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-toluic acid). 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 \(\beta\) 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 \(\beta\) 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) 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 \(\alpha\) 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 \(\beta\) 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 \(\beta\) relaxation\(^4–5\) 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 temperature dependence of the shear-mechanical \(\alpha\) 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\(^6\)

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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.
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.
The first information that can be extracted from our measurement is the $\alpha$ process loss peak frequency $\nu_{\text{max}}$. This has been deduced from the imaginary part through a simple unbiased method. We fitted the closest six points to the maximum of $G''(\nu)$ as a function of $\log(\nu)$ with a second-order polynomial to identify the maximum $\nu_{\text{max}}$ and the corresponding frequency $\nu_{\text{max}}$. 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 $\nu_{\text{max}} = 1 \text{ mHz}$. $T_g$ is identified by a linear extrapolation of the last three points of $\log(\nu)$ as a function of $T$.

Time-temperature superposition (TTS) is a property of the $\alpha$ 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,
the response is only shifting its characteristic time and its amplitude if we cool the liquid. Mathematically speaking, the generic response $\gamma$ can be rewritten as

$$\gamma(v, T) = A(T) \Phi(v / v_{\text{max}}(T)),$$

where $v_{\text{max}}(T)$ is a characteristic frequency depending on $T$. Having found the two parameters $G''_{\text{max}}$ and $v_{\text{max}}$ at every given temperature, it is rather easy to check whether TTS applies for a given liquid.

In Figure 4 we report the imaginary part of the shear modulus divided by the maximum loss $G''_{\text{max}}$ as a function of the frequency $v$ divided by the frequency of the peak $v_{\text{max}}$ (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 4.** Shear loss $G''$ of liquids studied scaled by the maximum loss $G''_{\text{max}}$ as a function of the frequency $v$ divided by the frequency of the peak $v_{\text{max}}$ (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 $\alpha_{\text{min}}$. 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 $\log(v/\text{Hz})$ is plotted as a function the frequency (stars). Some points are selected (red circles), and their average is taken to calculate $\alpha_{\text{min}}$ (red line). Note that a Debye-like mechanical process with the same relaxation time would have a sharper drop of the $\alpha$ parameter reaching $-1$ at high frequencies.

**Figure 6.** Minimum value of the logarithmic slope ($\alpha = d \log G''/d \log v$) for the liquids studied: DC705 ($\circ$), DBP ($\square$), DEP ($\ast$), 1,2-propanediol ($\Diamond$), $m$-toluidine ($\triangle$).
parameters are adjusted in this function).

It seems to be more intense in comparison with the shear response.\textsuperscript{4,5}

The dashed line is an exponential function with prefactor $\tau_0 = 10^{-14}$ s and taking the value $\tau = (2 \times 10^{-14})^{-1} \approx 150$ s for $x = 1$ (no free parameters are adjusted in this function).

Figure 7. Characteristic time $\tau = 1/\nu_{\text{max}}$ of the shear loss as a function of the scaled temperature $T/T_k$ (full symbols) and as a function of $x = (T/T_{G_{\text{max}}}) (T/T_{G_{\text{min}}})$ (open symbols) for the liquids in which TTS applies: DC705 ($\bigodot$, $T_g = 224.0$ K) and 1,2-propanediol ($\bigodot$, $T_g = 157.8$ K). The dashed line is an exponential function with prefactor $\tau_0 = 10^{-14}$ s and taking the value $\tau = (2 \times 10^{-14})^{-1} \approx 150$ 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\textsuperscript{14} is rather low while in the shear-mechanical spectra it seems to be more intense in comparison with the $\alpha$ process. This is another important feature of our mechanical measurement: a weak dielectric secondary process is \textit{magnified} in the shear response.\textsuperscript{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 $\nu_{\text{max}}$ (i.e., at $\nu/\nu_{\text{max}} \leq 1$) 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 $\alpha$ 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 $\beta$ 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 $\beta$ 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\textsuperscript{17,18} that when TTS applies, the high-frequency decay of the dielectric loss is characterized by a power-law behavior $\nu^\alpha$ 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.\textsuperscript{19–21}

We have tested this conjecture for the mechanical response, finding the minimum value of the logarithmic derivative of $G''$, i.e. $\alpha_{\text{min}} = \frac{\text{d} \ln G''}{\text{d} \ln \nu_{\text{max}}}$. 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 $\alpha_{\text{min}}$ is reported in Figure 5 for the mechanical response of $m$-toluidine at $T = 186$ K. When $\alpha$ 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 $\alpha_{\text{min}}$. Note that a Debye process would have a characteristic behavior of the logarithmic slope showing a sudden drop of $\alpha$ at the relaxation frequency $\nu_{\text{max}}$.

In Figure 6 we report the value of $\alpha_{\text{min}}$ 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 $\beta$ relaxation is present since its intensity is enhanced in the mechanical spectrum compared to the dielectric.

Finally, we remark that the parameter $\alpha_{\text{min}}$ 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 $\beta$ parameter for example) come close to unity.\textsuperscript{22} The relaxation frequencies belonging to this high-temperature regime are currently outside the dynamical window of the PSG technique.\textsuperscript{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 supercooled liquids. The shoving model\textsuperscript{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.\textsuperscript{25}

The shoving model predicts that the relaxation time is related to the infinite-frequency shear modulus $G_{\infty}$ by the equation

$$\ln(\tau) = \ln \tau_0 + V_c G_{\omega}(T)/T$$  \hspace{1cm} (1)

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

$$G_{\omega}(T) \propto G_{\text{max}}''(T)$$  \hspace{1cm} (2)

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

$$\log(\tau) = \log \tau_0 + B G''_{\max}(T)/T \quad (3)$$

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 $x = (T_g/G''_{\max,\nu})(G''_{\max}/T)$. Note that here we find $G''_{\max,\nu}$ 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 $\tau(T_g) = (2\pi 10^3)^{-1}$ $\approx 150$ s).

The dashed line in Figure 7 represents the shoving model prediction (no adjustable parameters 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 technique, we have investigated the behavior of the mechanical $\alpha$ process and found evidence of the presence of a mechanical $\beta$ relaxation in dibutyl phthalate, diethyl phthalate, and $n$-toluidine. Time–temperature superposition for the mechanical susceptibility is found to hold (DC705 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 $\beta$ relaxation, finding that it well describes the experimental data.

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**References and Notes**

(6) The piezoelectric ceramic is PZ26 produced by FerroPerm (Denmark).
(9) All the shear-mechanical spectra reported in this work are available in the “Glass and Time: Data repository” found online at http://glass.ruc.dk/.
(15) Note that a number of problems could be present in such low-temperature measurements. There is the possibility of damaging the piezodiscs because of the sandwiched glass contracting; nevertheless, unknown memory effects could be induced in piezo-ceramics lowering repetitively their temperature when the stresses are not fully relaxed.
(23) The high-frequency limit of the PSG technique (10 kHz) is set by the geometrical and material properties of the piezo-electric discs. Above this frequency the response of the measuring device is dominated by the intrinsic resonances of the piezo-ceramics (see ref 1).