

Generalized Cauchy Relation for Elasticity of Amorphous Material

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The transition from a simple liquid into the amorphous solid state is accompanied by the appearance of a shear modulus in addition to the longitudinal modulus. Based on Brillouin spectroscopy we will show that this apparent increase of the number of independent elastic coefficients remains virtual because a linear relationship between the elastic moduli reduces the number of independent elastic constants to the number of one again. This linear relationship is a generalization of the well known Cauchy relation which usually only fits under special restrictions. The scope of validity of this linear relation will be discussed empirically on the base of Brillouin spectroscopy results of quite different material.

The static elastic behavior of isotropic liquids can be described by a single stiffness constant c_{11} (Voigt notation). Isotropic solids (e.g. glasses) additionally have a shear stiffness which can be described by c_{44} . The non-vanishing elastic constant c_{12} is determined by the isotropy condition $c_{12} = c_{11} - 2c_{44}$. As known from solid state physics, in the case of local central forces between the atoms further symmetry relations, the so called Cauchy Relations, may be applied. They lead to a further reduction of the number of independent elastic constants which describe the material. Combining the isotropy condition and the Cauchy Relation $c_{12} = c_{44}$ for isotropic solids yields the Cauchy Relation

$$c_{11} = 3 \cdot c_{44}. \quad (1)$$

Nevertheless, as reported in literature (e.g. [1]), the Cauchy Relation is usually not fulfilled. Brillouin Light Scattering (BLS) is able to detect the sound velocity v of the longitudinal and transverse polarized sound modes simultaneously, provided the spectrometer has a sufficiently high contrast. If the density ρ of the material is known, the elastic constants $c_{11} = \rho v_{long}^2$ and $c_{44} = \rho v_{trans}^2$ can be calculated. Therefore the ratio of c_{11} and c_{44} can be determined from one single Brillouin spectrum. Another special feature of the high probe frequency of BLS is the possibility to measure *dynamically clamped* sound velocities even in the liquid state. In general, the elastic and viscous properties (η) of liquids are frequency dependent [2, 3]:

$$c_{nn}^*(\omega) = c_{nn}^s + i\omega\eta_{nn}^*(\omega), \eta_{nn}^*(\omega) = \frac{(c_{nn}^\infty - c_{nn}^s)\tau_n}{1 + i\omega\tau_n} \quad (2)$$

where $f = \omega/2\pi$ is the probe frequency, $n = 1, 4$, c_{nn}^∞ are the so-called frequency clamped elastic moduli and τ is a characteristic relaxation time for the liquid. But, since the Brillouin peak frequencies are extremely high, we always measure c_{nn}^∞ (a solid-like property [4]) even far above the thermal glass transition T_g and therefore omit the superscript ∞ in the following. We were using a modified 6-pass Tandem Brillouin spectrometer (Sandercock Scientific Instruments) having a high contrast and a typical finesse of 100. With a Laser wavelength of 532 nm and the benefits of the 90A scattering geometry we measured at a fixed acoustic wavelength of 376 nm in the GHz frequency regime [5]. We performed Brillouin measurements on organic and inorganic canonical glass-formers which reach the solid state by thermal freezing. To test the Cauchy Relation (1) we take sound velocities from the (isotropic, glassy) solid state and calculate the ratio of c_{11} and c_{44} . As can be seen in table I, the Cauchy Relation obviously fails for all materials.

Substance	$\frac{c_{11}}{c_{44}}$	$A/\rho[10^6 \frac{m^2}{s^2}]$	B
DGEBA	4.7	2.66	2.98
PA6-3-T	4.5	2.43	2.96
I1	4.6	2.03	3.06
(LiCl) _{0.14} (H ₂ O) _{0.86}	4.3	3.88	3.15
Epoxy Resin	4.4	2.87	2.82

TABLE I: The following canonical glass former were measured temperature dependent: pure prepolymer DGEBA ($T_g = 247$ K), PA6-3T ($T_g = 414$ K, poly-trimethyl-hexamethyleneterephthalamid), oligomer I1 ($T_g = 279$ K, tert.-butyl-4-[1-(4-benzyloxyphenyl)-1-methylethyl]-phenyl-iso-phthalate) and an aqueous solution of 14 mol% LiCl ($T_g = 138$ K). The epoxy resin (see text below) was measured in a curing experiment. Parameter A and B were obtained by least square fits of (3) to the measured data.

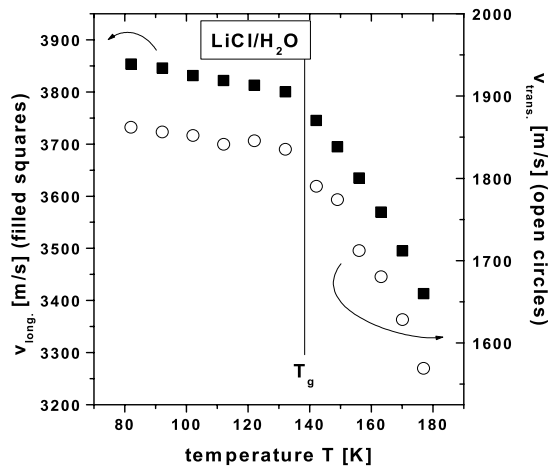


FIG. 1: longitudinal (filled squares) and transverse (open circles) hypersound velocities of LiCl below and above the glass transition at $T_g=138$ K.

Since the Cauchy Relation (1) is not fulfilled, we looked for the behavior of c_{11} as a function of c_{44} . This requires a possibility to vary both elastic constants significantly by means of a certain physical treatment of the material. As an example for all glass former we show sound velocity data of $LiCl/H_2O$ as a function of temperature in fig. 1. The kink of the sound velocity curves at the thermal glass transition $T_g = 138$ K can clearly be seen. Nevertheless, as can be seen in figure 2, c_{11} plotted as a function of c_{44} does not

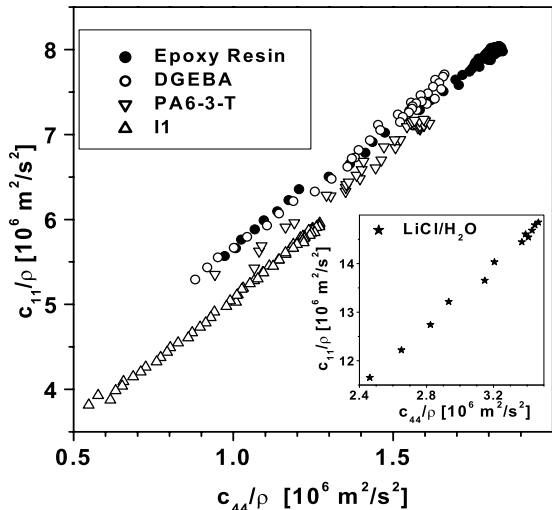


FIG. 2: Parametric plot of the squared hypersound velocities of several systems either during polymerization and vulcanisation (curing of epoxy resin) or around the thermal glass transition (DGEBA, PA6-3-T and I1). The insert shows the respective plot for $(\text{LiCl})_{0.14}(\text{H}_2\text{O})_{0.86}$ around its thermal glass transition. The corresponding parameters A and B are listed in table I.

show any kink but only a simple linear relation

$$c_{11}(t) = A + Bc_{44}(t). \quad (3)$$

Results of least square fits of (3) to the data in fig. 2 are given in table I.

Several conclusions can be drawn from both the experimental data given in fig. 2 and table I and the mathematical form of the linear relation (3): i.) The thermal glass transition separates two regimes with different elastic properties (Fig. 1). This separation indicated by the remarkable kink at T_g is completely hidden in the parametric plot Fig. 2. In both regimes, the same parameters A and B are valid. Therefore the ratio of the slopes of the dynamically clamped moduli c_{11} and c_{44} equals B in both the glassy state and the fluid. ii.) The validity of eq. (3) with constant parameters A and B has been shown for the vitrification of a variety of quite different inorganic and organic glass formers. Astonishingly, the parameters do not vary much for a wide range of chemically different materials (Table I). iii.) The parameter $B \approx 3$ (Table I) coincides with the coefficient of the classical Cauchy Relation (1), but $A > 0$ deviates from (1). Interpreting the linear relation (3) as a generalized Cauchy relation with specific temperature- and time-independent parameters

A and B for one special system or even a large class of amorphous materials, three important conclusions emerge: iv.) (3) does not only concern the linear elasticity but also non-linear elasticity (higher derivatives) [4]. v.) (3) implies that instead of two, only one elastic coefficient is sufficient to describe the elastic properties of a solid or solid-like amorphous material. vi.) On the practical side, (3) makes it possible to measure only one elastic coefficient and to calculate the remaining. As an example for this aspect we discuss the curing process of an epoxy resin, which again is

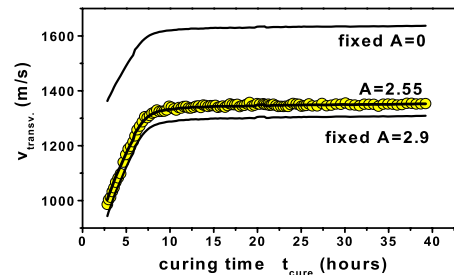


FIG. 3: Transverse (circles) hypersound velocities of epoxy resin vs. curing time at room temperature. The epoxy system is consisting of diglycidylether of bisphenol A (DGEBA) as prepolymer and diethylenetriamine (DETA) as hardener which forms an isotropic chemical network. The lines represent calculated shear sound velocities based on the longitudinal sound velocity under assumption of $B = 3$ and $A = 0$, $A = 2.55$ and $A = 2.9$

a process which transforms a liquid into an isotropic solid. Though the material goes through several different and non-equilibrium chemical states, the linear relation (3) holds (see fig. 2, table I), which broadens the empirical scope of validity. Since the scattering cross section for the transverse polarized sound mode is often very small, it may be difficult to measure the shear elasticity. In this case one precise measurement of longitudinal and transverse polarized sound wave velocities and the assuming $B = 3$ gives a good approximation for the shear elasticity. This is shown in fig. 3 where the longitudinal sound velocity (which can be easily and precisely measured) was used to calculate the sound velocity of the shear wave. Furthermore it can be seen in fig. 3 that the classical Cauchy Relation ($A = 0$ in (3)) clearly fails.

In summary we showed that an extension of the classical Cauchy relation can be applied to several isotropic materials. Up to now, no satisfying theory for this generalization of the Cauchy relation is known. Therefore the physical role of parameters A and B is still to be clarified.

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