Supercooled Liquid Dynamics Studied via Shear-Mechanical Spectroscopy

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We report dynamical shear-modulus measurements for five glass-forming liquids (pentaphenyltrimethyltrisiloxane, diethyl phthalate, dibutyl phthalate, 1,2-propanediol, and *m*-touluidine). The shear-mechanical spectra are obtained by the piezoelectric shear-modulus gauge (PSG) method. This technique allows one to measure the shear modulus ($10^5 - 10^{10}$ Pa) of the liquid within a frequency range from 1 mHz to 10 kHz. We analyze the frequency-dependent response functions to investigate whether time−temperature superposition (TTS) is obeyed. We also study the shear-modulus loss-peak position and its high-frequency part. It has been suggested that when TTS applies, the high-frequency side of the imaginary part of the dielectric response decreases like a power law of the frequency with an exponent −1/2. This conjecture is analyzed on the basis of the shear mechanical data. We find that TTS is obeyed for pentaphenyltrimethyltrisiloxane and in 1,2-propanediol while in the remaining liquids evidence of a mechanical β process is found. Although the high-frequency power law behavior $\omega^{-\alpha}$ of the shear loss may approach a limiting value of $\alpha = 0.5$ when lowering the temperature, we find that the exponent lies systematically above this value (around 0.4). For the two liquids without β relaxation (pentaphenyltrimethyltrisiloxane and 1,2-propanediol) we also test the shoving model prediction, according to which the relaxation time activation energy is proportional to the instantaneous shear modulus. We find that the data are well described by this model.

I. Introduction

The nature of the relaxation processes taking place in supercooled liquids approaching the glass transition has been a major subject of study for a number of years. Understanding how the different response functions are connected in such systems is still a fundamental goal to reach. It is not clear whether the various observables display some universal features approaching the glass transition. Although dielectric spectroscopy is the most common experimental tool, a more detailed characterization of their behavior can be obtained by measuring different quantities, like the *shear modulus*, that are important from a practical as well as theoretical point of view. Although this dynamic variable can be measured above $\sim 10^2$ Hz with conventional techniques, high-frequency data are scarce in the literature.

Motivated by these reasons, we employed the piezoelectric shear-modulus gauge (PSG)[1] method to measure the shear modulus of five glass-forming liquids. This technique allows us to measure the dynamic shear modulus of the supercooled liquids just above the glass transition where it takes values between 0.1 MPa and 10 GPa. By means of the PSG technique we can easily observe the α relaxation process in the shear response. The frequency range of the technique is wide ($10^{-3} - 10^4$ Hz), and we also observe a *mechanical* Johari−Goldstein β relaxation.[2] As shown before[3] indeed, this technique is sensitive to the secondary process, and we find evidence of the presence of a shear β relaxation[3−5] in some of the mechanical spectra reported here.

In section II we describe the experiment performed and the liquids studied reporting the frequency-resolved mechanical spectra. In section III we report the main findings of our study; in this section we present the analyzed data showing the
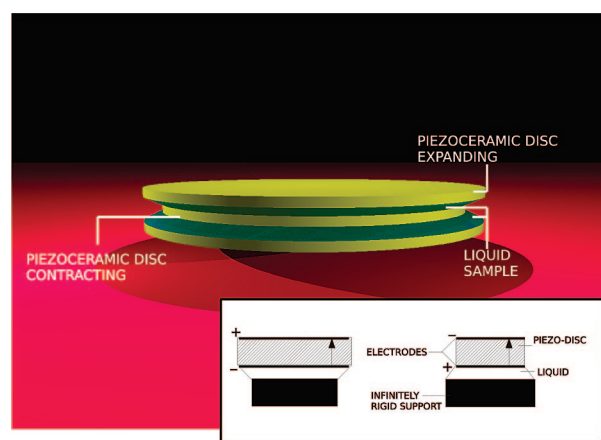

Figure 1. Pictorial representation of the shear transducer (PSG) during its expansion−contraction. The liquid sandwiched between the discs clamps their movement, inducing a measurable change in the piezoelectric capacitance of the disc system. The shear modulus can be deduced from this electrical capacitance. Inset: the one-disc equivalent system of the PSG. The applied electric field causes an expansion or a contraction depending on the polarization of the disc (represented by the arrow). See ref 1 for more details.

temperature dependence of the shear-mechanical α relaxation frequency and a test of some conjectures and models about the dynamics. Finally, we draw some general conclusions in section IV.

II. Experiment

The piezoelectric shear-modulus gauge (PSG) method is based on the piezoelectric properties of the material that composes the measuring device. The piezoelectric transducer is formed by three discs made of a special ceramic compound[6]

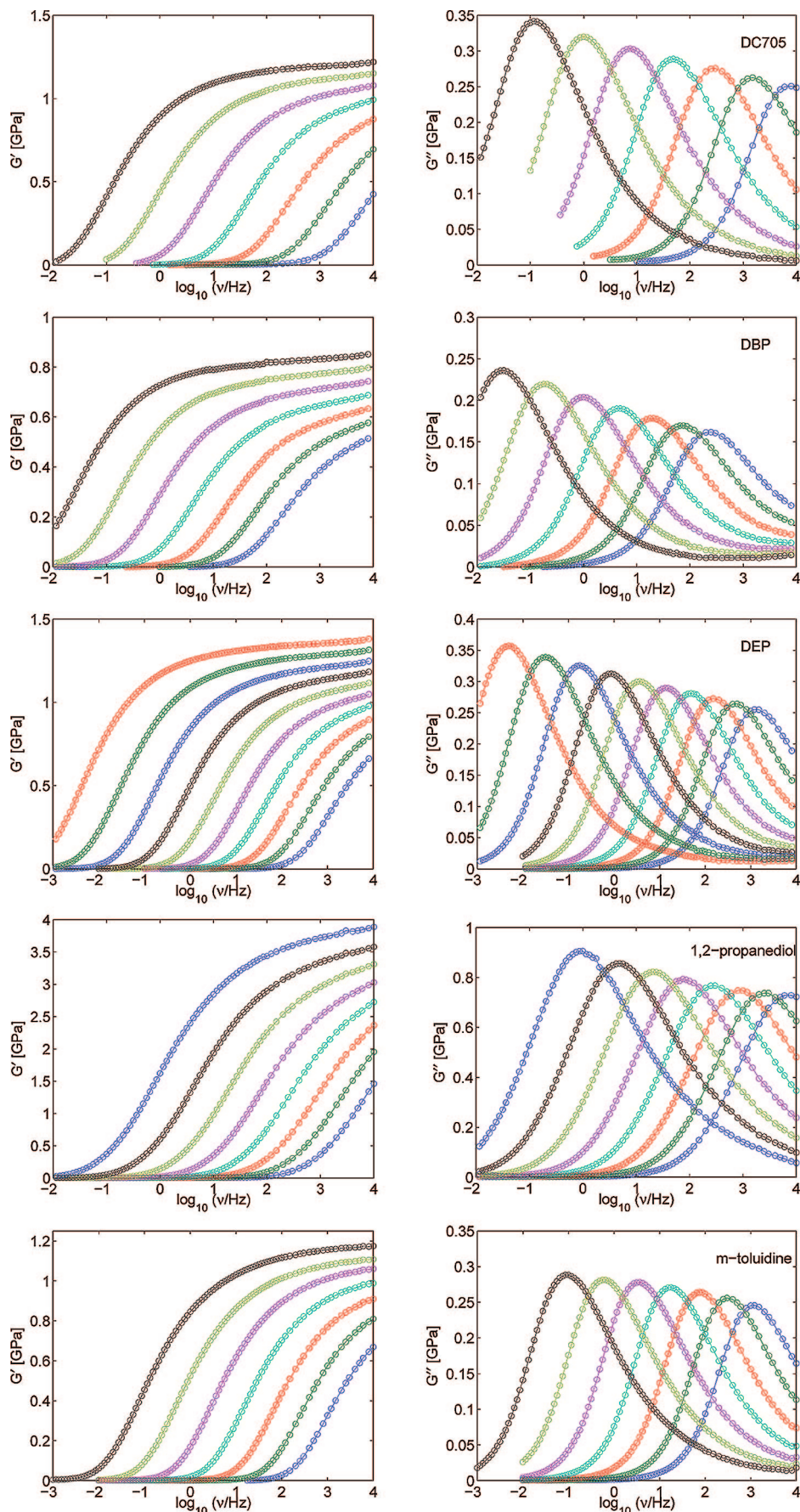* Corresponding author. E-mail: cmaggi@ruc.dk.

Figure 2. Real (left) and imaginary (right) part of the shear response of the liquids studied. (From top to bottom) spectra of DC705 taken at the temperatures (from right to left): 249, 246, 243, 240, 237, 234, and 231 K; of DBP at 188, 186, 184, 182, 180, 178, and 176 K; of DEP at 199, 197, 195, 193, 191, 189, 187, 185, 183, and 181 K; of 1,2-propanediol at 195, 192, 189, 186, 183, 180, 177, 173, and 171 K; and of *m*-toluidine at 198, 196, 194, 192, 190, 188, and 186 K.
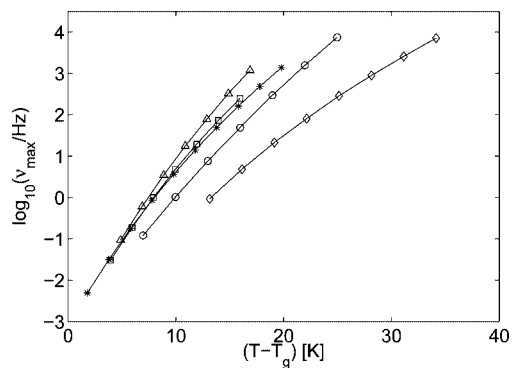
Figure 3. Frequency of the mechanical α peak as a function of the temperature for DC705 (○, T_g = 224.0 K), DBP (□, T_g = 172.3 K), DEP (∗, T_g = 179.5 K), 1,2-propanediol (◇, T_g = 157.8 K), and m-toluidine (△, T_g = 181 K).

that has a pronounced piezoelectric effect (see Figure 1). The working principle of the PSG is illustrated in the inset of Figure 1 where the one disc equivalent of the three-disc system is shown. The ceramic disc is covered with a silver layer on both faces constituting the electrodes. When a voltage is applied, each disc expands or contracts depending on its intrinsic polarization and on the direction of the acting electric field. The electric capacitance of the disc depends on its strain state so that if a material is partially clamping its motion, the measured capacitance will be lower than that of the free moving disc. Measuring accurately this electrical capacitance,[7] we can obtain the stiffness of the medium adhering to the disc. In other words, we can convert the electric impedance into the shear modulus knowing the exact relationship between the two.[1] The three-disc geometry, used in the experiment (main panel of Figure 1), is employed to reduce unwanted effect like the bending motion that would be present in a one-disc device. The interested reader can find details about the technique in ref 1.

The measurements are performed cooling the liquids via a home-built closed-cycle cryostat.[8] This has an absolute uncertainty on the temperature that is less than 0.2 K and a temperature stability better than 2 mK.

The liquids studied are the following: pentaphenyltrimethyltrisiloxane (DC705), dibutyl phthalate (DBP), diethyl phthalate (DEP), 1,2-propanediol, and m-touluidine. The DC705 is a diffusion-pump oil from Dow Corning; all the other liquids were acquired from Sigma-Aldrich. No filtration or purification of the samples was performed before the measurement.

All mechanical spectra are reported in Figure 2. Here the real part G' and the imaginary part G'' of the complex shear modulus $G(\nu,T)$ are presented.[9] The reactive and the absorbitive part of the shear response of the liquids studied are measured at several temperatures.

For the shear loss peak of the DC705 there is a clearly defined shear α process that shifts to lower frequencies as the temperature decreases. We have found no sign of a shear β relaxation in this liquid. This is also confirmed by the fact that the curve maintains the same shape, lowering the temperature as discussed below. We will see also that the high-frequency side of the shear-mechanical spectrum shows a pretty constant slope.

The shear response of DBP clearly shows a β relaxation. The shape of the imaginary part of the response function is strongly deformed at high temperatures where the α process is merged with the β. When the temperature is low enough, the high-frequency tail of the response functions shows a pronounced increase, signaling an emerging β relaxation. Unfortunately, the β loss peak lies at much higher frequencies than the upper limit

of our device. The dielectric β process of this liquid has been observed[10] to be around 10^6 Hz in a temperature window similar to the one of our mechanical experiment. This is consistent with the fact that the β relaxation is outside the PSG dynamical range since the shear-loss peak frequency is generally higher than the dielectric one[3] (usually the two peaks are within the same decade). For future studies on this liquid the upper frequency limit of the PSG could possibly be increased by slightly modifying the transducer geometry.

Evidence of a secondary loss peak is also found in the mechanical response of the DEP. The dielectric β relaxation process in DEP has been the subject of an accurate investigation in connection with the behavior of the entropy in the supercooled and in the glass state,[11] raising fundamental questions about the nature of fast molecular motions in ultraviscous liquids. Very recently, this dielectric β process has been shown to be intimately related to the results of positron annihilation lifetime spectroscopy.[12] We note that in those dielectric measurements the β loss peak is found at about 2×10^4 Hz at T = 179 K, consistent with the fact that mechanically this process is above the upper limit of the PSG. We shall see in section III that when the shear loss is plotted on a logarithmic scale, the low-frequency tail of the β relaxation is more clearly visible.

The spectra taken for 1,2-propanediol are characterized by an high shear modulus, and no signature of β relaxation is found. This hydrogen-bonded liquid has recently been studied in dielectric experiments and compared to polymers differing in chain length and in the number of OH groups.[13] These dielectric experiments did not reveal a visible β process, and a temperature-independent Cole−Davidson stretching parameter was found. These findings are fully in agreement with our shear spectra since the shape of the response function is very weakly temperature dependent as it will be stressed in the following.

Rather interesting mechanical spectra are found for m-toluidine. A weak, but nonzero, high-frequency tail of the loss response can be noted in Figure 2. This may hint to the existence of a shear β relaxation at frequencies around 1 MHz, consistent with recent broadband dielectric experiments performed on this liquid[14] where a β relaxation process could be resolved, but only in the glassy regime where the relaxation frequency reaches a value around 1 kHz at about 130 K. This could be a range in which this β process could start to be detected mechanically.[15]

Finally, we mention that we attempted to measure the frequency-resolved shear modulus also for 1,3-propanediol and for propylene carbonate. An anomalous shear response was found for these two liquids, however, signaling a probable crystallization.

III. Discussion

The first information that can be extracted from our measurement is the α process loss peak frequency ν_{max}. This has been deduced from the imaginary part through a simple unbiased method. We fitted the closest six points to the maximum of $\log(G''/\text{GPa})$ as a function of $\log(\nu/\text{Hz})$ with a second-order polynomial to identify the maximum G''_{max} and the corresponding frequency ν_{max}. These loss-peak frequencies are reported in Figure 3 as a function of the scaled temperature $(T - T_g)$. Here we define T_g as the temperature where the ν_{max} = 1 mHz. T_g is identified by a linear extrapolation of the last three points of $\log(\nu/\text{Hz})$ as a function of T.

Time−temperature superposition (TTS) is a property of the α process appearing in the susceptibilities of some supercooled liquids expressing the fact that the shape of the response function remains the same when the system is cooled. When TTS applies,
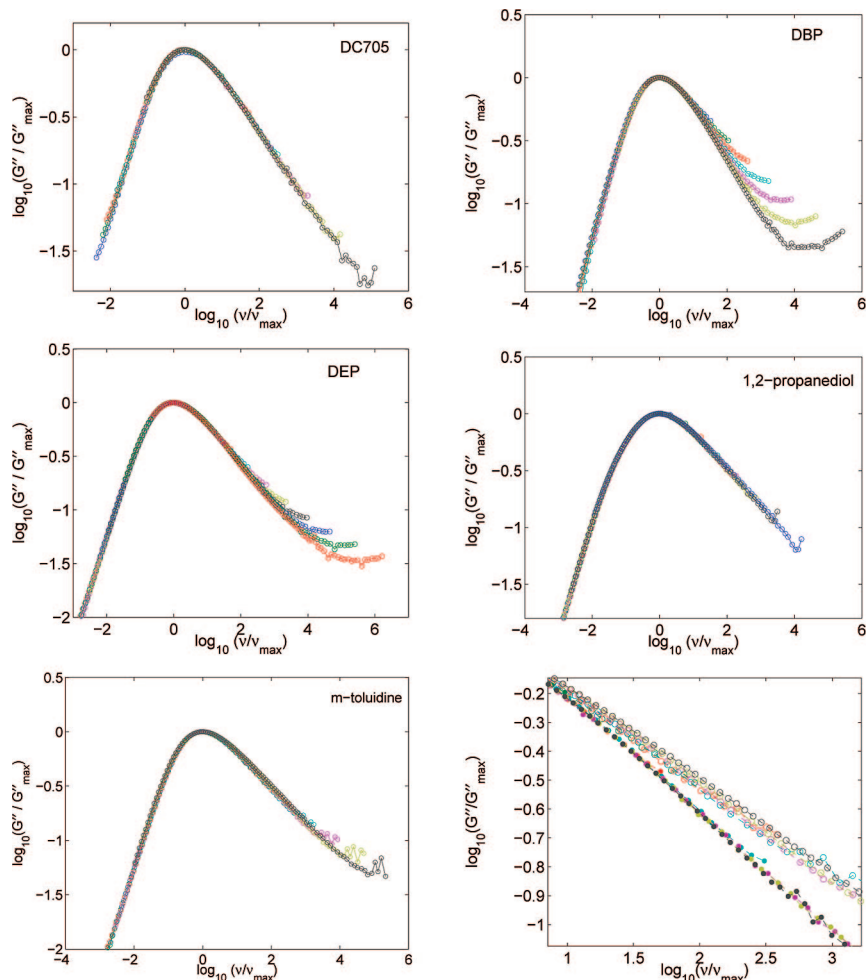
Figure 4. Shear loss G'' of liquids studied scaled by the maximum loss G''_{max} as a function of the frequency ν divided by the frequency of the peak ν_{max} (see also Figure 2): DC705, DBP, DEP, 1,2-propanediol, and m-toluidine. In the right-bottom panel we show a comparison between the scaled spectra of DC705 (full line, full symbols) and m-toluidine (dashed line, open symbols) on a smaller scale.
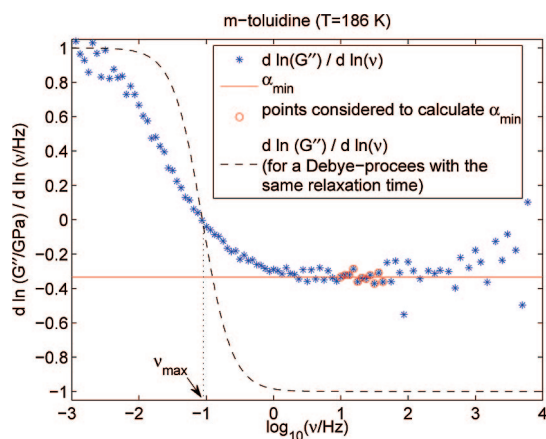

Figure 5. Representation of the procedure used to find the minimum logarithmic slope α_{min}. In this figure we report the analysis of the mechanical spectrum of m-toluidine at $T = 186$ K. The derivative of $\log(G''/\text{GPa})$ with respect to $\log(\nu/\text{Hz})$ is plotted as a function the frequency (stars). Some points are selected (red circles), and their average is taken to calculate α_{min} (red line). Note that a Debye-like mechanical process with the same relaxation time would have a sharper drop of the α parameter reaching -1 at high frequencies.

Figure 6. Minimum value of the logarithmic slope ($\alpha = \text{d} \ln G''/\text{d} \ln \nu$) for the liquids studied: DC705 ($\bigcirc$), DBP ($\square$), DEP ($*$), 1,2-propanediol ($\diamond$), m-toluidine ($\triangle$).

the response is only shifting its characteristic time and its amplitude if we cool the liquid. Mathematically speaking, the generic response χ can be rewritten as $\chi(\nu,T) = A(T)\Phi(\nu/\nu_{max}(T))$, where $\nu_{max}(T)$ is a characteristic frequency depending
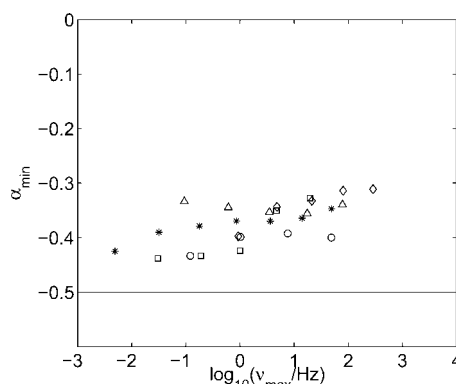
on T. Having found the two parameters G''_{max} and ν_{max} at every given temperature, it is rather easy to check wether TTS applies for a given liquid.

In Figure 4 we report the imaginary part of the shear modulus divided by G''_{max} as a function of ν/ν_{max}. This plot underlines that for some of the liquids (DC705 and 1,2-propanediol) the shape of the α process remains constant, lowering T. This is not the case for DBP and DEP where the curves are detaching at high frequencies. The lack of TTS is clearly related to the presence of a β peak; indeed, the logarithmic scale used in this
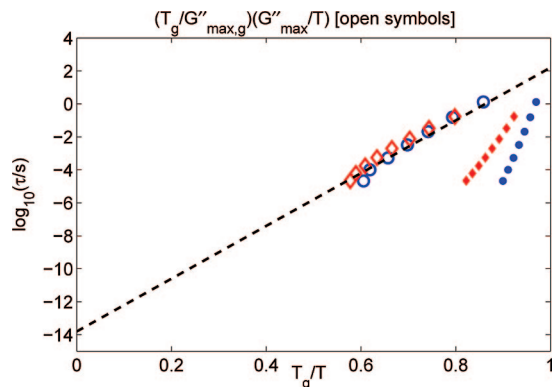
Figure 7. Characteristic time $\tau = 1/\nu_{max}$ of the shear loss as a function of the scaled temperature T/T_g (full symbols) and as a function of $x = (T_g/G''_{max,g})(T/G''_{max})$ (open symbols) for the liquids in which TTS applies: DC705 ($\bigcirc$, $T_g = 224.0$ K) and 1,2-propanediol ($\diamondsuit$, $T_g = 157.8$ K). The dashed line is an exponential function with prefactor $\tau_0 = 10^{-14}$ s and taking the value $\tau = (2\pi 10^3)^{-1} \simeq 150$ s for $x = 1$ (no free parameters are adjusted in this function).

plot makes the low-frequency tail of the secondary process more visible. For *m*-toluidine the situation is ambiguous. Indeed for this liquid TTS seems to apply, but if we look at the high-frequency end on a smaller scale (Figure 4, right-bottom) there is a sensitive difference between the curves. In this figure we report also the scaled spectra of DC705 that satisfy TTS on the small scale for an easier comparison. We also note that the dielectric strength of the secondary relaxation reported for *m*-toluidine[14] is rather low while in the shear-mechanical spectra it seems to be more intense in comparison with the α process. This is another important feature of our mechanical measurement: a weak dielectric secondary process is *magnified* in the shear response.[4,5]

An interesting feature of the spectra of 1,2-propanediol is underlined by the TTS plot in Figure 4. The portion of the spectrum at frequencies lower than ν_{max} (i.e., at $\nu/\nu_{max} \leq 1$) is slightly deformed. The shape of this response function is reproducible, and it seems to be almost temperature-independent in the temperature range explored in our experiment. This "shoulder" could be considered a peculiar feature of the mechanical relaxation of 1,2-propanediol since it is not found in dielectric spectra (see for example ref 13). Note that an additional process (with similar shape) close to the α relaxation is found in the case of tripropylene glycol in high-pressure conditions (see ref 16). Further studies of the dielectric relaxation of 1,2-propanediol at high pressure would be needed to better understand the origin of the shape of its mechanical response.

We want to stress again that, from our study, the lack of TTS seems to be intrinsically related to the presence of a secondary mechanical process. All the liquids studied here that show the β relaxation (as also confirmed by the dielectric measurements cited in section II) display a clear temperature dependence in the shape of the mechanical response function. Anyway, it is not generally clear how the presence of the β relaxation is related to the nature of a specific liquid. The understanding of the validity of TTS in some supercooled liquids requires the understanding of one of the most puzzling phenomena of ultraviscous liquids and glasses that is the secondary relaxation process.

It has been suggested from empirical observations[17,18] that when TTS applies, the high-frequency decay of the dielectric loss is characterized by a power-law behavior ν^α with exponent $\alpha = -1/2$. A theoretical explanation for this power-law dependence of the dielectric response has been proposed,

assuming the dominance of long-wavelength fluctuations.[19−21] We have tested this conjecture for the mechanical response, finding the minimum value of the logarithmic derivative of G'', i.e. $\alpha_{min} = [\text{d} \ln G''/\text{d} \ln \nu]_{min}$. It has to be noted that the extraction of this information is much more complicated for the shear loss than the dielectric response. This is due to the fact that the shear response is generally affected by a higher noise level than dielectric. An example of the procedure followed to extract α_{min} is reported in Figure 5 for the mechanical response of *m*-toluidine at $T = 186$ K. When α is plotted as a function of the frequency, a minimum can be identified within some data points. The average of these points is taken as the α_{min}. Note that a Debye process would have a characteristic behavior of the logarithmic slope showing a sudden drop of α at the relaxation frequency ν_{max}.

In Figure 6 we report the value of α_{min} as a function of the loss peak frequency for the temperatures where the minimum of the derivative of the logarithm was well-defined. We note that even if the behavior of this quantity for the liquids studied is compatible with a limiting $\alpha = -1/2$ at low temperatures, the data seem to lie systematically above the -0.5 line. We stress also that is easy to expect that an $\nu^{-1/2}$ behavior in the shear loss is disturbed more when a β relaxation is present since its intensity is enhanced in the mechanical spectrum compared to the dielectric.

Finally, we remark that the parameter α_{min} is not expected to monotonically decrease in a wider temperature range. Indeed, at higher temperatures the shape of the shear response should recover a simpler Debye-like shape where the stretching parameters (the KKW β parameter for example) come close to unity.[22] The relaxation frequencies belonging to this high-temperature regime are currently outside the dynamical window of the PSG technique.[23]

To conclude the analysis of our data, we want to present a comparison between the mechanical spectral features and a simple phenomenological model for the dynamics of super-cooled liquids. The shoving model[24] is based on the assumption that the relaxation in the supercooled liquid takes place with a local volume increase and that the activation energy is mainly elastic energy spent to shove aside the surrounding of the rearranging molecules. As has been reported, this model can be derived estimating the barrier height in a classical energy landscape approach.[25]

The shoving model predicts that the relaxation time is related to the infinite-frequency shear modulus G_∞ by the equation

$$\ln(\tau) = \ln \tau_0 + V_c G_\infty(T)/T \qquad (1)$$

where V_c is a characteristic volume in a relaxation process (V_c is assumed temperature independent) and τ_0^{-1} is the phonon-frequency ($\tau_0 \simeq 10^{-14}$ s). The determination of G_∞ is not necessary to test the model if TTS applies; indeed, if this property holds, we can write

$$G_\infty(T) \propto G''_{max}(T) \qquad (2)$$

since the constant factor A determining the amplitude of the complex response in $\chi(\nu,T) = A(T)\Phi(\nu/\nu_{max}(T))$ is the same for the real and the imaginary part Φ' and Φ''. Note that this proportionality does not apply when TTS does not hold. For example, in a case where the β relaxation is present the value of G_∞ is modified by the secondary process, and a more complicated fitting procedure would be needed to estimate the

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value of the infinite-frequency shear modulus. On the other hand, when TTS is satisfied, we can write the simple equation (using eq 2 in eq 1)

$$\log(\tau) = \log \tau_0 + BG''_{max}(T)/T \qquad (3)$$

where B is a constant factor. Equation 3 represents the prediction of the shoving model when TTS also applies: the logarithm of the relaxation time is a linear function of the quantity $G''_{max}(T)/T$. This is tested in Figure 7 for the liquids in which time−temperature superposition is found to hold (DC705 and 1,2-propanediol). In this figure the relaxation time (defined as $\tau = (2\pi\nu_{max})^{-1}$) is reported as a function of $1/T$ and as a function of G''_{max}/T. To report all the data in the same plot, the abscissa has been normalized to the unity as T_g/T and as $x = (T_g/G''_{max,g})(G''_{max}/T)$. Note that here we find $G''_{max,g}$ through a linear extrapolation of the last values G''_{max} to T_g previously identified to give $\nu_{max}(T_g) = 10^{-3}$ Hz (corresponding to $\tau(T_g) = (2\pi10^3)^{-1} \simeq 150$ s).

The dashed line in Figure 7 represents the shoving model prediction (no adjustable paremeters are used in this function) ending, at high temperature, at the physically reasonable prefactor 10^{-14} s.

IV. Conclusion

We have reported shear-mechanical spectra of five glass-forming liquids close to T_g. Via the PSG[1] technique, we have investigated the behavior of the mechanical α process and found evidence of the presence of a mechanical β relaxation in dibutyl phthalate, diethyl phthalate, and *m*-toluidine. Time−temperature superposition for the mechanical susceptibility is found to hold for the liquids without signature of β process (pentaphenyltrimethyltrisiloxane and 1,2-propanediol). The conjecture originally developed for the dielectric response that, when TTS applies, a $\nu^{-1/2}$ decay is found for the high-frequency part of the loss is checked for the shear response. We find that the data are consistent with a limiting $\nu^{-1/2}$ low-temperature behavior although the minimum slopes are systematically higher than -0.5. The shoving model has been tested for the two liquids without β relaxation, finding that it well describes the experimental data.

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