

The generalized Cauchy relation: a probe for local structure in materials with isotropic symmetry

R. Bactavatchalou^{1,2,3}, P. Alnot², J. Baller³, M. Kolle¹, U. Müller¹, M. Philipp^{1,3}, W. Possart¹, D. Rouxel², R. Sanctuary³, A. Tschöpe¹, Ch. Vergnat¹, B. Wetzel⁴ and J. K. Krüger¹

Laboratoire Européen de Recherche Universitaire Saarland- Lorraine- Luxembourg at

Universität des Saarlandes¹, Université Henri Poincaré, Nancy I², Université du Luxembourg³, Institut für Verbundwerkstoffe TU Kaiserslautern 67663 Kaiserslautern

E.mail: r.bactavatchalou@mx.uni-saarland.de

Abstract. The elastic properties of the isotropic state of condensed matter are given by the elastic constants c_{11} and c_{44} . In the liquid state the static shear stiffness c_{44} vanishes whereas at sufficient high probe frequencies a dynamic shear stiffness may appear. In that latter case the question about the existence of a Cauchy relation appears. It will be shown that a pure Cauchy relation can appear only under special conditions which are rarely fulfilled. For all investigated materials, including ceramics, liquids and glasses, a linear relation between c_{11} and c_{44} called generalized Cauchy relation is observed, which, surprisingly, follows a linear transformation.

Introduction

The number of independent elastic constants of isotropic solids is by symmetry reduced to the number of two [9]. In Voigt notation these elastic constants are the longitudinal modulus c_{11} and the shear modulus c_{44} . For crystals, so-called Cauchy relations (CR) may be valid which reduce the number of independent elastic constants given by symmetry [1, 2]. In cubic Sodium chloride the CR $c_{12} = c_{44}$ is observed which reduces for this crystal the number of independent elastic constants from three to two without forcing isotropy.

For isotropic solids like glasses or nanoceramics the existence of a CR is not expected to be found because the prerequisites needed for the existence of CR (s. below) are not fulfilled. As a matter of fact, instead of a pure CR a generalized CR (gCR) is observed for all isotropic materials studied so far. This gCR is equivalent to a linear transformation between c_{11} and c_{44} . This holds true even for liquids, provided the measurements are performed at sufficiently high probe frequencies [6]. In that case so called frequency-clamped longitudinal and shear stiffnesses are measured. The current paper tries to elucidate the physical background of the appearance of the gCR.

Experimental

1.1. Nano-compacted CeO₂

This material consists of compacted nano-crystallites of Cerium Oxide (CeO₂). The symmetry axes of the CeO₂ grain are oriented at random so that the global symmetry is isotropic. The grains themselves have cubic symmetry. Using the X-ray method of Warren and Averbach the average grain diameter was estimated to be $d=26\text{nm}$. The mass density is $\rho=7300\text{ kg/m}^3$. The porosity is less 1%.

1.2. The reactants: DGEBA and DETA

The reactants for the epoxy (s. below) are **diglycidyl ether of bisphenol A** (DGEBA) of commercial grade (DER 331 from DOW Plastics) and **diethylene Triamine** (DETA from Bayer). DETA remains at the temperatures of interest a liquid of low viscosity. At ambient temperature DGEBA is a super cooled liquid which usually crystallizes only ($T_m=315\text{K}$) if nucleation is forced, e.g. by the injection water droplets. As measured by Brillouin spectroscopy or by refractometry the glass transition temperature of DGEBA is $T_g=243\text{K}$.

1.3. The Brillouin technique

All data reported in the following were measured by means of Brillouin spectroscopy, which is a contact less and non-destructive inelastic light scattering method to determine hypersonic properties of matter. The measurements were performed by using a modified six-pass Tandem Brillouin spectrometer combined with the so-called 90A-scattering geometry [4]. It is the advantage of the 90A-scattering geometry that it yields an acoustic wavelength independent of the refractive index of the sample. The measurements were made using an optical wavelength of 532 nm yielding a fixed acoustic wavelength of 376 nm. Since the samples we deal with in the following have isotropic symmetry only pure longitudinal and pure transversal polarized acoustic modes appear. The frequencies of the longitudinal (L) and the transverse (T) polarized sound modes are labelled as $f_L^{\infty,90A}$ and $f_T^{\infty,90A}$. They can be measured simultaneously.

The label ∞ denotes the measurement of high frequency clamped quantities which means that all relevant relaxation frequencies ω_r are small in comparison to the probe frequency.

In this case the related sound velocities $v_L^{\infty,90A}$ and $v_T^{\infty,90A}$ can be calculated from the following relation:

$$v_{L,T}^{\infty,90A} = f_{L,T}^{\infty,90A} \cdot \frac{532\text{nm}}{\sqrt{2}}$$

Using the mass density ρ of the material under investigation, the longitudinal, c_L^{∞} , and the shear elastic, c_T^{∞} , constants can be calculated from the related sound velocities v_L^{∞} and v_T^{∞} : $c_{ii}^{\infty} = c_{L,T}^{\infty} = \rho \cdot (v_{L,T}^{\infty})^2$ with $i=1,4$ (Voigt notation) [9].

3. Results and Discussion

For crystalline solids it is well known that additional physical conditions like the so-called Cauchy relations (CR) [1,2] may reduce the number of independent elastic constants in comparison to those given by symmetry. The CR holds true only if the crystal fulfils the following prerequisites: the atoms interact only with central forces, every atom is a centre of inversion and the particle interaction must be free of anharmonicities. For cubic crystals the only Cauchy relation (cCR) which remains is

$$\text{cCR : } c_{12} = c_{44} \quad (1)$$

Consequently, the number of independent elastic constants reduces from three to two. At a first sight it is not clear whether there should exist a CR for disordered materials showing isotropic symmetry on a macroscopic scale. In order to study that question we start from the idea that the isotropic material of interest is a nanoceramic made up from nanocrystals of cubic symmetry. For the sake of simplicity we assume the condition of constant strain to be valid. An orientational average over the randomized ensemble of nanocrystals yields [3] the elastic constants of the isotropic state eq. 2a-c and the isotropy condition [9] eq.2d:

$$\langle c_{11} \rangle^{\text{iso}} = \frac{1}{5} \cdot (3 \cdot c_{11} + 2 \cdot c_{12} + 4 \cdot c_{44}) \quad (2a)$$

$$\langle c_{12} \rangle^{\text{iso}} = \frac{1}{5} \cdot (c_{11} + 4 \cdot c_{12} - 2 \cdot c_{44}) \quad (2b)$$

$$\langle c_{44} \rangle^{\text{iso}} = \frac{1}{5} \cdot (c_{11} - c_{12} + 3 \cdot c_{44}) \quad (2c)$$

$$\langle c_{11} \rangle^{\text{iso}} - \langle c_{12} \rangle^{\text{iso}} = 2 \cdot \langle c_{44} \rangle^{\text{iso}} \quad (2d)$$

If the cubic building units fulfil the cCR of eq.1 we obtain from eq.2d immediately a CR for the isotropic state:

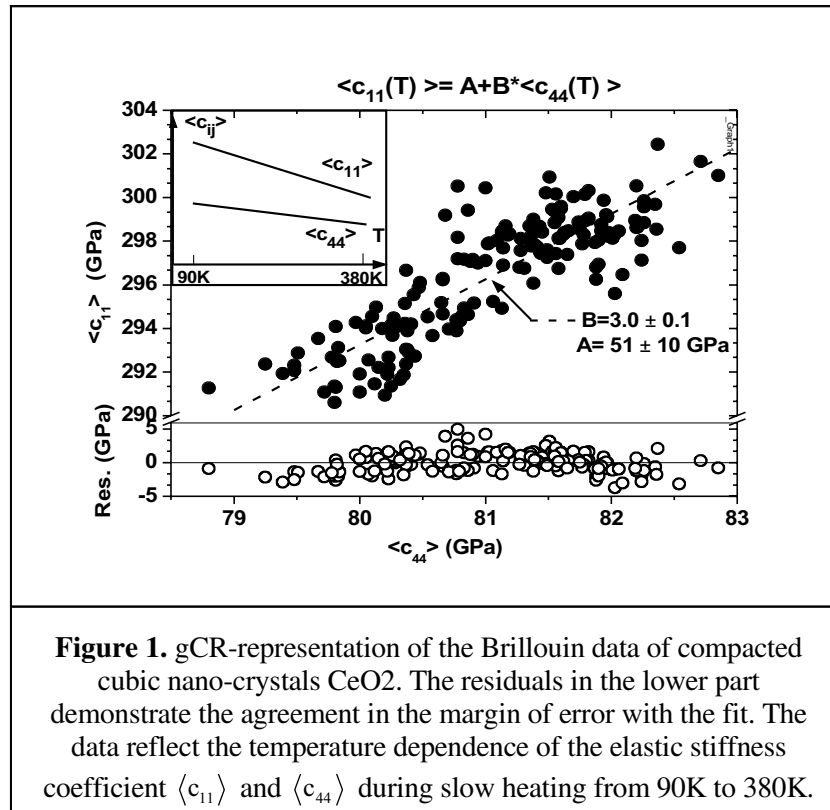
$$\text{iCR : } \langle c_{11} \rangle^{\text{iso}} = 3 \cdot \langle c_{44} \rangle^{\text{iso}} \quad (3a)$$

Eq.3a implies that, under certain additional conditions the elastic properties of isotropic solids can be described by only one elastic constant. In addition, eq.3a implies that $\langle c_{44} \rangle^{\text{iso}} = 0$ is accompanied by $\langle c_{11} \rangle^{\text{iso}} = 0$ which means that an eventual elastic instability concerns both remaining elastic constants of the macroscopic isotropic state.

If, on the other hand, the cubic nanocrystals do not fulfil the cCR the iCR (eq.1) is not expected to hold true. For the last case the compacted nanocrystalline material n-CeO₂ seems to be a good example. The macroscopic cubic crystal does not fulfil the cCR [5]. Based on these data we have calculated the elastic constants of the randomized nanocrystalline ceramic for room temperature and obtain $c_{11} - 3c_{44} = 45 \text{ GPa}$. The CR for the isotropic ceramic of n-CeO₂ obviously is violated because already the local building units, the cubic nanocrystals, do not follow a cCR. This estimation is roughly confirmed by experimental data obtained from consolidated *n-CeO₂*. The insert of Fig. 1 sketches the temperature dependence of the elastic stiffness coefficient $\langle c_{11} \rangle^{\text{iso}}$ and $\langle c_{44} \rangle^{\text{iso}}$ of this material during slow heating from 90K to 380K. In this temperature regime, *CeO₂* has no phase transition and the elastic constants behave linearly with temperature. The main part of Fig. 1 shows a plot of $\langle c_{11} \rangle^{\text{iso}}$ vs. $\langle c_{44} \rangle^{\text{iso}}$ with the temperature being a parameter. Surprisingly, the empiric data show a linear relation between c_{11} and c_{44} ,

$$\langle c_{11} \rangle^{\text{iso}} = 3 \langle c_{44} \rangle^{\text{iso}} + A \quad (2)$$

with the shift parameter $A \sim 51 \text{ GPa}$. This latter result is close to the number 45 GPa estimated above.



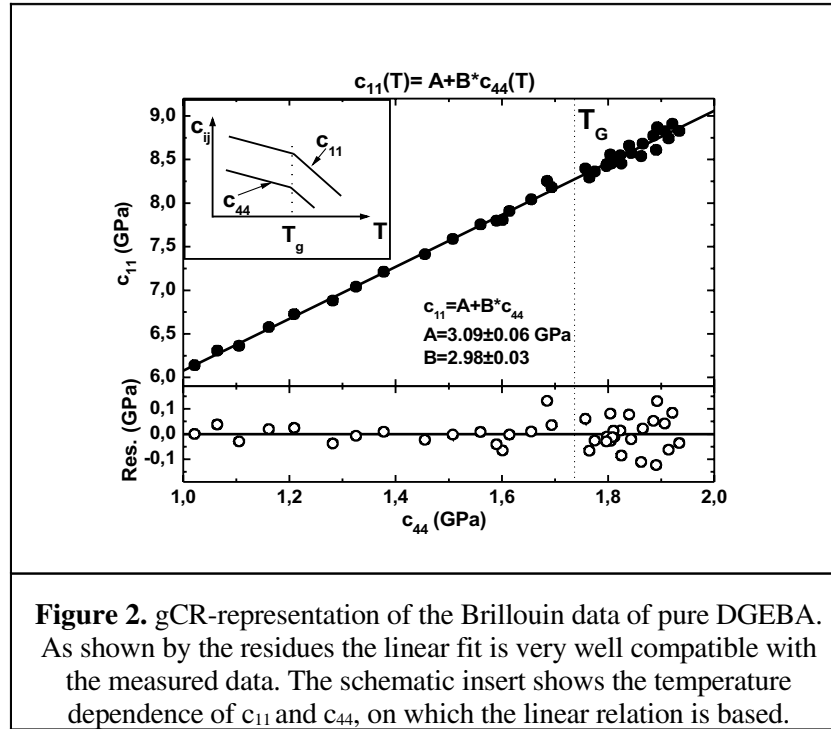
The difference between 51 and 45 may be due to imperfect grain boundaries or simply due to experimental errors. Eq.2 has also been called a generalized Cauchy relation (gCR) [6] and concerns only macroscopically isotropic materials. It should however be stressed that the theoretical estimation is based only on room temperature elastic data, whereas the experimental data cover a temperature range of 290 K. Reversing the arguments, this result signifies that the cCR of cubic CeO2 is violated to the same degree in the whole temperature range from 90 K to 380 K. We can therefore conclude that for isotropic n-ceramics with cubic symmetry of the building units there exists an identity between the difference $c_{12} - c_{44} = A$ and the shift factor A of the gCR. Since A measures for a cubic crystal the deviation from fulfilling the Cauchy relation, we can try to generalize this argument in interpreting the shift factor within the gCR as a measure of the violation of the Cauchy relations of the local structure on the length scale of typical lattice constants.

It is hard to believe that amorphous materials like polymers, viscous liquids or nanocomposites fulfil the prerequisites for a CR like local inversion symmetry or the absence of anharmonicity [7]. For liquid argon Mountain et al. [8] have predicted a generalized Cauchy relation:

$$c_{11}^{\infty} = 3 \cdot c_{44}^{\infty} + P(p, T, \dots) \quad (3)$$

where P is a parameter which depends on pressure, temperature and in materials other than argon on further parameters. The label ∞ indicates that the measurements were performed at sufficient high probe frequencies in order to establish a dynamical shear stiffness. Eq.3 resembles very much eq.2 despite the fact that A is understood as a constant and P is not. Therefore it was very interesting to test experimentally eq.3 for more complicated liquids than argon but still using high probe frequencies.

For this purpose we have studied amorphous materials of different morphologies: the viscous molecular liquid DGEBA in comparison to differently cured networks of epoxy (DGEBA/DETA).



The insert of figure 2 shows schematically the temperature dependence of the elastic constants c_{11}^{∞} and c_{44}^{∞} of the viscous liquid DGEBA. At our Brillouin frequencies both elastic constants are dynamically clamped but show a kink-like behaviour at the glass transition temperature T_g . Because neither of the three Cauchy relations mentioned above is believed to be valid for amorphous DGEBA a iCR is not expected to hold true between c_{11}^{∞} and c_{44}^{∞} . Surprisingly the longitudinal modulus c_{11}^{∞} depends linearly on the shear stiffness c_{44}^{∞} with a tangent of 3, thus it follows a gCR with a constant shift factor A , as confirmed by the residuals. The shift parameter $A \sim 3$ GPa is strongly reduced in comparison to that of n-CeO₂ but is a significant quantity compared to the absolute values of c_{11}^{∞} of DGEBA. Eq. 3 is therefore transformed to simplified generalized Cauchy relation with a constant shift factor A which henceforth will be called gCR:

$$gCR: \quad c_{11}^{(\infty)} = 3 \cdot c_{44}^{(\infty)} + A \quad (4a)$$

In comparison to the interpretation of A for CeO₂ the interpretation of the shift parameter for DGEBA is not obvious. Evidently, the symmetry argument amongst the Cauchy relations, “any molecular site is a centre of inversion symmetry”, makes no sense in an amorphous material. On the other hand even in liquids there exists some short range order for which tentatively the appearance of Cauchy relations can be discussed. In this context the shift factor A of the gCR as observed for amorphous materials eventually measures the degree of deviation from CRs compatible with the local (crystalline) order of the sample of interest. For viscous liquids, where the gCR has been verified using the temperature as a parameter, the quantity A has an additional meaning. It gives the value of $c_{11}^{\infty} > 0$ at $c_{44}^{\infty} = 0$ and defines therefore a limiting temperature T_{∞} above which the liquid can no more be “solidified” independent on the magnitude of the probe frequency. In that case c_{11}^{∞} becomes a pure compression modulus K^{∞} . The tangent of three reflects the global isotropic symmetry of the material

under investigation. It should be stressed that the evaluation of a gCR requires a suitable parameter like temperature, pressure, etc which forces the elastic moduli $c_{11}^{(\infty)}$ and $c_{44}^{(\infty)}$ to change according to these parameters. It is worth noting that for all (existing) derivatives a kind of ideal Cauchy relation holds true:

$$\frac{\partial^{(n)} c_{11}^{(\infty)}}{\partial x^{(n)}} = 3 \cdot \frac{\partial^{(n)} c_{44}^{(\infty)}}{\partial x^{(n)}} \quad n = 1, 2, \dots \quad (5)$$

with x being the parameters T, p, t, \dots . Eq.5 implies that even if $c_{11}^{(\infty)}(x)$ and $c_{44}^{(\infty)}(x)$ are strongly non-linear functions of x , the derivatives at every x has strictly to follow this relation. The gCR can be written in alternative forms:

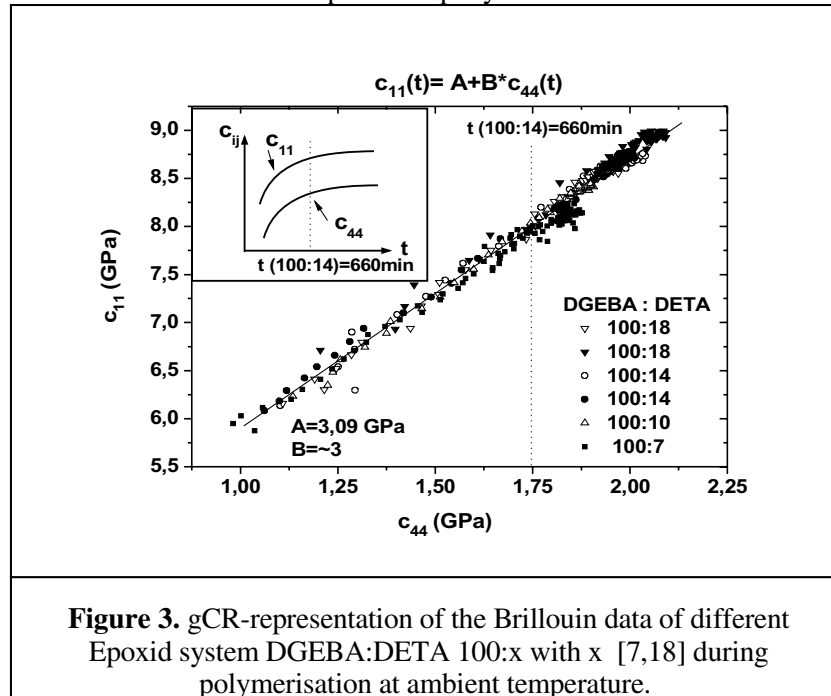
$$c_{12}^{(\infty)} = c_{44}^{(\infty)} + A \quad (4b)$$

$$\sigma^{(\infty)} = \frac{1}{2} \left(\frac{A + c_{44}^{(\infty)}}{A + 2 \cdot c_{44}^{(\infty)}} \right) \quad (4c)$$

$$K^{(\infty)} = A + \frac{5}{3} \cdot c_{44}^{(\infty)} \quad (4d)$$

where $\sigma^{(\infty)}$ is the Poisson ratio and $K^{(\infty)}$ is the compression modulus. If the shift parameter A goes to zero the Poisson ratio approaches $\sigma^{(\infty)} = 0.25$. For vanishing shear stiffness $c_{44}^{(\infty)} = 0$ the Poisson ratio $\sigma^{(\infty)}$ goes, as expected, to 0.5

Having learned, that n-CeO₂ and DGEBA both follow a gCR but with drastically different shift factors A , the question appeared how the magnitude A would be modified if the local structure of a global isotropic material is changed in a slight, in a systematic and in a continuous mode. In order to realize that idea we have mixed DGEBA with DETA at different concentrations and we have subsequently cured the mixtures in order to produce epoxy networks of different amounts of crosslink's.



During the curing process the material passes continuously across non-equilibrium states and yields strongly non-linear $c_{11}^{\infty} = c_{11}^{\infty}(t)$ - and $c_{44}^{\infty} = c_{44}^{\infty}(t)$ -curves (insert in fig. 3). From the chemical point of view the cured epoxy is still very similar to the reactants but its physical properties changes drastically.

Consequently, taking the curing time as a parameter the function $c_{11}^{\infty} = c_{11}^{\infty}(c_{44}^{\infty})$ is not believed to be a linear one, thus, at a first sight a gCR is not expected to be observed. The experimental reality (fig. 3) delivers again a gCR, which yields the surprising result that even a drastic increase of chemical crosslinks does not change the shift parameter A. In this context there is no more surprise that even for different initial concentrations of the DGEBA/DETA-mixture (100:7, 100:10, 100:14 and 100:18) the shift parameter A remains, in the margin of error, the same constant. It is worth noting that the curing process starts in the liquid phase and ends up in either a rubbery or a glassy state, depending on the concentration of DETA. However, for increasing DETA concentration the absolute values of $c_{11}^{\infty}(t)$ and $c_{44}^{\infty}(t)$ increase.

4. Conclusion

The observation that all isotropic materials studied so far follow a linear transformation is an astonishing result. Even more surprising is the fact, that a forced change of the local structure within the isotropic state does not demand different shift parameters. A possible explanation for this strange but almost universal behaviour might be as follows: Although the local structure is changed the degree of violation of the related Cauchy relation is maintained. Of course, this is a working hypothesis and further experimental and theoretical work has to be done in order to understand the physical background of the generalized Cauchy relation. The technical relevance of this relation turns out to be the reduction of necessary experimental work: Once one pair (c_{11} , c_{44}) has been measured, only the measurement of one of the elastic constants is sufficient in order to determine the other one.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft, especially by SFB277, the Ministère de la Culture, de l'Enseignement Supérieur et de la Recherche du Grand-Duché Luxembourg and the Centre National de la Recherche Scientifique, France.

References

- [1]M. Born, K. Huang *Dynamical Theory of Crystal Lattice* (Oxford: Clarendon, 1968)
- [2]G. Grimvall *Thermophysical Properties of Materials* (Selected Topics in Solid State Physics
- [3] vol 18) ed E. P. Wohlfahrt (North-Holland, Amsterdam, 1986)
- [4]S. Sengupta *Lattice Theory of elastic constants* (Trans Tech Publications Ltd. Switzerland, 1988)
- [5]J.K. Krüger *Optical Techniques to Characterize Polymer Systems* ed H. Bässler (Elsevier, Amsterdam, 1989)
- [6]A. Nakajima et al Phys Rev B, Vol 50, Number 18, 11-11-94
- [7]J.K. Krüger, J. Baller, A. le Coutre, Th. Britz, R. Peter, R. Bactavatchalou, J. Schreiber Phys.Rev. B **66** (2001) 12206
- [8]A. Sommerfeld *Vorlesungen über theoretische Physik, vol 2, Mechanik der deformierbaren Festkörper* (Harri Deutsch, Frankfurt a. M, 1989)
- [9]R. Zwanzig, R.D. Mountain J. Chem. Phys **43** (1965) 4464
- [10]Daniel Royer, Eugène Dieulesaint *Ondes élastiques dans les solides, vol I*, (Masson, Paris, 1999)