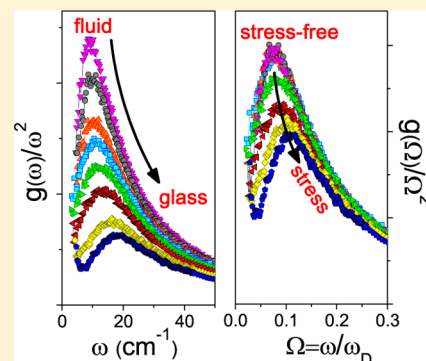


Stress-Induced Modification of the Boson Peak Scaling Behavior

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ABSTRACT: The scaling behavior of the so-called boson peak in glass-formers and its relation to the elastic properties of the system remains a source of controversy. Here the boson peak in a binary reactive mixture is measured by Raman scattering (i) on cooling the unreacted mixture well below its glass-transition temperature and (ii) after quenching to very low temperature the mixture at different times during isothermal polymerization. We find that the scaling behavior of the boson peak with the properties of the elastic medium — as measured by the Debye frequency — holds for states in which the elastic moduli follow a generalized Cauchy-like relationship, and breaks down in coincidence with the departure from this relation. A possible explanation is given in terms of the development of long-range stresses in glasses. The present study provides new insight into the boson peak behavior and is able to reconcile the apparently conflicting results presented in literature.



■ INTRODUCTION

It is now well-established that the density of vibrational states, $g(\omega)$, of amorphous materials differs in a characteristic way from that of crystalline ones. Whereas the low-frequency $g(\omega)$ in crystals is well-predicted by the Debye model, the lack of long-range periodicity is responsible for the universal presence, in amorphous materials, of an excess contribution over the Debye prediction, evidenced as a peak in the reduced $g(\omega)/\omega^2$ — the so-called boson peak (BP). This anomalous feature appears in the signal detected by several techniques, such as inelastic neutron scattering,¹ low-temperature calorimetry,² nuclear inelastic scattering,^{3,4} Mössbauer,⁵ Raman,⁶ and hyper-Raman spectroscopy.^{7,8} Despite the long-standing interest in this characteristic feature, it remains a source of controversy.^{9–16}

An approach that conveys information without invoking any model is studying the changes of these excess vibrational modes under the application of external stimuli such as temperature and pressure or by varying the sample conditions such as the volume available to the system, the thermal history, or the number of bonds between the molecules. Without exception, available results are all in agreement: the BP shifts toward higher frequencies and decreases in intensity when the sample becomes stiffer (increase in elastic constants).^{3,4,12,14–22} Recently, it has been proposed to quantitatively test the role played by the changes in the elastic properties by scaling the BP data with the Debye frequency, a quantity defined by the elastic medium. The question of whether such a scaling is able to generate a master curve of the data and hence whether the variations of $g(\omega)$ can be explained in terms of elastic medium transformations is still highly debated. So far, the accumulated

evidence is apparently in favor of opposite views: on one hand, the BP evolution in sodium silicate glasses (cooled,¹⁵ compressed,¹² hyperquenched,³ and permanently densified samples⁴) and in an epoxy-amine mixture during chemical vitrification¹⁹ is controlled by changes in the system's elasticity, according to the Debye scaling law; on the other hand, the BP variations in network-forming glasses like silica and GeO₂ upon cooling,^{14,16,23} in permanently densified silica,¹⁷ and in few polymers under pressure^{20,21} are stronger than the elastic medium transformation, and the Debye scaling does not work. In light of such controversial results, the question we face is the following: *Do these results really conflict, or rather is there a general explanation in terms of the elastic properties of the systems?*

It is well known that by changing the thermal history or the thermodynamic path to the glass transition, the obtained glasses present different elastic properties, both in terms of sound velocity and in terms of acoustic attenuation,^{24,25} because of the different amount of internal stresses that develop for the inability of the system to comply with the need to respond to the external stimuli.^{26–29} The stress-induced modification of elastic properties in the glass can influence the vibrational dynamics and may have a role in the evolution of the BP. To test this issue, starting from a reactive mixture in the fluid phase and combining the system's ability to achieve the glassy phase both by decreasing the temperature (thermal vitrification) and by increasing the number of bonds among the constituent monomers (chemical vitrification^{30–33}), we gen-

Received: June 3, 2013

Revised: October 24, 2013

Published: October 24, 2013

erate glasses with progressively different, either increasing or decreasing, residual stresses. The introduction of significant levels of internal stress in the system leads to a clear departure of the elastic moduli from the generalized Cauchy relation. Our results from Raman (RS) and Brillouin light scattering (BLS) provide evidence that the scaling of the BP with the properties of the elastic medium — as measured by the Debye frequency — breaks down when the Cauchy-like relationship starts failing and tends to be recovered when the amount of residual stress is reduced.

■ EXPERIMENTS AND DATA TREATMENT

Our system is an epoxy–amine mixture of diglycidyl ether of bisphenol A (DGEBA) and diethylenetriamine (DETA) in the 5:2 stoichiometric ratio. The two monomer types are mutually reactive and polymerize by stepwise addition with a rate of reaction strongly controlled by the temperature. At $T = 275$ K, the reaction runs out in ~ 2.5 days. The polymerization proceeds until the particles diffuse, and the unreacted sites can become close to each other, then stops when the average particle diffusion decreases to vanishing levels.^{34,35} When the reaction stops, the system has evolved spontaneously into a glassy structure (in the reacted mixture $T_g^{\text{reacted}} \approx 300$ K), while the changes of density and sound velocity have significantly increased the elastic moduli. As shown in ref 19, throughout the isothermal reaction the elastic moduli fulfill within the errors the Cauchy-like relationship, and the BP scaling law remains Debye-controlled despite the changes in the chemical structure produced by the reaction process. At any time t during the polymerization, moreover, the system — as a usual glass former with its own glass-transition temperature $T_g(t)$ — can also be forced to reach the glassy phase by decreasing the temperature. Exploiting this versatility, we have designed the following two experiments to push the system into states with different amounts of residual stress: (i) The first is a cooling experiment of the unreacted mixture from above to well below the glass transition ($T_g^{\text{unreacted}} = 231$ K). The freshly prepared mixture is progressively cooled from 275 to 80 K, and each temperature step is performed at ~ 2 K min^{-1} . Because the rate of reaction at lower temperature is further reduced, the advancement of reaction is prevented, and only the thermal vitrification route remains viable. The system is always in equilibrium above T_g , while the chosen cooling rate is fast enough to induce an *increasing* amount of unrelaxed stress in the glassy structure when the temperature is decreased below T_g .²⁸ (ii) The second is a quench experiment performed during the isothermal polymerization of the mixture. At different times, as reaction proceeds at 275 K, the partially polymerized mixture is quenched to 73 K at ~ 2 K min^{-1} and then brought back to the reaction T . The effect of an isothermal polymerization is combined with the effect of cooling to obtain at the same T glasses with higher polymerization level and *decreasing* amount of unrelaxed stress.

In all experiments, the two reagents were mixed and stirred for ~ 2 min and then transferred in the measurement cell (a cylindrical pyrex vial of inner diameter 10 mm). Raman spectra were acquired in the frequency range 3–1700 cm^{-1} , using a Jobin Yvon U1000 in the HV and VV polarization geometries, where V and H indicate the polarization perpendicular and parallel to the scattering plane. At temperatures lower than ~ 220 K, the subtraction of a luminescence background was needed to restore the symmetry of the Stokes and anti-Stokes intensities after reduction by $[n(\omega) + 1]\omega$, where $n(\omega) + 1$ is

the Bose population factor. The reduced spectra were then normalized to the intensity of the molecular vibration peaks at high frequency ($\omega > 600$ cm^{-1}). The depolarization ratio, $\rho(\omega) = I_{\text{HV}}(\omega)/I_{\text{VV}}(\omega)$, has the constant value 0.75 ± 0.02 in the frequency range 5–100 cm^{-1} , independent of temperature and consistent with the value 0.77 ± 0.03 that we measured during the polymerization process. The depolarized Raman spectra $I_{\text{HV}}(\omega)$ have been used to analyze the BP behavior. The low-frequency Raman spectrum consists of two main contributions, the vibrational part $I_{\text{BP}}(\omega)$ related to the BP and the quasielastic component $I_{\text{QES}}(\omega)$ usually assigned to fast relaxational processes. To isolate the vibrational part of the spectrum, $I_{\text{QES}}(\omega)$ has been described with a Lorentzian tail³⁶ and then subtracted. The remaining contribution $I_{\text{BP}}(\omega)$, however, does not directly represent the vibrational density of states $g(\omega)$. The problem of deriving from the Raman intensity a quantity proportional to $g(\omega)$ can be treated along a theoretical or a phenomenological approach. Theoretical treatments have led to contrasting types of relationship between $I_{\text{BP}}(\omega)$ and $g(\omega)$. In one case, $I_{\text{BP}}(\omega)$ is directly proportional to the vibrational density of states, according to^{37–39}

$$I_{\text{BP}}(\omega) = C(\omega) \frac{n(\omega) + 1}{\omega} g(\omega) \quad (1)$$

This expression is formally similar to that valid for the one-phonon incoherent neutron scattering spectrum, which differs only by the light-to-vibration (Raman) coupling coefficient $C(\omega)$. Another treatment predicts instead that $g(\omega)$ contributes to the shape of the Raman spectrum via the convolution of the Pockels-constant correlation functions with the strain susceptibilities;⁴⁰ therefore, the Raman intensity is not proportional to the vibrational density of states. More simply, in the phenomenological approach used here, $C(\omega)$ is defined as the Raman scattering intensity divided by the incoherent inelastic neutron scattering intensity, the latter being directly linked to $g(\omega)$. If $C(\omega)$ is known, then a quantity proportional to $g(\omega)$ can be directly obtained from the Raman signal. It is worth noting that in this approach eq 1 does *not* represent the theoretical relationship between $I_{\text{BP}}(\omega)$ and $g(\omega)$ but is only an *effective* relation. In the past, considerable effort has been invested in determining $C(\omega)$ from comparing Raman with neutron scattering data, searching for a general behavior. In the BP frequency region, $C(\omega)$ turns out to be reasonably approximated by a linear frequency dependence for all investigated systems.^{6,41–44} Therefore, as in ref 19, we have used $C(\omega) \propto \omega$ and divided $I_{\text{BP}}(\omega)$ by $[n(\omega) + 1]\omega^2$ to obtain from the Raman spectra a quantity that approximates the reduced density of vibrational states in the BP region. We denote this quantity $g_{\text{R}}(\omega)/\omega^2$. Moreover, in our treatment, as it has been shown for several glasses,^{6,23} we assume that $C(\omega)$ does not change appreciably with T , neither during reaction. As we will discuss later, neglecting such variations or assuming a slightly different $C(\omega)$ frequency dependence in the BP region has no appreciable effect on the conclusions of this work.

Brillouin spectra were acquired in the 90°-scattering geometry using a Sandercock-type 3 + 3-pass tandem Fabry–Pérot interferometer, with $\lambda = 532$ nm and no selection of the polarization for the scattered light (VU). This configuration allows to detect both longitudinal acoustic modes, which scatter light without change of polarization, and transverse acoustic modes, which scatter light with change of polarization. The corresponding sound velocities have been calculated as $v_{\text{L,T}} =$

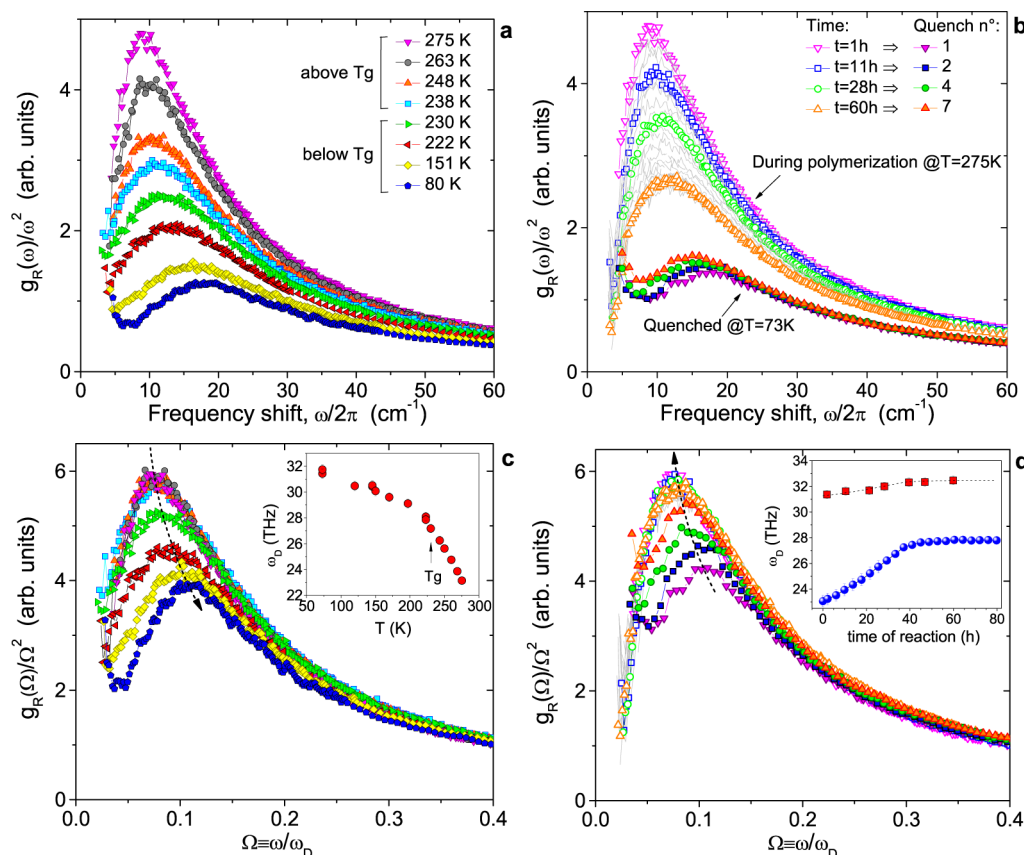


Figure 1. (a) Reduced density of vibrational states from Raman spectra, $g_R(\omega)/\omega^2$, for the unreacted DGEBA–DETA 5:2 mixture at different temperatures as indicated in the legend. (b) $g_R(\omega)/\omega^2$ for the DGEBA–DETA 5:2 mixture at different reaction times during the isothermal polymerization at 275 K (data from ref 19 — gray lines and open symbols) and after quenching at 73 K some partially polymerized states (solid symbols), as indicated in the legend (other intermediate quenches not shown). (c) Reduced density of vibrational states after rescaling by the Debye frequency ω_D . Symbols are the same as in panel a. Inset: ω_D as function of the temperature. (d) Reduced density of vibrational states after rescaling by the Debye frequency ω_D . Symbols are the same as in panel b. Inset: ω_D as function of the reaction time during the isothermal polymerization at 275 K (●) and after quenching at 73 K seven partially polymerized states (■).

$\nu_{L,T}\lambda/(2n \sin \theta/2)$, where $\nu_{L,T}$ are the frequencies of the acoustic modes, n is the refractive index of the sample, and θ is the scattering angle. The resulting values have been processed along with the results of previous BLS and inelastic X-ray scattering (IXS) experiments¹⁹ to obtain the longitudinal and transverse sound velocities in the high-frequency, solid-like limit. (Details are given in the Appendix.)

RESULTS

Figure 1a shows the obtained $g_R(\omega)/\omega^2$ for the unreacted mixture in a wide temperature range, above and below the glass transition. The BP evolution is clearly visible: as the temperature decreases, the BP shifts toward higher frequencies and decreases in intensity. The change is of $\sim 100\%$ in frequency position and $\sim 400\%$ in height when T decreases from 275 to 80 K.

Figure 1b shows the same quantity, $g_R(\omega)/\omega^2$, measured during the polymerization at 275 K, and after quenching at 73 K the sample at different extents of polymerization. On increasing the number of covalent bonds under constant T and P the system changes from liquid to glass, and the BP shows qualitatively similar changes to those observed on cooling the unreacted mixture. However, the BP evolution of the quenched states reveals a nontrivial behavior. In fact, each quench produces, as expected, an additional moving of the BP position

toward higher frequencies and a significant decrease in height, but this effect is not of the same amount at different extents of polymerization. Indeed, the first quench, performed after 1 h of reaction, doubles the frequency of the BP maximum and reduces its intensity by ~ 3.5 times; the last quench, performed on the fully polymerized mixture after 60 h of reaction, increases the frequency of the BP maximum by $\sim 30\%$ and reduces its intensity by ~ 1.6 times. As a result, the BP measured at 73 K at increasing extents of polymerization shifts to lower frequencies and increases in height, clearly in contrast with the evolution that would be expected in *equilibrium* at fixed T . In the following, we will consider these variations of the BP in relation to the transformation of the elastic medium.

To quantify the elastic medium transformation, we calculate the variations of the Debye frequency:

$$\omega_D = (6\pi^2 \rho N_A N_F / M)^{1/3} \langle v \rangle \quad (2)$$

where N_A is Avogadro's number, N_F is the average number of atoms per molecule in the sample, M is the average molar weight, and ρ is the density obtained using the procedure described in ref 45. $\langle v \rangle$ is the Debye sound velocity, defined as

$$\frac{1}{\langle v \rangle^3} = \frac{1}{3} \left[\frac{1}{(v_L^\infty)^3} + 2 \frac{1}{(v_T^\infty)^3} \right] \quad (3)$$

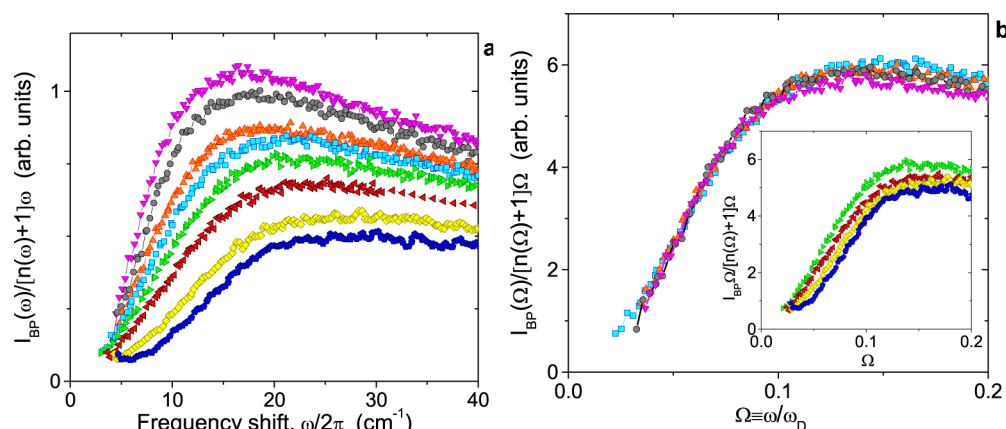


Figure 2. (a) Reduced Raman spectra, representing the quantity $C(\omega)g(\omega)/\omega^2$, during cooling of the unreacted DGEBA–DETA 5:2 mixture (same symbols as in Figure 1). (b) Reduced Raman spectra after rescaling by the Debye frequency, ω_D , for temperature above (mainframe) and below T_g (inset). Symbols are the same as in panel a.

where v_L^∞ and v_T^∞ are the solid-like longitudinal and transverse sound velocities, respectively.^{15,19} It should be emphasized that when the system undergoes a vitrification process, whether physical or chemical, the sound velocities become viscoelastic properties and acquire an intrinsic frequency dependence. While an IXS experiment, performed in the terahertz frequency region, always probes v_L^∞ , the sound velocities measured by BLS in the gigahertz frequency region are, in the fluid phase, still affected by viscoelastic effects and must be processed adequately to obtain v_L^∞ and v_T^∞ . (See the details in the Appendix.) Using the density data and the proper values of sound velocities, we calculate the Debye frequencies ω_D reported in the inset of Figure 1c,d.

Figure 1c,d shows the evolution of the reduced density of vibrational states corrected for the elastic medium transformation, that is, rescaled in Debye frequency units. It appears to be a more complex behavior than that reported so far in the literature, including regions of Debye scaling and regions of non-Debye scaling of the BP. In particular: (i) In the cooling experiment, the corrections for the properties of the elastic medium completely remove the differences in the BP at temperatures above T_g . As T decreases below T_g , the Debye scaling for the BP breaks down. The influence of temperature becomes stronger than the transformation of the elastic continuum, and specifically, the *rescaled* spectra progressively move to higher frequency and decrease in intensity (see the arrow in Figure 1c), thus indicating an actual progressive loss of vibrational states compared with the system at equilibrium. (ii) In the quench experiment, the Debye-scaling properties that characterize both the liquid and the glassy phase of the isothermal polymerization get lost. Again, the BP in Debye units stays higher in frequency but lower in intensity compared with the master curve at equilibrium, confirming a deficit of vibrational states. However, it should be noted that in this case the *rescaled* spectra have an opposite trend (see the arrow in Figure 1d): they move to lower frequency and increase in intensity, suggesting an eventual match with the master curve generated during polymerization.

A comment should be made concerning the effect of our approximations for the Raman coupling coefficient $C(\omega)$ on these results. To determine whether these approximations affect in a significant way the observed scaling behavior of the BP, we directly examine the scaling properties of the Raman signal divided by $[n(\omega) + 1]\omega$, the so-called reduced Raman

spectra (Figure 2a). These spectra represent the net quantity $C(\omega)g(\omega)/\omega^2$. In Figure 2b, we scale with the Debye frequency the reduced Raman spectra obtained in the cooling experiment. Compared with Figure 1b, we see that in the relevant frequency window they exhibit the same scaling behavior as $g_R(\omega)/\omega^2$, crossing from a Debye (mainframe) to a non-Debye scaling (inset). The same good agreement is found in the quench experiment. We conclude that the scaling properties of the BP are reasonably well-reproduced by $g_R(\omega)/\omega^2$, independently from details of the $C(\omega)$ frequency dependence and its eventual variation with temperature and reaction time.

The complex scenario presented above, has to be considered in connection with the evolution of the elastic properties. In particular, we report the behavior of the real part of the longitudinal, M' , and transverse modulus, G' , measured by BLS as $M' = \rho v_L^2$ and $G' = \rho v_T^2$, where v_L and v_T are the longitudinal and transverse sound velocities at the BLS frequency. Figure 3 shows M' versus G' . It is known that the elastic properties of an *isotropic amorphous system at equilibrium* satisfy a generalized

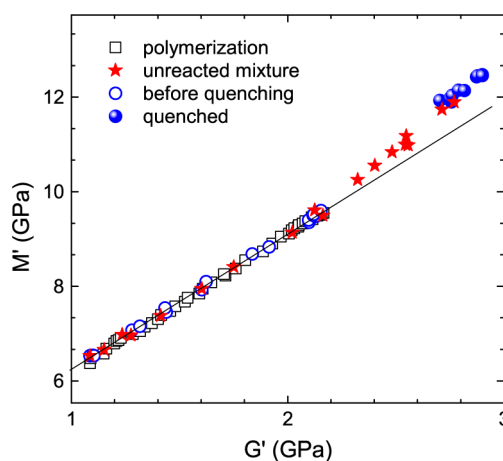


Figure 3. Real part of the longitudinal modulus M' versus real part of the transverse modulus G' of the DGEBA–DETA 5:2 mixture during the isothermal polymerization reaction at 275 K (\square),⁴⁵ under cooling the unreacted mixture (\star), and after quenching at 73 K the sample at different extents of polymerization (\bullet). Open circles represent the elastic moduli in the partially polymerized states at 275 K before quenching. Error bars are comparable to the symbol size. The solid line is the Cauchy-like relation $M' = (3.16 \pm 0.08) + (2.99 \pm 0.02)G'$.

Cauchy-like relation, $M' = A + 3G'$.^{45–47} Such relation is theoretically derived for the high-frequency elastic moduli M'_∞ and G'_∞ of any isotropic material in which particles interact by means of two-body central forces,⁴⁸ and its validity is found to extend to the apparent moduli $M'(\omega)$ and $G'(\omega)$ of viscoelastic liquids at finite frequencies.⁴⁵

We see in Figure 3 that the same Cauchy-like relation, $M' = (3.16 \pm 0.08) + (2.99 \pm 0.02)G'$, connects in our system the elastic moduli during the polymerization at 275 K as well as the moduli of the unreacted mixture for temperatures above and only slightly below T_g . Instead, a clear departure from this line occurs in the low-temperature region and in the quenched states. A suggestive correlation seems to emerge between the BP scaling behavior and the fulfillment of the Cauchy-like relation.

DISCUSSION

Our experimental data indicate a change in the elastic properties of the investigated samples that affects, on the one hand, the BP scaling and, on the other hand, the mutual relationship between the elastic moduli. In the following, we discuss a possible explanation in terms of the distribution of internal stresses in the disordered material and the development of long-range stresses in its arrested glassy phase.

As a preliminary consideration, we observe that in our experiments we study a material that vitrifies either by a physical (thermal) or by a chemical (polymerization) route. The chemical process strongly modifies from a microscopic point of view the material, implying changes in its chemical local structure,³³ but, in this case, the BP behavior can be fully explained by the elastic medium transformation, and the Cauchy-like relation is always fulfilled.¹⁹ So the reason for the observed failure of these features has to be searched in elastic modifications that occur on length scales larger than a few atoms or molecules. We also notice that local stresses developed at atomic level are always present in the disordered state due to misfits in the topological structure of the amorphous material or to locally distributed elastic constants.^{13,49–54} While internal stresses average to zero over microscopic scales in the fluid sample, a stress field over larger length scales may arise when the molecular motions slow down. This field can extend over long scales in the unrelaxed state and eventually to the entire sample in the case that appropriate annealing procedures are not adopted, as it is well-known in glass technology and it is the case in our cooling and quench experiments. It is known as well, on the basis of experimental evidence, that long-range stresses not released within an out-of-equilibrium glassy matrix not only induce altered values of the elastic moduli^{26,27} but also change the relationship between them, leading to violation of the generalized Cauchy-like relation.²⁸

The development of elastic anisotropy in the material due to unrelaxed stresses could explain the observed deviations from the Cauchy-like relationship. In fact, if isotropy is progressively lost due to a growing stress-field, then the conditions under which the validity of the Cauchy-like relation is predicted are no longer met.⁴⁸ It is worth noting that following this interpretation the length scale breaking the Cauchy-like relation as seen by our experiment, should be that of the volume probed by BLS. In fact, while it is true that microscopic stresses are always present in the disordered state, it is also true that the technique measures sound velocities averaged over the scattering volume ($\sim 10 \times 10 \times 10 \mu\text{m}$): when the probed

phonons travel in the presence of stresses which are randomly distributed with a characteristic volume much smaller than the sampled volume, the system still appears as homogeneous and isotropic on the BLS scale, and only a peak broadening normally arises; if the sampled volume is smaller than the characteristic volume for stresses, then variations in sound velocity of the probed phonons will be recorded. The Cauchy line in Figure 3 therefore characterizes, independently from the stiffening path, the states in which the system appears as isotropic over this scale. As expected, the data clearly confirm the presence of residual long-range stresses in the arrested glassy structure of the unreacted mixture and in all of the quenched states of the partially polymerized sample. In particular, the data for the unreacted mixture deviate from the Cauchy-like behavior by following a linear trend with slope higher than three and indicate that in our not-annealed sample a stress field able to cause anisotropy over the length scale probed by BLS starts to develop at a temperature not far below T_g .

The development of anisotropy in the material provides a basis to understand the failure of the Debye scaling for the BP as well. In fact, under this condition eq 3 does not properly represent the Debye sound velocity any more. This is defined, in the general case, by the average of the inverse third power of the phase velocity $v_s(\hat{k})$ in the long-wavelength limit of the three ($s = 1, 2, 3$) acoustic branches

$$\frac{1}{\langle v \rangle^3} = \frac{1}{3} \sum_s \int \frac{d\Omega}{4\pi} \frac{1}{v_s(\hat{k})^3} \quad (4)$$

which reduces to eq 3 only in the isotropic case. Therefore, when a deviation from the Cauchy-like relation is detected, the frequency obtained according to eq 2 is not the correct value that would scale the density of vibrational states in the Debye model. Indeed, the scaling of the BP does not work in the arrested glassy states of the unreacted mixture and in all quenched states of the partially polymerized sample.

Following the same reasoning, one can expect that if $\langle v \rangle$ is chosen according to eq 4, then the BP curves shown in Figure 1 will scale even in the anisotropic solid. This means that it will still be possible to find a different frequency value ω_D^* able to generate a master curve of the data. Indeed, our data from the cooling experiment are in reasonable agreement with this expectation in a wide range of temperatures below T_g , while the agreement progressively deteriorates at the lowest temperatures (Figure 4). As a possible explanation we notice that this expectation is still derived within the Debye's theory, which is based on crude approximations, whose limitations are more evident under extreme conditions. Thus, the residual deviation from the scaling performed by using ω_D^* may indicate that changes of the BP begin not to be solely given by changes of the Debye frequency.

In fact, going deeper into the analysis, it is interesting to note that when the spectra do not scale with ω_D — that is, when the representation $[g(\omega)/\omega^2]\omega_D^3$ versus ω/ω_D is no longer generating a master curve — the spectra can better be scaled on each other using different scaling factors for the BP position and intensity (Figure 5). Thus, independently from the Debye approximation and the validity of the Debye scaling, the spectral shape of the BP remains unchanged. This indicates that changes in the distribution of modes around the BP occur in a way that the scaled spectral shape remains essentially unaffected, despite the fact the system undergoes strong

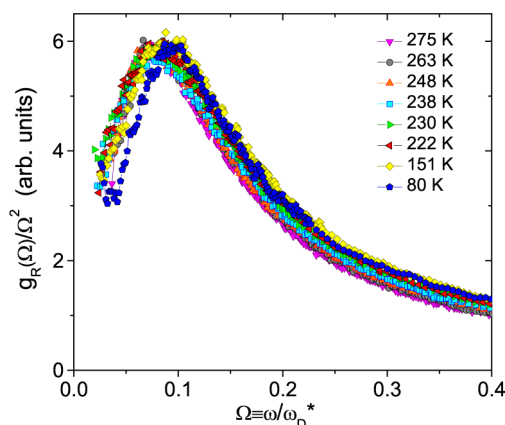


Figure 4. Reduced density of vibrational states, $g_R(\omega)/\omega^2$, for the unreacted mixture at different temperatures after rescaling by an appropriate frequency value ω_D^* . Symbols are the same as in Figure 1a. At temperature below T_g , ω_D^* is higher than the measured Debye frequency ω_D and coincident with the value ω_y shown in Figure 6

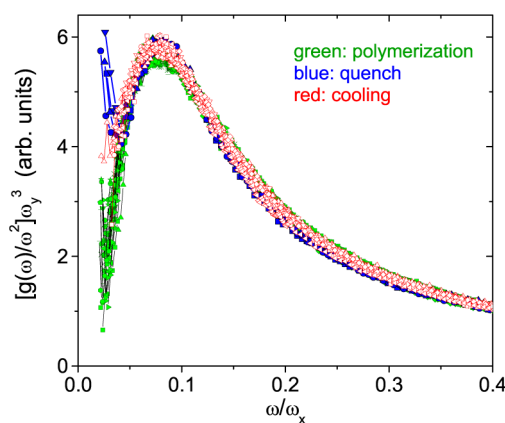


Figure 5. Master curve obtained from $g(\omega)/\omega^2$ shown in Figure 1a,b, by plotting $[g(\omega)/\omega^2]\omega_y^3$ versus ω/ω_x . The spectra refer to the DGEBA-DETA mixture at different reaction times during isothermal polymerization at 275 K (green symbols), the unreacted mixture at different temperatures (red symbols), and the mixture after quenching at 73 K some partially polymerized states (blue symbols). The spectra acquired during polymerization and at temperatures above T_g are scaled by using the measured value of the Debye frequency, that is, $\omega_x = \omega_y = \omega_D$. The spectra acquired in the quenched states and at temperatures below T_g are scaled by using appropriate factors $\omega_x \neq \omega_y \neq \omega_D$ reported in Figure 6. Notice that the BP retains the same scaled spectral shape.

changes of physical and chemical nature. Our case broadens the class of materials where invariance of the BP spectral shape has been observed^{3,4,14–17,19–21,23} and offers an example of invariance even against the formation of chemical bonds between the constituent molecules.

In the case of non-Debye scaling, by denoting with ω_x and ω_y^{-3} the factors that scale, respectively, the BP position and intensity on the master curve generated under a stress-free condition, we always find in our system $\omega_D < \omega_y < \omega_x$. This result is shown in Figure 6 for the unreacted mixture as a function of T . We remark that it is in agreement with the behavior of the BP position and intensity observed in silica as a function of T , considering that silica becomes stiffer (higher elastic moduli) when T increases.¹⁶ On the contrary, studies of BP as a function of pressure^{20,55} report an increase with P in the

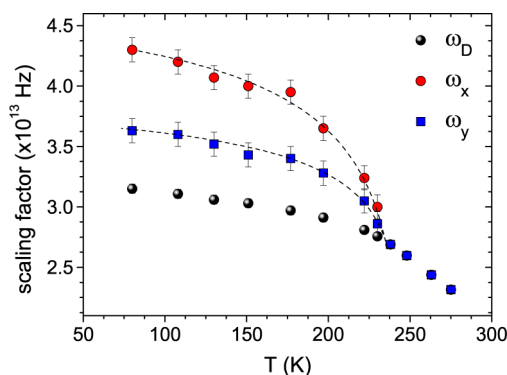


Figure 6. Debye frequency, ω_D , compared with the frequencies ω_x and ω_y used to scale $g(\omega)/\omega^2$ in Figure 5 for the unreacted mixture as a function of T . Dashed lines are only guides for the eyes.

BP intensity relative to the Debye level ($\omega_y < \omega_D$), while the BP frequency in Debye units increases ($\omega_x > \omega_D$). The difference in the intensity behavior could indicate a difference in the effect of T and P on the vibrational modes in the glass under stress, which in the first case experiences negative pressure rather than positive. However, additional experimental evidence is needed to assess the generality of this observation.

All together, our results can help provide a rationale for the apparently conflicting conclusions of previous investigations of BP scaling behavior. The key point is that existing studies are limited to glass-formers below their glass transition and hence always under a condition in which, if the sample is not properly annealed, a stress-field over long scales may have developed. However, on the basis of our results, if the amount of stress retained within the glassy structure is small, such that deviations from the Cauchy-like relationship cannot be appreciated within the experimental uncertainty, then the BP is expected to scale reasonably well with the elastic properties of the medium; otherwise, one expects that the BP scaling does not work. To test this expectation, we check the validity of the Cauchy-like relation in all of the so-far studied systems (Figure 7). Available M' and G' data for systems in which the BP evolution is not

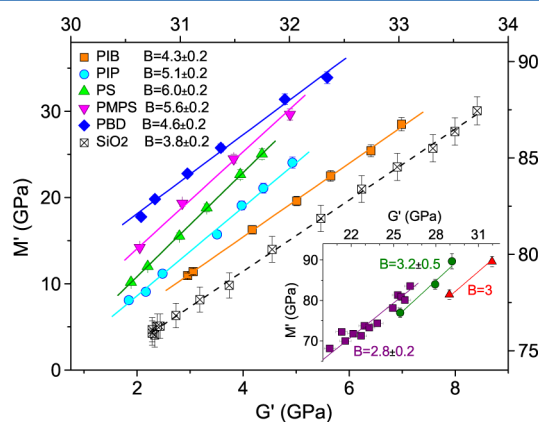


Figure 7. Longitudinal modulus M' versus transverse modulus G' of vitreous silica under cooling (square with X; data from ref 16, to be read on the right and top axes) and of five polymers under pressure (see legend; data from ref 21). For clarity, the data of PS, PMPS, and PBD are vertically shifted by +2, +6, and +9, respectively. The lines are a linear fit, $M' = A + BG'$. Inset: M' versus G' in sodium silicate glasses — cooled (■, data from ref 15), hyperquenched (▲, data from ref 3), and permanently densified (●, data from ref 4).

Debye-controlled are collected in the main panel of Figure 7, while data for systems in which the BP reasonably scales with ω_D are presented in the inset. Surprisingly, all of the data in the main panel exhibit an angular coefficient (B) significantly higher than three, suggesting the presence of long-range stresses in the investigated samples, while the data in inset are all compatible with a long-range isotropic condition ($B \approx 3$).

To this regard, the data in inset for the hyperquenched and annealed glass³ merit a comment. In the thin hyperquenched films ($\sim 100 \mu\text{m}$), the presence of microscale residual stresses is anyhow expected, but a long-range isotropic condition can be still realized if micrometric and randomly oriented anisotropic regions develop during the hyperquench process. However, the only two points available for the elastic moduli and the small difference in ω_D ($\sim 5\%$) between the two glasses being compared make this case not decisive for our test.

CONCLUSIONS

By a combination of experiments performed during polymerization and quenching of a reactive mixture, we provide evidence of a correlation existing between breakdown of the Debye scaling of the BP and violation of the Cauchy-like relationship between longitudinal and transverse elastic moduli. In the framework of such a correlation, which is corroborated by the data for all systems available, it is possible to accommodate the apparently conflicting conclusions presented in literature concerning the BP scaling behavior.

A possible interpretation is given in terms of the distribution of internal stresses in the disordered material and the development of long-range stresses in its arrested glassy phase. In particular, the development of stress-induced anisotropy over the length scale probed by our experiments is able to explain the measured deviations from the Cauchy-like relationship and the failure of the Debye scaling as well, thus providing a physical rationale for their correlation. In conclusion, when the system appears as isotropic, the elastic moduli measured by BLS follow the Cauchy-like relation, and the changes of the BP result to be solely given by the change of these moduli, which under this condition provide the correct values to be used in the calculation of the Debye frequency; when the elastic moduli deviate from the Cauchy-like relation, their value does not provide a measure of the BP changes, either because these values do not provide a true measure of the Debye frequency of the sample or because the changes of the BP are not solely given by changes of the Debye frequency. We would like to emphasize that our argumentation does not establish a connection between the length scale of the BP vibrations and the length scale of the internal stresses developed in the glass sample. Therefore, it is not in contradiction with the common idea that a few tens of atoms or molecules participate in the BP vibrations.

Moreover, independently from the validity of the Debye scaling, the BP spectra can always be scaled into a single master curve by means of two parameters, one for the frequency and one for the intensity; in the case that the elastic moduli fulfill the Cauchy-like relation, these parameters are equal and coincident with the value of the Debye frequency calculated in the isotropic approximation. Therefore, while there seem to be different scaling regimes governed by the distribution of residual stresses in the glass, the BP appears to have a characteristic shape independent from the vitrification path.

The present study encourages quantitative studies of residual stresses over different length scales in glasses and stimulates us

to investigate further their influence on BP and elastic constants.

APPENDIX: DERIVATION OF SOLID-LIKE SOUND VELOCITIES

BLS and IXS measurements as a function of time during isothermal polymerization of the DGEBA–DETA reactive mixture at 275 K were previously reported;^{19,33} in the present work, BLS measurements have been extended as a function of temperature by cooling the unreacted mixture from 275 to 80 K and after different quenches (to 73 K) of the mixture at different times of polymerization. From these experiments, we have derived the appropriate solid-like velocities v_L^∞ and v_T^∞ that are needed to calculate ω_D in all of the experimental conditions of the present study, as follows:

(i) During the isothermal polymerization at 275 K, v_L^∞ is directly measured by IXS, and v_T^∞ , which is not accessible in the IXS experiment, is obtained using the Cauchy-like relation $M' = (3.16 \pm 0.08) + (2.99 \pm 0.02)G'$ that connects the longitudinal modulus $M' = \rho v_L^2$ and the transverse modulus $G' = \rho v_T^2$ at all frequencies, with ρ the density.⁴⁵ The v_T^∞ data as a function of the polymerization time are shown in Figure 8a with a solid line.

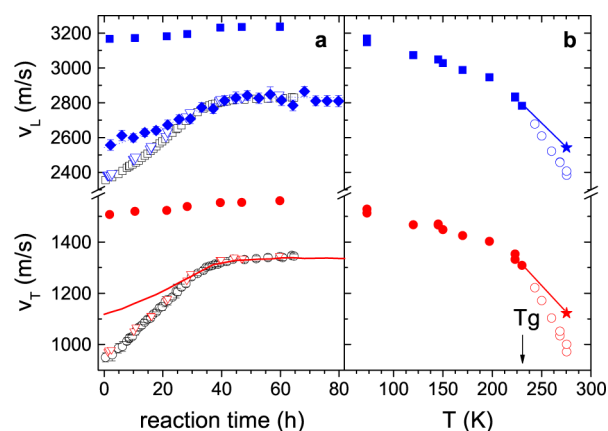


Figure 8. (a) Longitudinal and transverse (\square , \circ) sound velocity measured by BLS during isothermal polymerization at 275 K¹⁹ and after quenching at 73 K some partially polymerized states (\blacksquare , \bullet). The velocities at 275 K measured just before and after the quench procedure are indicated with triangles. The BLS values during polymerization are compared with their high-frequency values v_L^∞ (\blacklozenge) and v_T^∞ (solid line), which are obtained by IXS¹⁹ and using the Cauchy-like relation.⁴⁵ (b) Longitudinal (\square , \blacksquare) and transverse (\circ , \bullet) sound velocity measured by BLS in the unreacted mixture as a function of temperature. A star indicates the longitudinal high-frequency value v_L^∞ measured by IXS at 275 K. The solid line above is the linear interpolation of this value to the value measured by BLS at $\sim T_g$, and the solid line below is the high-frequency transverse sound velocity estimated from the longitudinal one using the Cauchy-like relation.

(ii) In the quenched states at 73 K, the system is well into the glassy phase, and BLS directly measures the solid-like elastic values of both v_L^∞ and v_T^∞ . The data are reported as solid circles and squares in Figure 8a.

(iii) For the unreacted mixture under cooling, in the temperature region below T_g , the sound velocities measured by BLS already correspond to the high-frequency values v_L^∞ and v_T^∞ (solid symbols in Figure 8b), while in the temperature region above T_g , the IXS measurement made at the beginning

of the isothermal polymerization provides the value of v_L^∞ at 275 K. (This value is marked with a star in Figure 8b). Joining this last point to the point at $T \approx T_g$ by assuming a linear dependence on temperature, as observed for the BLS data (open symbols), allows us to obtain v_L^∞ also in the viscoelastic fluid. The corresponding values of v_T^∞ are obtained from the Cauchy-like relation;⁴⁵ these results are reported in Figure 8b with a solid line.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank M. Mattarelli for the helpful discussions.

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