Unique Dynamic Correlation Length in Supercooled Liquids

Claudio Maggi,[a] Bo Jakobsen,[b] and Jeppe C. Dyre[c]
DNRF Centre "Glass and Time", IMFUFA, Department of Sciences, Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark
(Dated: March 1, 2010)

We present a direct comparison of the number of dynamically correlated molecules in the shear-mechanical and dielectric relaxations of the following seven supercooled organic liquids: triphenylethylene, tetramethyl-tetraphenyl-trisiloxane, polyphenyl ether, perhydrosqualene, polybutadiene, decahydroisoquinoline, and tripropylene glycol. For each liquid we observe that the numbers of dynamically correlated molecules in the shear and in the dielectric relaxation are proportional. We show that this proportionality can be explained by the constancy of the decoupling index of the shear and dielectric relaxation times in conjunction with time-temperature superposition. Moreover the value of this proportionality constant is related to the difference in stretching of the shear and dielectric response functions. The most significant deviations from unity of this constant are found in a liquid with strong hydrogen bonds and in a polymer.

INTRODUCTION

The dynamical processes taking place in a supercooled liquid are complex. This is due to the fact that the motion of the molecules of a liquid close to the glass transition is intrinsically collective. When the liquid enters this ultra-viscous regime [1], the rearrangement of a particle involves the motion of many of its neighbors. The idea that the dynamics becomes more and more cooperative has led to searches for a growing length scale as the dynamics slow-down upon cooling. So far no standard static correlation has revealed a detectable growing correlation length arising in the supercooled phase. On the other hand, *dynamic correlations* [2] may account for the evolution of the correlation length scales involved in the glass transition. Recently Berthier, Biroli and co-workers invented a simple and powerful method to estimate the four-point susceptibility, χ_4 [3–5]. The central idea is to estimate the four-point function via a more accessible three-point function. The function χ_4, which cannot be easily measured directly, can be approximated from the temperature evolution of any measured dynamic variable.

We can measure the frequency-dependent dielectric susceptibility, $\epsilon(\omega)$, and shear modulus, $G(\omega)$ using the same cryostat and covering overlapping temperature-frequency ranges [6–8]. The *piezo-shear-gauge* (PSG) technique [8] allows us to measure the dynamic shear modulus of a supercooled liquid close to its glass transition (where G typically assumes values between 0.1 MPa and 10 GPa) in a wide frequency range ($10^{-3} - 10^4$ Hz). In this work we extract and compare the number of dynamically correlated molecules in the structural (alpha) relaxation from two different dynamic variables: the dielectric susceptibility and the shear modulus.

[a]Electronic address: cmaggi@ruc.dk
[b]Electronic address: boj@ruc.dk
[c]Electronic address: dyre@ruc.dk

	Tg [K]	m	$I(T)$	(clear) β-relaxation
TPE	249	73	3.4 – 3.5	no
DC704	211	83	3.7 – 3.9	no
PPE	245	80	3.9-3.9	no
Squalane	167	64	0.4 – 2.9	yes
PB20	176	79	3.7	yes
DHIQ	179	154	3.8 – 8.3	yes
TPG	190	65	1.4 – 3.0	yes

TABLE I: Properties of the seven liquids studied (from Refs. [9–12, 18]). T_g is the glass transition temperature, m is the Angell fragility, I is the temperature index (the values of I are reported for the highest and lowest temperature studied). The last column indicates if the liquid has or not a clear secondary β-relaxation. All the data here refer to dielectric measurements.

We analyze below dielectric and shear-dynamic data collected and published by our group [9, 11], available on-line [12]. This study focuses on seven liquids: triphenylethylene ("TPE"), tetramethyl-tetraphenyl-trisiloxane ("DC704"), polyphenyl ether ("PPE"), perhydrosqualene ("squalane"), polybutadiene ("PB20"), decahydroisoquinoline ("DHIQ"), and tripropylene glycol ("TPG"). DC704, TPE, PPE, squalane and DHIQ are molecular van der Waals bonded liquids, TPG has hydrogen bonds, and PB20 is a polymer with molecular weight of 5000 g/mol. All liquids were used as acquired. The PPE used is the Santovac®5 vacuum pump fluid, and DC704 is the Dow Corning®704 diffusion pump fluid. All the other liquids were acquired from Sigma-Aldrich. All the experimental details about these measurements can be found in Refs. [6–9].

Some properties of the liquids [9–12, 18] are reported in Table I. Here the relaxation time τ is defined by the inverse loss peak frequency and the glass transition temperature T_g is defined as the temperature where the loss-peak is located at $2\pi 10^{-3}$ rad/s. The temperature dependence of the relaxation time around T_g is expressed

in terms of the Angell fragility index [13–16]

$$m = \left.\frac{d\log_{10}\tau}{d(T_g/T)}\right|_{T=T_g} \quad (1)$$

The temperature dependence of activation energy is quantified via the temperature index [17, 18]

$$I(T) = \frac{d\ln\Delta E(T)}{d\ln T} \quad (2)$$

where $\Delta E(T)$ is the activation energy defined by $\tau = \tau_0\exp(\Delta E(T)/k_BT)$. Table I reports the variation of $I(T)$ in the temperature interval studied [18]. Table I also reports presence of a clear Johari-Goldstain β-relaxation [19] in the dielectric spectrum of the liquid.

COMPARISON OF SHEAR-MECHANICAL AND DIELECTRIC RESPONSES

The studies carried out by our group [9, 11, 20, 21] focused on the temperature-dependence of the the shear-mechanical and dielectric α relaxation times (indicated with τ_G and τ_ϵ, respectively). Furthermore, comparison of the shape of these two relaxation functions was presented. The main conclusions of these studies may be summarized as follows:

(*i*) The relaxation time of the shear modulus is generally different from that of the dielectric susceptibility at the same temperature T. The shear-mechanical relaxation is always slightly faster than the dielectric, $\tau_\epsilon(T) \geq \tau_G(T)$. Nevertheless, the shear and dielectric characteristic alpha relaxation times evolve in a rather similar way in the liquids studied when T is changed. This was discussed in detail in [9] where the *decoupling index* $\tau_\epsilon(T)/\tau_G(T)$ was reported and its insignificant temperature dependence was established ($\tau_\epsilon(T)/\tau_G(T) \simeq$ const). This picture is also confirmed by other studies found in the literature [22–26].

(*ii*) The shear response function and the dielectric response function generally have different shapes. In liquids that do not show any detectable Johari-Goldstain β-relaxation [19] the shape of each frequency-dependent response is found to be almost temperature independent. This feature is referred as *time-temperature superposition* (TTS), and it is found to hold to a very good degree in the temperature-frequency range explored [9, 20] both for the shear and the dielectric relaxation [31].

(*iii*) For those liquids that have a clear beta-relaxation the alpha relaxations in the shear and dielectric spectrum seem to approach a temperature independent shape as the temperature is lowered. This has been presented in detail in Refs. [9, 20, 21, 31] suggesting that for the alpha process alone TTS applies, while in the full spectrum TTS is lost because of the presence of the beta process.

In the following we show that (*i*) and (*ii*) imply that the shear and the dielectric numbers of dynamically correlated molecules (for the liquids without clear beta relaxation) are proportional in the temperature range studied. Moreover, the same conclusion applies if we *assume* TTS (as suggested by (*iii*) and also done in [29]) to hold for the alpha process in those liquids that have a secondary relaxation. To understand this link it we first briefly recall how to approximate the four-point susceptibility.

ESTIMATION OF THE NUMBER OF DYNAMICALLY CORRELATED MOLECULES

The four-point correlator can be interpreted as the variance of the dynamics around its average value. One can estimate this function from the following equation (Refs. [3–5, 27–29])

$$\chi_4(\omega,T) \simeq \frac{k_B}{c_P}\left(\frac{\partial\tilde{\chi}'(\omega,T)}{\partial\ln T}\right)^2. \quad (3)$$

In this equation $\tilde{\chi}'$ is the normalized real part of the response function and c_P is the configurational heat capacity per molecule at constant pressure. The right-hand side of Eq. (3) is an approximation of χ_4, it actually represents a lower bound for this function. Nevertheless, this method is found to give values of the four-point susceptibility in good agreement with the actual values of χ_4 when these can be evaluated directly (for example in computer simulations) [4, 5]. The characteristic value of the four-point function (i.e., the typical number of correlated molecules in the relaxation, $N_{\rm corr}$) is associated with the maximum of χ_4,

$$N_{\rm corr}(T) = \max_\omega[\chi_4(\omega,T)]. \quad (4)$$

The maximum of this function is consistently found to close to a frequency close to the loss-peak frequency of the alpha dynamics.

The normalized response function $\tilde{\chi}'$ appearing in Eq. (3) is computed by subtracting a baseline parameter to the measured response (for example the dielectric susceptibility), subsequently dividing by the amplitude of the function [27]

$$\tilde{\chi}(\omega,T) = \frac{\chi(\omega,T)-\chi_\infty}{\Delta\chi}. \quad (5)$$

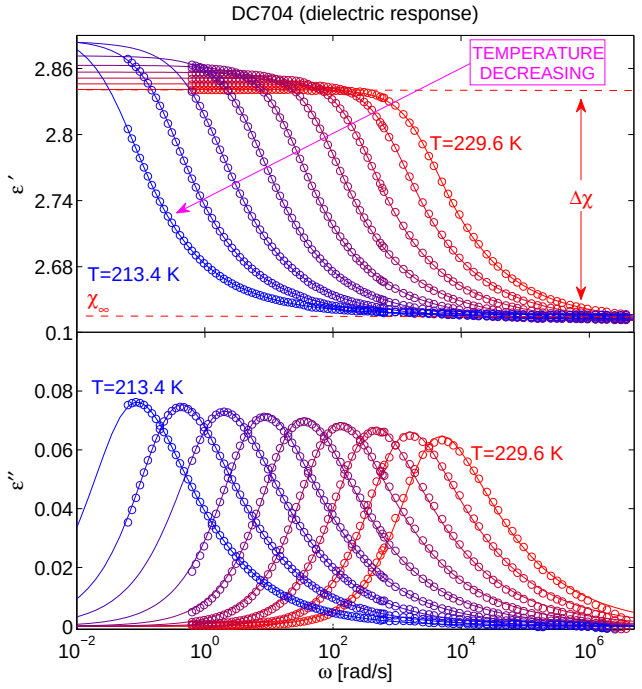

FIG. 1: Real and imaginary part (top and bottom respectively) of the dielectric response of DC704 measured at T =229.6, 227.6 225.5, 223.5, 221.5, 219.5, 217.5, 215.4, 213.4 K (open circles). The full lines are fits with the HN function Eq. (6). The amplitude $\Delta\chi$ and the baseline χ_∞ of the fitting function are shown graphically for the curve at T =229.6 K.

In this work we fit all response functions with the Havriliak-Negami (HN) function [30]

$$\chi(\omega,T) = \chi_\infty + \frac{\Delta\chi}{[1+(i\tau\omega)^\alpha]^\beta}. \tag{6}$$

The Appendix details how we introduce the assumption of TTS in the analysis of the spectra of the liquids presenting a beta process (this is done by fixing the α and β parameters of the function (6)). An example of the fitting is reported in Fig. 1 for the dielectric responses of DC704. The normalized functions are shown in the upper parts of Fig. 2.A (dielectric) and in Fig. 2.B (shear). The function χ_4 obtained from Eq. 3 is shown in Fig. 2 for the dielectric responses and the shear-mechanical response of DC704. Note that the maximum of these functions at the same temperature is located at different frequencies in the shear and the dielectric case (as is also the case for the loss peaks of the responses). Moreover, the shape of χ_4 is slightly different in the shear and in the dielectric case as discussed in detail below.

Once we have determined the maximum of χ_4, the quantity $N_{\rm corr}$ can be obtained via Eq. (4). In this way two independent estimates of the number of dynamically correlated molecules can be obtained: the number of correlated molecules in the shear relaxation N_G and in the dielectric relaxation N_ϵ. Note that for comparing these two numbers knowledge of c_P is unnecessary, being only a constant multiplicative factor in Eq. (4).

From Fig. 3 we can appreciate the growth of the shear and diellectric $N_{\rm corr}$ upon cooling. The minimum increase of N_ϵ is of a factor ∼1.6 in TPE and its maximum increase is of a factor ∼5.7 found in TPG. The relaxation times of the responses studied grow at least four orders of magnitude in all liquids.

Let us now see the form assumed by the equations (3) and (4) if TTS applies. To do this let us consider the very general expression for a (normalized) response function obeying TTS:

$$\tilde{\chi}(\omega,T) = \phi(\omega\tau(T)). \tag{7}$$

This is the case of Eq. 6 if the parameters α and β are kept constant. Differentiating the real part of Eq. (7) with respect to $\ln T$ (as in Eq. (3)) we obtain

$$\frac{\partial\phi'(\omega\tau(T))}{\partial\ln T} = \omega\frac{d\phi'(x)}{dx}\frac{\partial\tau(T)}{\partial\ln T}. \tag{8}$$

where the prime indicates the real part and we have introduced $x \equiv \omega\tau(T)$. The maximum of the function (8) can be estimated setting $\omega = \tau^{-1}$ (a minor correction term is present in the case of very large stretching [29]):

$$N_{\rm corr} \propto \left[\max_\omega\left(\frac{\partial\phi'(\omega\tau(T))}{\ln T}\right)\right]^2 = f^2(1)\left(\frac{\partial\ln\tau(T)}{\partial\ln T}\right)^2 \tag{9}$$

where $f(x) = (d\phi'(x)/dx)$. From Eq. (9) it is clear that the growth of N is determined uniquely by the growth of the relaxation time upon cooling if TTS strictly holds. If (as stated in (i)) the decoupling index has a negligible temperature-dependence ($\tau_\epsilon(T)/\tau_G(T) \simeq$ const) then

$$\left(\frac{\partial\ln\tau_\epsilon(T)}{\partial\ln T}\right)^2 \simeq \left(\frac{\partial\ln\tau_G(T)}{\partial\ln T}\right)^2. \tag{10}$$

This means that the decoupling index of the characteristic number of correlated molecules in the shear and dielectric relaxation is also constant as T is lowered:

$$\frac{N_\epsilon(T)}{N_G(T)} \simeq \text{const} \tag{11}$$

where the constant is determined by the stretching of the shear and dielectric relaxations. In other words, the growth of N_G and N_ϵ is identical upon cooling, while their difference in absolute values is set by the different (temperature independent) shape of the two response functions.

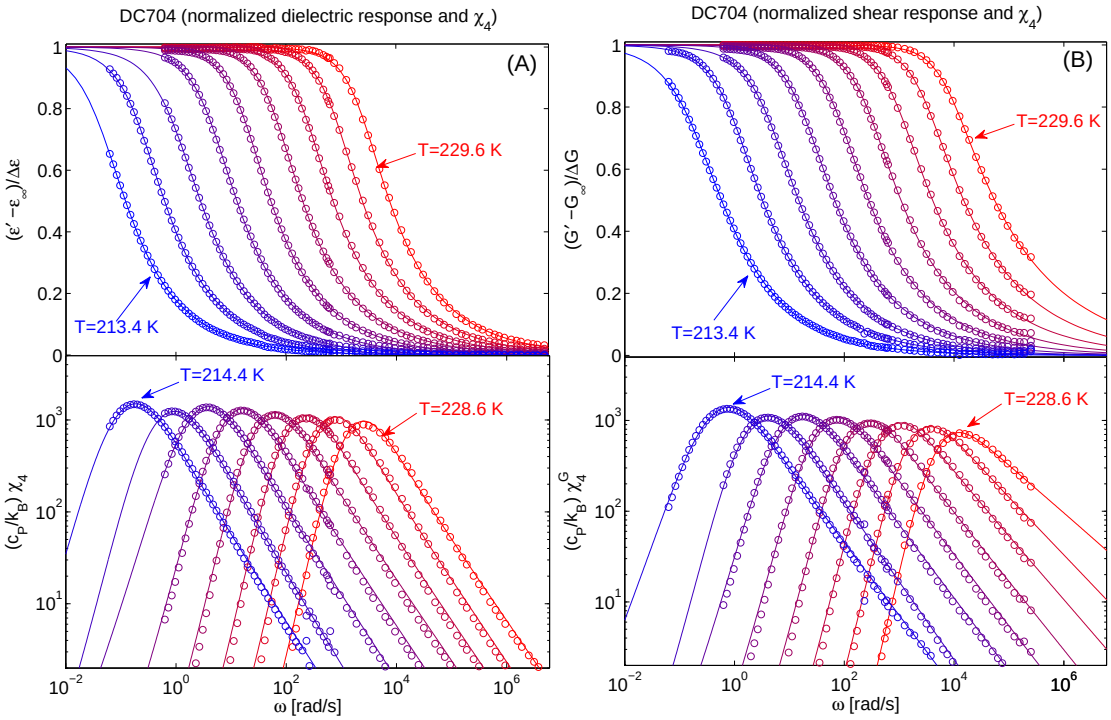

FIG. 2: (**A-Top**) Normalized real part of the dielectric response for DC704 at T = 229.6, 227.6 225.5, 223.5, 221.5, 219.5, 217.5, 215.4 and 213.4 K. The full lines are the corresponding (normalized) fits to the HN functions. (**A-Bottom**) $(c_P/k_B)\chi_4 = (\partial\tilde{\chi}'(\omega,T)/\partial \ln T)^2$ for the dielectric (left) and shear (right) relaxation at T= 228.6, 226.6, 224.5, 222.5, 220.5, 218.5, 216.4 and 214.4 K. The full line are the corresponding $(c_P/k_B)\chi_4$ computed form the fitting HN functions. (**B**) Same as A for the shear-mechanical response

COMPARISON OF THE SHEAR AND DIELECTRIC NUMBERS OF DYNAMICALLY CORRELATED MOLECULES

The results expected from the constant decoupling index and TTS can be readly checked. Plotting $N_\epsilon(T)$ versus $N_G(T)$ as in Fig. 4 we check that these quantities approximatively differ only by a multiplicative factor in the temperature range studied for all liquids considered in this work. As seen in the inset of Fig. 4 all the data collapse onto the line $N_\epsilon \propto N_G$ if we multiply N_ϵ by the value $\langle N_G/N_\epsilon\rangle$ where the average is taken over the temperature range studied.

We test Eq. (11) directly in Fig. 5. As seen from this figure the decoupling index $N_\epsilon(T)/N_G(T)$ of the number of correlated molecules in the dielectric and shear relaxation is very weakly temperature dependent and it does not show any clear trend of a systematic increase or decrease. Note that, while $N_\epsilon(T)/N_G(T)$ stays constant, N_ϵ and N_G both grow significantly upon cooling for all liquids (see Fig. 3).

In Fig. 6 we test further the constancy of the decoupling index. Fig. 6 demonstrate the validity of Eq. (10). The equality $(\partial \ln \tau_\epsilon/\partial \ln T)^2 = (\partial \ln \tau_G/\partial \ln T)^2$ seems to hold to a good approximation as expected from $\tau_\epsilon(T)/\tau_G(T) \simeq$ const.

We stress once again that the multiplicative factor between the shear and dielctric $N_{\rm corr}$ (i.e., the constant appearing in Eq. (11)) is determined by the shape of the shear and dielectric response. Indeed, the function $f(1)$ defined in Eq. (9) depends on the form of the relaxation functions that set $N_\epsilon/N_G \simeq [f_\epsilon(1)/f_G(1)]^2$. When the response is modelled by the HN function (6), the value of $f(1)$ depends only on the parameters α and β:

$$f(1) = -\alpha\beta\,\mathrm{Re}[i^\alpha/(1+i^\alpha)^{1+\beta}]. \qquad (12)$$

From Eq. (12) it is easy to understand that if the dielctric response function has approximatively the same shape as the shear-mechanical one, the constant of Eq. (11) is close to unity. This is the case of DC704 as can be seen from Figs. 5 and 7.A for which Eq. (12) gives consistently $N_\epsilon/N_G \simeq [f_\epsilon(1)/f_G(1)]^2 \simeq 1.35$ using the values α and β obtained from the fitting.

If the dynamic shear modulus is instead much broader than the dielectric response (as shown in Fig. 7.B for TPG), N_ϵ/N_G is significantly larger than unity (as seen

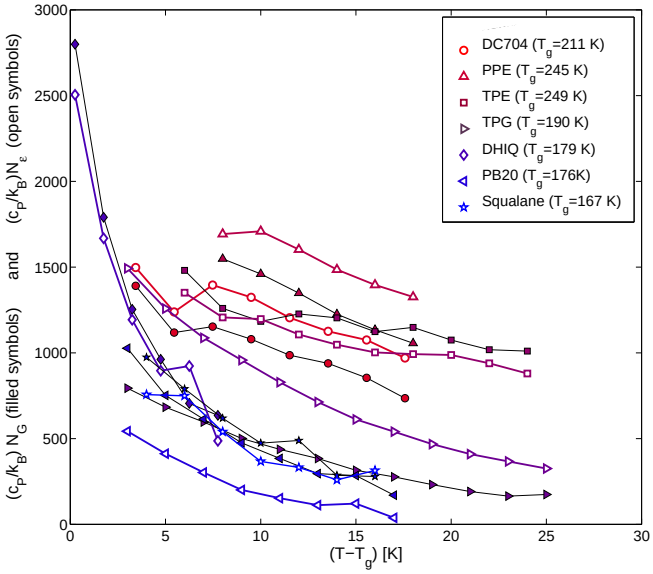

FIG. 3: The quantity $(c_P/k_B)N_{\rm corr}$ for shear (filled symbols) and dielectric (open symbols) as a function of $(T - T_g)$ for the liquids studied (see legend). T_g is the glass transition temperature for the dielectric relaxation from Ref. [9] (see legend and Table I).

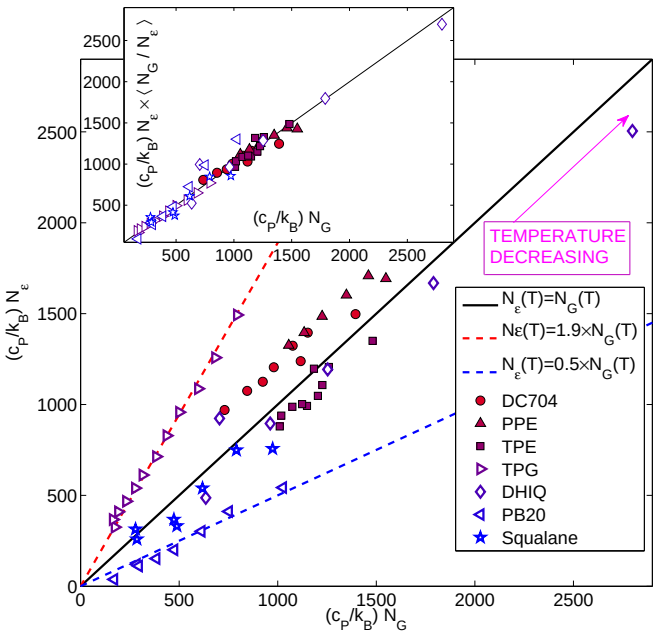

FIG. 4: Characteristic number of correlated molecules in the dielectric relaxation plotted versus the characteristic number of correlated molecules in the shear mechanical relaxation at the same temperatures for the seven glass-forming liquids (see legend). The full line indicates $N_\epsilon = N_G$ while the dashed lines represents $N_\epsilon = \lambda N_G$ (with λ =1.9 and 0.5 respectively for the upper and the lower line). In the inset we show the data collapse on the line $N_\epsilon \propto N_G$ obtained when we multiply N_ϵ by the value $\langle N_G/N_\epsilon \rangle$ where the average is taken over the temperature range studied.

in Fig. 5). Also for this liquid we can check that the value of this ratio is consistent with the equations given above obtaining $N_\epsilon/N_G \simeq 1.97$.

Finally we want to stress that the stretching of the relaxation function does not only significantly affect $N_{\rm corr}$, but also the full shape of the function $\chi_4(\omega)$ as calculated from Eq. (3). This is illustrated in Fig. 8. If the stretching of the shear and dielectric response functions is similar as in DC704 (see Fig. 7.A), N_ϵ/N_G is close to one, but also the shapes of $\chi_4^G(\omega)$ and $\chi_4^\epsilon(\omega)$ are quite similar as seen in Fig. 8.A.

If the two response functions have significantly different stretching, the corrresponding four-point susceptibilities will have quite different shapes. This is the case of TPG whose dielctric response function is more "Debye-like" than the shear-mechanical one (Fig. 7.B). In this case the functions χ_4^G is clearly broader than χ_4^ϵ as seen in Fig. 8.B.

CONCLUSIONS

We have compared the shear-mechanical and dielectric characteristic number of dynamically correlated molecules for seven supercooled liquids close to the glass transition. The number of dynamically correlated molecules in the shear-mechanical relaxation is generally different from that of the dielectric relaxation. Nevertheless, these quantities are approximatively proportional in the explored temperature range. For five of the seven liquids studied the ratio between the shear and dielectric characteristic number of correlated moleculues is close to the unity. The most significant deviations from this unitary ratio are found in a liquid with strong hydrogen bonds and in a polymer. Finally, we showed that the difference in these absolut numbers arises from the different stretching of the dielectric and shear response functions.

Center for viscous liquid dynamics "Glass and Time" is sponsored by The Danish National Research Foundation (DNRF).

[1] Jeppe C. Dyre *Rev. Mod. Phys.* **78**, 953 (2006).
[2] M. D. Ediger *Annu. Rev. Phys. Chem.* **51**, 99 (2000).
[3] L. Berthier, G. Biroli, J.-P. Bouchaud, et al. *Science* **310**, 1797 (2005).
[4] L. Berthier, G. Biroli, J.-P. Bouchaud, et al. *J. Chem. Phys.* **126** 184503 (2007).
[5] L. Berthier, G. Biroli, J.-P. Bouchaud, et al. *J. Chem. Phys.* **126** 184504 (2007).

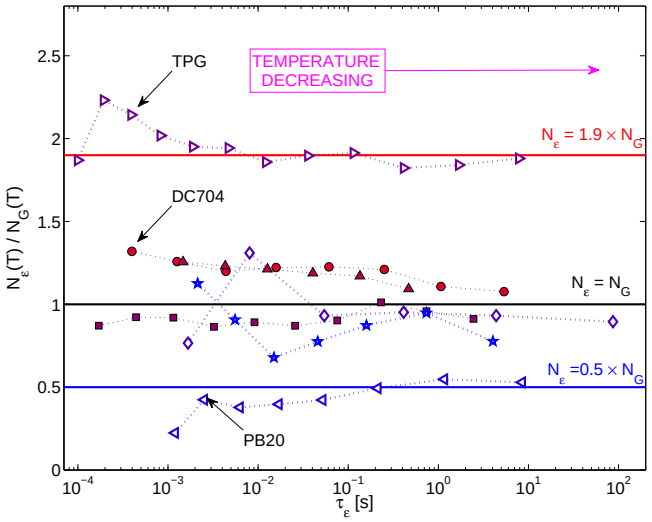

FIG. 5: Ratio between the characteristic number of dynamically correlated molecules in the shear and in the dielectric relaxation at the same temperature as a function of the (dielectric) relaxation time for different liquids (same symbols as in Fig. 4). The full lines represent $N_\epsilon = \lambda N_G$ with $\lambda = 1.9,1,0.5$ respectively from top to bottom.

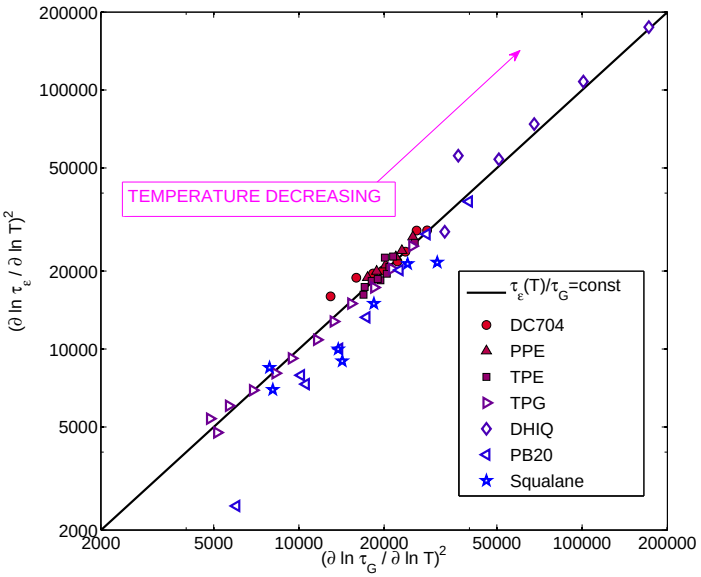

FIG. 6: $(\partial \ln \tau_\epsilon/\partial \ln T)^2$ plotted versus $(\partial \ln \tau_G/\partial \ln T)^2$ for the seven liquids (see legend). The full line represents $(\partial \ln \tau_\epsilon/\partial \ln T)^2 = (\partial \ln \tau_G/\partial \ln T)^2$ (Eq. 10).

[6] B. Igarashi, T. Christensen, E. H. Larsen et al., *Rev. Sci. Instrum.* **79**, 045105 (2008).

[7] B. Igarashi, T. Christensen, E. H. Larsen et al., *Rev. Sci. Instrum.* **79**, 045106 (2008).

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

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

[10] K. Niss and B. Jakobsen, MS thesis, Department of Mathematics and Physics IMFUFA, Roskilde University, 2003.

[11] K. Niss, B. Jakobsen and N. B. Olsen *J. Chem. Phys.* **123**, 234510 (2005).

[12] All the shear-mecahnical an dielectric spectra analyzed in this work together with more recent data [20, 21] are available in the "Glass and Time: Data repository" found online at *http://glass.ruc.dk/data*.

[13] D. J. Plazek and K. L. Ngai, *Macromolecules* **24**, 1222 (1991).

[14] R. Böhmer and C. A. Angell, *Phys. Rev. B* **45**, 10091 (1992).

[15] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.***99**, 4201 (1993).

[16] R. Richert and C.A. Angell. *J. Chem. Phys.* **108** (21) 9016, (1998).

[17] Dyre, J. C. and Olsen N. B. *Phys. Rev. B* **69**, 042501 (2004).

[18] Tina Hecksher, Albena I. Nielsen, Niels Boye Olsen, Jeppe C. Dyre *Nature Phys.* **4**, 737 (2008)

[19] G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970).

[20] C. Maggi, B. Jakobsen, T. Christensen et al. *J. Phys. Chem. B* **112** 16320 (2008).

[21] B. Jakobsen, C. Maggi, T. Christensen et al. *J. Chem. Phys.* **129** 184502 (2008).

[22] N. Menon, S. R. Nagel, and D. C. Venerus, *Phys. Rev. Lett.* **73**, 963 (1994).

[23] Claus F. Behrens, Tine G. Christiansen, Tage Christensen, Jeppe C. Dyre, and Niels B. Olsen Phys. Rev. Lett. **76**, 1553 (1996).

[24] R. Zorn, F. I. Mopsik, G. B. McKenna, L. Willner, and D. Richter, *J. Chem. Phys.* **107**, 3645 (1997).

[25] R. D. Deegan, R. L. Leheny, N. Menon, S. R. Nagel, and D. C. Venerus, *J. Phys. Chem. B* **103**, 4066 (1999).

[26] K. Schrøter and E. Donth, *J. Chem. Phys.* **113**, 9101 (2000).

[27] F. Ladieu, C. Thibierge and D. L'Høte *J. Phys.: Condens. Matter* **19** 205138 (2007).

[28] C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco et al. *Phys. Rev. E* **76** 041510 (2007).

[29] S. Capaccioli, G. Ruocco and F. Zamponi *J. Phys. Chem. B* **112**, 10652 (2008).

[30] S. Havriliak and S. Negami *Polymer* **8** 161 (1967)

[31] A. I. Nielsen, T. Christensen, B. Jakobsen, et al *J. Chem. Phys.* **130**, 154508 (2009)

APPENDIX: Analysis details

Note that, although we consider the real part of $\tilde{\chi}$ when computing the four-point susceptibility, we fit simultaneously the real and imaginary part with Eq. (6). This is done minimizing the (generalized) residual χ^2 for a complex variable x, i.e.: $\chi^2 = \sum_j (x^j_{exp} - x^j_{th})^* \cdot (x^j_{exp} - x^j_{th})$ where the star indicates the complex conjugate.

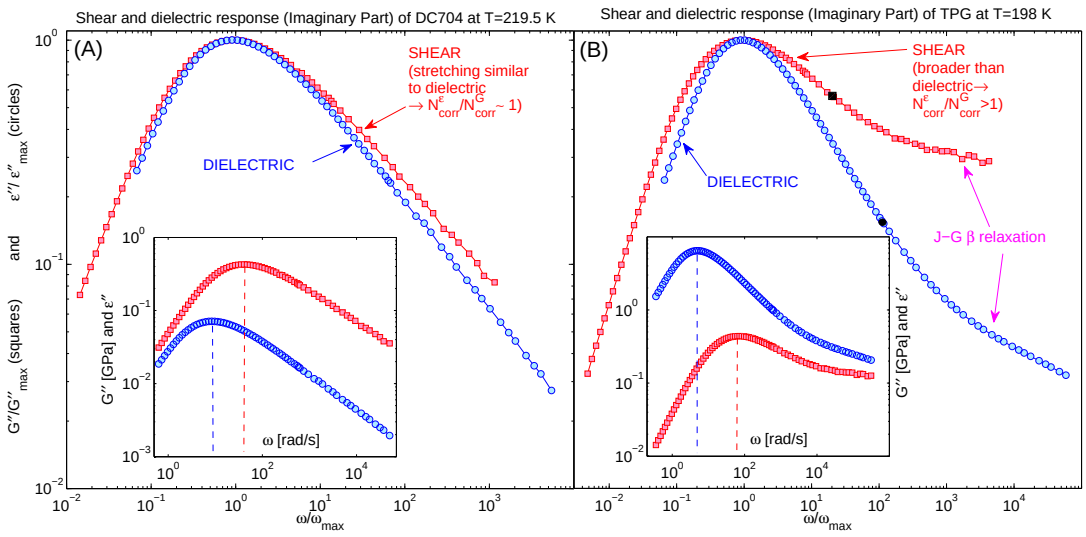

FIG. 7: (**A**) Comparison of (normalized) imaginary part of the shear and dielectric response function of DC704 at the same temperature T =219.5 K (main panel). The amplitude of the functions is normalized to the loss maxima ($\epsilon''_{\max}$ and $G''_{\max}$) and they are plotted vs $\omega/\omega_{\max}$ for an easier comparison of the shapes. In the inset we show the two susceptibilities as they are are measured. (**B**) Same as (A) for TPG at T =198 K. The black symbols indicate the last point included in the fitting (see Appendix).

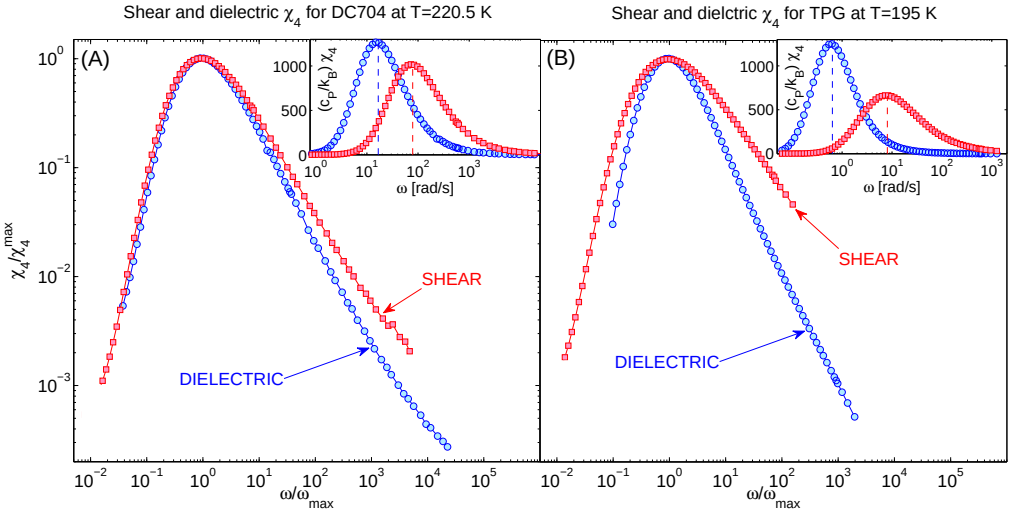

FIG. 8: (**A**) Comparison of the shear and dielectric four-point susceptibility of DC704 at the same temperature T =220.5 K (main panel). The amplitude of each function is normalized to the maximum ($\chi_4^{\max}$) and it is plotted vs $\omega/\omega_{\max}$ for an easier comparison of the shapes. In the inset we show χ_4^G and χ_4^ϵ calculated from Eq. 3. (**B**) same as (A) for TPG at T =195 K.

A further remark on the computation of χ_4 is that Eq. (3) involves the derivative with respect to the temperature that is, in practice, performed as finite difference. After obtaining the normalized curves we consider two successive functions measured at different temperatures T_1 and $T_2(< T_1)$. Each frequency scan of a response function is carried in a way that each curve has points in the same frequencies. The derivative appearing in Eq. (3) is then computed, at the single frequency, as follows:

$$\left[\frac{\partial\tilde{\chi}'(\omega,T)}{\partial \ln T}\right]_{T=(T_1+T_2)/2} \simeq \frac{\tilde{\chi}'(\omega,T_1)-\tilde{\chi}'(\omega,T_2)}{\ln T_1 - \ln T_2}$$

Here we illustrate how we introduce the assumption

of TTS in the analysis of the spectra of the liquids presenting a secondary relaxation process (as TPG, DHIQ, Squalane and PB20). This is done by fixing the stretching parameters in (6) for the fitting in the following way.

First we fit the spectrum at the lowest temperatures (with free stretching parameters) where the secondary process is well separated from the α relaxation. We exclude from this fit some of the high frequency data (affected by the secondary relaxation). To select which data to remove from the minimization we plot the logarithmic derivative of the imaginary part of the response (that is $\alpha = \partial \ln \chi'' / \partial \ln \omega$) that shows a minimum α_{min} at the frequency ω_{min} where the α process meets the secondary relaxation. The frequencies larger than this ω_{min} are not considered in the fitting.

Once the parameters are found from this low-temperature spectrum they are fixed to fit all the other spectra up to high temperature. In those fits we also exclude the high frequency points from the computation in the same way illustrated above.

When this procedure is completed χ_4 is estimated form the obtained fitting functions. All the liquids with a secondary process have been treated in this way. Note that analyzing the data in this manner we are implicitly assuming TTS. A final remark is that if we compute χ_4 from the original (normalized) relaxation function, instead that from the fitting functions, we find a relative difference beteween the heights of the maxima only of a few percents.