Different glassy states, as indicated by a violation of the generalized Cauchy relation

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\textbf{Abstract.} Using Brillouin spectroscopy as a probe for high-frequency clamped acoustic properties, a shear modulus $c_{44}^\infty$ can be measured in addition to the longitudinal modulus $c_{11}^\infty$ already well above the thermal glass transition. On slow cooling of the liquid through the thermal glass transition temperature $T_g$, both moduli show a kink-like behaviour and the function $c_{11}^\infty = c_{11}^\infty(c_{44}^\infty)$ follows a generalized Cauchy relation (gCR) defined by the linear relation $c_{11}^\infty = 3c_{44}^\infty + \text{constant}$, which completely hides the glass transition. In this work we show experimentally that on fast cooling this linear transformation becomes violated within the glassy state, but that thermal ageing drives the elastic coefficients towards the gCR, i.e. towards a unique glassy state.
1. Introduction

Additional relations which reduce the number of independent elastic stiffness coefficients are known in solid-state physics and are called Cauchy relations \[ 1, 2 \]. Such relations hold only if apart from the usual symmetry conditions the crystal obeys additional constraints on the local symmetry, molecular interacting forces, lattice defects and lattice anharmonicity. For cubic crystals fulfilling these significant constraints, the relevant relation \[ c_{12} = c_{44} \] applies, which reduces the initially three independent elastic constants to only two. If we tentatively combine this relation with the isotropy condition \[ c_{12} = c_{11} - 2c_{44} \] we obtain a Cauchy relation for the solid-like isotropic state \( c_{11} = 3c_{44} \), which in turn reduces the number of independent elastic constants to one. Taking into consideration that the additional conditions on the local symmetry, the absence of defects and the absence of anharmonicity are hardly fulfilled for solid or solid-like amorphous materials, we do not expect \( c_{11} = 3c_{44} \) to hold for amorphous solids. On the other hand, theoretical work \[ 3, 4 \] proposes a generalized Cauchy relation (gCR) between the high-frequency elastic shear and compression moduli, \( G^\infty = c_{44}^\infty \) and \( K^\infty \) of liquids:

\[
K^\infty = \frac{5}{3}G^\infty + 2(P - nk_B T)
\]

with \( P \): external pressure, \( T \): temperature, \( n \): particle density. Using \( K^\infty = c_{11}^\infty - \frac{3}{3}c_{44}^\infty \) one finally obtains \( c_{11}^\infty = 3c_{44}^\infty + 2(P - nk_B T) \). This gCR adds to the ideal Cauchy relation a term which depends on pressure and temperature.

In a recent publication it was shown \[ 5 \] that the high-frequency elastic shear and longitudinal moduli, \( c_{44}^\infty \) and \( c_{11}^\infty \), of several thermal and chemical glass-formers obey a more specific gCR. Using Brillouin spectroscopy (BS) as a probe for high-frequency clamped acoustic properties, it was shown that on slow cooling of glass-forming samples through the thermal glass transition (TGT) the longitudinal stiffness modulus \( c_{11}^\infty(T) \) follows the linear transformation

\[
c_{11}^\infty(T) = A^0 + Bc_{44}^\infty(T)
\]

(\( A^0 \), \( B \): temperature- and pressure-independent material constants; \( T \): temperature, common parameter). In our recent investigation we found for all materials under investigation, within the margin of error, \( B = 3 \). Therefore, we will use in the following the notion ‘gCR’ implying \( c_{11}^\infty(T) = A^0 + Bc_{44}^\infty(T) \). Astonishingly, the TGT is completely hidden in the elastic data representation described by equation (1). Much more surprising was the observation \[ 5 \] that even the \((c_{44}^\infty, c_{11}^\infty)\) data measured during the non-equilibrium chemical process of curing (polymerization) yield a linear transformation, \( c_{11}^\infty(t) = A^0 + Bc_{44}^\infty(t) \) with \( B = 3 \), where \( t \) is the curing time. This observation raises the questions of whether
(i) non-equilibrium processes do not violate the gCR at all, or whether
(ii) the curing process was still slow enough to allow the elastic moduli at every curing time \( t \) to develop their equilibrium values.

If hypothesis (i) holds, the validity of relation (1) for the liquid state as well as for the solid state would be less exciting. If, on the other hand, hypothesis (ii) holds, then, during every time interval \( [t, t + \delta t] \), the acoustic phonon bath comes to thermal equilibrium. In that case we expect elastic frequencies collected during such a short time interval to be equilibrium properties although the underlying curing process is a non-equilibrium process. Taking into account that recent results obtained from time domain BS performed on DGEBA (diglycidylether of bisphenol A) indicate the existence of an equilibrium glassy state [6], but also keeping in mind that excessive cooling from the liquid to the glassy state bears the risk of creating non-equilibrium states, the question arises of whether the experimental Cauchy representation found on slow cooling of DGEBA into the glassy state represents ‘equilibrium properties’ or not. With this question resolved, the validity of the gCR could turn out to be a versatile tool for discriminating between mechanical equilibrium and non-equilibrium.

From this viewpoint, it is highly interesting to elucidate the question of whether fast cooling of the liquid to the non-equilibrium glassy states is able to violate the gCR and, if this happens, whether these non-equilibrium states relax towards equilibrium and, if they do so, on what timescale and to what end this happens. Again using DGEBA as a model system, the current paper addresses these questions.

2. Experimental details

All data reported in the following were measured with BS using the 90A scattering geometry [7, 8] detecting simultaneously the longitudinal sound frequency, \( f_{L,T}^{90A} \), and the transverse sound frequency, \( f_{T}^{90A} \). Using this scattering technique together with a laser wavelength of 532 nm we made measurements at a fixed acoustic wavelength of 338.68 nm in the gigahertz regime. In this case the related sound velocities \( v_{L,T}^{90A} \) and \( v_{T}^{90A} \) can be calculated from the following relation:

\[
v_{L,T}^{90A} = f_{L,T}^{90A} \frac{532 \times 10^{-9}}{2 \sin(\pi/4)}. \tag{2}
\]

Using the mass density \( \rho \) of DGEBA, the adiabatic elastic moduli can be calculated from the relation \( c_{ii} = c_{L,T} = \rho v_{L,T}^2 \) (\( i = 1, 4 \)). Since we usually have no access to \( \rho(T) \), we approximate equation (1) by

\[
v_L^{\infty}(T) \left[ v_T^{\infty}(T) \right] - A = B v_T^{\infty} \tag{3}
\]

using \( A = A^0/\rho(T) \) and \( v_L^{\infty}(T) = c_{L,T}^{\infty}(T)/\rho(T) \), where \( v_L^{\infty}(T) \) are the clamped sound velocities related to the moduli \( c_{L,T}^{\infty}(T) \) with \( i = 1, 4 \). Usually \( \rho(T) \) varies only little with \( T \); in that case equation (3) is expected to be representative of equation (1). Because there is no risk of confusion, we will skip in the following the indices 90A and \( \infty \).

Cooling and heating of the sample were performed in an optical top-loading cryostat using helium as a contact gas. For the forced cooling experiments the cryostat including the contact gas atmosphere was cooled down to about 77 K. Subsequently, the film-like sample was introduced into the cryostat by fast top-loading and then the sample was quenched to the lowest possible temperature. The average cooling rate was estimated to be below 10 K min\(^{-1}\). The temperature was measured with a calibrated rhodium–iron resistance.
The DGEBA product was of commercial grade and no further purification was carried out. DGEBA shows at extremely slow cooling an intrinsic TGT at $T_g = 243$ K [6]. It is well known [5, 6] that bulk DGEBA is a fragile liquid and crystallizes only under special circumstances where nucleation is forced, e.g. by rough surfaces and water droplets. We used thin glass cuvettes (a Bor silicate glass of type BK7) with smooth surfaces as sample holders.

3. Influence of stress on elastic properties

A crucial problem for our BS measurements evolves from the development of internal stresses within the DGEBA sample. The increasing sticking of the DGEBA sample on the supporting glass windows during cooling through the TGT in combination with the fact that BK7 glass has a much lower volume expansion coefficient than DGEBA results in internal stresses below the glass transition. As soon as any slip in the BK7/DGEBA interface is blocked due to the sticking at the glass transition of DGEBA, the expected thermal contraction is pinned and internal stresses within the DGEBA sample will develop. From our experience we can remove these residual stresses in different ways:

(a) On very fast cooling of the sample far below the glass transition temperature we can induce cracks at the BK7/DGEBA interface and additionally within the DGEBA volume. According to our experience, these cracks completely release the residual stresses. BS measurements can only be performed if the volume crack density is not high, in order to give the laser light a chance to pass through the sample without internal refraction. This technical problem can always be solved by repeating the quenching trials.

(b) On very slow cooling there is a good chance that the DGEBA sample as a whole delaminates at $T_g$ from the BK7 window. The change of the slope of the sound frequency curves clearly indicates whether this delamination has taken place or not.
Figure 2. A gCR representation of the Brillouin data of figure 1. In the lower part of the figure the corresponding residuals are given. The effect of internal stresses is indicated by the arrows. The residuals indicate the accuracy of the data with respect to the model given by equation (3).

(c) If this delamination does not take place immediately at $T_g$, the slope of the sound frequency curves decreases in comparison to those of the equilibrium glassy branches. According to our experience, this hindered delamination takes place at intermediate fast cooling rates. Under these conditions the delamination takes place spontaneously somewhere in the glassy state. It should be stressed that we have no deterministic influence on the delamination process; in particular, we do not control the surface properties of the BK7 windows. Figure 1 shows the effect of delamination during moderate cooling and of the accompanying release of residual stresses for the longitudinal as well as for the transverse polarized phonon mode within the glassy state.

A clear hint as regards the action of internal stress due to the non-slipping situation at the DGEBA/BK7 interface is obtained from the methodical deviations of the statistical residuals of the measured data (circles in figure 2) from equation (3). In fact, the residual stress yields negative deviations from the gCR.

4. Equilibrium and non-equilibrium behaviour

On extremely slow cooling the formation of internal stress can be widely avoided by the above-mentioned delamination process at $T_g$. The results of such a measurement are shown in figure 3 and the related gCR is depicted in figure 4. As expected, both sound frequency versus temperature curves show a kink at about the intrinsic glass transition temperature of 243 K [6]. According to the small residuals shown in figure 3 both frequency curves behave piecewise linearly in the temperature interval investigated. Figure 4 demonstrates that the frequency data measured under
Figure 3. $f_L$ and $f_T$ for DGEBA as a function of temperature $T$. The straight lines are fitted curves. The residuals in the lower part demonstrate the agreement of the data with a piecewise straight-line model.

these conditions obey perfectly the gCR with $A = (2.66 \pm 0.07) \times 10^6$ and $B = 2.98 \pm 0.2$. Thus, within the margin of error, $B = 3$ holds ($c_{11} = 3c_{44}$ would be the classic Cauchy relation). The residuals show that the linearity of the data representation is almost perfect and that the TGT is completely hidden in this parametrical representation.

If we tentatively accept a kinetic interpretation (see e.g. [9]) of the TGT, we have to assume that $T_g$ could be shifted to lower temperatures, provided the cooling process was slowed down further. In that case the sound frequencies of the phonon branches of the glassy state would be higher in comparison to those measured at higher cooling rates. Thus, the ‘high-temperature part’ of the gCR would be stretched. Provided that the relation between the slopes of the frequency curves $(\partial_T(f_L(T < T_g))/\partial_T(f_T(T < T_g))) = 3$ remained invariant under this slower cooling procedure, the same gCR would result as for faster cooling. In other words, the gCR would remain a linear function but would become ambiguous in its physical meaning. Consequently, the gCR would turn out to be rather insensitive to deviations from equilibrium. If, on the other hand, the slopes of the frequency curves of the new hypothetical glassy state changed their relation in comparison to the previous one, the gCR would become violated for the new glassy state. Keeping in mind that within this approach the more slowly cooled sample is closer to equilibrium, such a behaviour seems not to be very likely. In order to clarify this point we have tested whether the apparent instability of the gCR with respect to equilibrium is a general feature of the gCR. For this purpose we have used quenching procedures in order to create forced non-equilibrium glassy states. During this fast cooling we are not able to record Brillouin data simultaneously. Therefore we cannot say anything about the evolution of the elastic behaviour during the fast cooling process. As will be shown below, we were able, however, to measure the sound frequency evolution at intermediate cooling rates.
Figure 4. A gCR representation of the Brillouin data of figure 3. In the lower part of the figure the corresponding residuals are given. The residuals indicate the perfect compatibility of the measured data with the gCR represented by the straight line.

Figure 5 shows $v_T^2 = v_L^2 (v_T)$ representations as derived from measured Brillouin data obtained from different quenching procedures. As mentioned above, these quenching procedures can be controlled only roughly. Figures 5(a), (b) and (d) show Brillouin data measured during heating of the quenched sample from the glassy to the liquid state. Figure 5(c) shows the Cauchy representation of Brillouin data measured on intermediate fast cooling of the DGEBA sample. The open circles in figure 5 give the measured data; the straight lines give the gCR. From figure 5 it is evident that non-equilibrium glassy states produced by quenching lead to a violation of the gCR. In contrast to the stressed samples, the quenched samples of figure 5 show significant positive deviations from the gCR. Moreover, these deviations are able to relax during the heating procedure towards the gCR even if the samples are still deeply in the glassy state (figures 5(a), (b)).

Figure 5(c) demonstrates how the violation of the gCR takes place if the BS measurements are performed during intermediate fast cooling (about 3 K h$^{-1}$). It is evident that even if the sample is moderately cooled into the glassy state, significant positive deviations from the gCR can be produced. Representative for all temperature-dependent measurements after quenching, we show in figure 6 the temperature dependence of the longitudinal and shear sound velocities corresponding to the Cauchy representation of figure 5(b). As is seen from figure 6 we have spread the plot axis for both phonon frequency curves such that the longitudinal and transverse phonon branches almost coincide within the liquid phase. In the glassy phase the slope of the transverse mode becomes smaller in comparison to that of the longitudinal mode. According to the related frequency–temperature plots the different ageing processes presented by figures 5(a), (b) and (d) end up on the ‘equilibrium glass branches’ of the longitudinal and transverse polarized modes.
Figure 5. gCR representations for different quenching and heating cycles. The residuals indicate the deviations of the measured data from the gCR represented by the straight lines. Parts (a), (b), (d) represent Brillouin data measured on heating after different quenching procedures. Part (c) shows a cooling run using an intermediate fast cooling. For further explanations, see the text.

The low-temperature branch of figure 5(a) merges at $T - T_g = 16$ K. The slope of this branch amounts to about $m = 4$ in comparison to $B = 3$. The low-temperature branch of figure 5(b) even merges at $T - T_g = 21$ K. The slope of this branch amounts to $m = 4.8$. In figure 5(d) the onset of the deviation from the gCR occurs only at the TGT. It is worth noting that the large slopes of the Cauchy representations within the glassy state are due to

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Figure 6. Sound frequency curves $f_L(T)$ and $f_T(T)$ of the longitudinal and transverse polarized phonon modes as a function of temperature $T$ measured after quenching to about 77 K.

a lag of the high-frequency clamped shear stiffness behind the longitudinal stiffness. No excess of the slope ($m > B = 3$) was ever observed above $T_g$.

The heating runs which led to figures 5(a), (b) and (d) were performed with different accumulation times for the Brillouin spectra, implying different but badly specified effective heating rates. However, the average heating rates are estimated to be lower than 3 K h$^{-1}$. It seems that smaller effective heating runs favour an earlier meeting of the measured data with the $gCR$, but there seem to exist other factors which influence the ageing process.

5. Aspects of ageing

In order to elucidate the observed significant ageing behaviour within the glassy state of DGEBA, we have performed specific cooling and heating cycles within the glassy state of this material. After having quenched the sample to 120 K we performed a first heating experiment (run 1) in figure 7, which we stopped at 195 K. This is more than 40 K below $T_g$. The slope of the low-temperature branch is $m = 4.15$ in comparison to $B = 3$ in the liquid state. Subsequently we cooled the sample again to 120 K and then heated the sample to $T_g - 10$ K. The slope of the low-temperature branch had then decreased to $m = 3.92$. A further cooling to 137 K and a subsequent heating to ambient temperature yields for the glassy state a slope of $m = 3.48$. These results confirm the above-anticipated ageing process within the glassy state. This thermal relaxation process converges in all our experiments versus a unique glassy state, which we have reported recently on the basis of time domain Brillouin measurements [6] as the equilibrium glassy state of DGEBA. We definitely found no relaxations towards the liquid state which exceed the sound frequency data within the temperature representation of the equilibrium glassy state. This result is based on at least 15 different quenching cycles. According to [6] the structural $\alpha$-relaxation shows a cut-off at the intrinsic glass transition temperature $T_g = 243$ K with $T_0 \simeq T_g - 25$ where
Figure 7. gCR representations for different consecutive quenching and heating cycles. All measurements were performed on heating. The straight line represents the gCR for the equilibrium state. For further explanations, see the text.

$T_0$ is the Vogel–Fulcher–Tamann (VFT) temperature. It is therefore likely that the dynamical processes involved in the ageing process have little in common with the structural $\alpha$-relaxation process. We do not want to compare time constants found in the gCR representation during ageing in the glassy state with time constants reported for the hypersonic velocities in the liquid state [6]. There is no hint of a direct connection between the two processes. The gCR representation is sensitive to small differences in the behaviour of the longitudinal and the transverse elastic constants. This could involve different timescales to the relaxation behaviour of elastic moduli versus temperature. It is well known that the timescales related to translational and rotational diffusion differ significantly when approaching $T_g$ [10].

In favour of this view are the facts that

(i) the temporal evolution of the ageing process is much faster than that of the $\alpha$-process above, but very close to that of the glass transition, and that

(ii) we found ageing well below the VFT temperature $T_0$.

As a consequence, the liquid state of DGEBA seems to be a forbidden state below $T_g$ and the glassy state which is approached during the thermal ageing appears as an ‘equilibrium glassy state’ of DGEBA for $T < T_g$. Of course, we cannot exclude the possibility of existence of another state that is lower lying energetically, but if it exists, this state must be separated from our highly preferential glassy state by such high potential barriers that eventually lower-lying states are virtually inaccessible. In order to be observable in a Brillouin experiment, the molecular non-equilibrium excitations have to couple to the transverse and longitudinal polarized sound modes and their relaxation times have to be in a time window accessible to this kind of experiment. It is worth noting that, if this coupling is weak, or if the relaxation times are too fast or
too slow in comparison to our experimental timescale. BS is ineffective as regards the testing of ageing phenomena. In addition, even if we believe that the features found for DGEBA are representative for other materials, it should be stressed that our existing database is too small for verifying the universality of our results.

6. Conclusions

Inspection of the high-frequency clamped moduli of differently quenched DGEBA samples has shown that moderate degrees of quenching are sufficient to violate the gCR. Thus, the gCR can be used as a sensitive probe for detecting deviations from the internal equilibrium of the elastic constants. Inspecting deviations from the generalized Cauchy behaviour we were able to detect significant ageing processes within the quenched glassy states. Nevertheless, there is no proof yet for the reverse statement, that no deviation from gCR implies a rigorous absence of any non-equilibrium behaviour. But in fact the elastic properties measured during these ageing processes converge towards a unique glassy state which was recently demonstrated to be an equilibrium glassy state.

Consequently, the gCR turns out to be a versatile probe for mechanical non-equilibrium situations. Investigations of materials other than DGEBA are necessary in order to verify the degree of universality of the interpretations derived from the results found for DGEBA.

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