Dielectric and Shear-Mechanical Dynamic Heterogeneities in Supercooled Liquids

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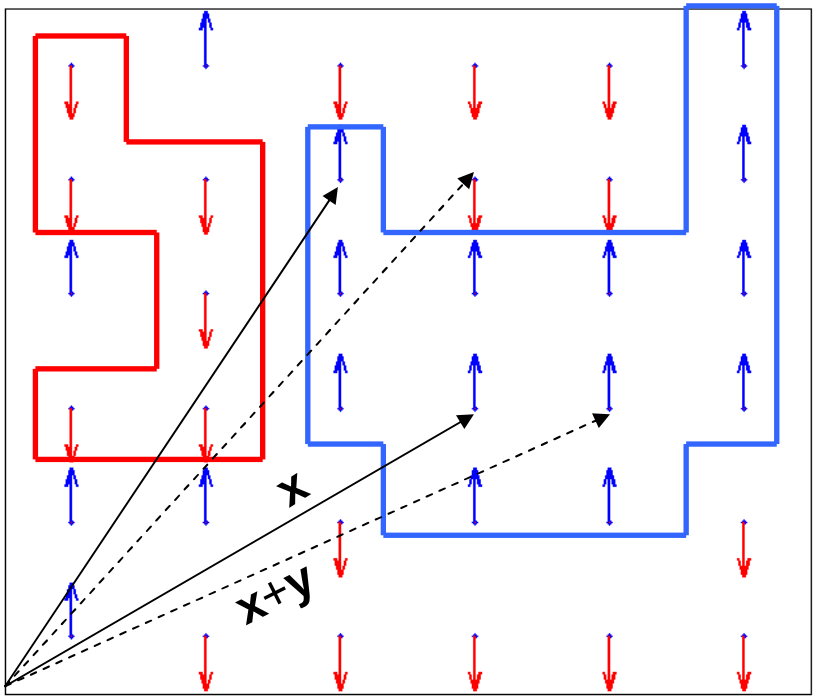
Outline

- Heterogeneities and four-point correlations
- Dielectric and shear-mechanical dynamic heterogeneity
- The case of a mono-alcohol with an additional dielectric relaxation
- Conclusions

The study of heterogeneities is inspired by *spin-glasses*[1]

- The spin-spin correlation is zero when averaged over space: $[\langle s_x s_{x+y} \rangle]_x = 0$
- Introduction of the E.A. parameter: $[\langle s_x s_{x+y} \rangle^2]_x \neq 0$
- Dynamic generalization of the E.A. param. to study the dynamics above Tc:

$$[\langle s_x(0) s_{x+y}(0) s_x(t) s_{x+y}(t) \rangle]_x \underset{t\to\infty}{\to} [\langle s_x s_{x+y} \rangle^2]_x$$



[1] M. Mezard, G. Parisi and M. Virasoro, *Spin-Glass Theory and Beyond*, World Scientific, Singapore

Dynamic heterogeneity and its lower bound from the FDT[2]

- Generalization for any variable of a supercooled liquid:

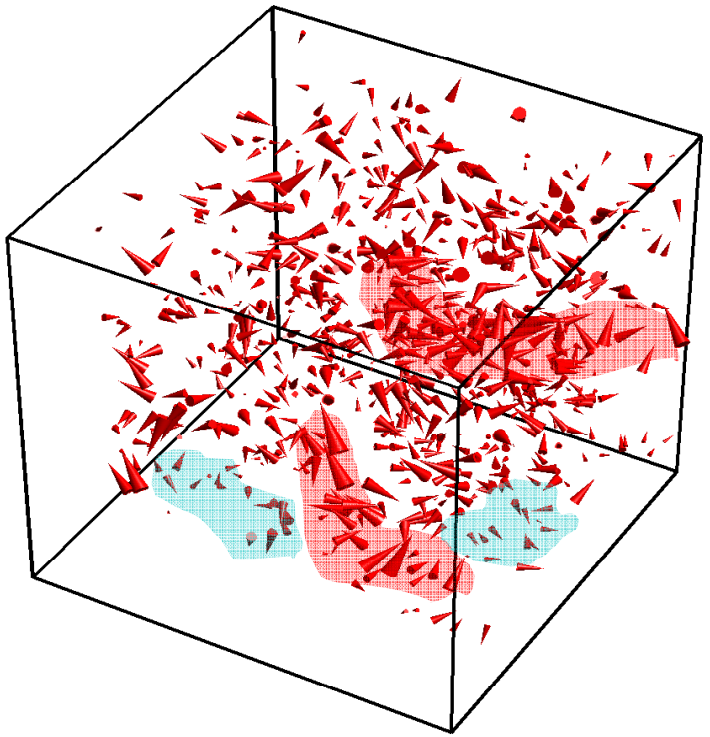
$$\frac{1}{N}\chi_4(t) = [[\langle \mathcal{O}_x(0)\mathcal{O}_x(t)\mathcal{O}_{x+y}(0)\mathcal{O}_{x+y}(t)\rangle]_x]_y - [[\langle \mathcal{O}_x(0)\mathcal{O}_x(t)\rangle]_x]^2$$

- Three point correlation and the Schwartz inequality:

$$\frac{1}{N}\chi_T(t) = [[\langle h_x(0)\mathcal{O}_{x+y}(0)\mathcal{O}_{x+y}(t)\rangle]_x]_y$$

$$[\frac{1}{N}\chi_T(t)]^2 \le \frac{1}{N}\chi_4(t)\times[[\langle h_x(0)h_y(0)\rangle]_x]_y$$

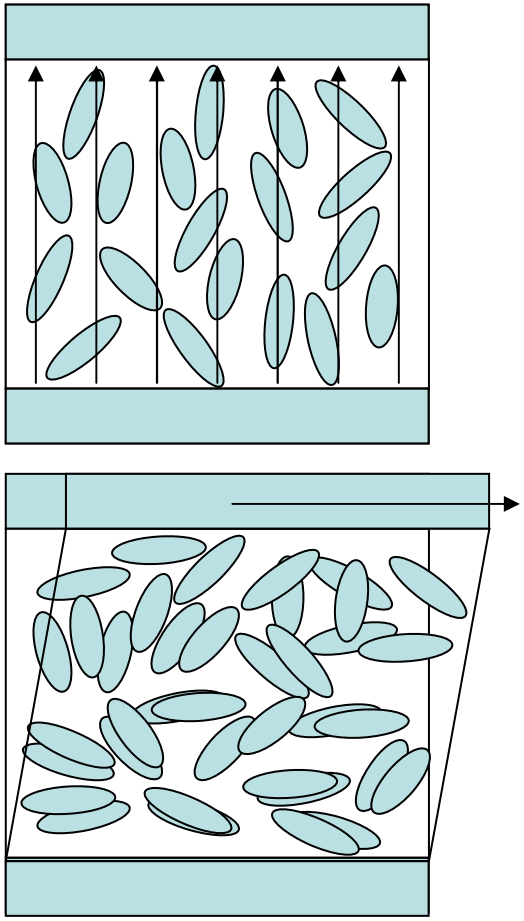
- FDT $\chi_4(t) \simeq \frac{T^2\chi_T{}^2(t)}{c_P} = \frac{1}{c_P}\left(\frac{\partial C(t,T)}{\partial \ln T}\right)^2$



[2] L. Berthier, G. Biroli, J.-P. Bouchaud, et al. *Science* **310**, 1797 (2005)

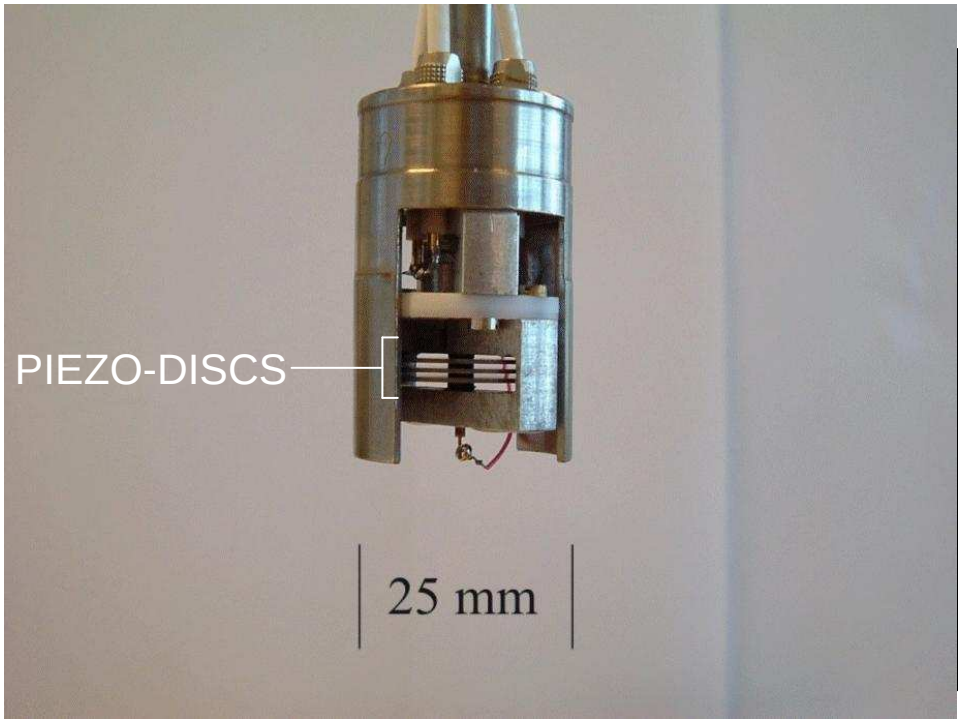
Dielectric and shear-mechanical linear response

- The dielectric response is related to the dynamics of molecular dipoles
- The shear-modulus represents the resistance that the system opposes to a volume-preserving deformation



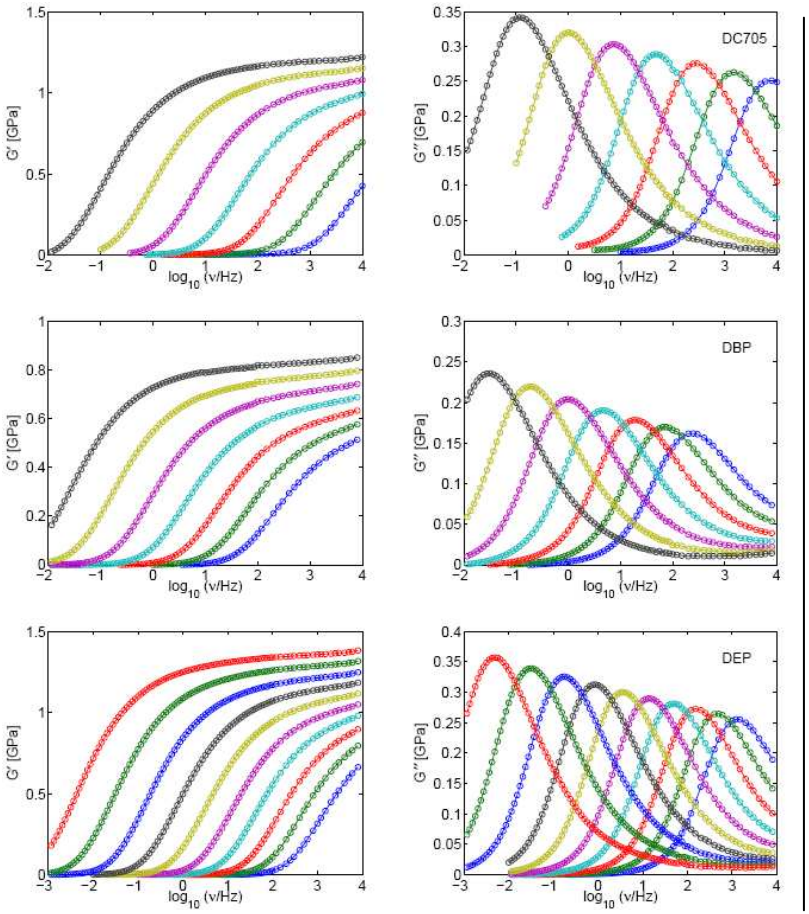
Broad-band mechanical spectroscopy: the PSG technique[3]

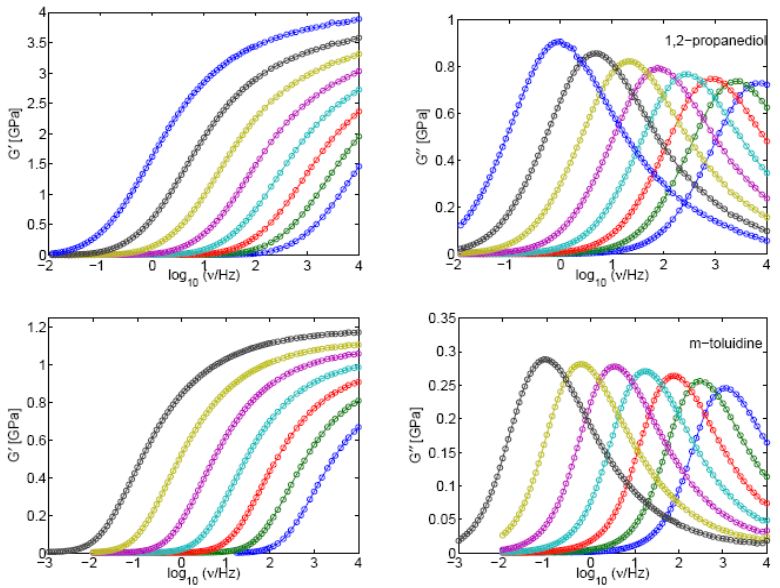
- The Piezoelectric Shear Gauge is composed by tree piezoelectric discs
- These discs expand-contract under the action of the applied electric filed
- The discs capacitance is determined by the shear-modulus of the liquid adhering to them.

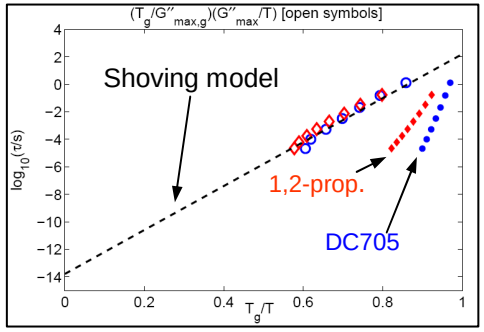


[3] T. Christensen and N. B. Olsen, *Rev. Sci. Instrum.* **66**, 5019 (1995).

Broad-band mechanical spectroscopy: many informations on super-cooled liquids[4]







Shear-data available on line at *http://glass.ruc.dk/data* !

[4] C. Maggi, B. Jakobsen, T. Christensen et al. ArXiv 0806.1400v2

Extraction of the dynamic heterogeneity[5]

- The response function needs to be normalized

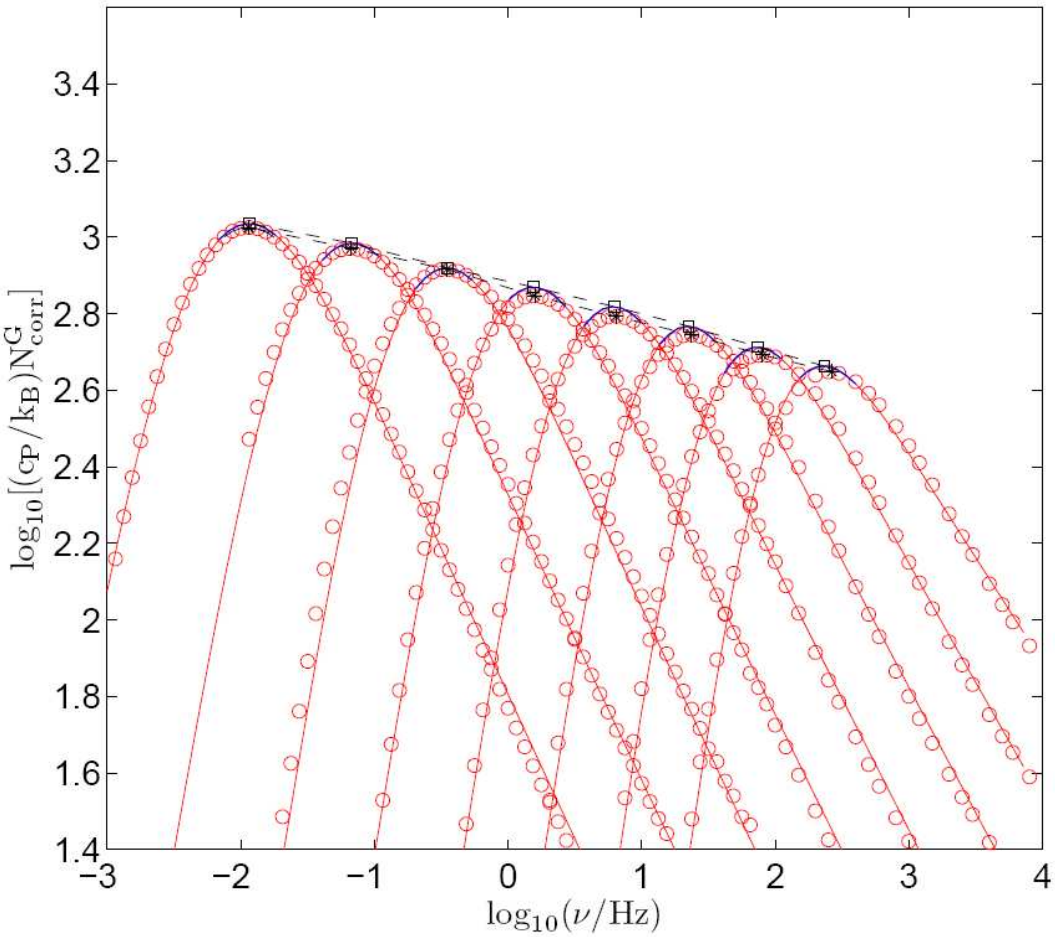
$$\chi_4(\omega) = \frac{1}{c_P}\left(\frac{\partial \tilde{\chi}(\omega,T)}{\partial \ln T}\right)^2$$

- The parameters are obtained fitting with the HN function

$$\chi(\omega) = \chi_\infty + \Delta\chi/[1+(i\omega\tau)^\alpha]^\beta$$

- The *characteristic* dynamic heterogeneity is found

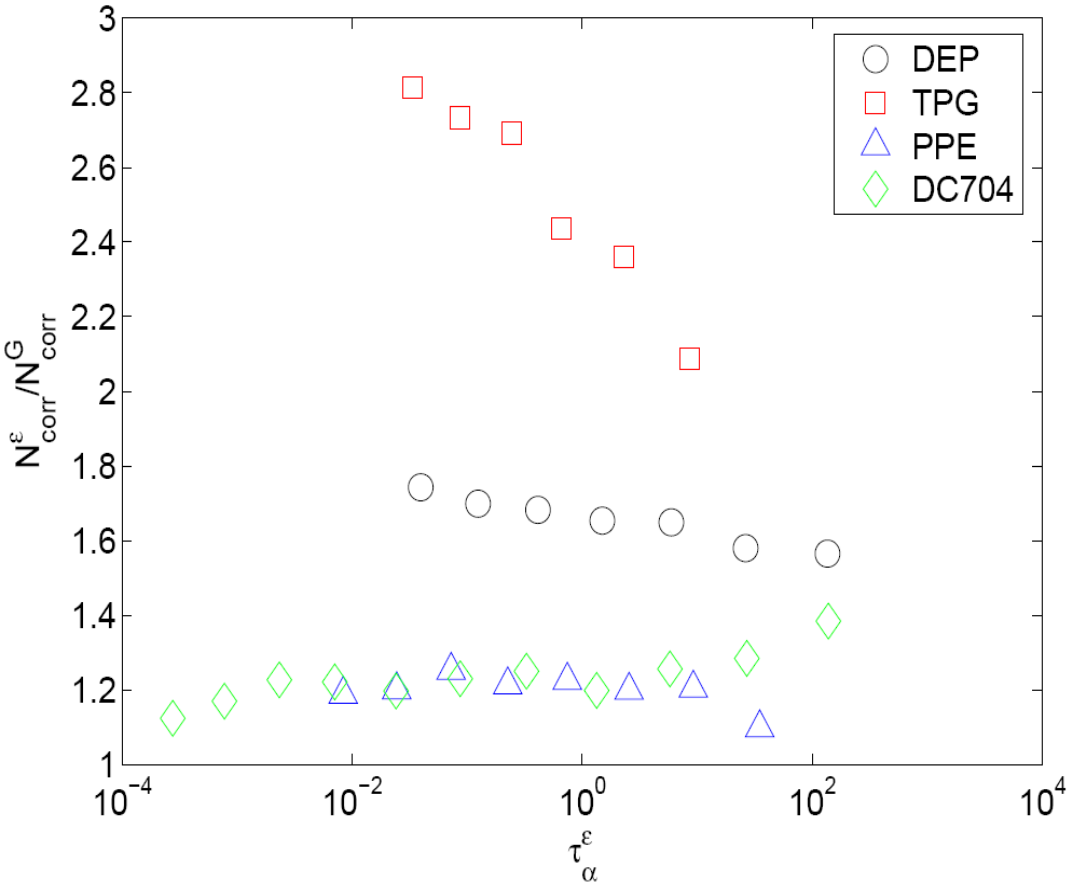
$$N_{corr} \simeq \max_{\omega}\left\{\frac{1}{c_P}\left(\frac{\partial \tilde{\chi}(\omega,T)}{\partial \ln T}\right)^2\right\}$$



[5] C. Dalle-Ferrier, C. Thibierge, C. Alba-Simioneso, *PRE.* **76**, 041510 (2007).

Comparison of the heterogeneities[6]

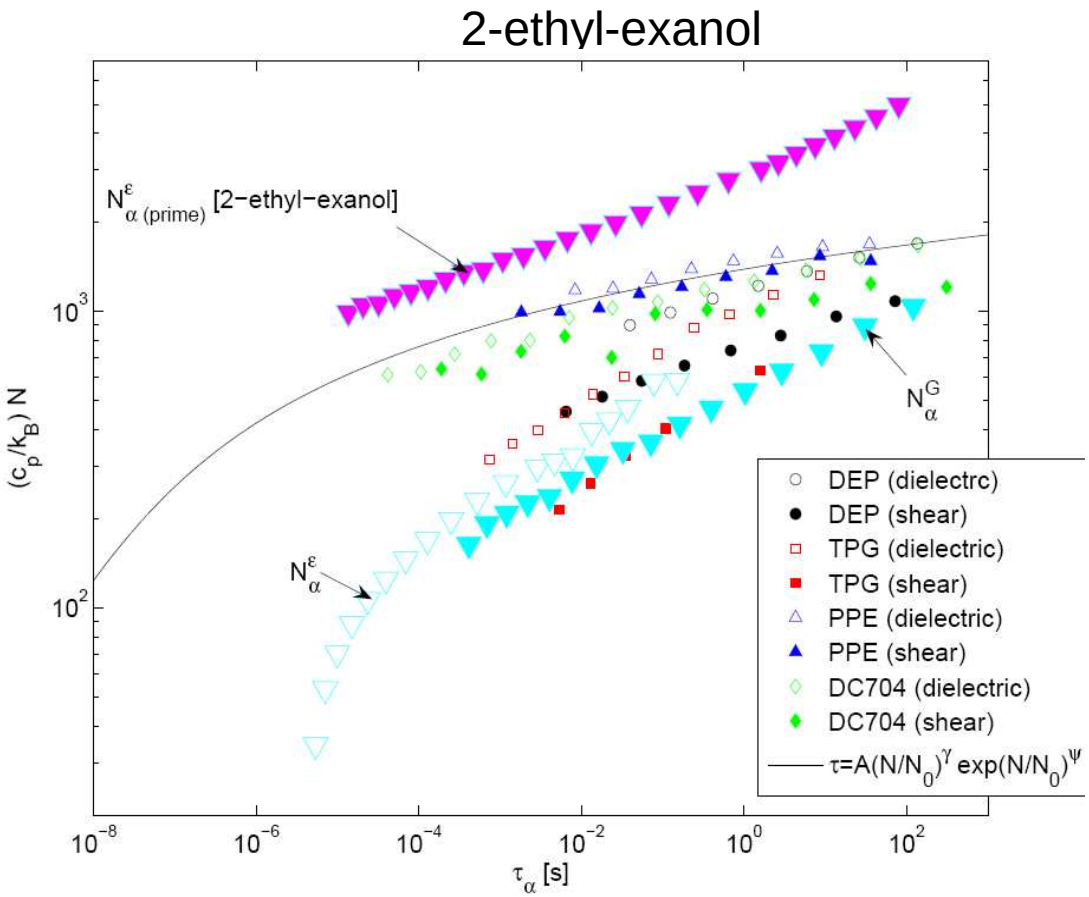
- The heterogeneity increases as temperature decreases
- The heterogeneity increases following the relaxation time
- The dielectric heterogeneity it is *always greater* than the shear-mechanical one



[6] B. Jakobsen, K. Niss and N. B. Olsen *J. Chem. Phys.* **123**, 234511 (2005).

The case of a mono-alcohol with an additional relaxation process[7]

- Some mono-alcohols show an additional (very intense) Debye-like dielectric relaxation process
- This process has not been detected in calorimetric measurements and density fluctuations
- We do not find this additional process in the shear-mechanical dynamics
- The behavior and the value of the heterogeneity of the different processes help us in classification



[7] B. Jakobsen, C. Maggi. et al. arXiv:0805.4519v2.

Conclusions

- **Our analysis shows that:**

1) The dynamic correlation volume of the dielectric dynamics is *systematically larger* than the correlation volume of the shear-mechanical dynamics
2) The study of the heterogeneity clearly distinguishes between multiple processes as in the case of mono-alcohols with additional dielectric processes (alpha prime).

Acknowledgements:

Glass and Time

C. Dalle-Ferrier

C. Alba-Simionesco

Thank you for your attention!