

SUPPLEMENTARY INFORMATION

Multimodal character of shear viscosity response in hydrogen bonded liquids

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Time Temperature Superposition

Figures 2, 3 and 4 of the manuscript show several master curves obtained after applying time-temperature superposition. As we previously commented detailed characterization of Debye-like and α relaxation characteristic times by BDS evidences that there exists some degree of "themorheological complexity" on the T-dependence of these two processes. Under experimental uncertainty and for the purposes of this work, however, this effect can be regarded as negligible or too small to significantly alter the qualitative features underlined in the master curves. On the one hand, measurements were carried out at small temperature intervals and over 2.5-3 decades to assure the superposition of a significant part of the curves, so that roughly n temperatures are used to construct a master curve extending n decades in frequency. On the other hand, the magnitude of the "themorheological complexity" itself is quantitatively small (around 0.2 decade difference over 4.5 decade of characteristic times¹) and time-temperature superposition is applied on a quite narrow temperature range. As an example, figure 5a) shows represented by crosses the equivalent dielectric characteristic times obtained after applying to the experimental dielectric times $\tau_D(T_{ref})$ and $\tau_\alpha(T_{ref})$ the shift factors used to construct the master plots shown in figures 2, 3 and 4. As it can be seen, actually measured (τ_D , τ_α) and calculated or shifted values (crosses) lay within the uncertainty

between the different phenomenological approaches available to parametrize characteristic relaxation times by mechanical means. Moreover, such small difference between the shift factor and the actual T-dependence of the processes could not qualitatively change the presence of a maximum or an intermediate power law regime, as these features extend in frequency more than the mentioned deviation.

Dielectric and calorimetric measurements and analysis

In previous works we explored new routes for measuring and analyzing the Debye-like and α -dielectric relaxation of MAs. Details about measurement conditions, data analysis, fitting models and comparison with calorimetry results can be found in references^{1,2}. Figure 1 in this supplement shows comparison of the imaginary part of shear viscosity and the derivative of the real part of permittivity. The nice correspondence between the Debye-like relaxation and the crossover to pure viscous flow on the one hand, and between α -relaxation and the high frequency peak of $\eta''(\omega)$ on the other are evident. The comparison in figure of the present supplement supports the statements in the manuscript and the results shown in figure 5 of the manuscript.

¹ S. Arrese-Igor, A. Alegría, and J. Colmenero. Dielectric relaxation of 2ethyl-1hexanol around the glass transition by thermally stimulated depolarization currents. *J. Chem. Phys.*, **2015**, 142, 214504.

² S. Arrese-Igor, A. Alegría, and J. Colmenero. On the non-exponentiality of the dielectric Debye-like relaxation of monoalcohols *J. Chem. Phys.*, **2017**, 146, 114502.

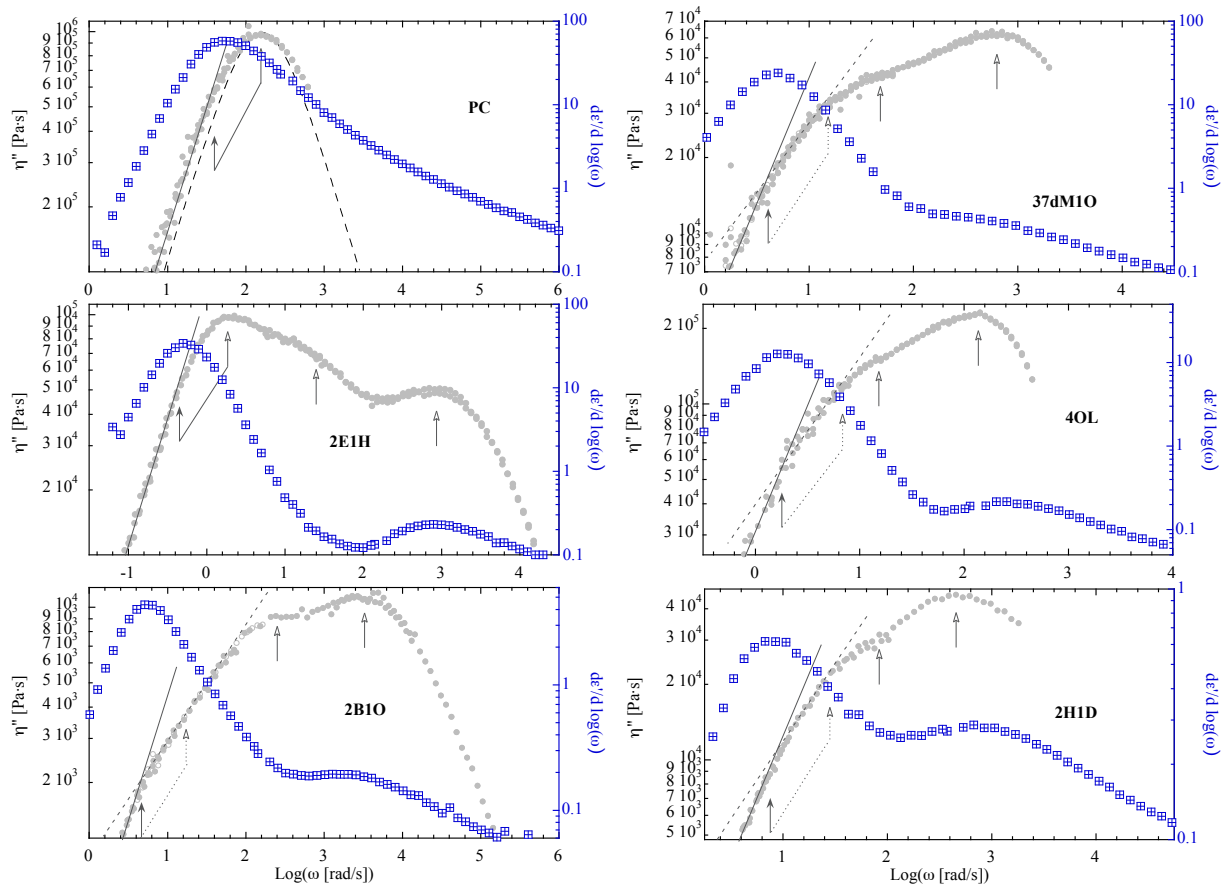


FIG. 1: Comparison of the imaginary part of the shear viscosity (grey circles) and the derivative of the real part of the permittivity (blue squares). Shear data are exactly the same as those in figure 4 of the manuscript. Dielectric permittivity data was derived with respect to $\log\omega$ to better resolve overlapped Debye-like and α relaxations, see references^{1,2} for more details.