Cauchy-like relation between elastic constants in amorphous materials

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It is well known that in addition to the longitudinal modulus, viscoelastic liquids show a shear stiffness at sufficiently high probe frequencies due to structural relaxations. For probe frequencies that are large compared to the structural relaxation frequency, the measured elastic longitudinal and shear moduli become so-called clamped properties (c_{11}^∞ and c_{44}^∞, respectively). During freezing or polymerization of amorphous liquids, these clamped moduli behave in a strongly nonlinear fashion as a function of temperature or polymerization time. Based on Brillouin spectroscopy data we will show that there exists a linear relation between c_{11}^∞ and c_{44}^∞ over a large temperature or polymerization time range. Surprisingly, the parameters of this linear relation between the elastic moduli vary only little for different materials. Implications for the nonlinear elastic behavior at the glass transition will be discussed on the basis of mode Grüneisen parameters.

The elastic behavior of simple isotropic liquids is fully described by the static longitudinal modulus c_{11}^s (Voigt notation), the corresponding shear modulus c_{44}^s is zero.[1] In contrast, isotropic solids show in addition to the longitudinal modulus c_{11} the shear modulus c_{44}. Between the components of the related elastic stiffness tensor the isotropy relation[2,3] $c_{11} = c_{12} + 2c_{44}$ holds. If in addition the atoms interact through a central potential, the Cauchy identity $c_{12} = c_{44}$ may hold and together with the isotropy relation one obtains a reduction to only one independent elastic constant[4] $c_{11} = 3c_{44}$. However, this Cauchy identity for the isotropic state is usually not fulfilled.[5] In applying the concept of an elastic property to a fluid Zwanzig *et al.*[6] have calculated a generalized Cauchy relation $c_{11}^\infty = 3c_{44}^\infty + f(T,p)$ for an isotropic liquid, which contains an additive term $f(T,p)$ depending on temperature and thermodynamic pressure. c_{11}^∞ and c_{44}^∞ are the so-called *frequency clamped* elastic moduli which will be found in liquids only at sufficiently high frequencies.[6–9] For argon this additive term $f(T,p)$ was estimated to be rather small.[6] A Cauchy-like relation at the transition from the liquid to the solid state was recently reported by Yamura *et al.*[10] Based on Brillouin spectroscopy these authors have reported a relation between $c_{11}^\infty(t)$ and $c_{44}^\infty(t)$ for a curing epoxy resin. Despite a significant nonlinear behavior of the elastic constants as a function of curing time t they found a linear relationship (LR),

$$c_{11}^\infty(t) = A + B c_{44}^\infty(t), \tag{1}$$

between the clamped elastic moduli throughout the polymerization process where A and B are material constants that are independent of t. The question arises whether LR (1) is a special property valid only for the resin investigated by Yamura *et al.*[10] or whether it represents a more general rule for a solid or solidlike amorphous state. Therefore, the main emphasis of this paper is the verification and generalization of LR (1) and the specification of the parameters A and B. Based on Brillouin investigations we will show that LR (1) is not restricted to chemical freezing but also applies to the

thermal freezing of liquids. We will show that the dimensionless parameter B appears to be three as predicted by the generalized Cauchy relation.[6] Parameter A essentially remains constant during the chemical or thermal solidification process. Furthermore, we will investigate the implications of LR (1) for the anharmonic elastic properties around the thermal glass transition.

In the following we restrict our discussion to the elastic data obtained within the high frequency limit (i.e., measuring frequency clamped moduli) and therefore omit the superscript ∞. Of course we are interested in LR (1) but since we usually have no access to the mass density we approximate LR (1) by

$$v_1^2[v_4^2(x)] = \tilde{A} + B v_4^2(x), \tag{2}$$

with $\tilde{A} = A/\rho(x)$ and $v_i^2(x) = c_{ii}(x)/\rho(x)$, where $v_i(x)$ with $i = 1,4$ are the hypersound velocities of the longitudinal and transverse polarized modes, respectively. x denotes either temperature T or curing time t. Usually $\rho(x)$ varies only little with x, therefore LR (2) is expected to be a good approximation of LR (1).

All data reported in the following experiments were measured with a modified six-pass Tandem Brillouin spectrometer (Sandercock Scientific Instruments) having a high contrast and a typical finesse of 100. Using 90A-scattering geometry[11,12] we detected the longitudinal (L) and transverse (T) polarized sound modes simultaneously (Fig. 1). With an optical wavelength of 532 nm and a fixed acoustic wavelength[11] of 376 nm, we measured in the GHz regime. An influence of acoustic relaxation processes on the presented data could be almost excluded by the absence of excessive acoustic attenuation and by the fact that the optoacoustic dispersion function[12] and the optical refractive index had approximately the same values. It is worth noting that significant acoustic relaxation processes would cause the breakdown of LR (2). More experimental details are to be published elsewhere. In order to verify LR (2) it was essen-
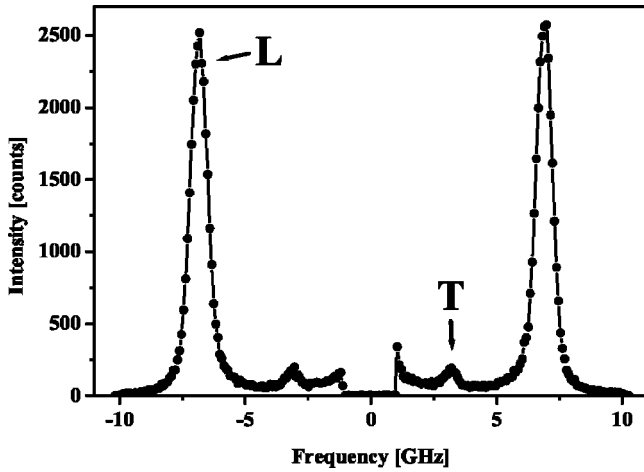
FIG. 1. Brillouin spectrum of PA6-3-T at 387 K in the glassy state. The central line (Rayleigh peak) is suppressed.

TABLE I. Parameters $\tilde{A}$ and B of LR (2), for error details see text. First four substances were measured in a curing experiment, last four substances were measured temperature dependent.

Substance	$\tilde{A}\left[10^6 \frac{m^2}{s^2}\right]$	B
DGEBA:DETA 100:10	2.60 ± 0.05	2.96 ± 0.03
DGEBA:DETA 100:14 I	2.83 ± 0.09	2.81 ± 0.05
DGEBA:DETA 100:14 II	2.87 ± 0.03	2.82 ± 0.02
DGEBA:DETA 100:18	2.61 ± 0.04	2.96 ± 0.02
DGEBA ($T_g = 247$ K)	2.66 ± 0.07	2.98 ± 0.05
PA6-3-T ($T_g = 414$ K)	2.43 ± 0.09	2.96 ± 0.06
I1 ($T_g = 280$ K)	1.90 ± 0.02	3.18 ± 0.02
$(LiCl)_{0.14}(H_2O)_{0.86}$ ($T_g = 138$ K)	3.88 ± 0.02	3.15 ± 0.06
Mean $\pm$ standard error of mean	2.72 ± 0.2	2.98 ± 0.05

tial to select substances with elastic moduli that strongly vary with temperature or curing time.

We performed four Brillouin measurements on curing epoxy systems consisting of diglycidylether of bisphenol A (DGEBA) as prepolymer and diethylenetriamine (DETA) as hardener with three different mixing ratios. As an experimental result Fig. 2(a) shows hypersound velocities as a function of curing time for the mixing ratio of 100 mass parts DGEBA and 14 mass parts DETA as a representative example.

As expected, the temporal evolution of $v_1(t)$ and $v_4(t)$ is nonlinear. The squared sound velocities derived from the Brillouin data of each of the four mixtures can be described by LR (2) with parameters $\tilde{A}$ and B (Table I).

It is clear that for this material the parameters $\tilde{A}$ and B are not only significant for the initial and the final state ("chemically frozen" network) but also for all intermediate chemical states, even for the nonequilibrium states involved in the curing process. We have also tested the statistic compatibility

of the measured data with our model function LR (2). In order to check the apparent linearity of our $v_1^2 = v_1^2(v_4^2)$ representations we give in Fig. 3 a representative example including the deviations between the measured data and the related fit values. The statistical distribution of the residuals around zero confirms the applicability of the linear fit.

In order to prove the validity of LR's (1) and (2) for isotropic materials other than curing epoxy resins we extended our investigations to organic and inorganic canonical glass formers. Figure 2(b) shows related sound velocities of
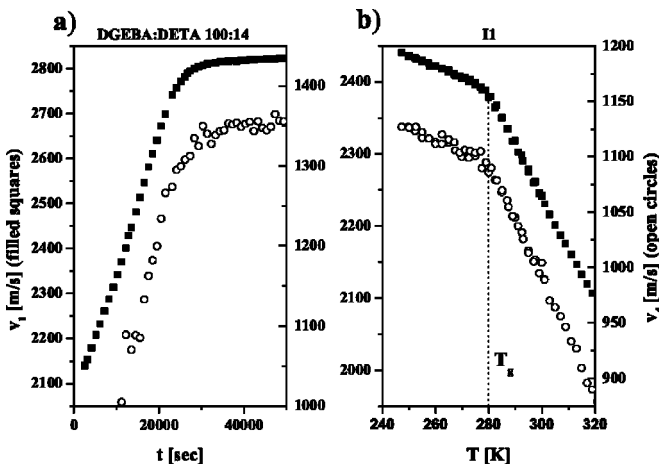

FIG. 2. Evolution of the longitudinal (filled squares) and transverse (open circles) hypersound velocities of (a) DGEBA-DETA (100:14) mixture versus curing time. (b) I1 below and above the glass transition at $T_g = 280$ K.
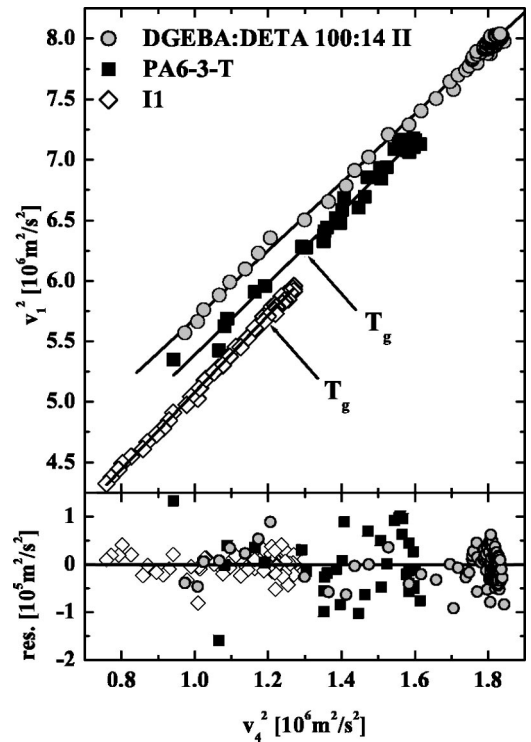

FIG. 3. Linear fits of the squared hypersound velocities of a curing epoxy resin DGEBA:DETA 100:14 II and of a temperature-dependent investigation of PA6-3-T and I1 (upper part). The residuals of the respective fit show the validity of LR (2) (lower part).

the longitudinal and the transverse polarized hypersonic modes $v_1(T)$ and $v_4(T)$ in the vicinity of the thermal glass transition of the oligomer I1 (tertiary-butyl-4-[1-(4-benzyloxyphenyl)-1-methylethyl]-phenyl-iso-phthalate, denoted as compound 11 by Krüger *et al.*[13]). Although the $v_1(T)$ and $v_4(T)$ curves both show a clear kink at the thermal glass transition temperature T_g the squared sound velocities follow LR (2) (Fig. 3) for the liquid as well as for the glassy state. Further studies on chemically rather different freezing liquids such as DGEBA, poly-trimethyl-hexamethylen-terephthalamid (PA6-3-T), and an aquaeous solution of 14 mol % LiCl suggest a broad applicability of the relation LR (2) between the clamped squared sound velocities v_1^2 and v_4^2 of isotropic materials (Table I). Since the thermal glass transition temperature of PA6-3T is almost within the center of the measured $v_4^2(T)$ interval this material is a good candidate to test the simultaneous validity of LR (2) for the liquid and for the glassy state (Fig. 3). The statistic reliability of the linear fit with respect to the measured data is obvious, the distribution of the residuals around zero confirm the validity of LR (2) for this material for temperatures above T_g as well as below T_g with same parameters $\tilde{A}$ and B. As a consequence, the thermal glass transition temperature is completely hidden in the LR (2) representation.

The standard errors of $\tilde{A}$ and B obtained by a linear least-squares fit are below 2%. The maximum change of the mass density either during polymerization or during thermal freezing is in total less than 5% in our experiments. This as well as the following systematic influences on the Brillouin-frequencies may lead to a slight bending of the $v_1 = v_1(v_4)$ curves especially at small sound velocities: (i) continuous polymerization during data accumulation of a spectrum, (ii) weak skewed transverse phonon lines due to the interference with the wings of strong Rayleigh lines, and (iii) the onset of acoustically relevant relaxations at short curing times, etc. Therefore the fit parameters might be slightly biased but the deviation of our estimations from the unbiased parameters are expected to be below 10%. A closer look at Table I shows that all the materials investigated in this study follow LR (2) with the values of B closely grouped together. Taking into account the above-mentioned maximum error interval of $\pm 10\%$ we find that according to Table I all the individual B data have a nonzero overlap of their error intervals. Especially $B = 3$, appearing in the generalized Cauchy relation given by Zwanzig *et al.*[6] is within the intersection of these error intervals. Thus, within the margin of errors we take $B = 3$ as a reliable estimate for all materials investigated so far. Furthermore the standard error of the mean value for B (Table I) is consistent with this assumption. $\tilde{A}$ is much more specific for the systems investigated in this study but in any case $A \neq 0$ demonstrates the clear incompatibility of the Cauchy identity. Setting $B = 3$ as a fixed parameter in the fit procedure, the $\tilde{A}$ values change little and the squared error sums remain almost constant. Under these conditions $\tilde{A}$ can be determined by measuring only one single pair of v_1, v_4 values which, of course, can be done in an experimentally comfortable temperature/time regime. Since the Brillouin scattering cross section for transverse phonons in isotropic

materials is often extremely small it may happen that measuring v_4 can be quite demanding and time consuming. In this case LR (2) can be very helpful in order to get estimates of $v_4(x)$ on the base of measured $v_1(x)$.

The validity of LR (1) for the relationship between $c_{44}(x)$ and c_{11} ($x = t$ or T) yields a relationship between the derivatives of the elastic constants,

$$\partial^n c_{11}/\partial x^n = B \partial^n c_{44}/\partial x^n, \qquad (3)$$

provided the derivative of the order $n(\geqslant 1)$ exists. Expanding c_{11} and c_{44} in a Taylor series up to the order of N, Eq. (3) together with the assumed universality $B = 3$ implies the reduction of the total number of expansion coefficients necessary to describe the temperature/time dependence of $c_{11}(x)$ and $c_{44}(x)$ from $2N$ to $N + 1$. In the case $x = T$ the expansion to first order reflects the thermal anharmonicity of the related sound mode. In order to examine this aspect we discuss the behavior of mode Grüneisen parameters in the vicinity of the thermal glass transition of canonical glass formers. The significant role of acoustic anharmonicity in terms of mode Grüneisen parameters (MGP) was shown for polyvinylacetate, polymethylmethacrylate, and polystyrene by a jump[14,15] in the MGP at T_g, which in turn reflects a significant change of the related elastic potential during the freezing process. According to Brody *et al.*[16] the temperature dependence of the elastic moduli around T_g can be formally taken into account by introducing MGP's,

$$\gamma_i[f_i^{\vec{q}}(T), \rho(T)] = -\frac{d \ln[f_i^{\vec{q}}(T)]}{d \ln[\rho(T)]} = \frac{\rho(T_g)[df_i^{\vec{q}}(T)/dT]}{f(T_g)[d\rho(T)/dT]}, \quad (4)$$

where $i = 1,4$ is the polarization (longitudinal and transverse, respectively), $\vec{q}$, $f^{i,\vec{q}}(T)$ are wave vector (omitted in the following) and frequency of the acoustic mode, T is the temperature, and $\rho(T)$ is the mass density of the sample. Using Eq. (4), the following expansions for the temperature dependencies of the elastic stiffness coefficients can be given:

$$c_{ii}(T) = c_{ii}(T_g)[1 - \alpha^{l,g}(1 + 2\gamma_i^{l,g})(T - T_g)], \qquad (5)$$

where α^l and α^g are the volume expansion coefficients of the liquid ($T > T_g$) and the glassy state ($T < T_g$), respectively. By introducing the following short notations: $k^{l,g} = 2c_{11}(T_g)/(1 + 2\gamma_4^{l,g})$ and $\Delta\gamma_{4-1}^{l,g} = \gamma_4^{l,g} - \gamma_1^{l,g}$ (each for liquid and glassy phase) and $\Delta\gamma_{1,4}^{l-g} = \gamma_{1,4}^l - \gamma_{1,4}^g$ (each for longitudinal and transverse polarized mode) and combining Eqs. (4) and (5) we obtain the following relationship that yields the parameters A and B:

$$c_{11}^{l,g} = \underbrace{k^{l,g}\Delta\gamma_{4-1}^{l,g}}_{=A} + \underbrace{\left(\frac{c_{11}(T_g)}{c_{44}(T_g)} - \frac{k^{l,g}\Delta\gamma_{4-1}^{l,g}}{c_{44}(T_g)}\right)}_{=B} c_{44}^{l,g}. \qquad (6)$$

Equation (6) clearly shows that the experimental observation $A > 0$ implies for both the liquid and the glassy state that the MGP's of the transverse polarized sound modes exceed those of the longitudinal ones. Moreover, Eq. (6) approaches the

Cauchy identity ($A \rightarrow 0$) in as much the difference $\Delta \gamma_{4-1}^{l,g}$ between the longitudinal and transverse MGP's vanishes. In other words, the Cauchy identity only holds true if the influence of the elastic anharmonicities are similar for the longitudinal and transverse acoustic modes. A further result that emerges directly from the fact that LR (1) holds true below and above T_g with same parameters A and B, concerns the ratio $\Delta \gamma_{4-1}^{l} / \Delta \gamma_{4-1}^{g}$ of the differences of the MGP's within the liquid and the glassy phase in relation to the ratio of the absolute MGP's $\gamma_4^{l,g}$ and $\gamma_1^{l,g}$ of each phase,

$$\frac{\Delta \gamma_{4-1}^{l}}{\Delta \gamma_{4-1}^{g}} = \frac{1 + 2\gamma_4^{l}}{1 + 2\gamma_4^{g}} = \frac{1 + 2\gamma_1^{l}}{1 + 2\gamma_1^{g}}. \qquad (7)$$

The magnitude of the ratio (7) does not depend on the phase for which it is measured. A similar relation exists for the ratio between the differences $\Delta \gamma_1^{l-g} / \Delta \gamma_4^{l-g}$ of the MGP's within each phase,

$$\frac{\Delta \gamma_1^{l-g}}{\Delta \gamma_4^{l-g}} = \frac{1 + 2\gamma_1^{g}}{1 + 2\gamma_4^{g}} = \frac{1 + 2\gamma_1^{l}}{1 + 2\gamma_4^{l}}. \qquad (8)$$

For ideal glass formers the l term on the right-hand side of Eq. (8) is an equilibrium quantity that is nonzero. This means, that the ratio of the jumps of the MGP's at T_g is determined by equilibrium properties according to Eq. (8). Thus, LR (1) imposes strict conditions on the anharmonic acoustic properties of the glassy phase via Eqs. (6)–(8), if those of the liquid phase are given (and vice versa).

To give numerical values we estimated the density of PA6-3-T, $\rho(T_g) = 1080$ kg/m^3 by using the density at ambient temperature[17] $\rho = 1120$ kg/m^3 and typical volume expansion coefficients for such polymers as can be found in any textbook of polymer physics. Using $\alpha^g \approx 3 \times 10^{-4}$ and $\alpha^l \approx 5 \times 10^{-4}$ as typical values for the glassy and liquid state, respectively, one can furthermore estimate the Grüneisenparameters [Eq. (4)] $\gamma_1^g = 3.3, \gamma_4^g = 4.8$ and $\gamma_1^l = 5.5, \gamma_4^l = 9.6$. The same approximation gives elastic moduli and parameter A of LR (1) to be $c_{11}(T_g) = 6.5$ GPa, $c_{44}(T_g) = 1.3$ GPa, and $A = 2.6$ GPa. Since the density of all materials investigated in this study is near 1000 kg/m^3 all values for $\tilde{A}$ given in Table I can be multiplied by a factor of 1000 to obtain a reasonable approximation for A as used in LR (1).

In summary, we have experimentally found the following

(i) There exists a linear transformation between the clamped shear and longitudinal elastic stiffness coefficients of polymerizing or freezing viscous liquids, which is reminiscent of a Cauchy-like relation for the isotropic solid state.

(ii) The parameter B corresponds to that of the Cauchy identity of the isotropic state.

(iii) For a given material the additive parameter A does neither depend on temperature nor on the degree of chemical reaction in the case of curing epoxies, thus even strong changes of the chemical morphology do not alter this parameter.

(iv) The proposed Cauchy-like relation does not only concern the relationship between the linear elastic constants, but also the acoustic mode Grüneisen parameters describing nonlinear elastic properties of the isotropic state. Although the longitudinal and the transverse mode Grüneisen parameters behave discontinuously at the thermal glass transition these discontinuities are again strictly related to each other. If the difference between the mode Grüneisen parameters vanishes the additive parameter A disappears yielding the Cauchy identity.

(v) The proposed Cauchy-like condition can be used to calculate the temperature dependence and/or time dependence of the shear modulus c_{44} on the basis of pure c_{11} data combined with only one single c_{44}-data point. This feature can be used to predict c_{44} data in cases where they are hard to measure, or can simply reduce the amount of experimental work.

The range of validity of the Cauchy-like relation is still not clear but under investigation. Theoretical concepts of a generalized Cauchy relation for liquids and amorphous solids as well as further empirical data may help to understand especially the role of the additive parameter A.

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