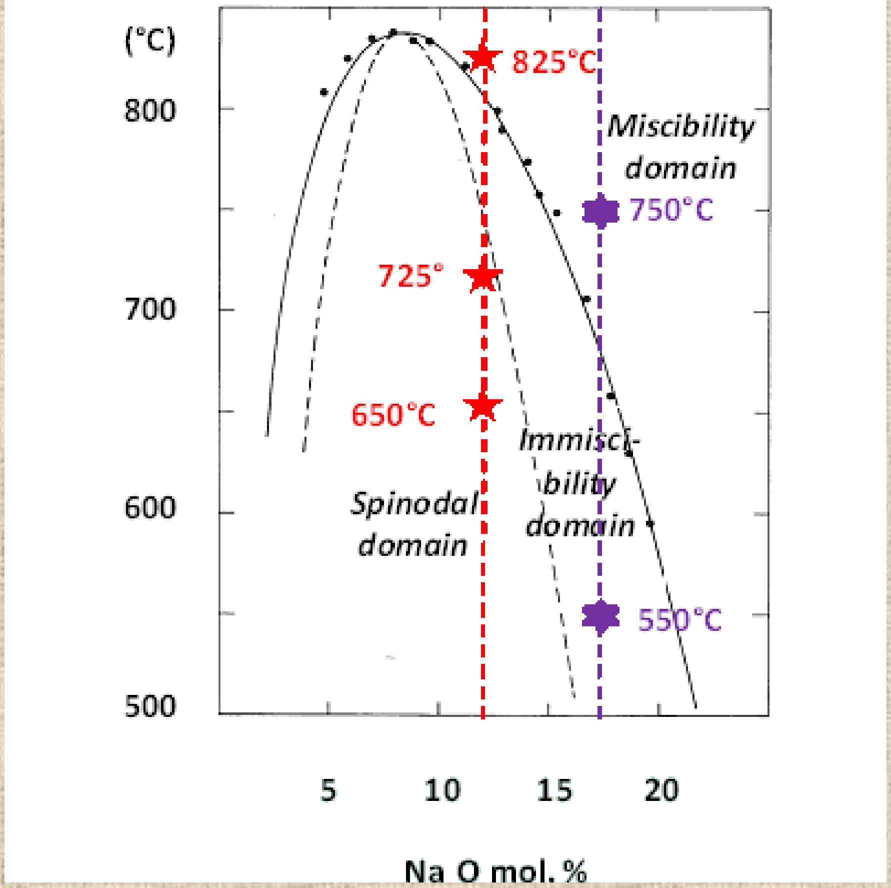
What about oxide glasses?

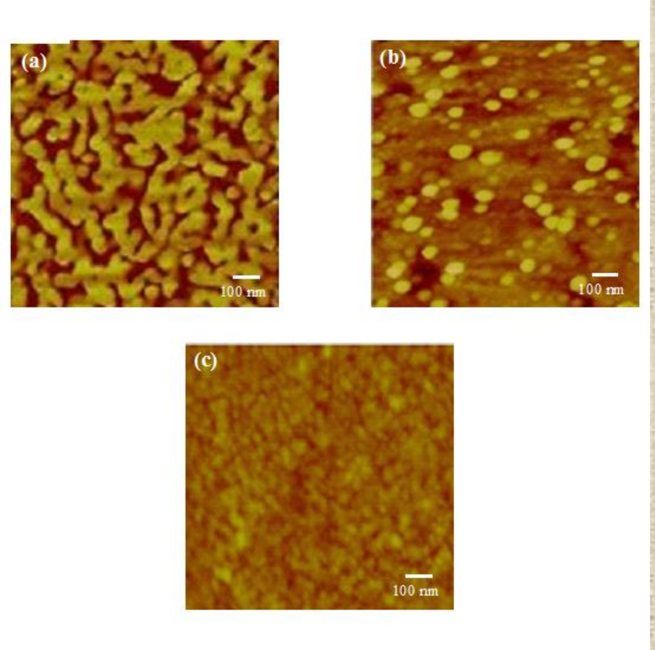
→ Oxide glasses : chemical and topological heterogeneity

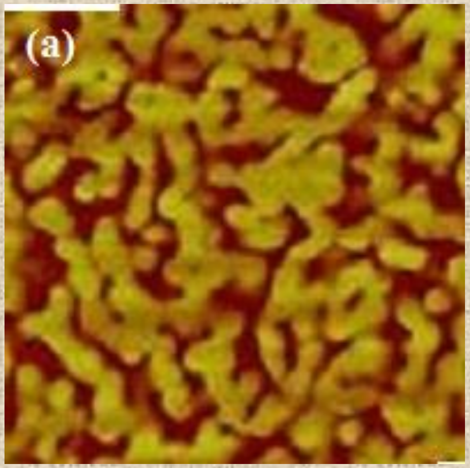
→ Dynamics and nature of relaxation are depending on the spatial scale

Composition choose

Composition xNa_2O- (1-x) SiO_2



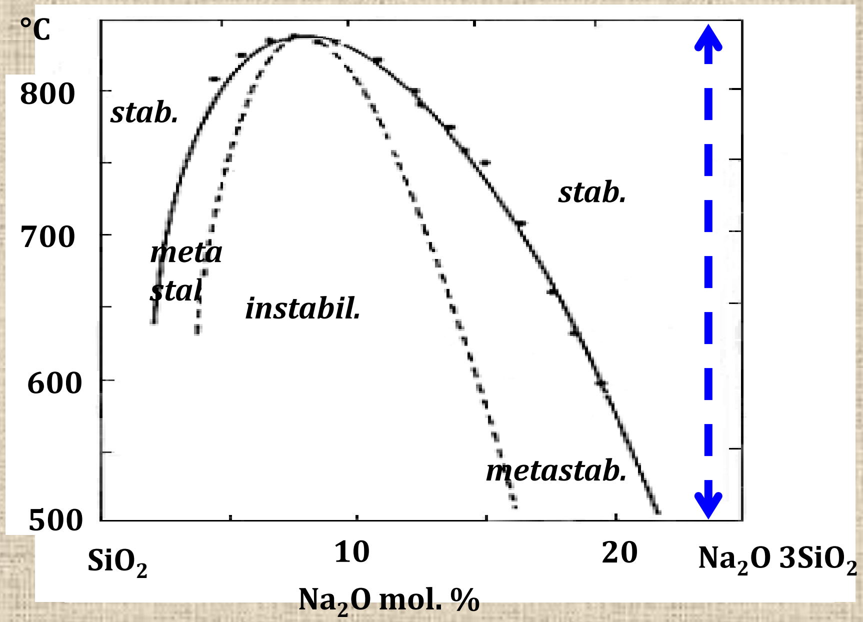




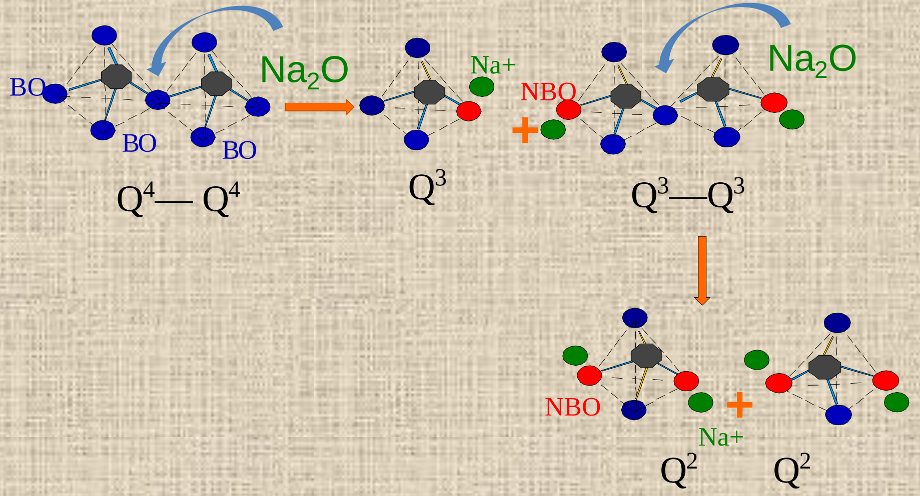
Composition choose

Composition $0.27\ Na_2O - 0.73\ SiO_2$

✓ *Tg(DSC) = 730K*



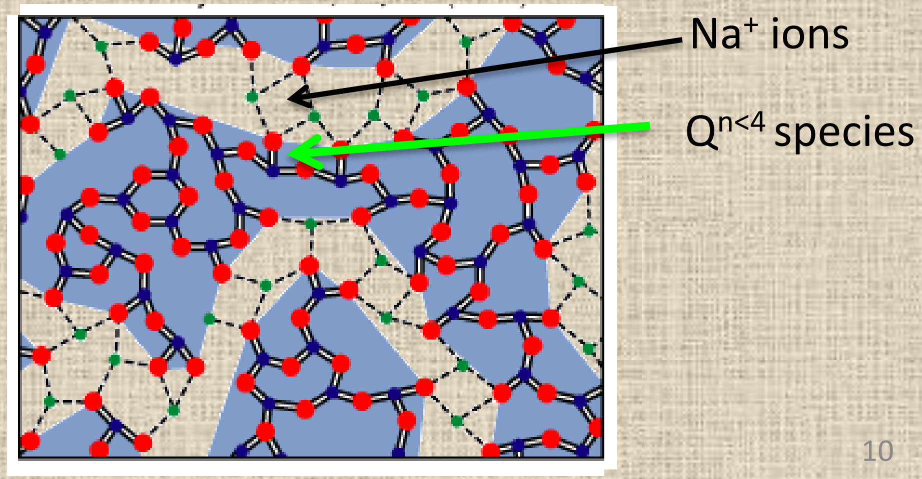
Short distance

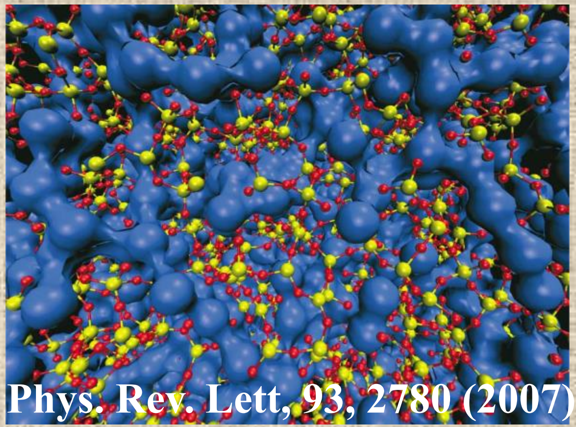


Long distance

Modified random model

Greaves, JNCS (1985)



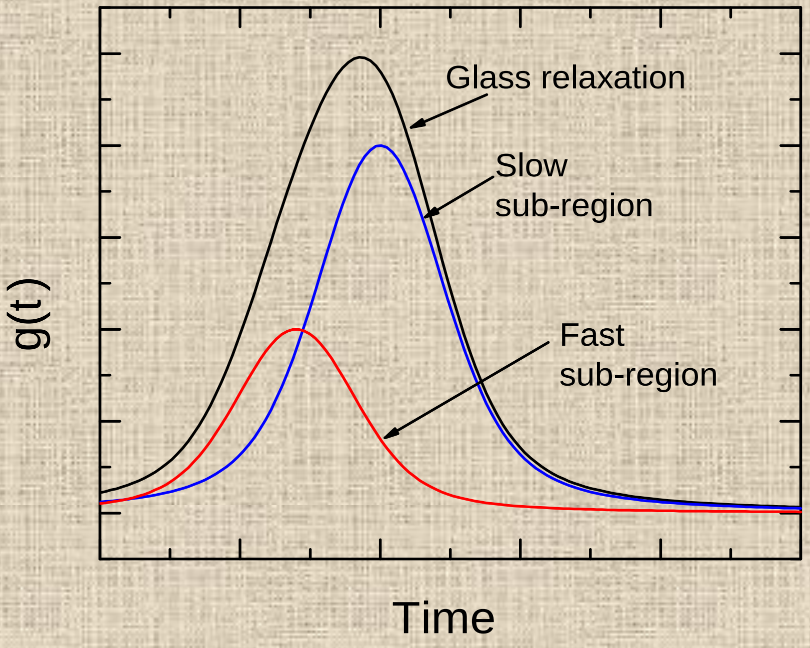


Phys. Rev. Lett, 93, 2780 (2007)

Neutron scattering + Molecular Dynamics calculations

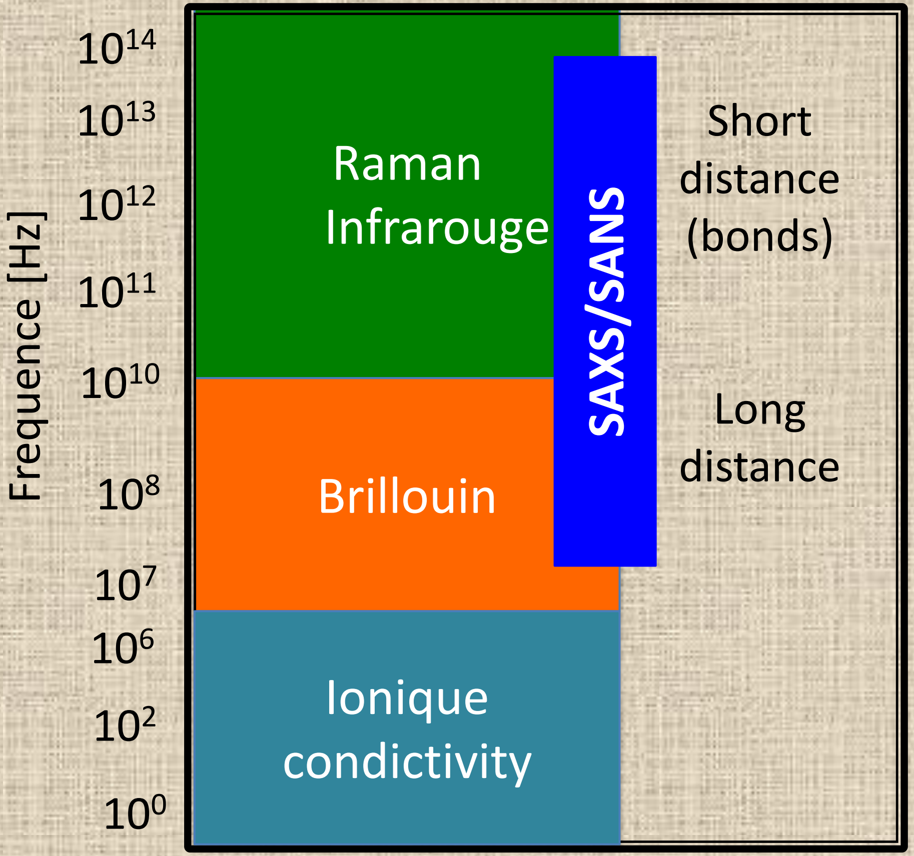
Wich scale?

Idea



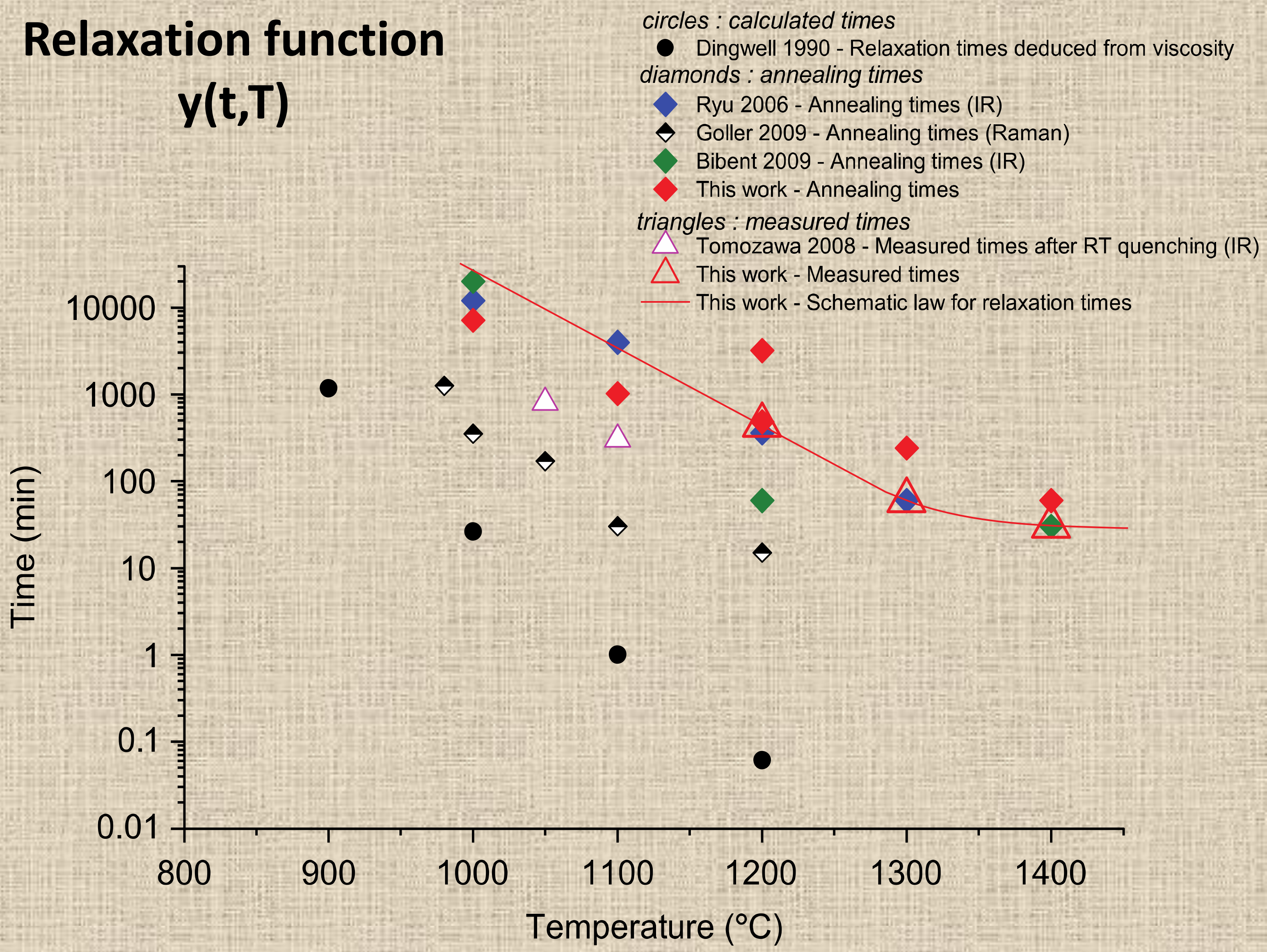
R. Ritchert, J. Phys. Cond. Mat. (2002)

tools



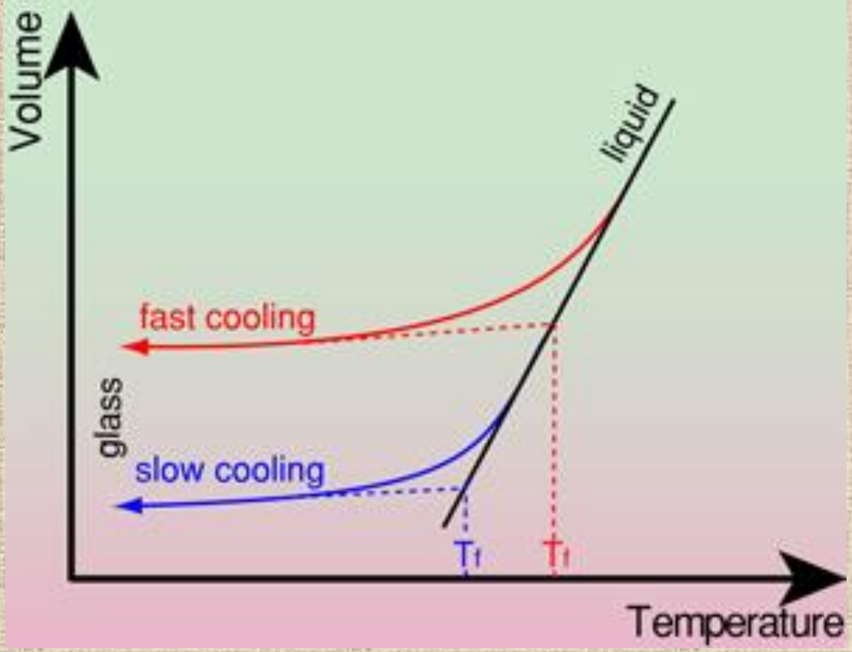
Structural relaxation

Relaxation function y(t,T)



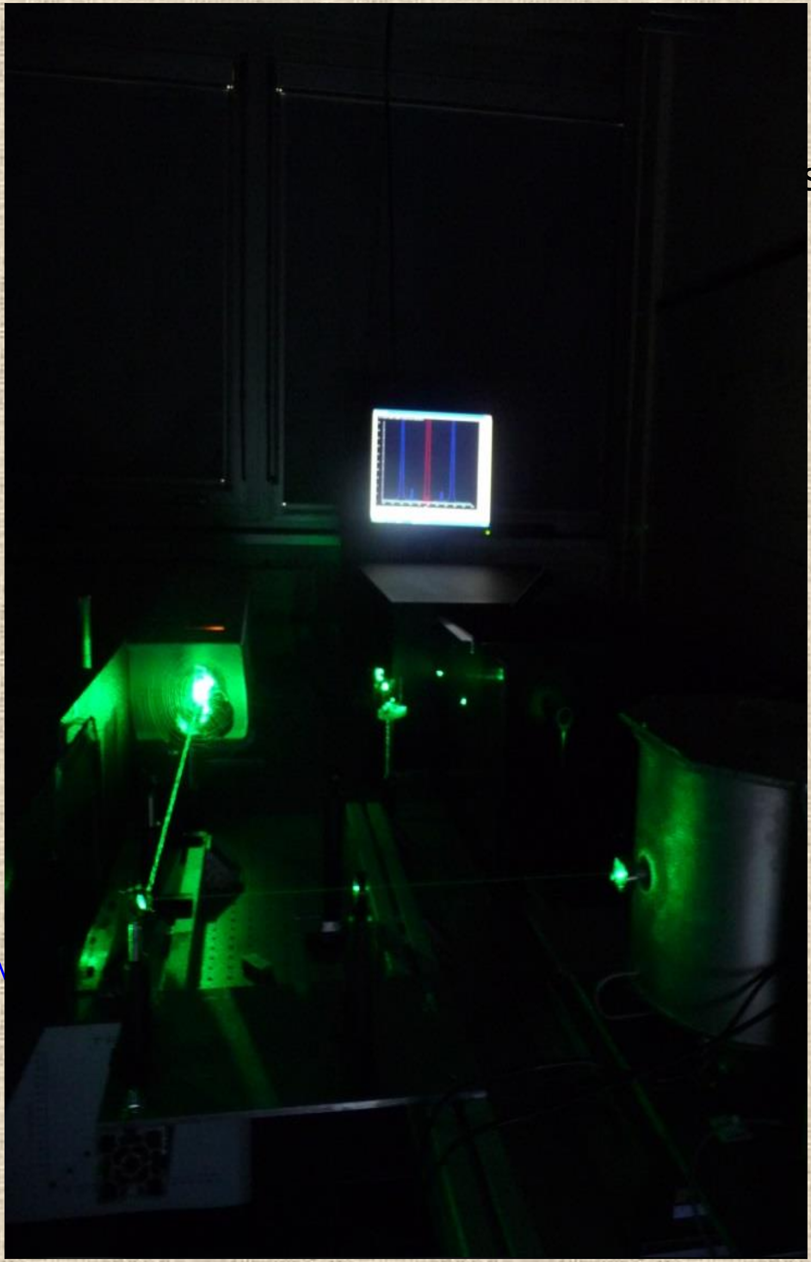
Structural relaxation

Which relaxation function y(t) ?



- ✓ Longitudinal acoustical mode frequency (measured by Brillouin scattering)
- ✓ Relative intensity of an Raman lines

Tool description



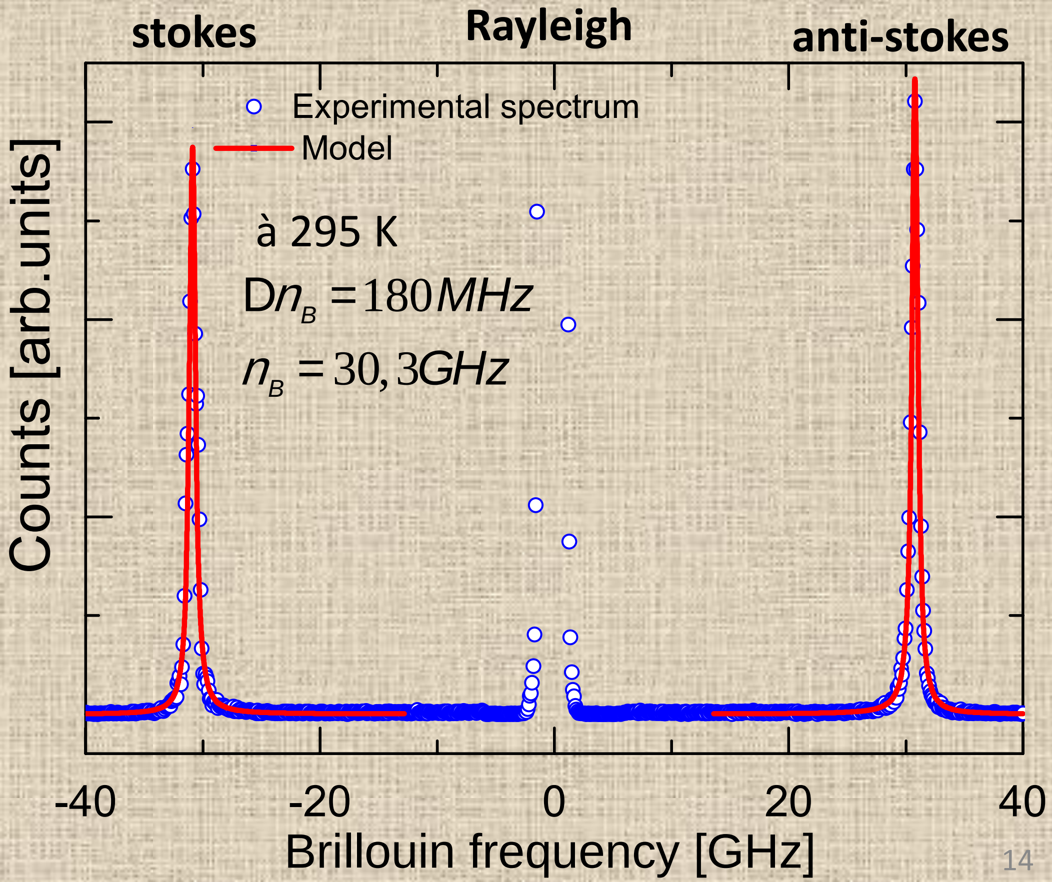
s)

N

Spectrum analysis

$$I = I_{Dho} \, Ä \, I_{instr}$$

$$I_{Dho} = \frac{l}{4p} \frac{4Dn_B n_0^2}{(n^2 - n_0^2) + 4n^2 Dn_B}$$

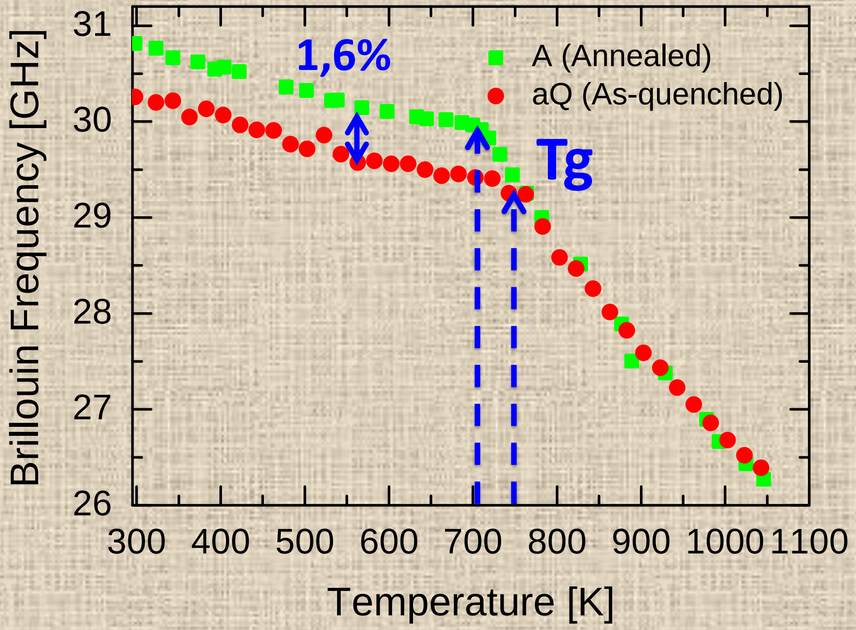


Brillouin scattering vs Temperature

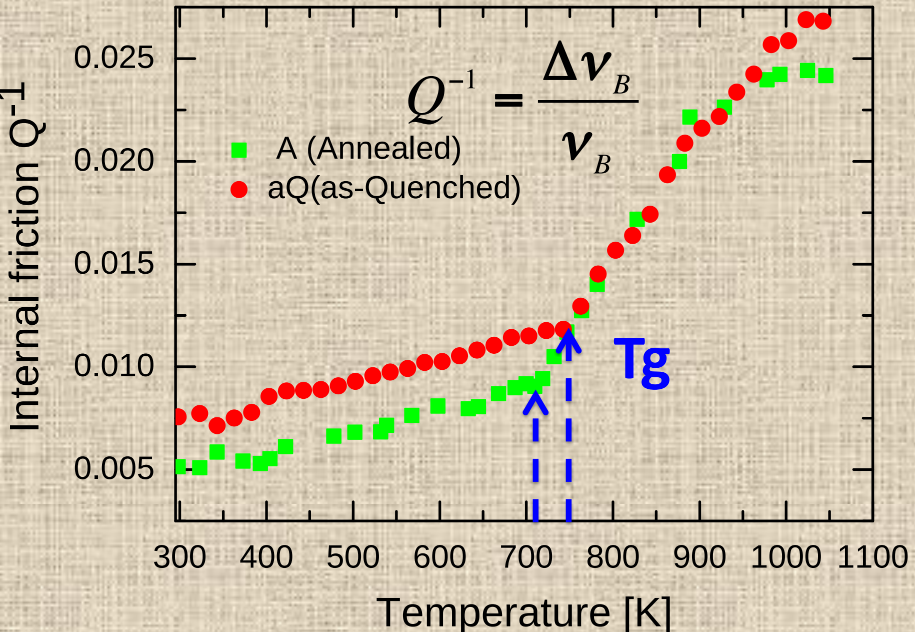
Brillouin frequency variations

● ***As quenched glass***

🟩 ***Annealed glass***



Internal friction variations

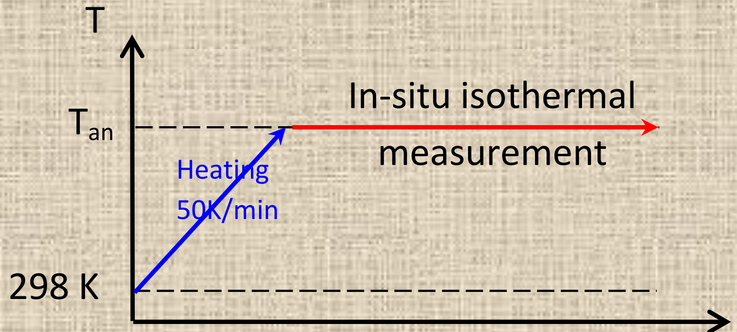


$$Q^{-1} = \frac{\Delta \nu_B}{\nu_B}$$

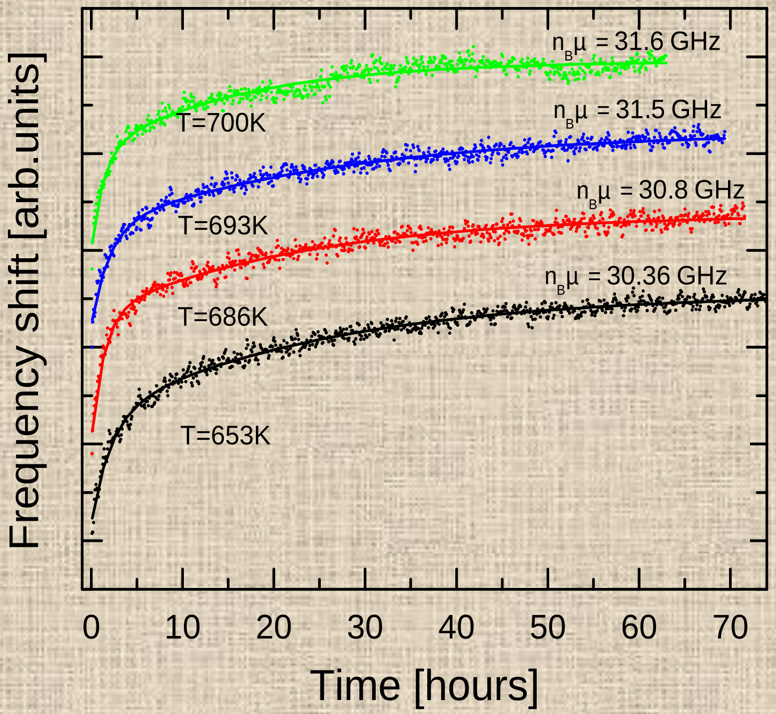
➔ Two signatures of a long distance relaxation

Brillouin scattering vs Temperature & time

Experimental procedure for relaxation study

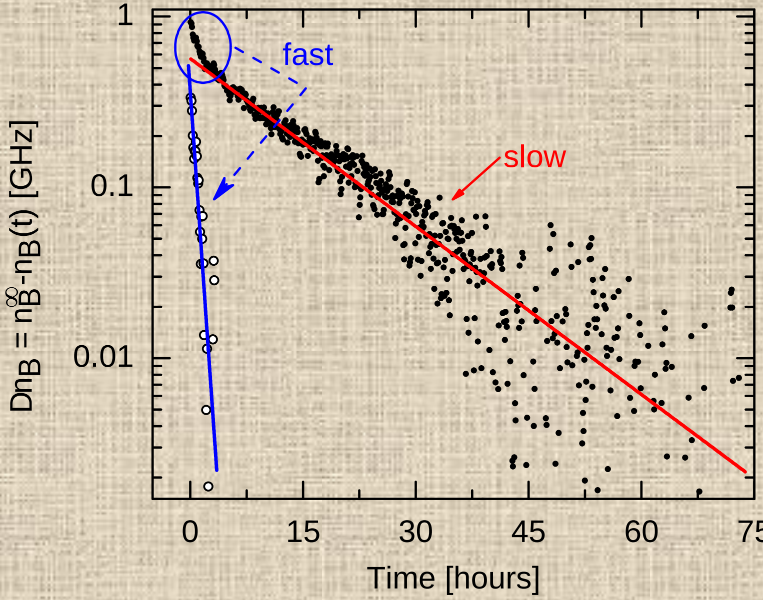


Relaxation kinetics



analyse

Exponential decomposition



➔ **bi-exponential model**

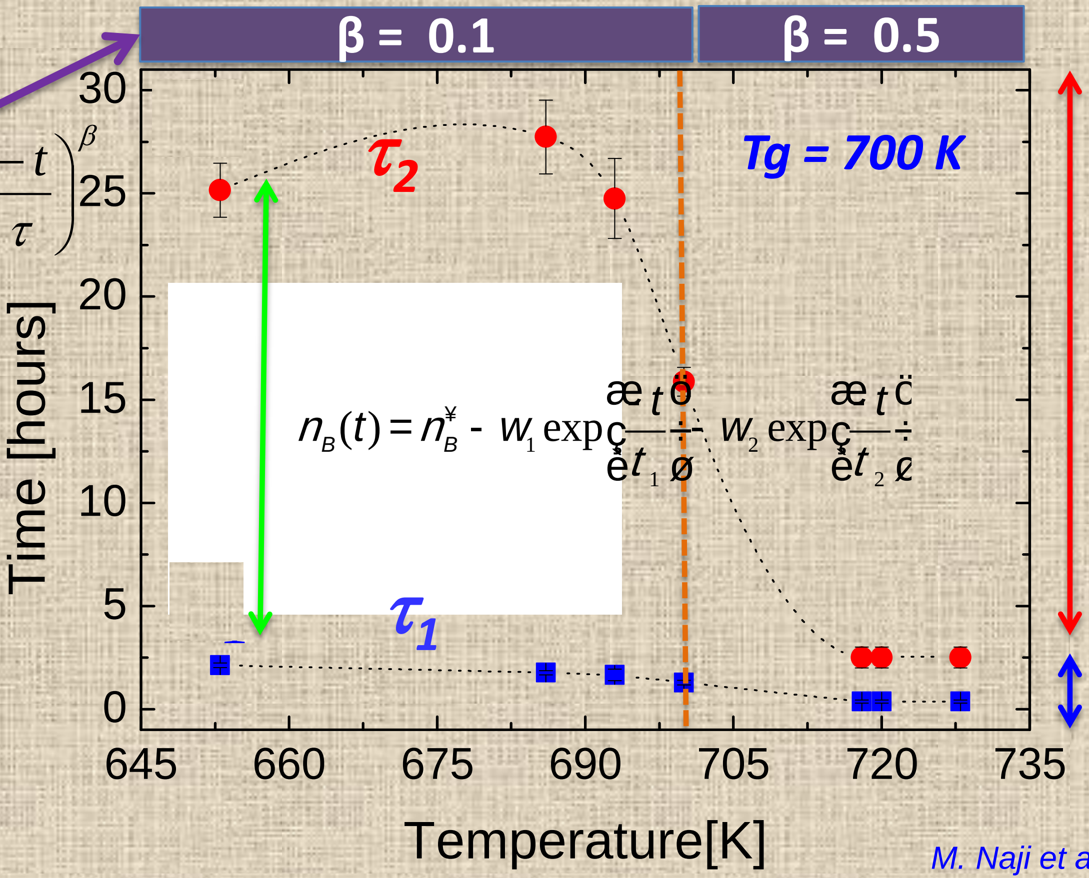
$$n_B(t) = n_B^{\infty} - w_1 \exp\left(\frac{t}{\tau_1}\right) - w_2 \exp\left(\frac{t}{\tau_2}\right)$$

➔ **Strechted exponential**

$$n_B(t) = n_B^{\infty} - w\exp\left(\frac{t}{\tau}\right)^{b}$$ with $0 < b \le 1$

Evidence of heterogeneous dynamics

$$v_B(t) = v_B^{\infty} - w\,exp\left(\frac{-t}{\tau}\right)^{\beta}$$



Slow Dynamics

Fast dynamics

M. Naji et al. J.Phys.Chem.B (2013)
M.Naji et al. Physics Procedia (2013)

→ **T < Tg** : two relaxations τ_1 & τ_2
one order of magnitude, or
small β strong heterogeneity

→ **T > Tg** : weak heterogeneity

➔ Evidence of an **heterogeneous dynamics at long distance**

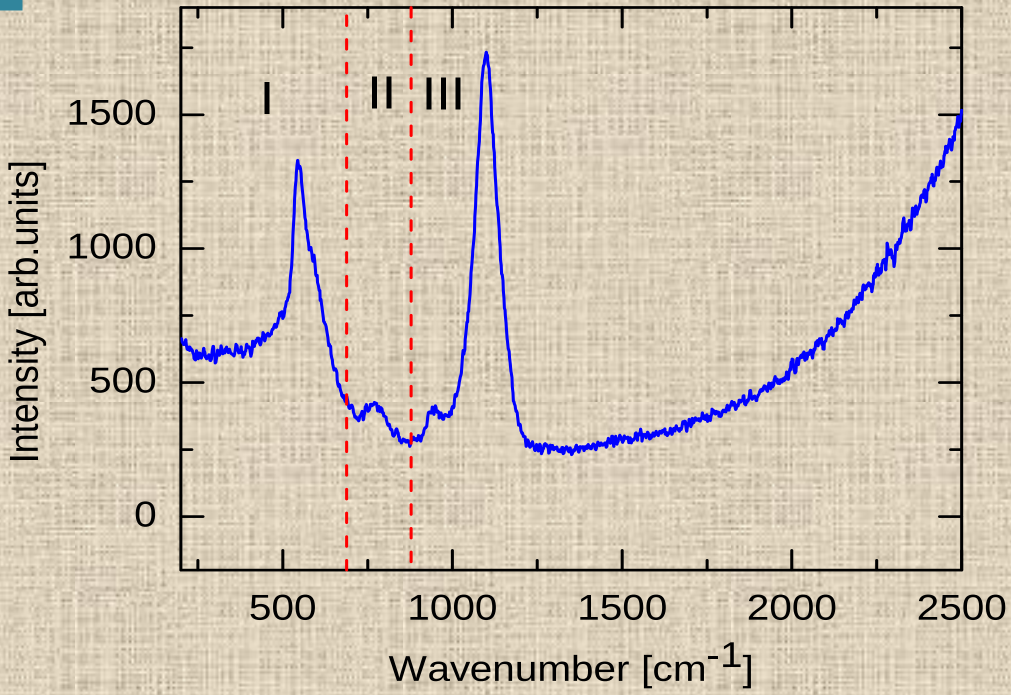
structurale relaxation at short distance: Raman

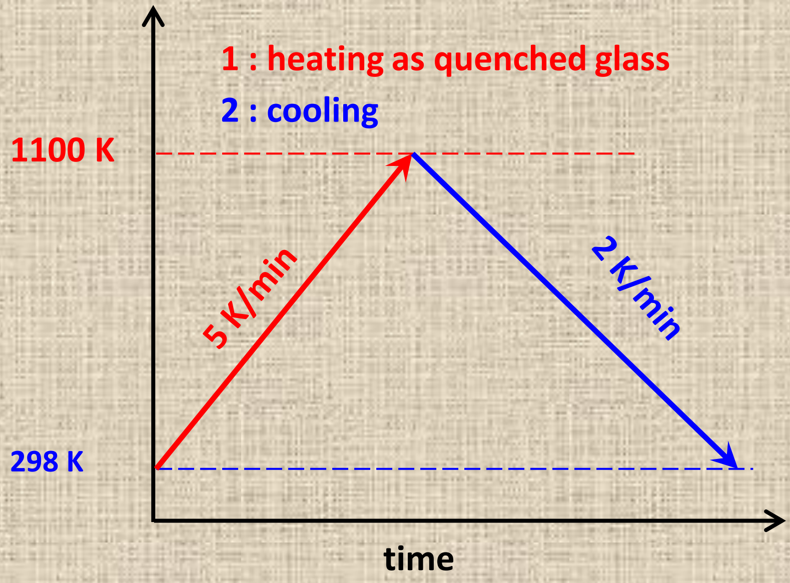
Raman modes of the Raman spectrum

Region I: 3, 4, 5 et 6 tetrahedra rings

Region II: Si-O-Si interterahedral bonds

Region III: Si-NBO/BO in Q^n species



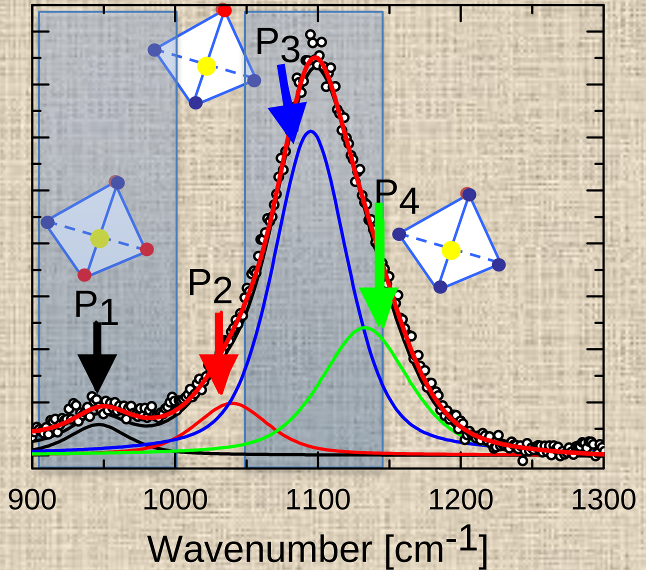


Experimental process : in situ heating and cooling

short range by Raman vs temperature

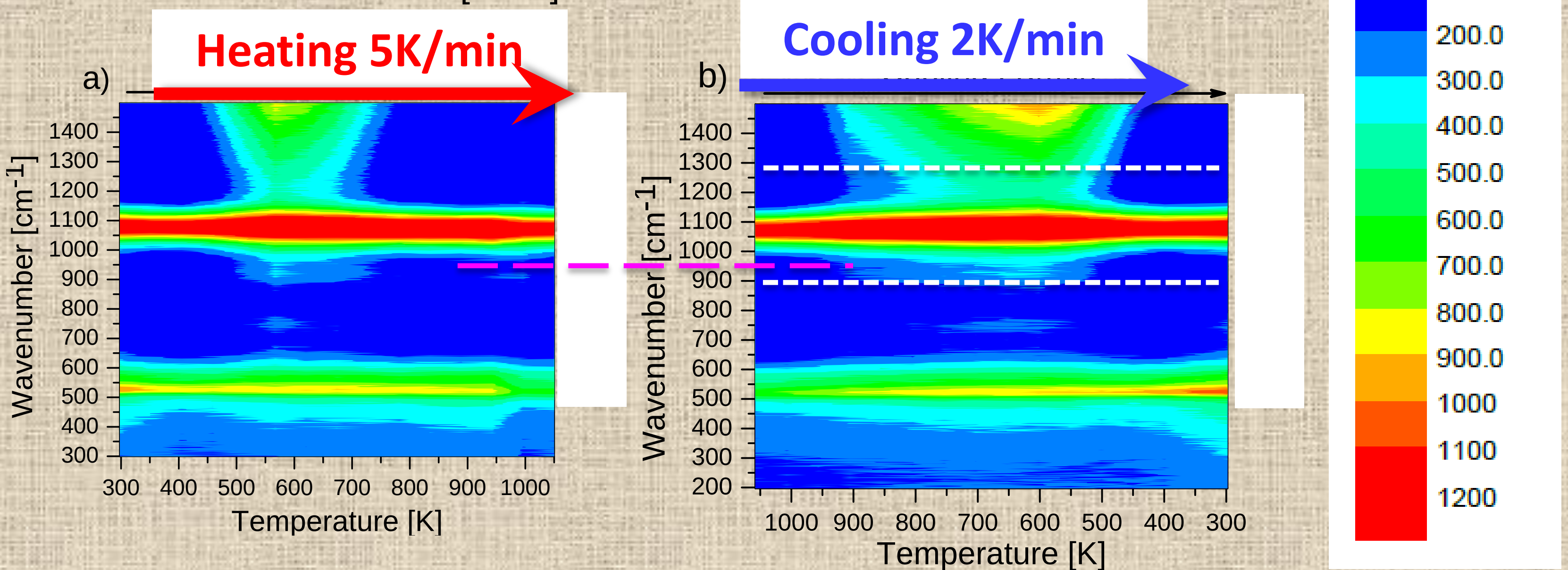
Analyse in individual compounds

4 gaussian bands



- P1 Mode ➔ stretching Si-NBO in Q^2 species
- P2 Mode ➔ stretching Si-BO
- P3 Mode ➔ stretching Si-NBO in Q^3 species
- P4 Mode ➔ stretching Si-NBO in Q^4 species

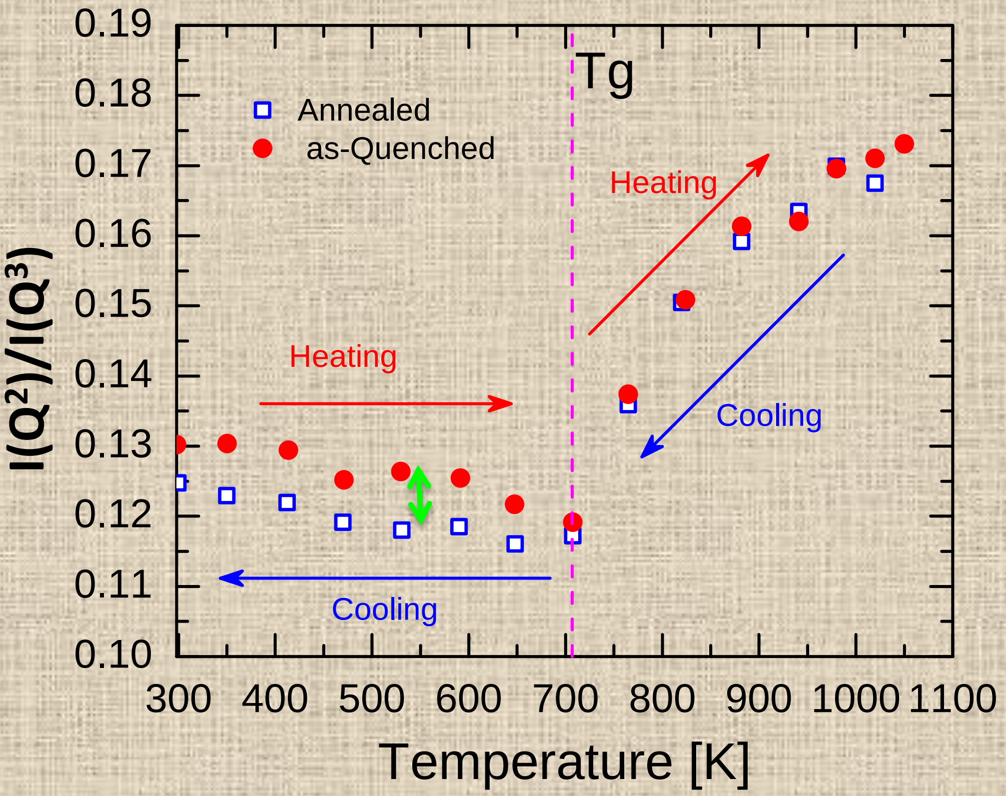
D. De Sousa Meneses Vibrational Spectroscopy, 65, 50-57 ***2013***.
W.J. Malfait, J. Raman Spec. 2009



✓ quasi-Reversible

Evidence of relaxation at short range

Variations of Q^2 line relative intensity with the temperature



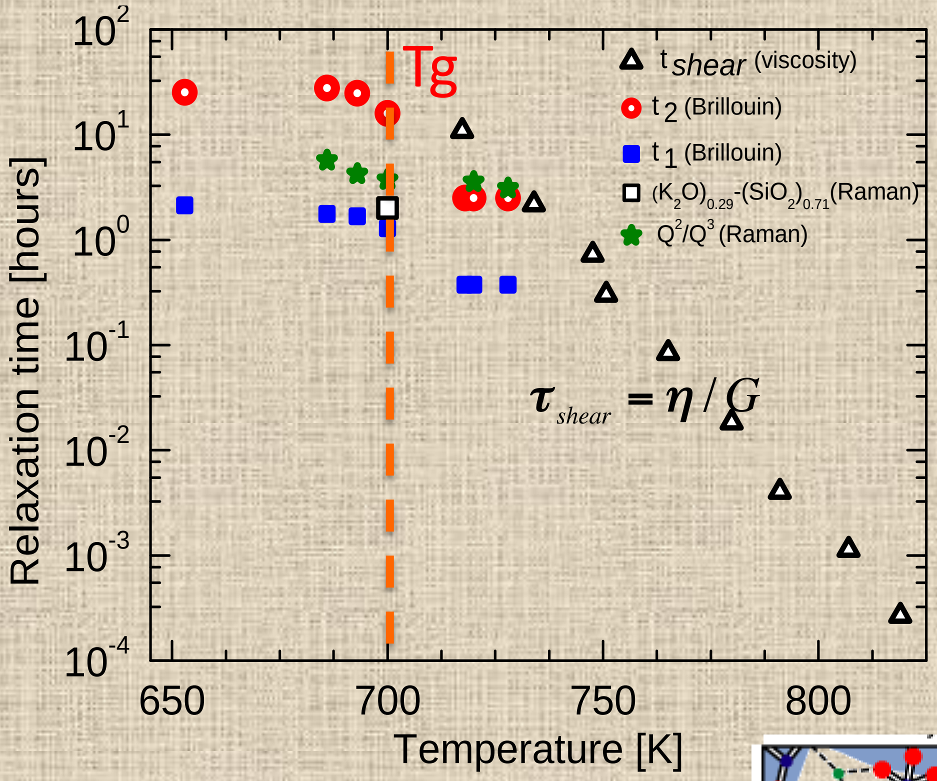
- ~~Reduction of number of Q^2 (Si-O) species by relaxation ?~~
- Variation of the Raman cross section (Environment change) ?

The well known NMR measurements exclude the first hypothesis

the intensités of Q^2/Q^3 ratio→ good probe for structural relaxation

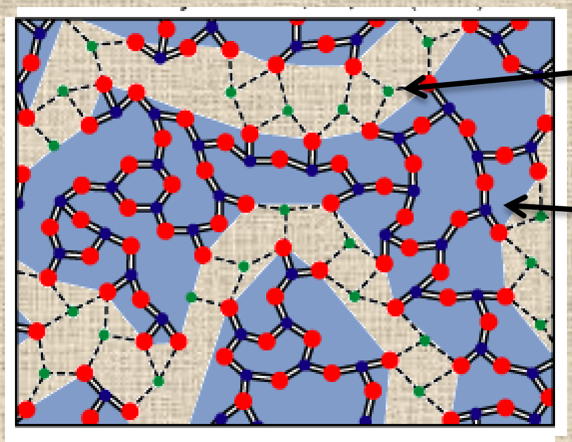
Discussion

Comparaison of several relaxation dynamics
(Brillouin, Raman, viscosité)



Temps de relaxation Raman (Q^2/Q^3) relaxation time : close from the **fast** Brillouin τ_2

The Brillouin **slow relaxation** time τ_1 is consistent with shear relaxation time deduced from the viscosity : Si—O--Si

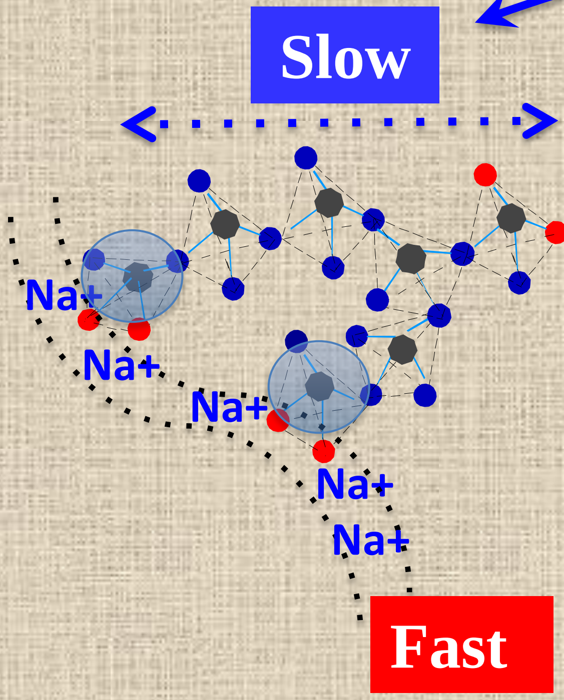


Na^+ ions

$Q^{n<4}$ species

Conclusion

Relaxation scenario at T < Tg and heterogeneous dynamics



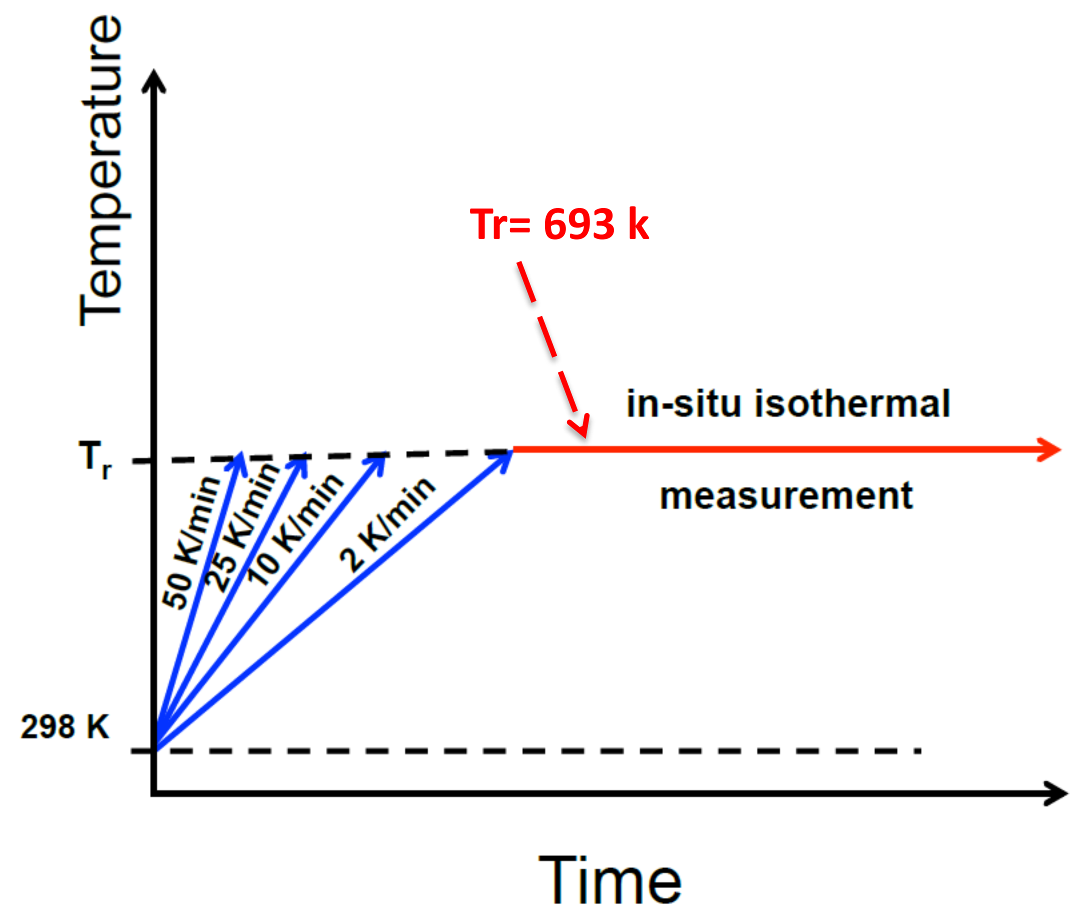
The **Brillouin** **slow relaxation** time τ_1 is consistent with shear relaxation time deduced from the **viscosity** : Si—O--Si

Temps de relaxation **Raman** (Q^2/Q^3) relaxation time : close from the **fast** **Brillouin** τ_2

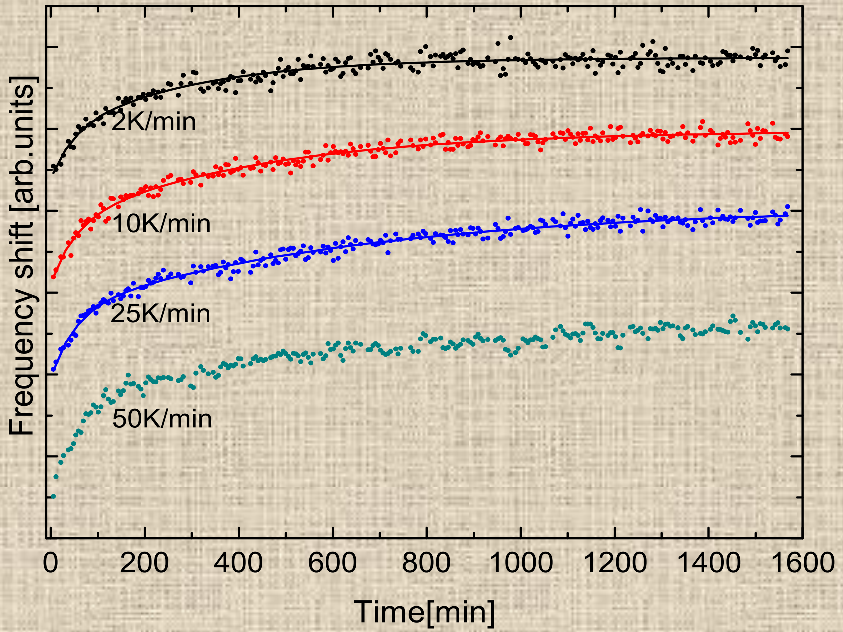
Effet de la vitesse de montée en température

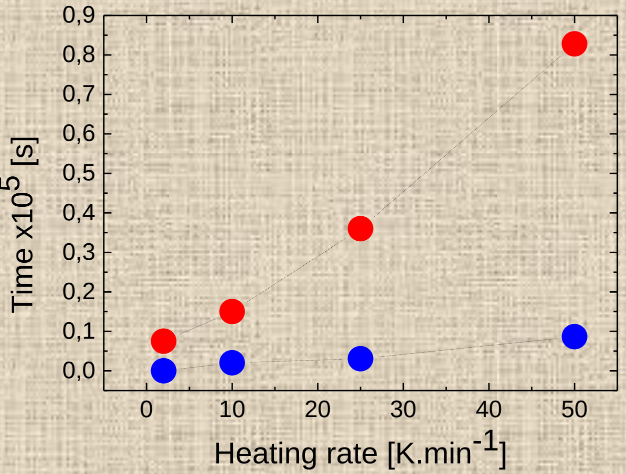
Thinks are they so simple?

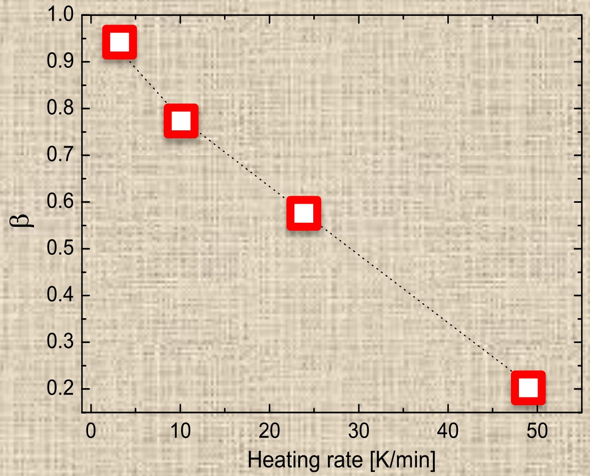
Effect of heating rate



Effect of heating rate







$$n_B(t) = n_B^{\infty} - w_1 \exp\left(\frac{t}{\tau_1}\right) - w_2 \exp\left(\frac{t}{\tau_2}\right)$$

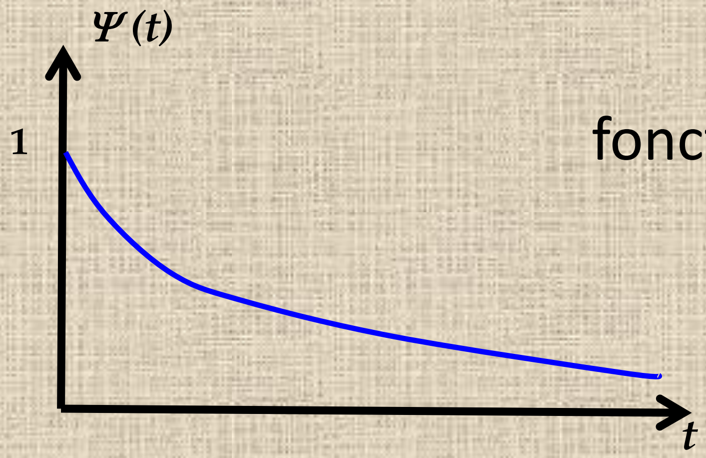
$$\nu_B(t) = \nu_B^{\infty} - w\, exp\left(\frac{-t}{\tau}\right)^{\beta}$$

Effect of heating rate

Idea of time relaxation distribution function

Modelisation using fractional Brownian dynamics

G. Kneller, J; Chem. Phys. (2010)



fonction de relaxation = superposition d'exponentielles

$$\Psi(t) = \int_0^\infty d\lambda \, p(\lambda) e^{-\lambda t}$$

$p(\lambda)$ représente ici le spectre de taux de relaxation

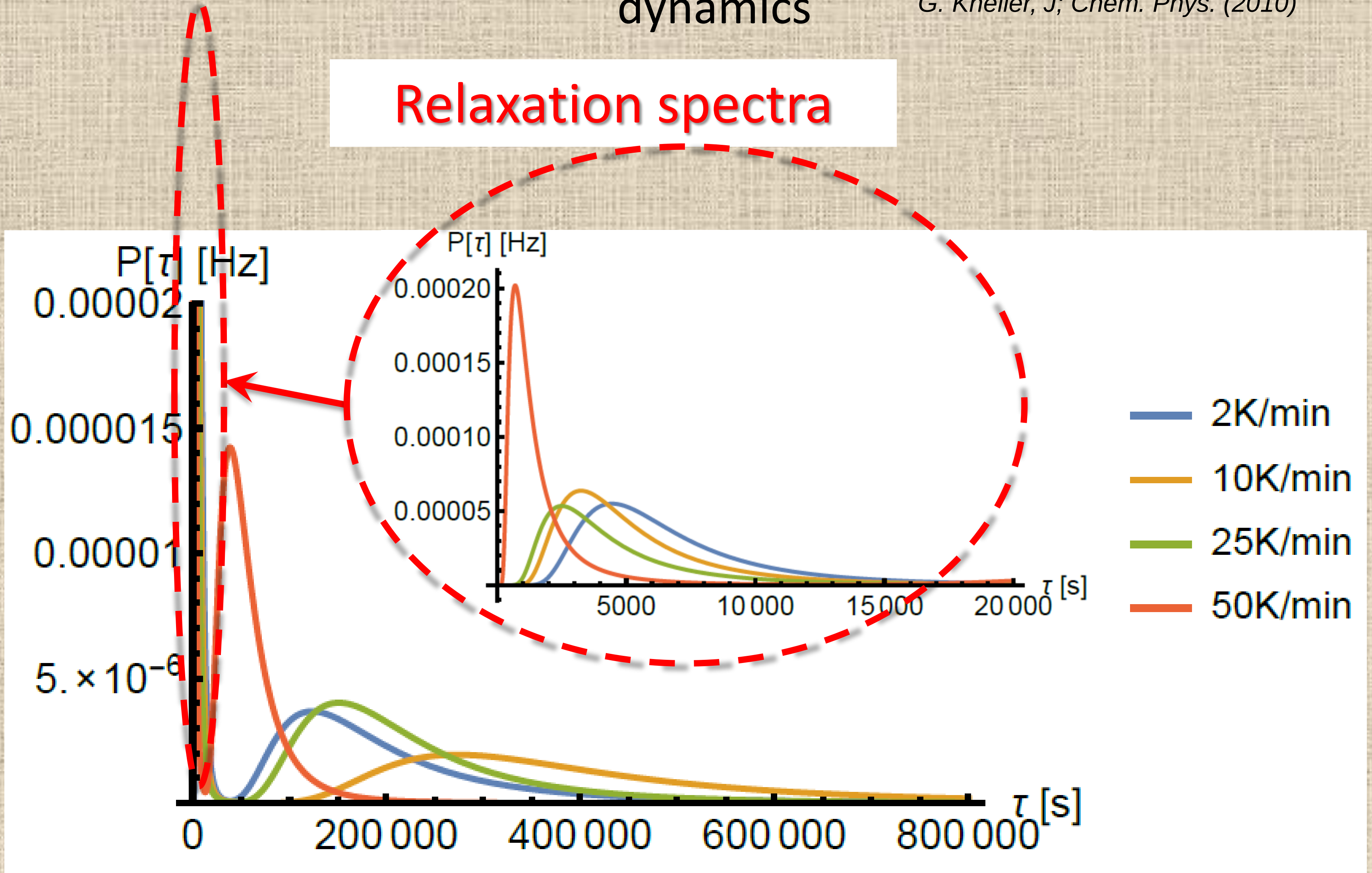
Effect of heating rate

Idea of time relaxation distribution function

Modelisation using fractional Brownian dynamics

G. Kneller, J; Chem. Phys. (2010)

Relaxation spectra



Relaxation structurale à courte distance: Infrarouge

Détails techniques

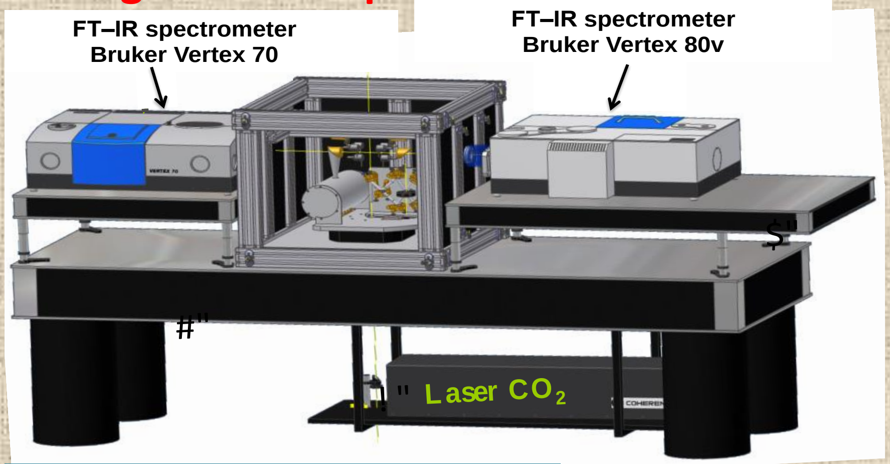
Dispositif expérimental : 2 spectromètres

développé au CEMHTI

spectromètre FT-IR, Bruker Vertex 80v

$\sigma = 400 - 1600$ cm^{-1}

Chauffage avec une platine résistive T ~1200 K



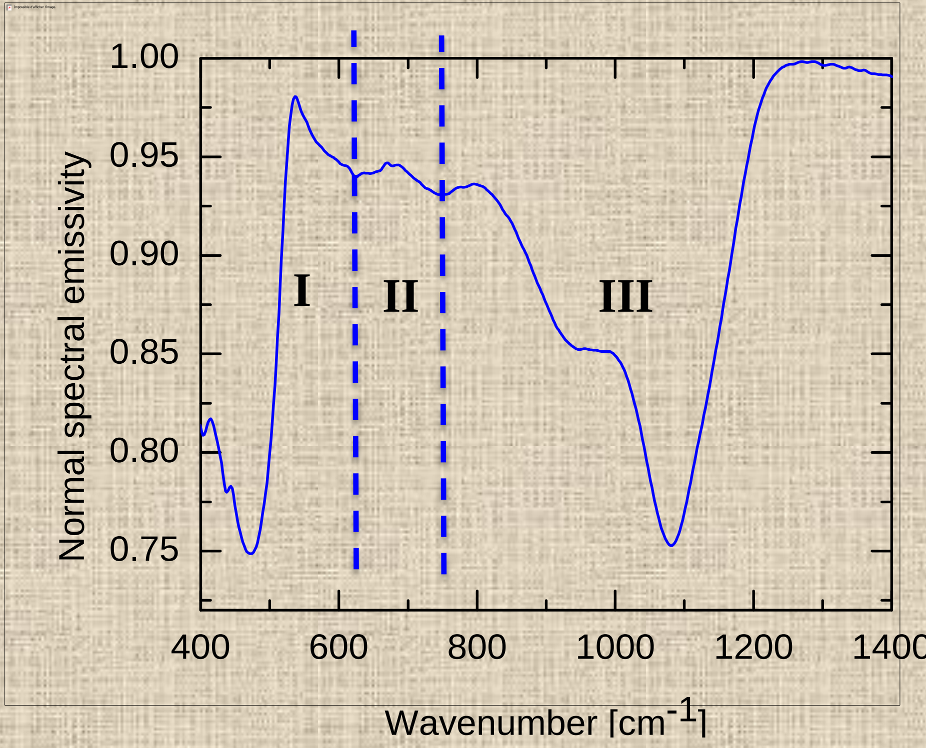
Calcul d'emissivité

Luminance du verre et celle du corps noir

$$E = \frac{TF\left(I_S - I_{RT}\right)}{TF\left(I_{BB} - I_{RT}\right)} \frac{P_{BB} - P_{RT}}{P_S - P_{RT}} E_{BB}$$

FT : Fourrier transform ; I : Interferogram; P: Planck's law ; BB : Black body ; S: Sample ; RT : Room Temperature

Spectre d'emissivité du verre



- région I : fléxion des liaisons O—Si—O
- région II : vibrations des liaisons Si—O—Si
- région III: vibration des liaison Si—BO/NBO dans les entités Q^n

Analyse des spectres

Région opaque : Lois de Kirchhoff et Fresnel

$$E(\omega) = 1 - \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$

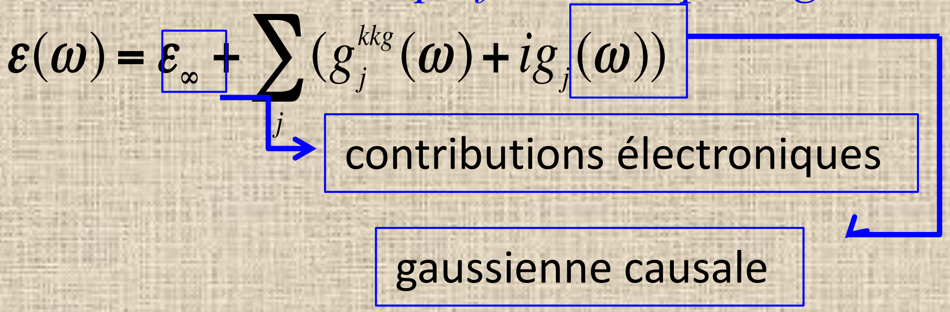
Logiciel Focus

avec :

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

fonction diélectrique

Modèle utilisant un profil d'absorption gaussien



$$\varepsilon(\omega) = \boxed{\varepsilon_\infty} + \sum_j (g_j^{kkg}(\omega) + i\boxed{g_j(\omega)})$$

contributions électroniques

gaussienne causale

Attribution des modes

ν_1 O-Si-O déformation

ν_2 Si-O-Si étirement, ν_6

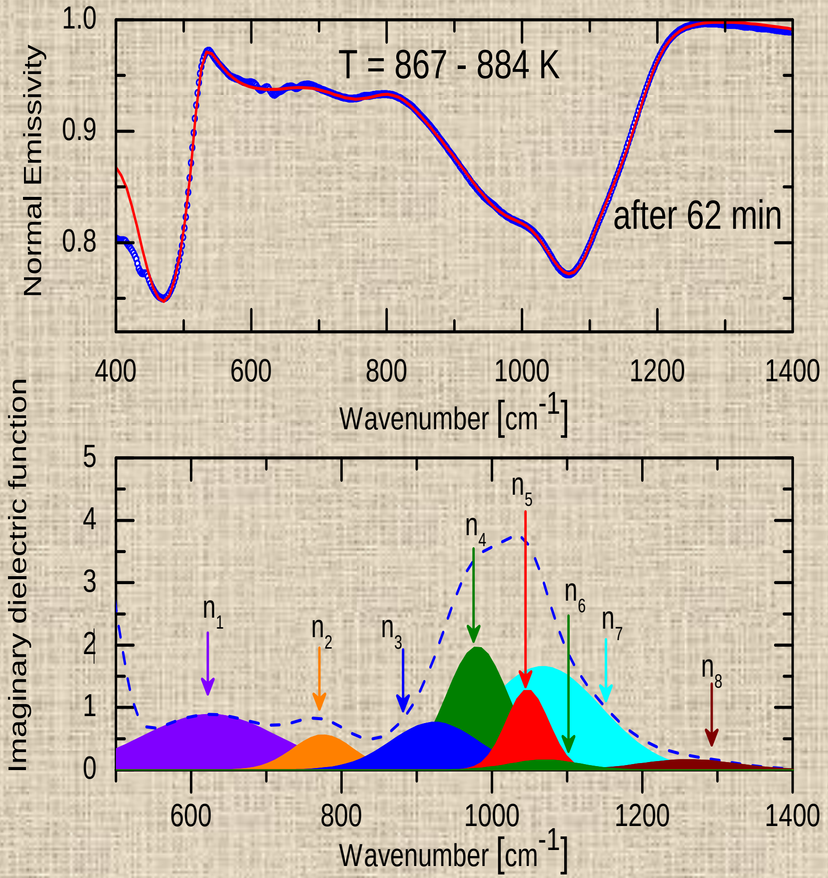
ν_3 Si-NBO étirement dans Q^2

ν_4 Si-NBO étirement dans Q^3

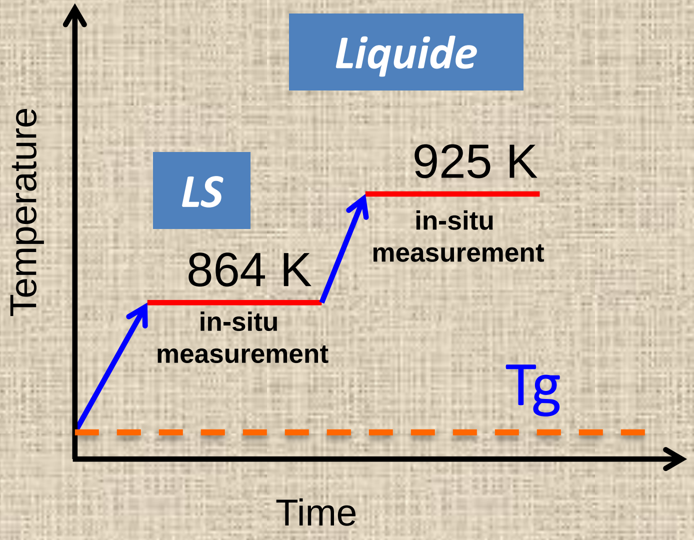
ν_5 Si-BO étirement dans Q^4

ν_7 Si-BO contribution des Q^2, Q^3, Q^4 au désordre dynamique

D. De Sousa Meneses Vibrational Spectroscopy, 65, 50-57 ***2013***.



Protocol expérimental



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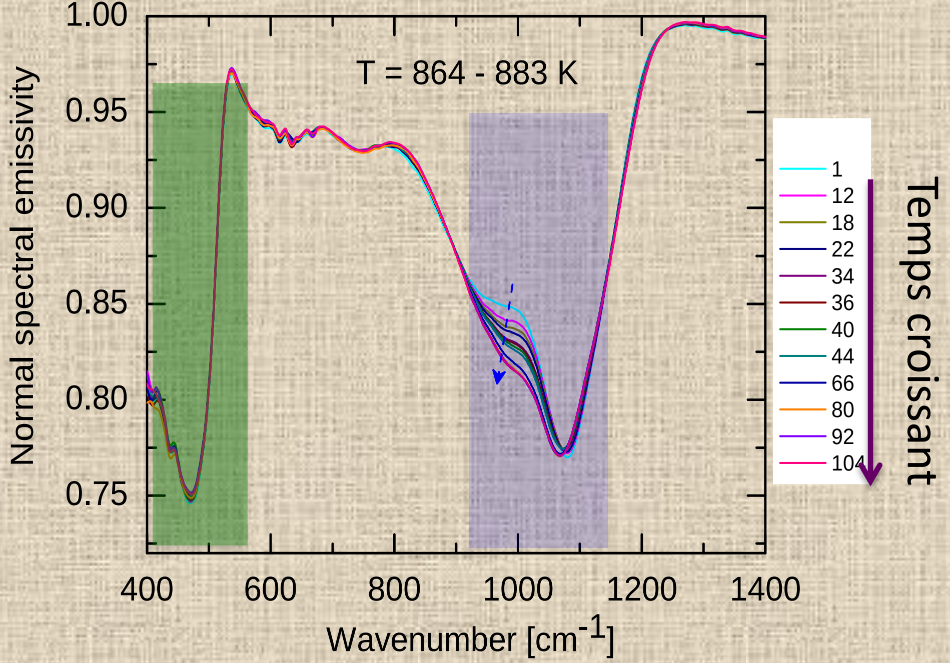
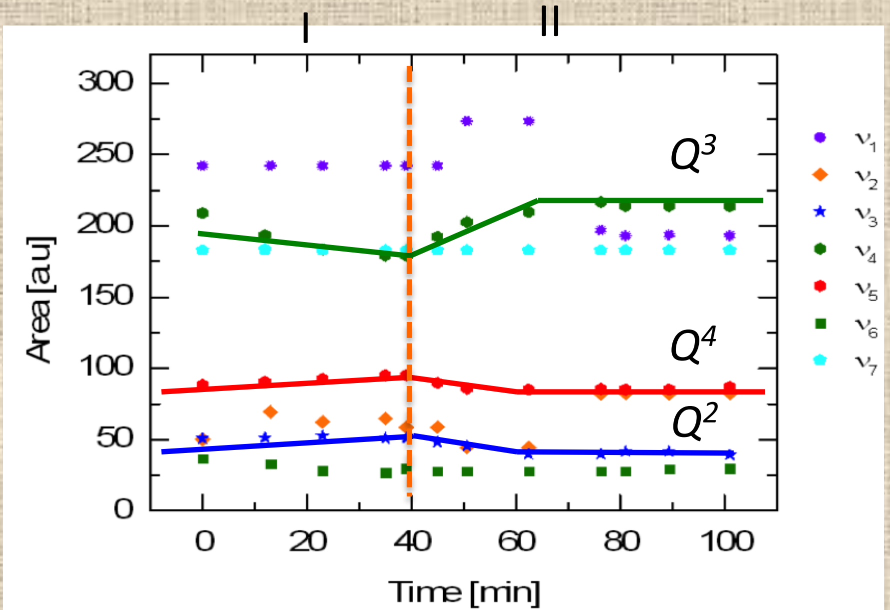


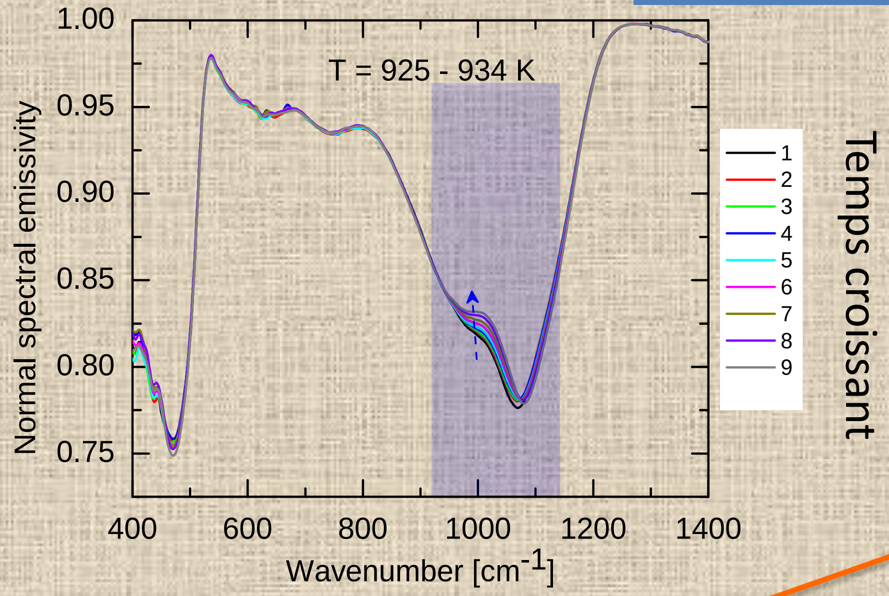


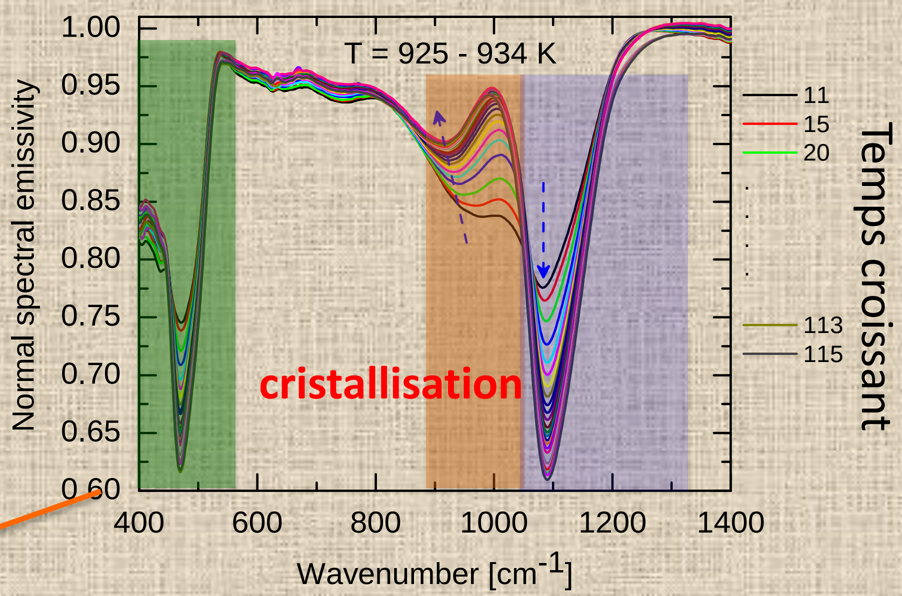
- Le phénomène de relaxation s'amorce.
- Augmentation de l'aire Q^3 et diminutions des aires Q^2, Q^4

1. Mise en place d'une réorganisation qu'on voit pas par Infrarouge.
2. Puis relaxation à courte distance, avec changement des populations Q^n.

Relaxation structurale à courte distance: Infrarouge

Liquide

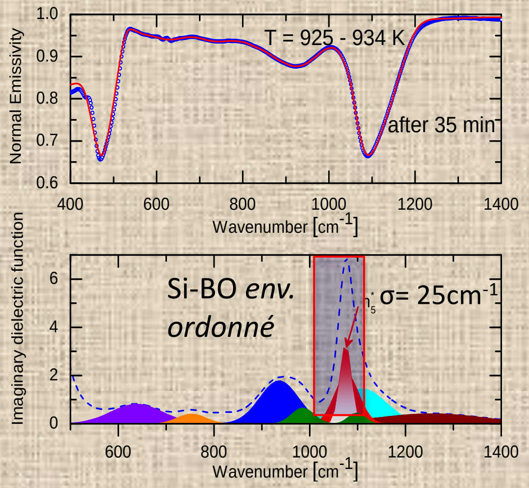


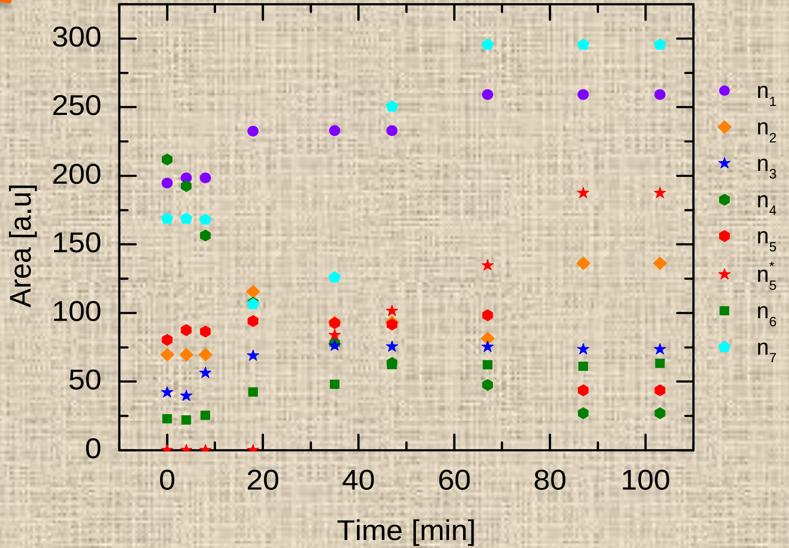


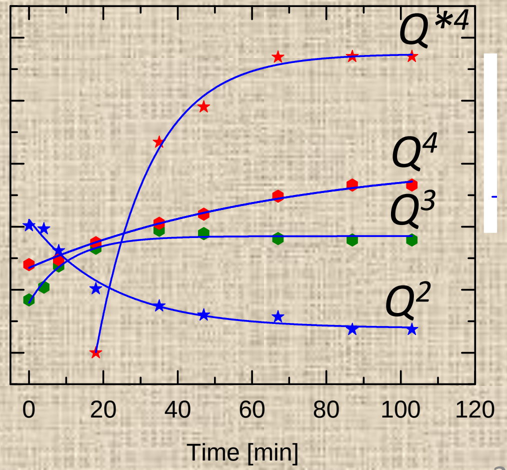
cristallisation

Ajout d'un mode supplémentaire:

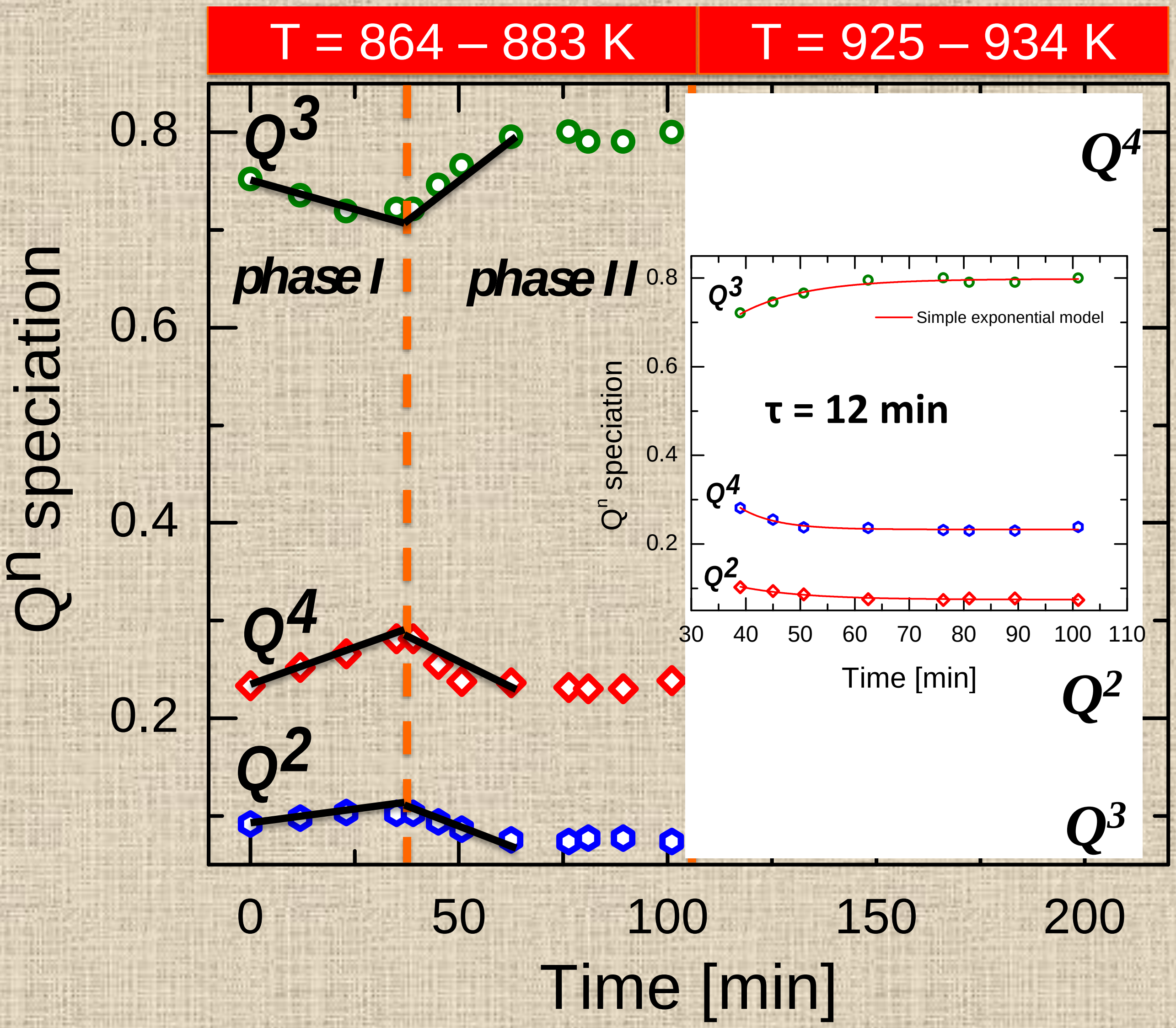
Q^4 (SiO_2-quartz)







Relaxation structurale à courte distance: Infrarouge



- ✓ Augmentation des entités Q^2.
- ✓ Augmentation des entités Q^4.
- ✓ Migration des Na^+ pour compenser la charge.

$$2Q^3 \Leftrightarrow Q^4 + Q^2$$

- ✓ Consommation de $2Q^3$.
- ✓ Le système atteint un minimum.

- ✓ Verre continue à évoluer, état plus stable.
- ✓ Augmentation des especesQ^4, apparition du mode supp, montre la formation d'une phase cristalline riche de SiO_{2-} quartz.

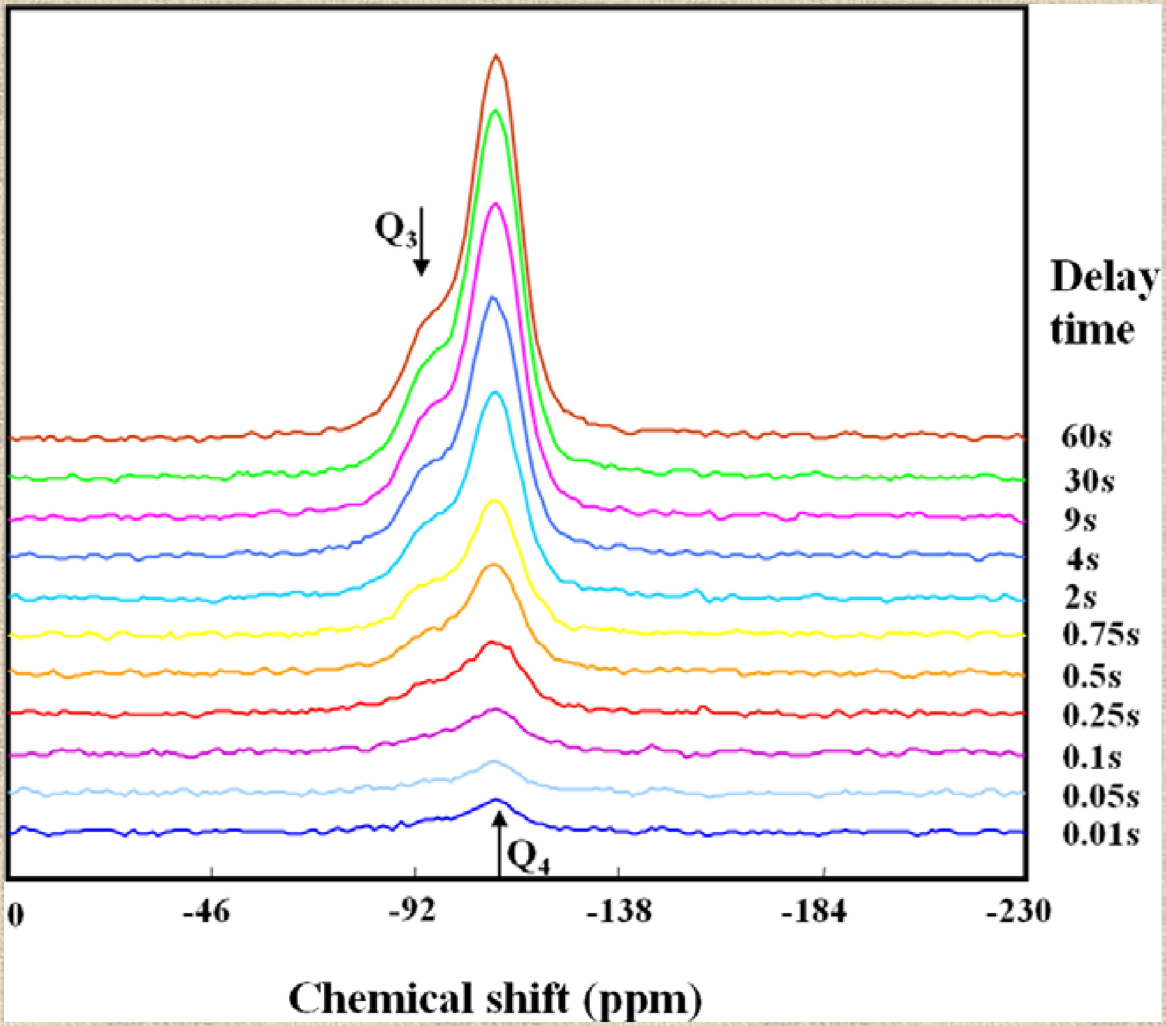
➔ Cristallisation et démixtion (formation des cristallites autour de la structure

➔ Réaction lente du système au début, mise en place d'une organisation à longue distance, puis une relaxation à courte échelle.

Etude par RMN de la distribution spatiale des ions Na^+ dans les verres $(SiO_2)_{1-x}(Na_2O)_x$

distribution spatiale des atomes porteurs de moments magnétiques (ici ^{29}Si) $\Rightarrow$relation masse-distance

$$m(r) \sim r^D$$



^{29}Si Chemical shift in $9Na_2O$–$91SiO_2$ glass (1000 ppm Gd_2O_3).

$M(t) = t^{\alpha}$ relaxation nucléaire de ^{29}Si

$$M(t) = c\int_{r_m}^{r_M} \left[1 - exp(-At/r^6)\right]\mu_0(r)dr$$

$$M(t) = c\,M_0[r = (At)^{1/6}]$$

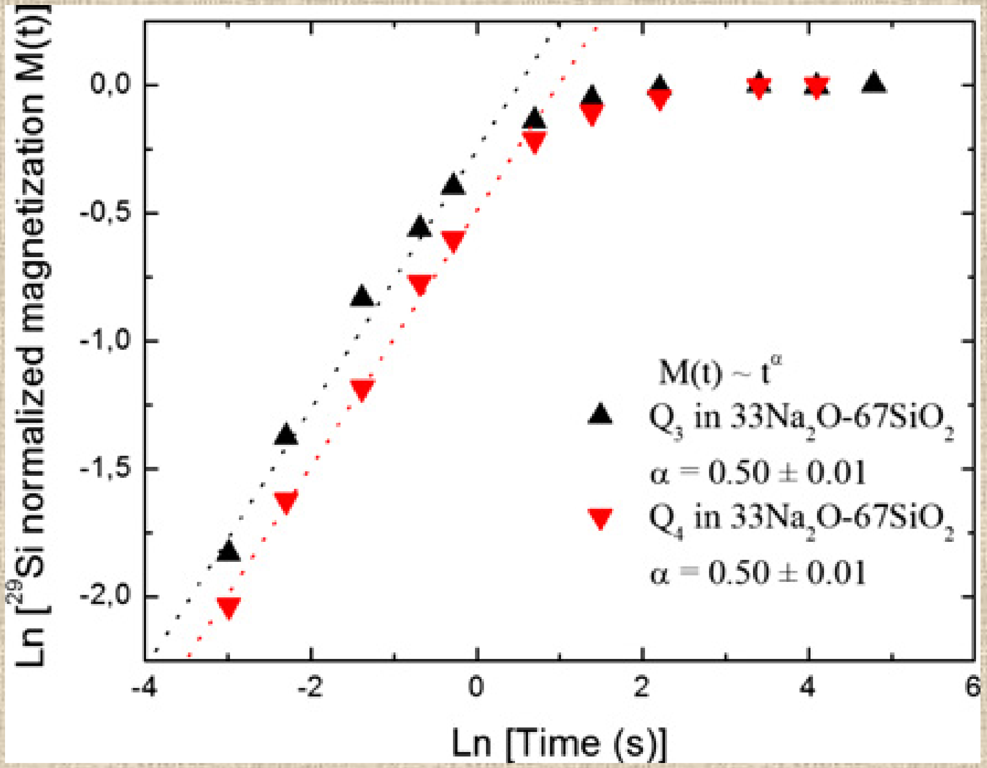
$M \propto r^D \propto t^{\alpha} \propto (At)^{D/6}$

$\Rightarrow \alpha = D/6$

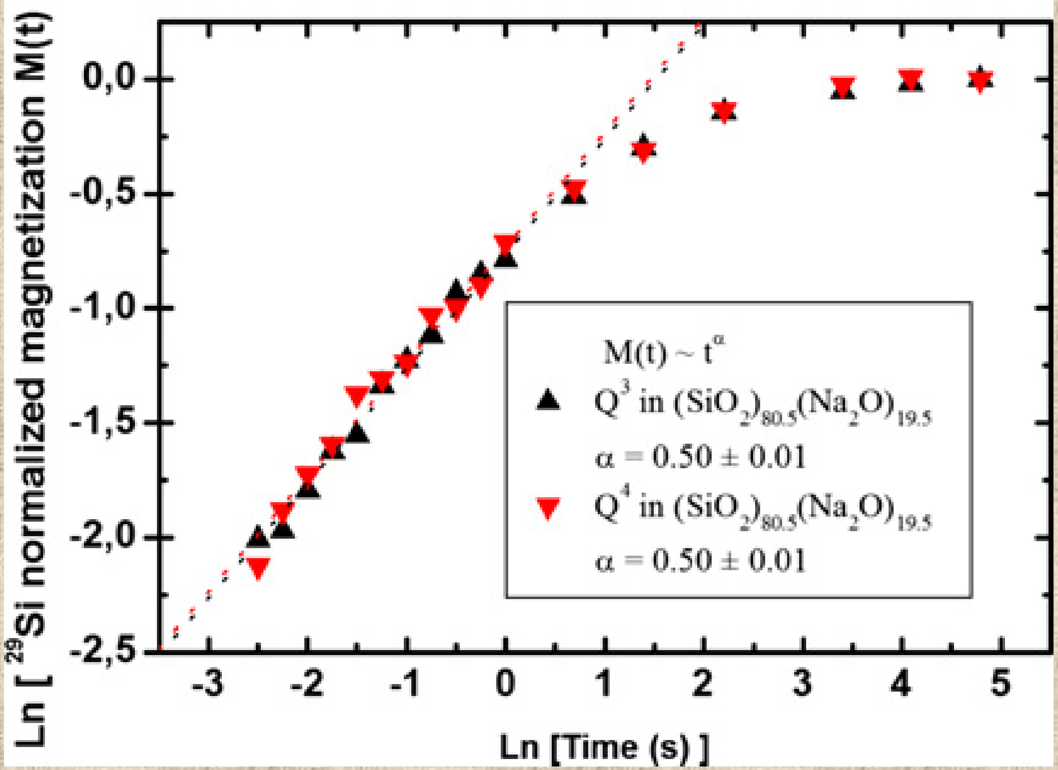
$(SiO_2)_{0.91}(Na_2O)_{0.09} \Rightarrow D = 2.46$

$(SiO_2)_{0.795}(Na_2O)_{0.195} \Rightarrow D \approx 3$

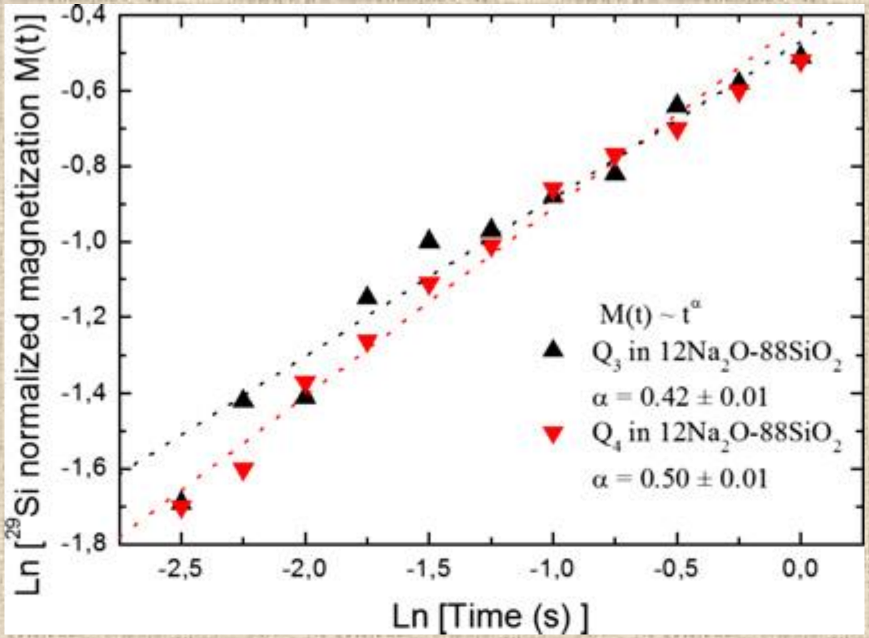
$(SiO_2)_{068}(Na_2O)_{032} \Rightarrow D \approx 3$



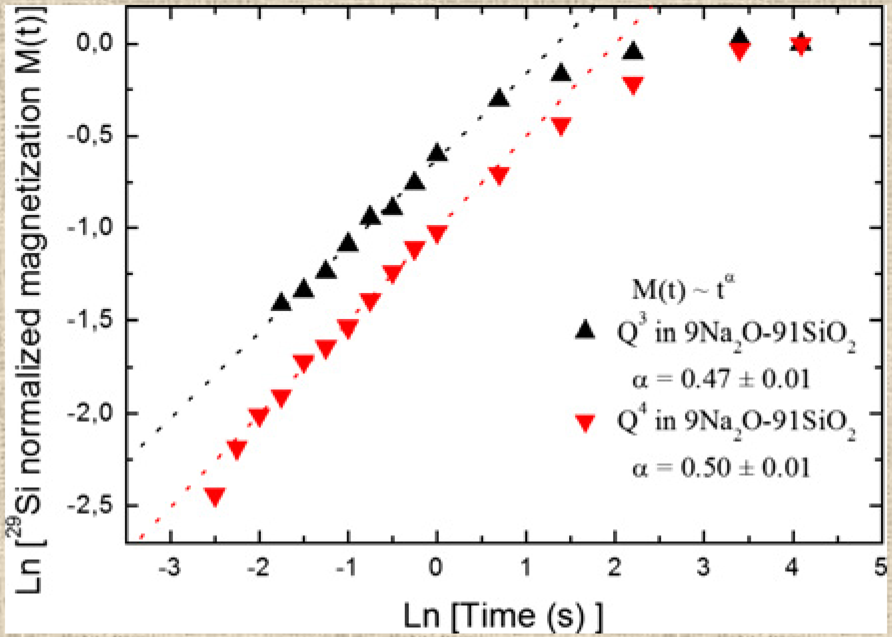
Logarithm of ^{29}Si normalized magnetization as a function of logarithm time delay for $33Na_2O–67SiO_2$ glass (e).



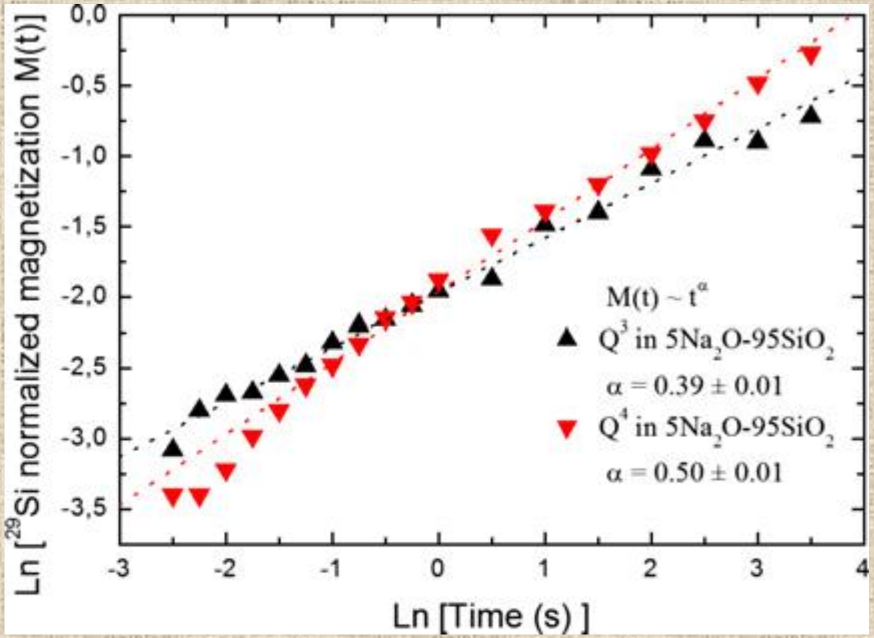
Logarithm of ^{29}Si normalized magnetization as a function of logarithm time delay for $19.5Na_2O$–$80.5SiO_2$ glass



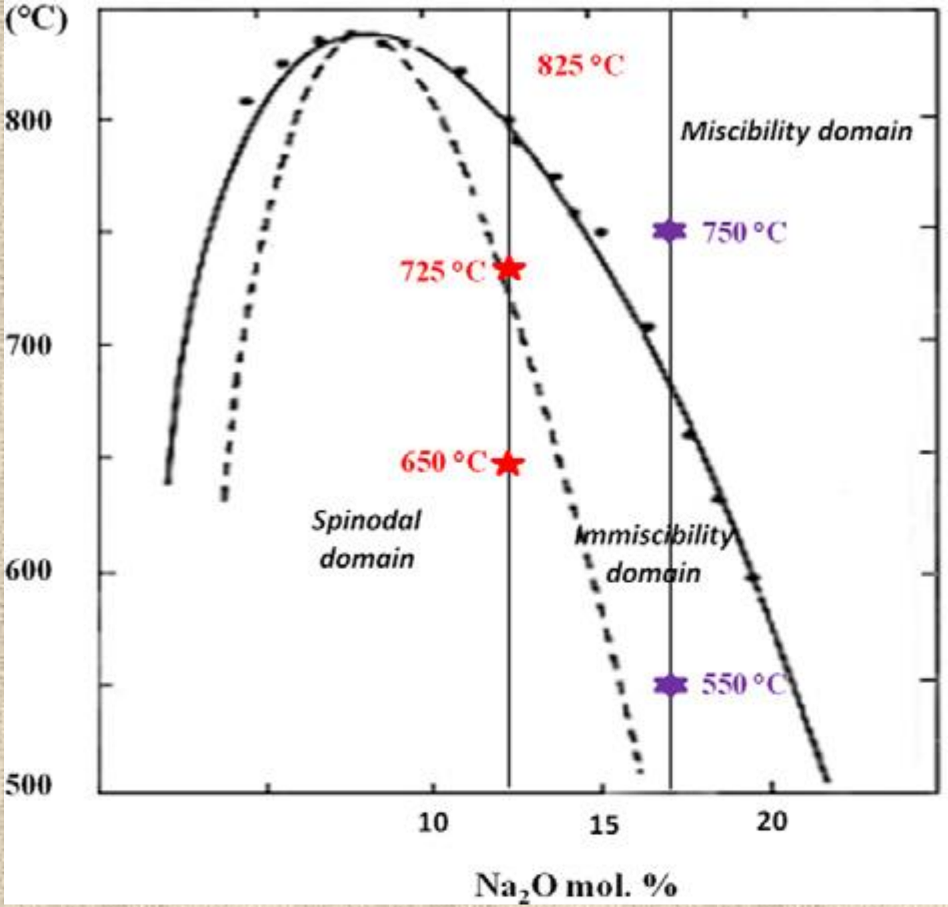
Logarithm of ^{29}Si normalized magnetization as a function of logarithm time delay for $12Na_2O$– $88SiO_2$ glass



Logarithm of ^{29}Si normalized magnetization as a function of logarithm time delay for $9Na_2O$–$91SiO_2$ glass



Logarithm of ^{29}Si normalized magnetization as a function of logarithm time delay for $5Na_2O$–$95SiO_2$ glass



$M \propto r^D \propto t^\alpha \propto (At)^{D/6}$

$\Rightarrow \alpha = D/6$

$(SiO_2)_{0.91}(Na_2O)_{0.09}$

$(SiO_2)_{0.795}(Na_2O)_{0.195}$

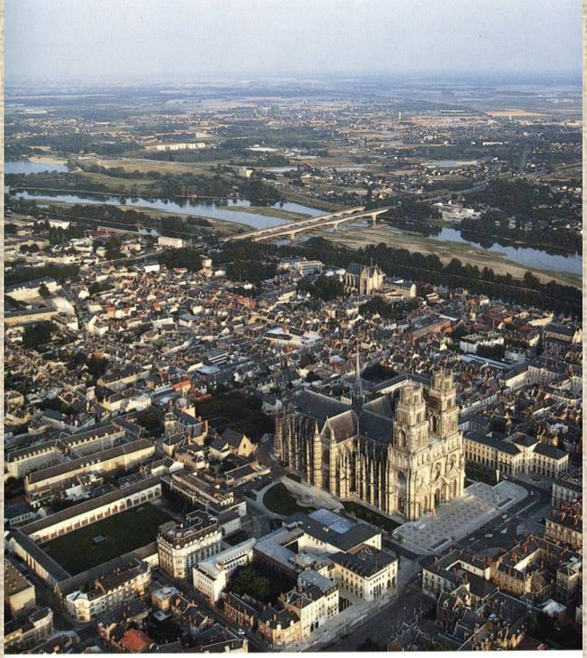
$(SiO_2)_{068}(Na_2O)_{032}$

$(SiO_2)_{0.91}(Na_2O)_{0.09} \Rightarrow D = 2.46$

$(SiO_2)_{0.795}(Na_2O)_{0.195} \Rightarrow D \approx 3$

$(SiO_2)_{068}(Na_2O)_{032} \Rightarrow D \approx 3$

Thank you for your attention



Orléans city

Joan of Arc City

along
Loire river

"Loire valley"
also named

"Kings valley"

University
Since 1306