A new control parameter for the glass transition of glycerol.

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Service de Physique de l'Etat Condensé (CNRS, MIPPU/ URA 2464), DSM/IRAMIS/**SPEC/SPHYNX**
CEA Saclay, France

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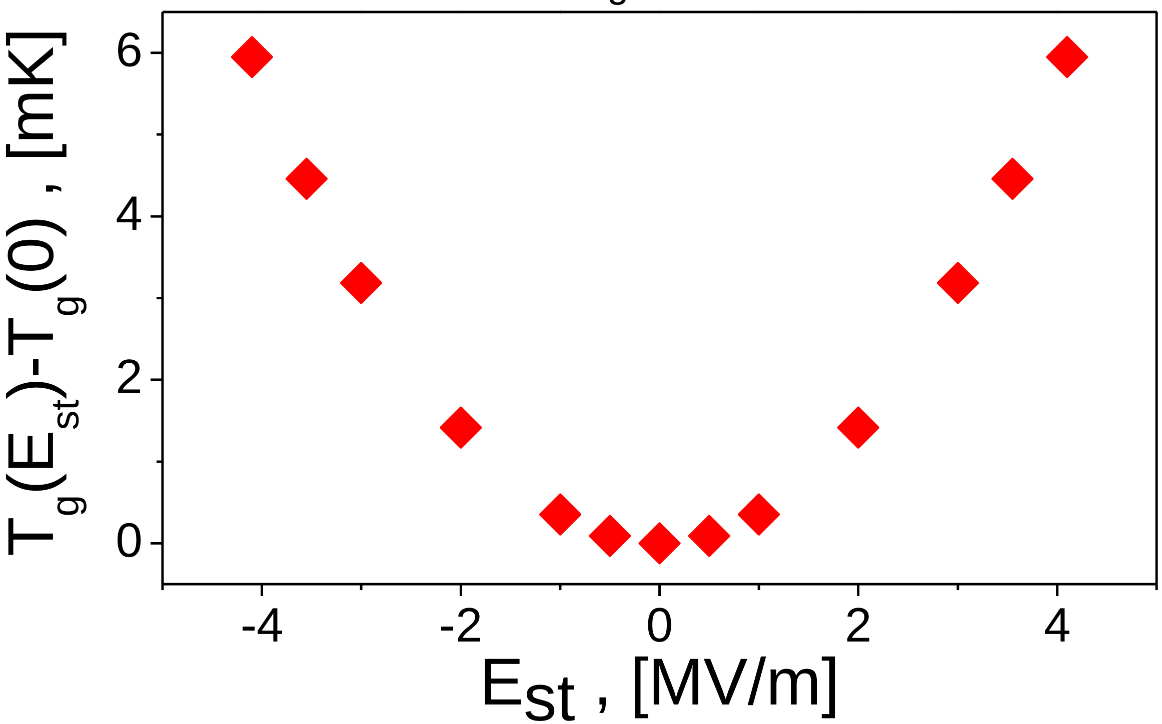
Additionnal Funding:

The most emblematic claim of this work :

Glycerol (T_g=187K at E_{st}=0)



- E_{st} is a new control parameter in Glycerol.

- Previously, the unique way to change Tg was the Pressure Π

- Small effect: discovered through a nonlinear technique (see L'Hôte, Tourbot, Ladieu, Gadige PRB 90, 104202 (2014))

- As for Π exp[ts], the most interesting is not $T_g(\Pi)$ in itself but what we learn about the glass transition when varying the control parameter.

Outline:

I) Motivations for nonlinear experiments

- What happens around Tg ?
- Dynamical Heterogeneities
- Special interest of nonlinear responses !

II) Our specially designed experiment

→ it works !

III) Results on Glycerol

- Order of magnitude and comparison to the Box model
- Relation to N_{corr}
- Tg shift

Summary and Perspectives.

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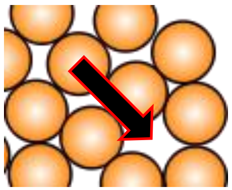
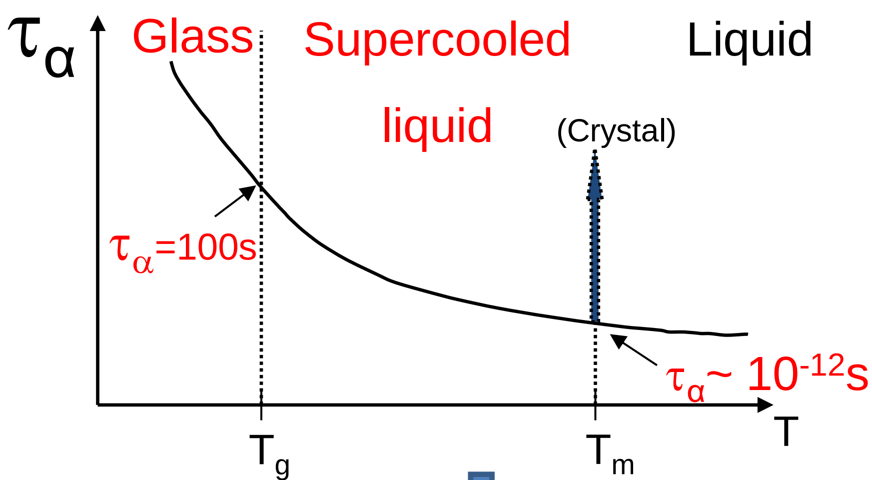
Summary and Perspectives.

What happens around Tg ?

Relaxation time τ_α



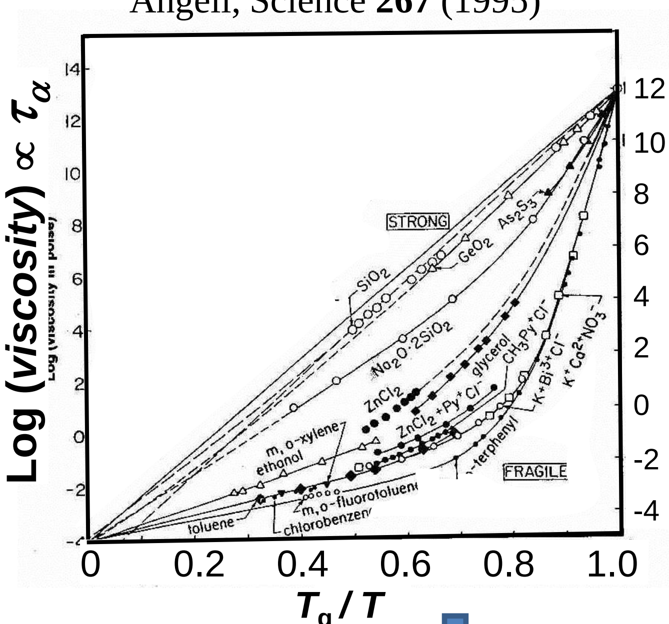


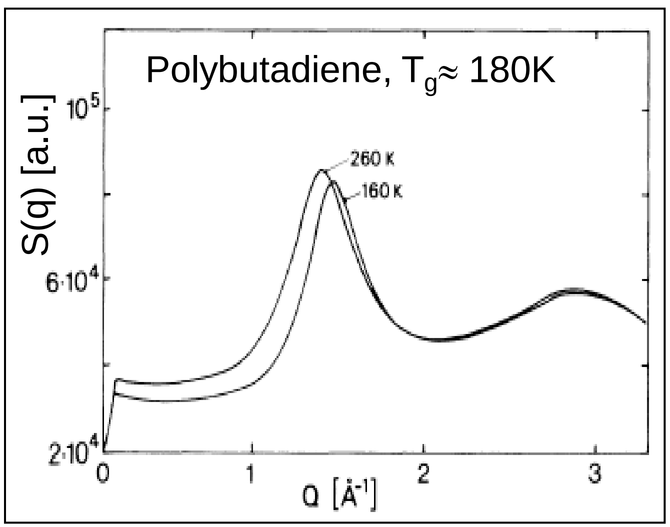
$$\eta \sim \tau_\alpha \sim e^{\frac{E_a}{T}}$$

E_a ↗ when T ↘

⇒ Correlations ↗ when T ↘

Angell, Science **267** (1995)





No (static) order

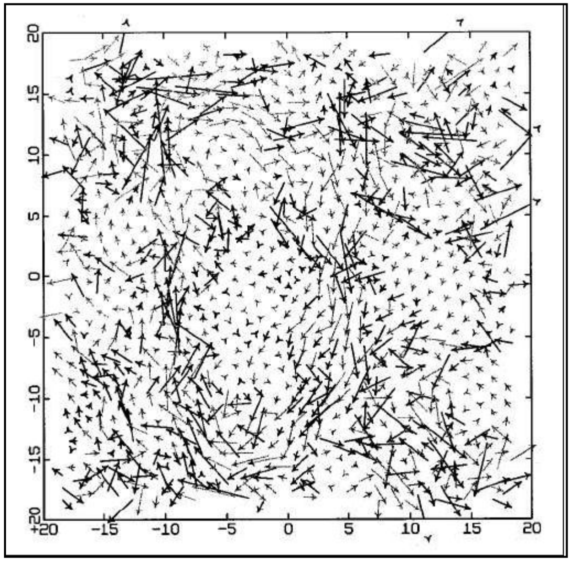
How to combine the existence of correlations with the absence of order ?

Dynamical Heterogeneities in supercooled liquids

- N_{corr} = average number of dynamically correlated molecules : $N_{corr} \propto \xi^3$

… directly observed in granular matter or in numerical simulations.

Example : numerical simulations on soft spheres :

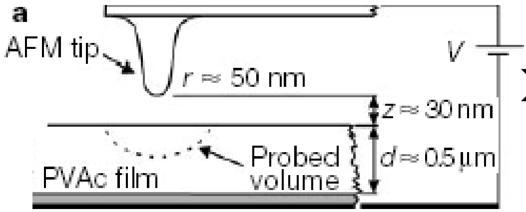


Hurley, Harowell, PRE, 52, 1694, (1995)

…Experimentally, the heterogeneous nature of the dynamics has been established through various breakthroughs:

- NMR experiments — Tracht *et al.* PRL81, 2727 (98), J. Magn. Res. 140 460 (99),…

- Local measurements — E. Vidal Russell and N.E. Israeloff , Nature 408, 695 (2000).



« clusters » of 30-90 monomers

- Hole burning experiments

When T↓: N_{corr} ***would*** ↑, which ***would*** explain why τ_α increases so much

Dynamical Heterogeneities and NHB.

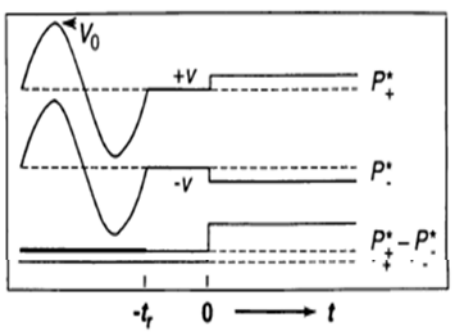
- Many improvements since Schiener, Böhmer, Loidl, Chamberlin Science, **274**, 752, (1996)

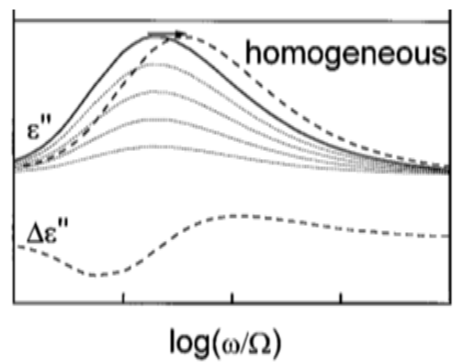
  e.g. R.Richert's group: PRL, **97**, 095703 (2006); PRB **75**, 064302 (2007); EPJB, **66**, 217, (2008); PRL, **104**, 085702, (2010)…

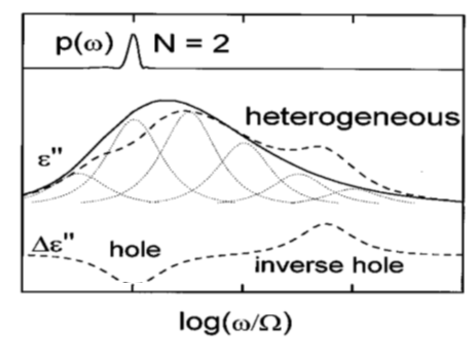
- The central idea in Schiener et al 's seminal paper in 1996:

Strong field (V_0) at Ω ⇒

- No distribution of τ ⇔ $\varepsilon(t,\omega)$: should be globally **shifted** in ω
- A distribution of τ's exists ⇔ $\varepsilon(t,\omega)$: should be mainly **modified close to Ω**







Non Res Hole Burning: ⇒supercooled dynamics IS heterogeneous (at least in time)

- … Can nonlinear experiments give MORE than originally expected ??....

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Summary and Perspectives.

The prediction of Bouchaud-Biroli (⇔B&B): PRB 72, 064204 (2005)

DH characterisation ⇔

$$g_4(\vec{r},t) = \left\langle \vec{p}(\vec{0},0)\,\vec{p}(\vec{0},t)\,\vec{p}(\vec{r},0)\,\vec{p}(\vec{r},t) \right\rangle_c$$

AND

N_{corr} « large enough »

$$E(t) = E\,e^{i\omega t}$$

$$\frac{P}{\varepsilon_0} = \chi_{Lin} E + \chi_3 E^3 + \ldots$$

$$\chi_3(\omega,T) = \frac{\varepsilon_0 \chi_s^2 a^3}{k_B T} N_{corr}(T) H\left(\omega \tau_\alpha(T)\right)$$

Natural scale of χ_3

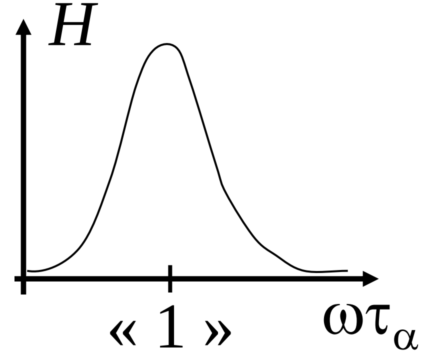
χ_s= static value of χ_{Lin}

a^3= molecular volume

N_{corr}= number of dynamic. correlated molec.

τ_α (T) : typical relaxation time

H: scaling function



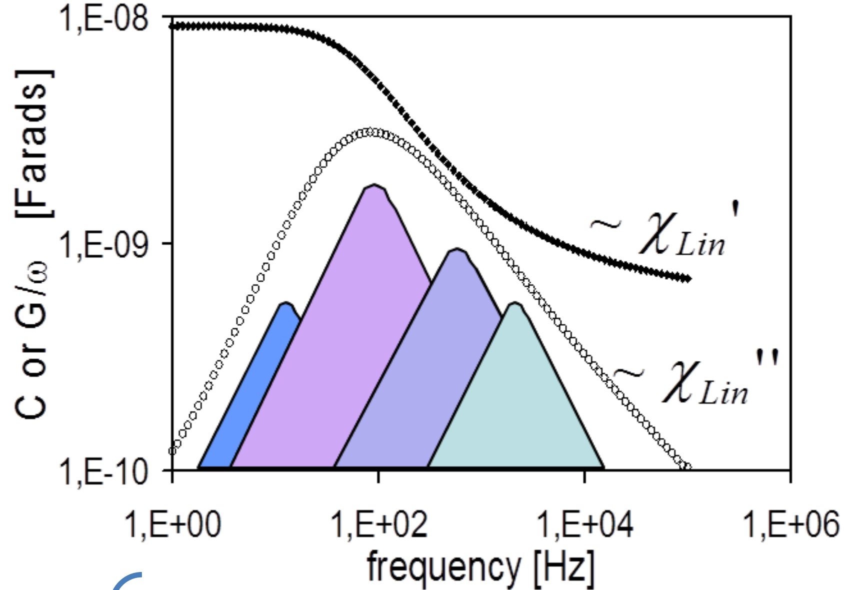
Systematic $\chi_3(\omega,T)$ measurements to test the prediction and possibly get $N_{corr}(T)$

The issue of interpretations : Box Model versus B&B

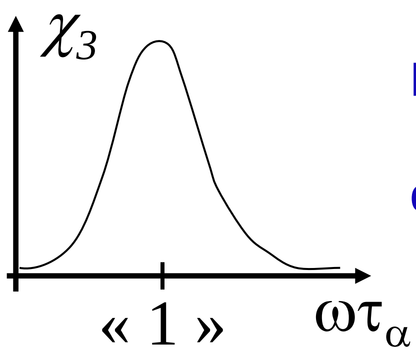
Box model assumptions (designed for NHB):

→ Each DH « k » has a Debye dynamics.
$\{\tau_k\}$ chosen to recover $\chi_{lin}(\omega)$ at each given T.

→ Applying E: each DH « k » is heated by δT_k (τ_{therm})
with $\tau_{therm} \sim \tau_k$.
⇔ as $\{\tau_k\} \sim \tau_\alpha$ heat diffusion **over one DH** takes a **macroscopic time** close to Tg.



$$\left\{ \begin{array}{c} \tau_k \dfrac{\partial(\delta T_k)}{\partial t} + \delta T_k = \dfrac{\text{heat power density}}{\text{c}} \\ (\text{heat power density} \sim \chi_k'' \, \omega \, \text{E}^2) \end{array} \right\} \xrightarrow{\delta T_k \sim E^2} \left\{ \begin{array}{c} P_k - P_{k,\,Lin} = \dfrac{\partial P_{k,Lin}}{\partial T} \delta T_k \sim E^3 \\ (P_{k,Lin} \sim \chi_k \, E) \end{array} \right\}$$



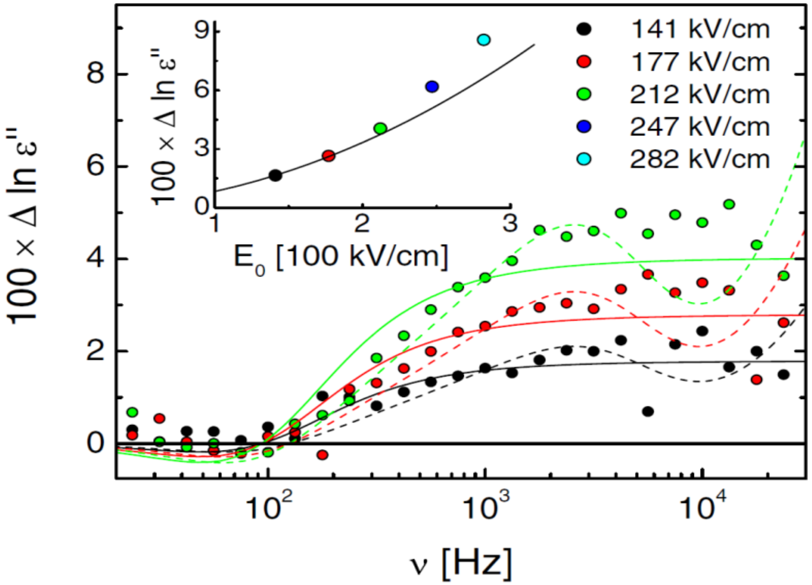
For a pure ac field $E_{ac}\cos(\omega t)$:
ω and T dependences are **qualitatively similar** in the Box model and in B&B

χ_3 does NOT contain N_{corr} (Box model is space free)

$\chi_3(\omega,T)$: $N_{corr}(T)$ or not ?

Some experiments done since B&B's prediction (2005)

Box model : $\delta \ln \varepsilon'' = \frac{-\mathrm{Im}(\chi_3^{(1)}) E^2}{\mathrm{Im}(\chi_{Lin})}$



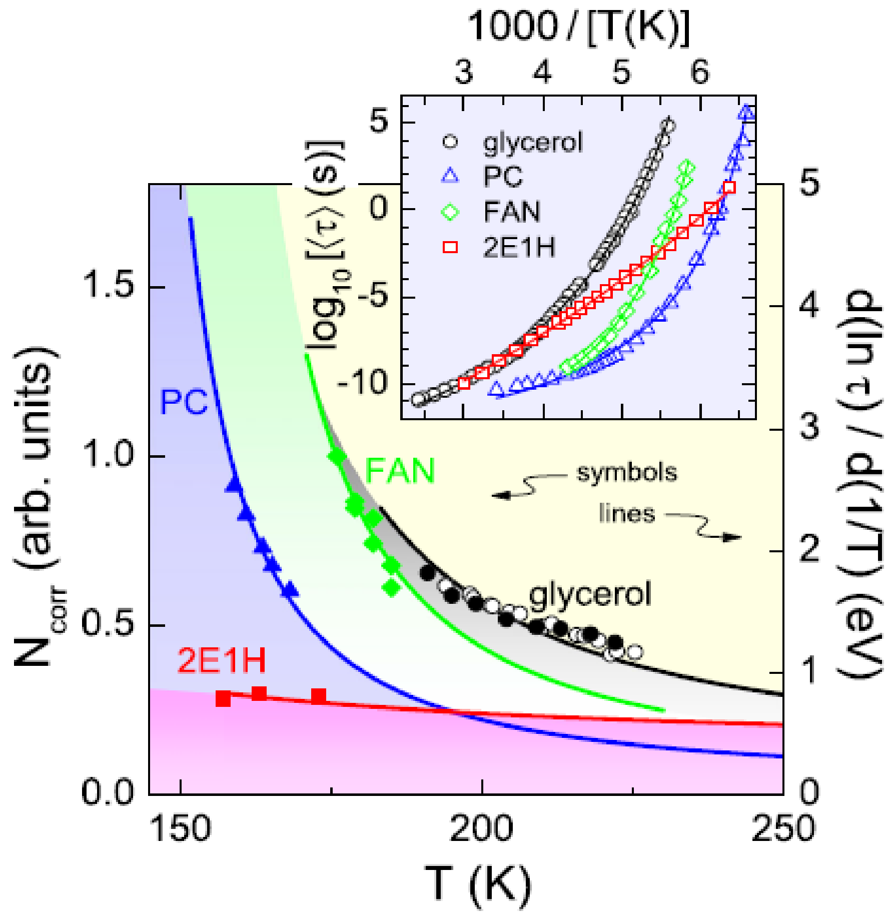
e.g. R.Richert's group: PRL, **97**, 095703 (2006); PRB **75**, 064302 (2007); EPJB, **66**, 217, (2008); PRL, **104**, 085702, (2010)…

→ Very good fits at 1ω (better than at 3ω)

→ Accounts for the transient regime at 1ω

→ Several liquids tested (Richert PRL (2007))

B&B: $\chi_3^{(1)}$ as well as $\chi_3^{(3)}$



→ Evolution of $N_{corr}(T)$ or of $N_{corr}(t_a)$

→ Several liquids tested (Bauer, Lunkenheimer, Loidl, PRL **111**, 225702 (2013))

→ Using E_{st} will shed a new light on this interpretation issue

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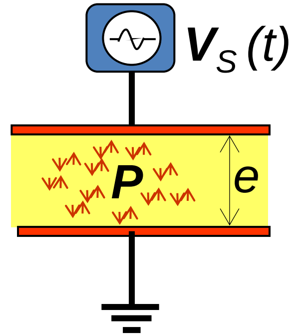
Summary and Perspectives.

Dielectric setup and orders of magnitude

Supercooled liquid, controlled T



For "low enough" E

$$\frac{P(t)}{\varepsilon_0} = \underbrace{\int_{-\infty}^{+\infty} \chi_{lin}(t-t')E(t')dt'}_{\text{Linear term}} + \underbrace{\iint\int_{-\infty}^{+\infty} \chi_3\left(t-t_1^{'}, t-t_2^{'}, t-t_3^{'}\right)E(t_1^{'})E(t_2^{'})E(t_3^{'})dt_1^{'}dt_2^{'}dt_3^{'}}_{\text{First non-linear term}} + \dots$$

$$E(t) = E_{ac}\cos(\omega t) + E_{st}$$

$$\frac{P(t)-P_{Lin}}{\varepsilon_0} = \frac{1}{4}E_{ac}^3 \operatorname{Re}\left[3\chi_3^{(1)}(\omega)e^{-j\omega t} + \chi_3^{(3)}(\omega)e^{-j3\omega t}\right] + 3E_{st}^2 E_{ac} \operatorname{Re}\left[\chi_{2;1}^{(1)}(\omega)e^{-j\omega t}\right] + \text{even harmonics}$$

$$\chi_3^{(1)}(\omega) = F.T.\{\chi_3\}(-\omega,\omega,\omega)$$

$$\chi_3^{(3)}(\omega) = F.T.\{\chi_3\}(\omega,\omega,\omega)$$

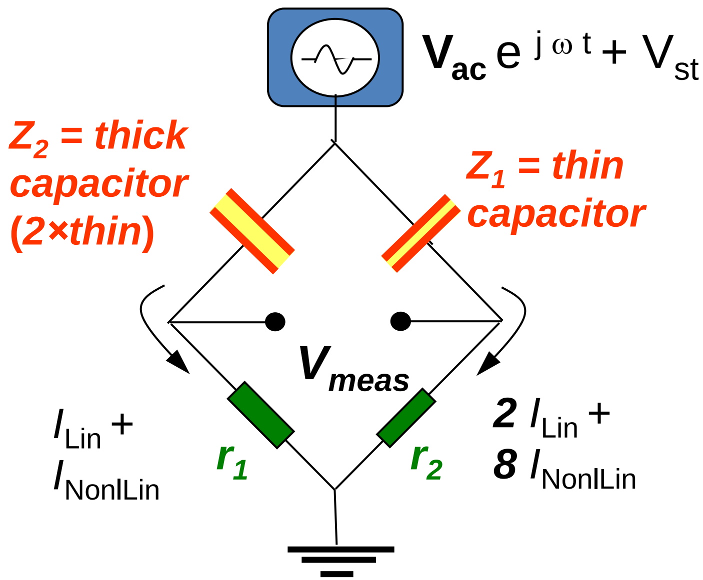
$$\chi_{2;1}^{(1)}(\omega) = F.T.\{\chi_3\}(0,0,\omega)$$

For $E \approx 1\text{MV/m}$, $\dfrac{\text{cubic terms}}{\text{linear term}} \approx 10^{-6}\text{-}10^{-4}$ $\Rightarrow$ Specially designed setup

Our setup to measure cubic susceptibilities

Bridge with two glycerol-filled capacitors of different thicknesses

C. Thibierge et al, RSI **79**, 103905 (2008))



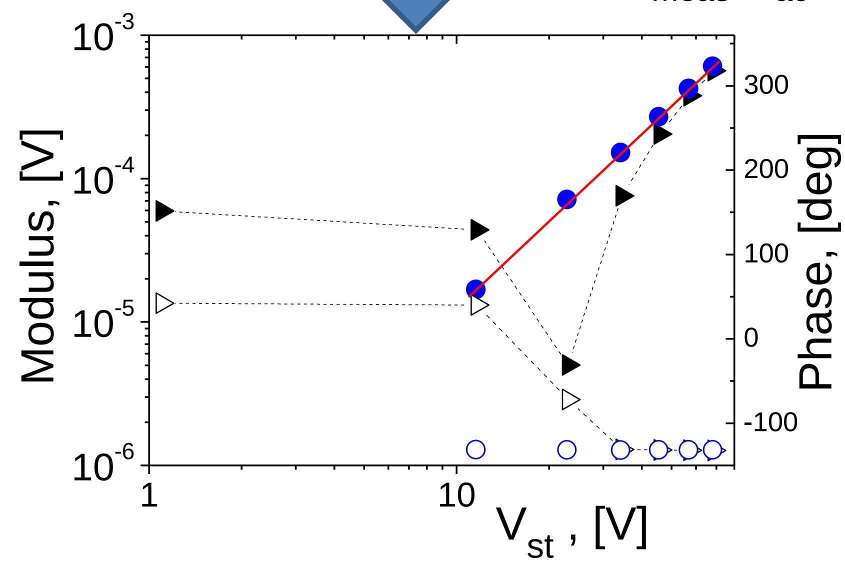
$$\underline{\text{N.B.:}}\quad I = S\frac{\partial P}{\partial t}$$

- when $r_1 Z_1 = r_2 Z_2$: P_{lin} cancels

gives P_{NonLin}

$$\left(\frac{P - P_{Lin}}{\varepsilon_0}\right)_{1\omega} = \frac{3}{4}E_{ac}^3\,\mathrm{Re}\left[\chi_3^{(1)}(\omega)e^{-j\omega t}\right] + 3E_{st}^2 E_{ac}\,\mathrm{Re}\left[\chi_{2;1}^{(1)}(\omega)e^{-j\omega t}\right]$$

$\Delta V = V_{meas}(V_{ac}, V_{st}) - V_{meas}(V_{ac}, 0)$



$\Delta V \sim V_{st}^2\, V_{ac}$

Phase (ΔV) = cte

$$\chi_{2;1}^{(1)} \propto \frac{\Delta V}{V_{st}^2 V_{ac}}$$

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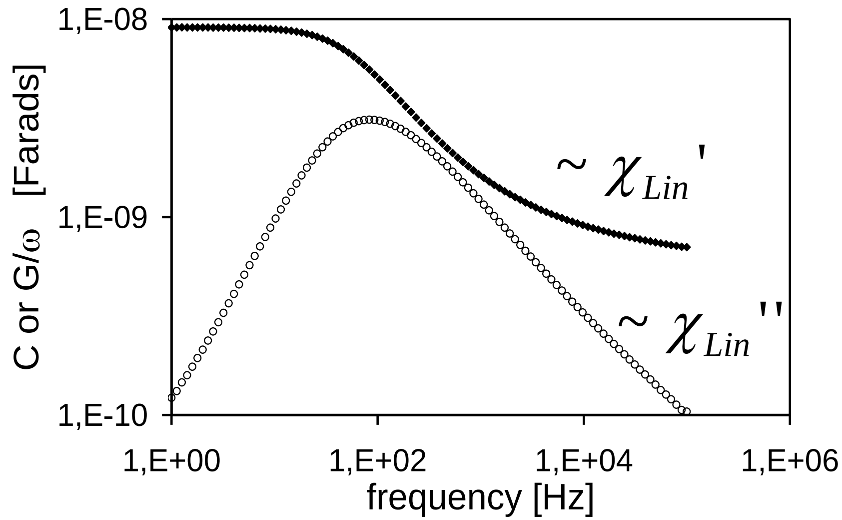
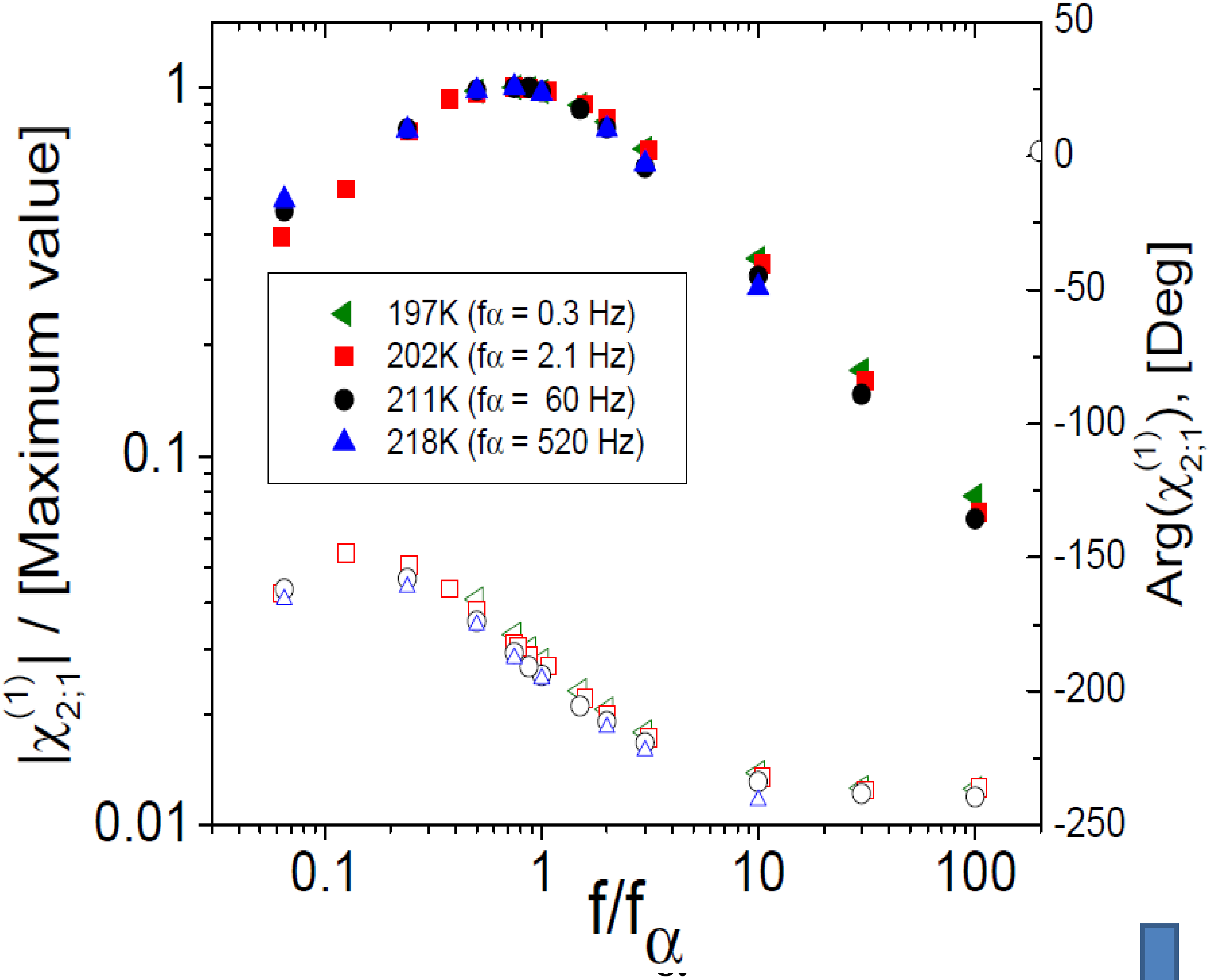
- NB: $\omega\tau_\alpha \equiv f/f_\alpha$

  $f_\alpha \Leftrightarrow$ peak of $\chi_{lin}''(\omega)$

  $|\chi_{lin}(\omega)|$ has no peak



Main features of $\chi_{2;1}^{(1)}(\omega,T)$



At constant T:

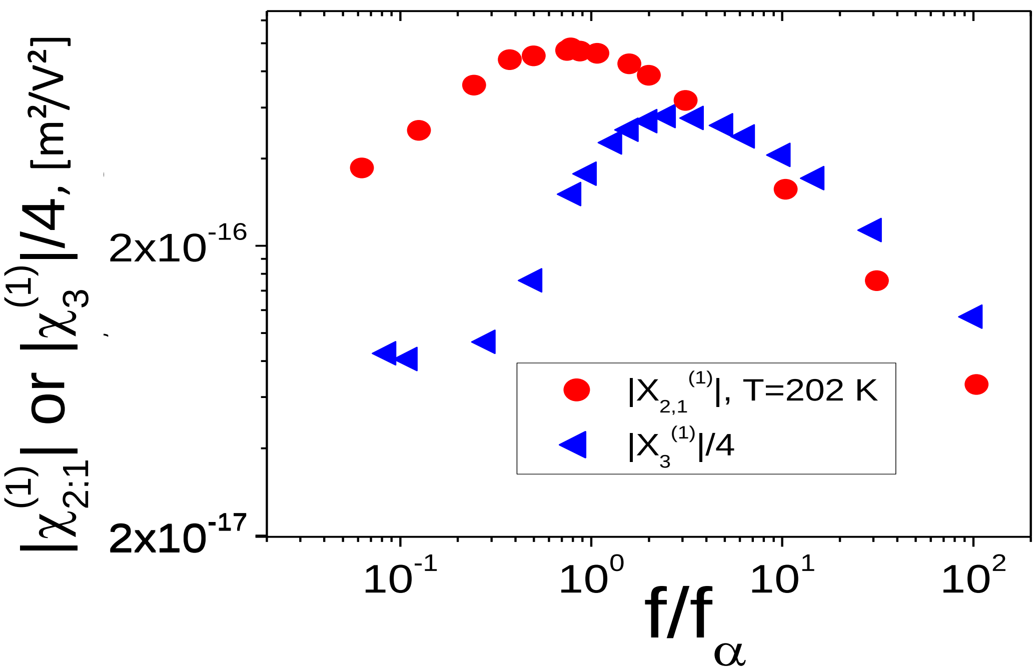
- humped shape for $|\chi_{2;1}^{(1)}|$
- maximum happens in the range of f_α

Scaling of the hump in T

Same qualitative trends as for $\chi_3^{(1)}$ and $\chi_3^{(3)}$

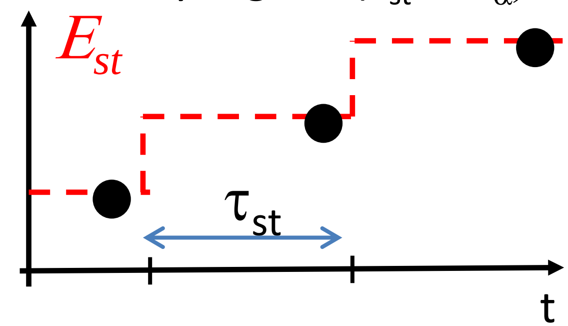
Comparing $\chi_{2;1}^{(1)}(\omega,T)$ and $\chi_3^{(1)}(\omega,T)$

$$\left(\frac{P-P_{Lin}}{\varepsilon_0}\right)_{1\omega} = \frac{3}{4}E_{ac}^3\,\mathrm{Re}\left[\chi_3^{(1)}(\omega)e^{-j\omega t}\right] + 3E_{st}^2E_{ac}\,\mathrm{Re}\left[\chi_{2;1}^{(1)}(\omega)e^{-j\omega t}\right]$$ ⇒ Compare $|\chi_3^{(1)}|/4$ and $|\chi_{2;1}^{(1)}|$



→ **Same order of magitude**

→ Measurements (●) are in the stationnary regime ($\tau_{st} >> \tau_\alpha$)



Varying E_{st} ⇔ ZERO dissipated power

In the Box Model : δT_k ~ dissipated power

Box model's prediction : $|\chi_{2;1}^{(1)}| << |\chi_3^{(1)}|$

(ions)

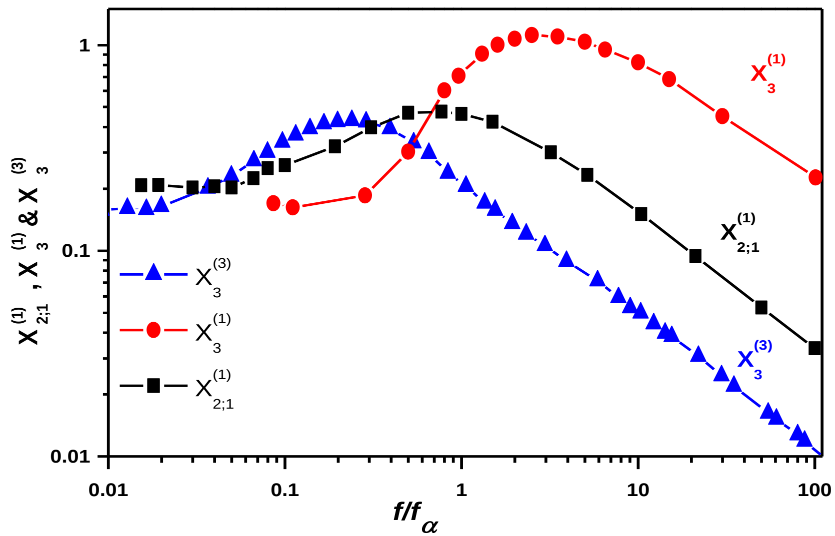
Box model's prediction is too small by a factor 300 for $|\chi_{2;1}^{(1)}|$

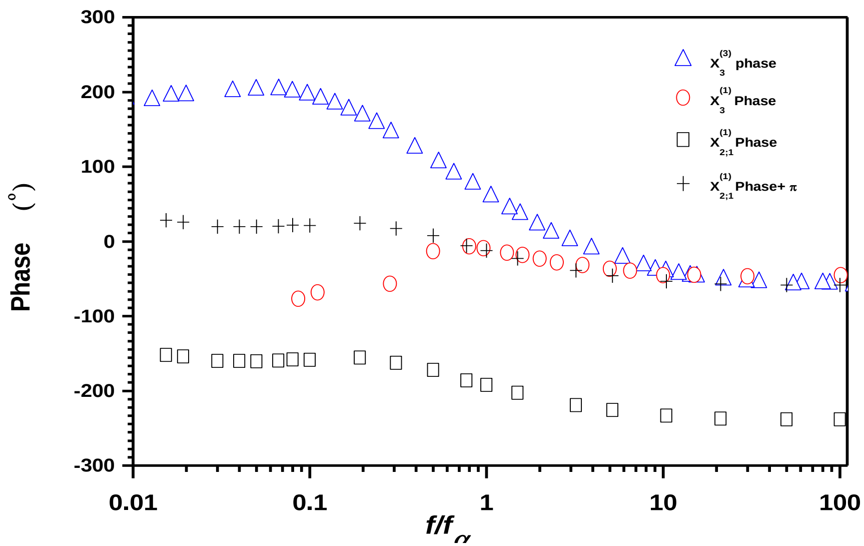
For the first time, Box Model is unable to account for a cubic response:

Decisive point for the interpretation issue …

The latest paper: Samanta, Richert, J.Chem.Phys. 142, (2015).

$$\Delta S \sim \varepsilon_0 (E_{static})^2 \frac{\partial(\Delta\chi_1)}{\partial T} \text{ plugged in } Ln(\tau_\alpha) = \frac{A}{T\,S_c(T)} \Rightarrow \delta T_g \sim (E_{static})^2$$





$\chi_{2;1}^{(1)}$: E_{static} entropy variation

$\chi_3^{(1)}$ *and* $\chi_3^{(3)}$: E_{ac} heating (box model)

Two different

mechanisms at play ?

Very unlikely due to the similarities of $\chi_{2;1}^{(1)}$, $\chi_3^{(1)}$, and $\chi_3^{(3)}$.

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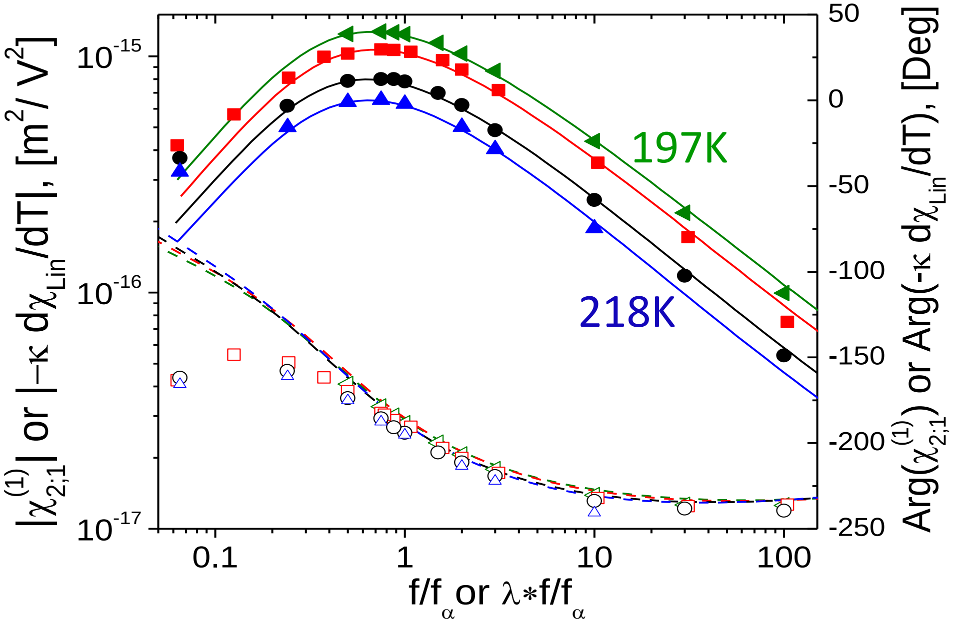
Comparing the ω dependences of $\chi_{2;1}^{(1)}(\omega,T)$ and of $\left(\frac{\partial \chi_{Lin}}{\partial T}\right)_{E_{st}=0}$



- For $f/f_\alpha > 0.2$:

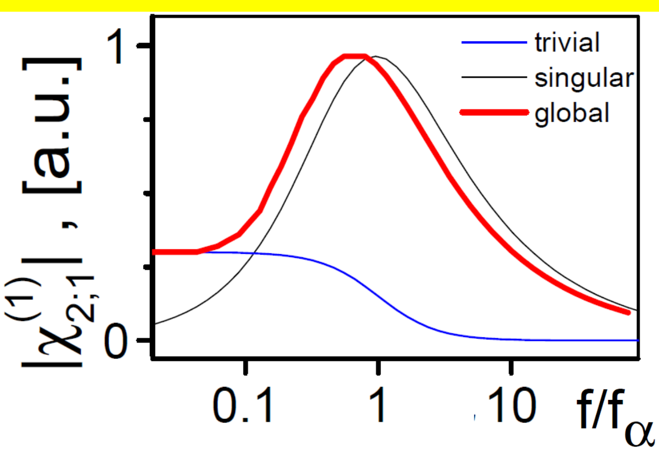
$$\chi_{2;1}^{(1)}(T,\omega) = -\kappa \left(\frac{\partial \chi_{Lin}}{\partial T}\right)_{0,T,\frac{\omega}{\lambda}}$$

with $\kappa \cong 1.2\times 10^{-16}\ \frac{Km^2}{V^2}$, $\lambda \cong 0.80$

∀ T

for both Re and Im parts

Direct link with $n_{corr}^{estim} \sim T\,\frac{d\chi_{Lin}}{dT}$ expected from Berthier et al., Science (2005); JCP, (2007); PRE (2007).



- For $f/f_\alpha < 0.2$: "Trivial" dominates

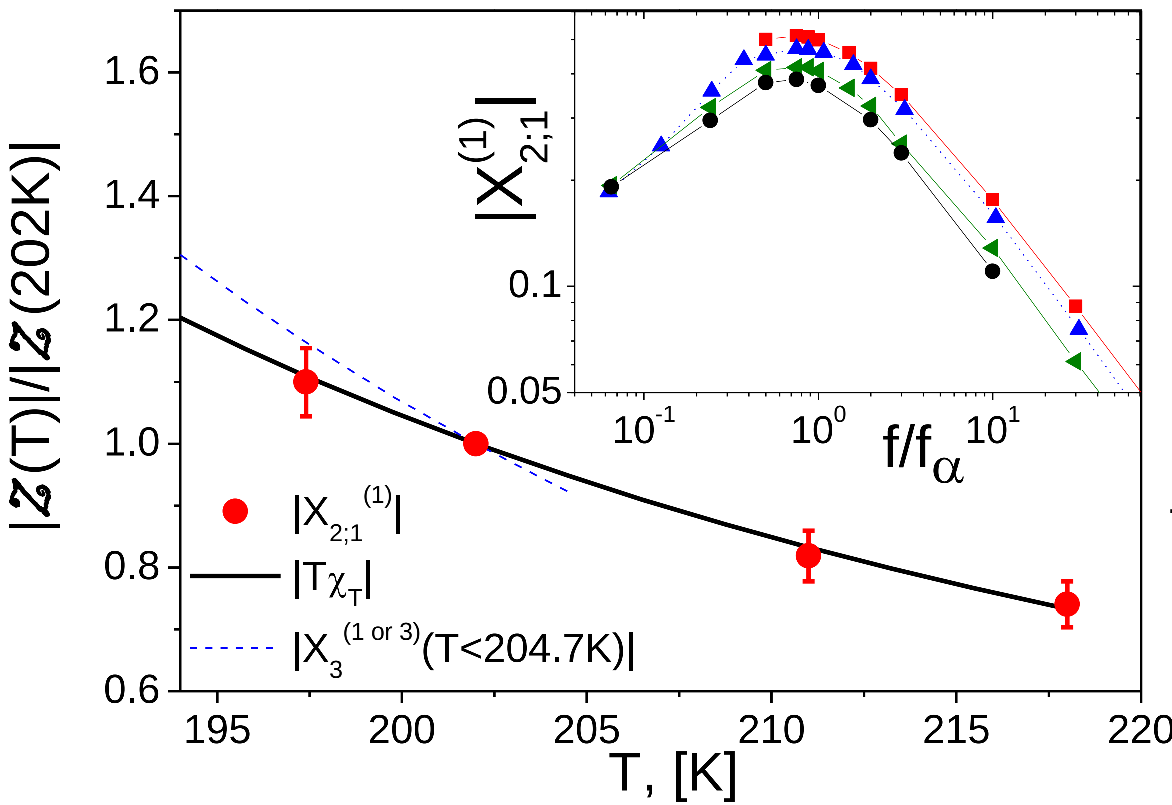
Reshuffling ⇒ Ideal gas at t >>τ_α

$$\Rightarrow \quad \chi_{2;1}^{(1)}(\omega,T) = -\kappa\left(\frac{\partial \chi_{Lin}}{\partial T}\right)$$

T-dependences of the dimensionless cubic susceptibility $X_n^{(k)}$

$$X_n^{(k)}(\omega,T) = \frac{\chi_n^{(k)}(\omega,T)}{\left(\frac{\varepsilon_0 \chi_s^2 a^3}{k_B T}\right)}$$

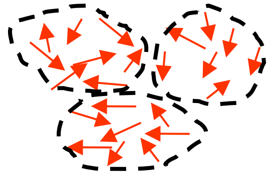
- is T-independent in the trivial limit (ideal gas)
- $= N_{corr}(T) H_n^k(\omega\tau_\alpha(T))$ if B&B's prediction holds



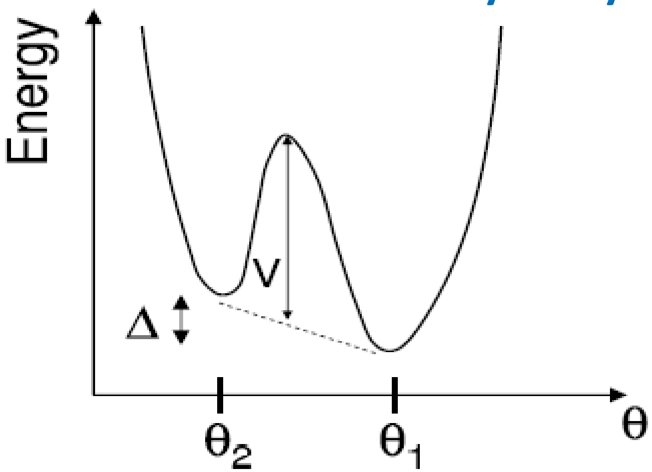
- "Trivial" $X_{2;1}^{(1)}$ looks OK
- Similar T dependences for $X_n^{(k)}$ and for $T\,\partial\chi_{Lin}/\partial T$

ω and T dependences **consistent with $X_{2;1}^{(1)} \sim N_{corr}$ (OK within MCT)**

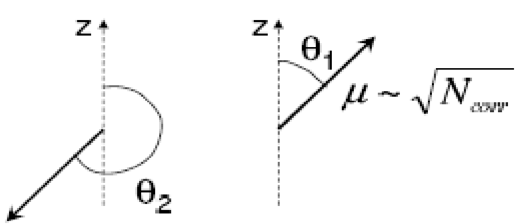
Can we fit nonlinear resp. ? The "toy model" as an attempt :



Each Dyn.Het. ⇔
$\mu = \mu_m \sqrt{N_{corr}}$
in a double well
(to get long τ),
of assymetry Δ



$\vec{E}$ //z



Simplest example: $\Delta=0=\theta_1$

$$\frac{\tau}{\mathrm{ch}\, e}\frac{\partial P}{\partial t} + P = \mathrm{M\,th}\, e$$

$$\text{where } \begin{cases} e = \dfrac{\mu_m \sqrt{N_{corr}}\, E(t)}{k_B T} \sim \sqrt{N_{corr}} \\ \mathrm{M} = \dfrac{\mu_m \sqrt{N_{corr}}}{N_{corr}\, a^3} \sim \dfrac{1}{\sqrt{N_{corr}}} \end{cases}$$

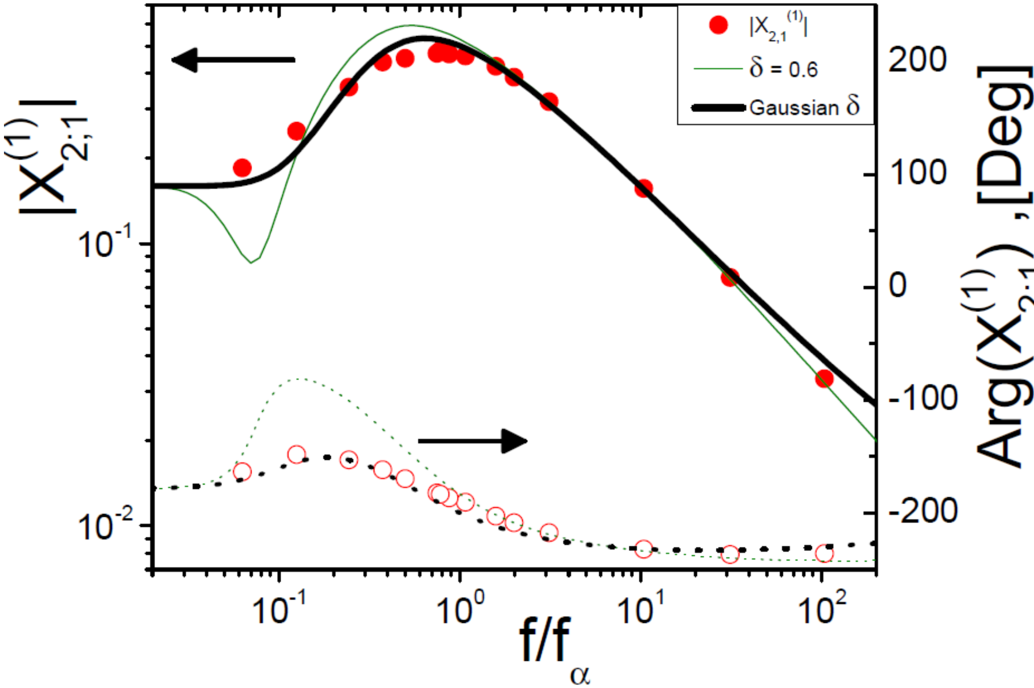
$$\left[\begin{array}{l} P_{Lin} \sim \mathrm{M}\, e \sim \dfrac{\sqrt{N_{corr}}}{\sqrt{N_{corr}}} E \\ P_3 \sim \mathrm{M}\, e^3 \sim \dfrac{\left(\sqrt{N_{corr}}\, E\right)^3}{\sqrt{N_{corr}}} \end{array}\right] \Rightarrow \left[\begin{array}{l} \chi_{Lin} \sim 1 \\ \chi_3 \sim N_{corr} \end{array}\right]$$

Two key points:
- $\mu \sim \sqrt{N_{corr}}$ ⇔ **Amorphous Order** («as» in S.G.)
- **Crossover to trivial is enforced at f<<fα**

→ can it fit the data ? …

Fits at Tg+17K:

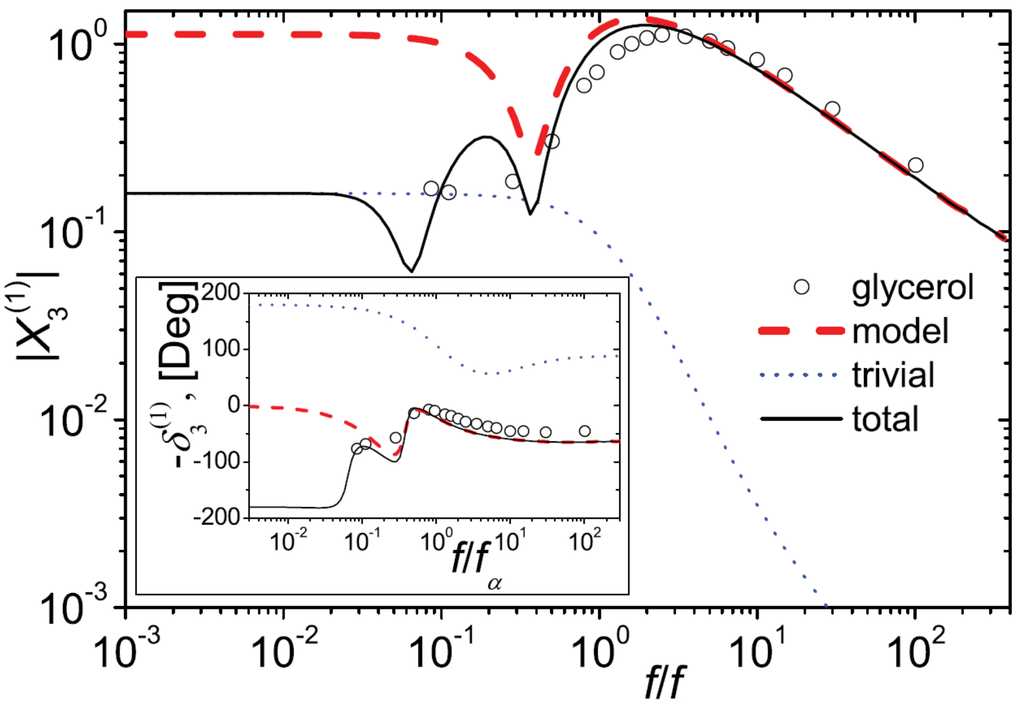
N_{corr}=10
δ=0.60



L'Hôte, Tourbot, Ladieu, Gadige PRB 90, 104202 (2014)

- N_{corr} has the right order of magnitude
- good fits for ALL the $X_n^{(k)}$
- … but with different values of N_{corr} (**toy** model)

N_{corr}=15
δ=0.60



Ladieu, Brun, L'Hôte, PRB **85**, 184207, (2012)

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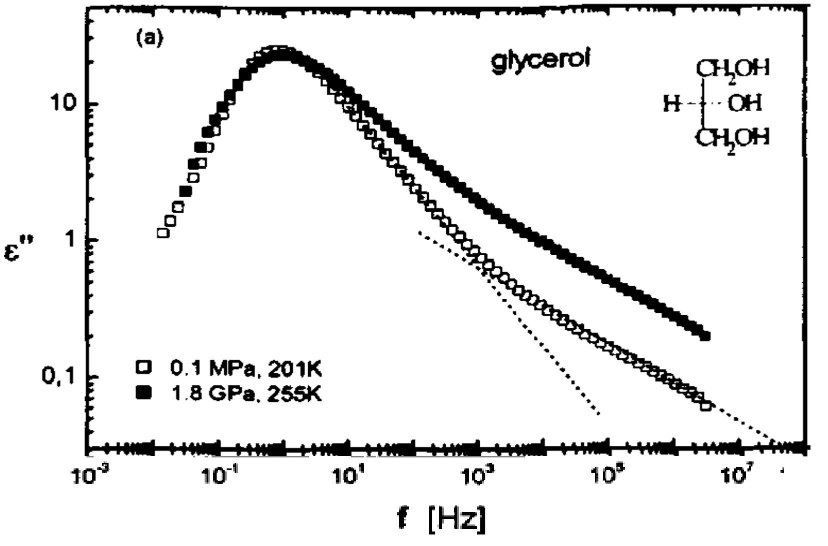
Translating $\chi_{2,1}^{(1)}$ as a δTg shift

Hensel-Bielowka et al. , PRE (2004)



Pressure experiments:

$\delta T_g(\Pi)$ is drawn from :

$$P(\omega;\Pi;T) \equiv P(\omega;0;T-\delta T_g(\Pi))$$

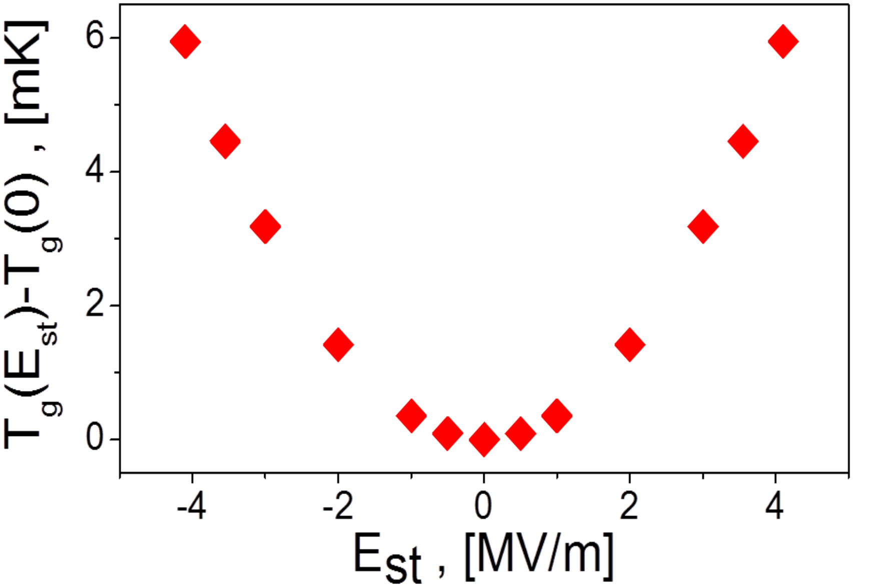
Same method for E_{st}:

$$P(\omega;E_{st};T) \equiv P(\omega;0;T-\delta T_g(E_{st}))$$

$\delta T_g(E_{st}) = 3\kappa E_{st}^2$

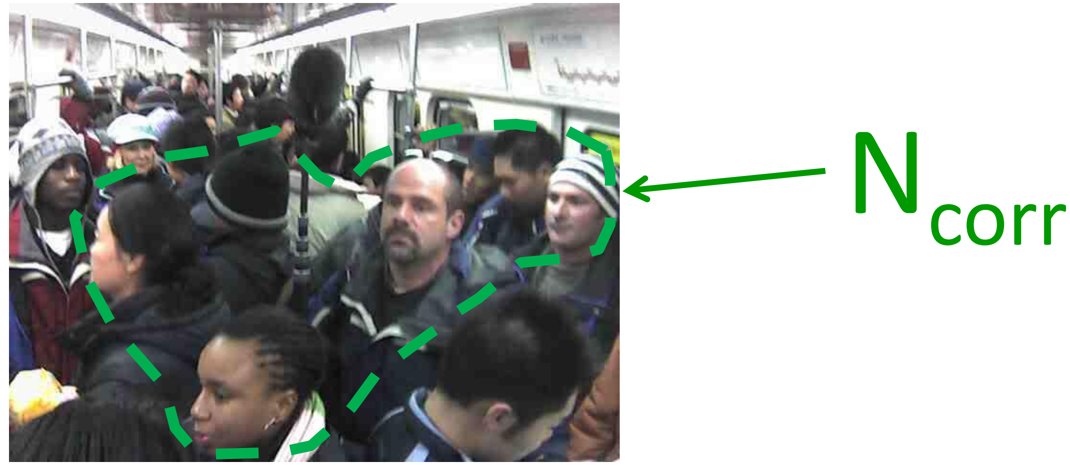
$$\chi_{2;1}^{(1)}(T,\omega) = -\kappa \left(\frac{\partial \chi_{Lin}}{\partial T}\right)_{0,T,\frac{\omega}{\lambda}} \text{ with } \lambda = 1$$

Slight trivial distortion of $\chi_{2,1}^{(1)} \Rightarrow \lambda \neq 1$



$\delta T_g = 3\kappa E_{st}^2 \Leftrightarrow$ E_{st} is a new control parameter in glycerol

A picture: D.H. ≈ overcrowded subway



Increasing Pressure …

Increasing E_{st} …

Density ↑… ⇒ Σ ↓ and τ_α ↑

E_{st} ↑… ⇒ Σ ↓ and τ_α ↑

Summary and Perspectives.

- Our very sensitive setup has successfully measured $\chi_{2;1}^{(1)}(\omega,T)$
- The interpretation issue is now clarified since :
  - the Box Model cannot account for the order of magnitude of $\chi_{2;1}^{(1)}$
  - Global consistency with $\chi_n^{(k)} \sim N_{corr}$:

    $\rightarrow$ ω and T dependences,

    $\rightarrow$ fits with the toy model

- Perspectives = systematic studies of N_{corr} ⇔ the scale on which the systems is **solid**, **during τ_α** :

  $\rightarrow$ study $\chi_3(\omega_1;\omega_2;\omega_3)$ in other directions than $(0,0,\omega)$ or $(\pm\omega,\omega,\omega)$

  $\rightarrow$ study $\chi_{2;1}^{(1)}$at high temperatures (no heating)

  $\rightarrow$ Study $\chi_{2;1}^{(1)}$ at higher fields or in other liquids

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