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SCALING BEHAVIOR OF THE RAMAN INTENSITY AND HETEROGENEOUS ELASTICITY DURING THE CHEMICAL VITRIFICATION OF AN EPOXY RESIN

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Abstract. The density of vibrational states of amorphous materials deviates from that expected from the Debye model, giving rise to a characteristic excess of states known as boson peak (BP). Despite the long-standing interest in this characteristic feature, its origin and behavior remain a source of controversy, in particular its scaling behavior and its relation to the elastic properties of the material. In this regard, the theory of elastic heterogeneity, based on the notion that the structural disorder induces spatially fluctuating local elastic moduli, offers an interesting reading key for the BP behavior. In this paper we consider the evolution of the Raman signal in the BP region, during the isothermal vitrification process of an epoxy resin induced by the progressive polymerization of the molecules in the system, and provide a critical discussion of the observed scaling behavior in the framework of the theory of heterogeneous elasticity.

1. Introduction

The boson peak. The vibrational spectrum, especially the density of states $g(\omega)$, of topologically disordered materials appears to differ in a characteristic way from that of ordered crystalline solids. Whereas the low-frequency $g(\omega)$ in periodic crystals is generally well predicted by the Debye's elasticity theory – *i.e.*, simply by counting the sound waves (phonon modes) compatible with the periodic boundary conditions one obtains the squared-frequency dependence $g(\omega) \sim \omega^2$ – the lack of long-range periodicity in amorphous materials is associated to the universal presence of an excess contribution over the Debye prediction. This shows up as a peak (typical frequency/energy scale: a few THz/meV) in the reduced density of states $g(\omega)/\omega^2$, which is called the boson peak (BP). This anomalous enhancement of vibrational modes is responsible for a number of thermodynamic anomalies in glasses at low-temperatures, like the excess in specific heat C_p over the T^3 dependence predicted by the Debye model, observed at $\sim 10-30$ K. In the same temperature range, the thermal conductivity presents a characteristic plateau. The BP is also associated to anomalous acoustic behavior at THz frequencies: the sound velocity shows a negative dispersion in the BP frequency region and there is a strong increase of the sound attenuation near the BP frequency (Monaco and Mossa 2009; Baldi *et al.* 2010, 2011). The universal presence of the BP in all disordered materials including biological matter (for example, proteins) has fascinated many researchers over the years, and has led to the belief that it is a manifestation of some sort of disorder. Notwithstanding, it has taken a long time to build a coherent picture of how disorder makes the vibrations of amorphous materials loose the simple character of plane-wave phonon modes, and of how it induces an excess of states over the Debye prediction and accounts for the associated anomalies in their propagation. This came out of a large body of investigations, including experimental, theoretical and numerical-simulation works.

It is not possible here to review the extensive literature generated by this issue. We only mention, without going into details, some of the different mechanisms that have been proposed to explain the BP and the associated anomalies: optical modes of very low frequency (Flubacher *et al.* 1959), onset of mechanical instability related to jamming (Silbert *et al.* 2005; Xu *et al.* 2007; Silbert and Silbert 2009), strongly anharmonic transitions between the local minima of the energy landscape (Lubchenko and Wolynes 2003) or crossover from a minima-dominated phase (with phonons) to a saddle-point-dominated phase (without phonons) (Grigera *et al.* 2003), localized modes associated with cohesive clusters (Duval *et al.* 1990), superstructural units (Buchenau *et al.* 1984; Carini Jr. *et al.* 2013) or locally favoured structures (Tanaka 2001), interaction of sound waves with soft-mode vibrations (Buchenau *et al.* 1991, 1992; Klinger and Kosevich 2001, 2002), vibrational instability of weakly interacting harmonic modes (Parshin *et al.* 2007), transverse vibrational modes associated with low-density defective structures (Shintani and Tanaka 2008), breakdown of the continuum approximation on the mesoscopic length scale (Wittmer *et al.* 2002; Leonforte *et al.* 2005; Leonforte *et al.* 2006; Monaco and Mossa 2009), vibrational states in the presence of spatially fluctuating elastic constants (Schirmacher *et al.* 1998; Schirmacher 2006; Schirmacher *et al.* 2007), broadening and shift of the transverse acoustic van-Hove singularity (Taraskin *et al.* 2001; Chumakov *et al.* 2011). Some of these suggestions are now out of date, others remain a matter of controversy (Chumakov *et al.* 2014), others instead are becoming part of a puzzle which is going to reassemble into an increasingly coherent picture (Marruzzo *et al.* 2013; Schirmacher *et al.* 2015). It is worth noting that beyond the aspects of difference in the mentioned explanations, a link between the BP and transverse degrees of freedom shows up as a real point of convergence.

Boson peak and elastic heterogeneity. In the recent years, inelastic scattering experiments and molecular dynamics simulations have much contributed to give insights into the nature of the high-frequency and small-scale vibrations of glasses. The development of high resolution inelastic x-ray scattering has opened the possibility to investigate with unprecedented accuracy the acoustic dynamics at THz frequencies, and has revealed that the propagation of acoustic excitations is strongly perturbed near the BP frequency, ω_{BP} (Baldi *et al.* 2010, 2011). Recent simulations of model glasses have provided clear evidence that a mechanical feature, elastic heterogeneity at the nanoscale (Duval and Mermet 1998; Yoshimoto *et al.* 2004; Tsamados *et al.* 2009; Mizuno *et al.* 2013a,b; DeGiuli *et al.* 2014), profoundly affects the main properties and even the very nature of acoustic excitations (Mizuno *et al.* 2014). More specifically, in the large length-scale limit, macroscopic elastic constants (shear, bulk and longitudinal moduli) are observed. As the length scale is reduced, heterogeneities of elastic moduli are detected on a mesoscopic length scale ξ (Tanguy 2015), the same length scale where the breakdown of both continuum mechanics (Leonforte *et al.* 2005; Leonforte *et al.* 2006) and Debye approximation (Monaco and Mossa 2009) has been demonstrated. The wave frequency corresponding to the wavelength $\lambda \sim \xi$ is very close to $\omega_{\mathrm{IR}} \sim \omega_{\mathrm{BP}}$, where ω_{IR} is the Ioffe-Regel limit, at which the mean-free path of the acoustic wave becomes equal to its wavelength, the mean-free path being a quantity inversely related to the sound attenuation. Remarkably, both the lifetime and the IR limit of the sound-like excitations have been shown to directly correlate with the width of the distributions of local elastic moduli. Altogether these results have indicated the BP frequency as an upper frequency limit of a Debye-like description of acoustic excitations in disordered systems, and have demonstrated that sound attenuation and BP are crucially related to elastic heterogeneities.

All these issues have indeed been rationalized within the mean-field theory of heterogeneous elasticity, based on the assumption that due to the structural disorder the elastic constants on a small scale may depend of the spatial location $\mathbf{r}$. In the theory as developed by Schirmacher *et al.* (2007), Marruzzo *et al.* (2013), and Schirmacher *et al.* (2015), the assumption of spatial fluctuations of G, the shear modulus, according to a Gaussian distribution leads to an expression of $g(\omega)$ that shows an excess over the Debye prediction in agreement with the BP phenomenology. The microscopic spatial fluctuations of $G(\mathbf{r})$ are transformed in the macroscopic limit into a frequency dependence of the shear modulus $G(\omega)$, which – by the dictate of causality – must acquire an imaginary part, proportional to the sound attenuation coefficient and to the inverse mean-free path. This disorder-induced mechanism of sound attenuation makes the concept of waves break down, once the mean-free path becomes comparable to the wavelength of the vibrational excitations (Ioffe-Regel limit), and the excitations become random-matrix-type states. Overall, the theory points to the conclusion that the BP arises from a steep increase of the sound attenuation at a frequency which marks the transition from wave-like excitations to disorder-dominated ones, and the excess vibrations are predominantly produced by the transverse degrees of freedom of local elasticity.

Raman scattering and elastic heterogeneity. The BP is observed in inelastic neutron and x-ray scattering experiments, for which the measured intensity is directly proportional to the vibrational density of states $g(\omega)$. A large number of studies, however, have probed the low-frequency vibrational properties of amorphous materials by using Raman scattering data, assuming a close connection between the Raman intensity, $I(\omega)$, and $g(\omega)$. Indeed, the low-frequency Raman spectra also present an anomalous behavior near the BP frequency, which shows up as a characteristic peak in the so-called reduced Raman intensity, $I^{red}(\omega) = I(\omega)/[n(\omega)+1]\omega$ with $n(\omega) = [\exp(\hbar\omega/k_{\mathrm{B}}T)-1]^{-1}$ the mean boson occupation number. This feature in the reduced Raman spectra is also inaccurately called BP, despite it differs in shape and position from the reduced density of states $g(\omega)/\omega^2$ as measured by inelastic neutron and x-ray scattering. For many years, the situation has been described by writing $I(\omega) = C(\omega)[n(\omega)+1]g(\omega)/\omega$, *i.e.*, by assuming for the Raman intensity a proportionality to the vibrational density of states, similar to that valid for incoherent neutron scattering but modified by a phenomenological frequency dependent factor $C(\omega)$, known as light-to-vibration coupling function. In principle, $C(\omega)$ can be determined by comparing Raman and neutron data. The idea behind using $C(\omega)$ is that, albeit approximately, the frequency dependence of this function might be the same for all systems. As a consequence, looking at the Raman intensity would be a way to look directly at the vibrational density of states, and then to follow the BP evolution when an external parameter (temperature, pressure or the amount of polymerization) is changed. Such a phenomenological approach, quite simple, is yet questionable due to the lack of a satisfactory theoretical basis.

A more recent theory has been able to describe the low-frequency Raman spectra of disordered materials on the same footing as their vibrational spectra, based on the assumption that the structural disorder induces not only spatially fluctuating elastic moduli, but also spatially fluctuating elasto-optic (Pockels) constants, through which the light couples to the vibrational degrees of freedom. The result of the theory is that the Raman intensity can be represented as an appropriate sum of the imaginary parts of longitudinal and transverse dynamic susceptibilities integrated up to a certain wavenumber cutoff related to the inverse correlation length of the spatially fluctuating Pockels constants (Schmid and Schirmacher 2004; Schirmacher *et al.* 2015). It is important to emphasize that $g(\omega)$ derived within the framework of heterogeneous elasticity, is also related to the dynamic susceptibilities, but the relation between the Raman intensity and $g(\omega)$ remains implicit within the theory. In particular, the relationship is not a direct proportionality, which raises doubts about the possibility to assess in a reliable manner, by using Raman scattering data, the way in which the vibrational spectrum is modified by changing an external parameter.

Heterogeneous elasticity and scaling properties of the boson peak. Great experimental effort has been devoted in the last years to measure vibrational spectra of materials in which an external parameter (temperature, pressure, density, thermal history, or number of bonds between the molecules) is changed. All results indicate that the BP shifts toward higher frequencies and decreases in intensity when the sample becomes stiffer (*i.e.*, the elastic moduli increase) (Monaco *et al.* 2006a,b; Caponi *et al.* 2007; Niss *et al.* 2007; Hong *et al.* 2008; Baldi *et al.* 2009; Caponi *et al.* 2009; Rufflè *et al.* 2010; Zanatta *et al.* 2010; Chumakov *et al.* 2011; Zanatta *et al.* 2011; Rossi *et al.* 2012). However, two different behaviors are recognized, with respect to the associated changes in the elastic properties. A number of BP data can be rationalized as an elastic-medium transformation, *i.e.*, they reflect a change in the Debye frequency ω_D (a quantity dependent on the longitudinal and transverse elastic moduli) (Monaco *et al.* 2006a,b; Baldi *et al.* 2009; Caponi *et al.* 2009, 2010; Ruta *et al.* 2010; Caponi *et al.* 2011a,b). In these cases, the modification of $g(\omega)/\omega^2$ disappears after correcting for the elastic-medium transformation: all data fall onto the same curve if replotted by scaling the frequency with the Debye frequency. Some investigations, on the other hand, reveal a deviation from this scaling law (Niss *et al.* 2007; Hong *et al.* 2008; Chumakov *et al.* 2011; Zanatta *et al.* 2011; Corezzi *et al.* 2013).

Modifications of the BP scaling behavior in disordered materials have been interpreted in terms of microscopic internal stresses, which may develop on a long-range scale in the glassy state (Corezzi *et al.* 2013). Underlying this interpretation there is the idea of a connection between the BP behavior and heterogeneities in the local elastic constants, consistent with the basis of heterogeneous-elasticity theory. Model calculations for a system with spatial fluctuations of the shear modulus have provided quantitative support (Schirmacher *et al.* 2015), suggesting an explanation in terms of changes that occur in the state of elastic disorder of the material, characterized by the parameter $\gamma \propto \langle \Delta G^2 \rangle / \langle G \rangle^2$ and the correlation length ξ of the distribution of G fluctuations. It has been argued that if the state of disorder is not changed, but just the value of the mean elastic constants or the density, then the modification of the vibrational spectrum by varying an external parameter can be described by an elastic transformation, and the Debye scaling law holds. A failure of this scaling arises from a change in the state of disorder.

In summary, the concept of elastic heterogeneity seems not only to explain the BP and the associated anomalies in disordered systems, but also to provide a key to understand its scaling behavior. With these premises, we reconsider Raman spectra measured several years ago during the isothermal polymerization of an epoxy resin (Caponi *et al.* 2009), a process that progressively transforms the initially fluid mixture into a solid glass through the formation of an increasing number of chemical bonds. The data were originally treated phenomenologically, by using the light-to-vibration coupling function $C(\omega)$ as explained in the next section, in order to derive a Raman *alter ego* of $g(\omega)$. The quantity extracted in this way, $g_{\mathrm{Raman}}(\omega)$, exhibited a clear modification by increasing the number of bonds between the molecules, and $g_{\mathrm{Raman}}(\omega)/\omega^2$ showed a profile strongly reminiscent of the BP measured by inelastic neutron and x-ray scattering. Also, all the data collapsed on a single curve when replotted taking the elastic-medium transformation into account. The aim of the present paper is to provide a physical reading of the observed Debye scaling of $g_{\mathrm{Raman}}(\omega)$ in the framework of the theory of elastic heterogeneity.

2. Results and discussion

Scaling properties of $g_{\mathrm{Raman}}(\omega)$. Caponi *et al.* (2009) measured the Raman spectra during the polymerization-induced vitrification process of an epoxy resin under isothermal condition. The quantity in the focus of the data analysis was $g_{\mathrm{Raman}}(\omega)$, obtained from the Raman intensity starting from the phenomenological relation $I(\omega) = C(\omega)[n(\omega) + 1]g(\omega)/\omega$, which introduces the function $C(\omega)$ as an invention to correct the relationship between the Raman intensity and the density of states in analogy to the relationship valid for incoherent neutron scattering. Assuming that $C(\omega)$ is approximately proportional to ω in the region of interest, with a proportionality constant $\mathscr{A}$ non-dimensionless, it results that $I(\omega)/[n(\omega)+1] \approx \mathscr{A}g(\omega)$ is a quantity that has not the physical dimensions of the density of states $g(\omega)$, but still, is numerically proportional to it, and monitors how it changes when an external parameter of the system is modified. Within this phenomenological approach, $I(\omega)/[n(\omega)+1]$ has been called $g_{\mathrm{Raman}}(\omega)$, and the variation of $g_{\mathrm{Raman}}(\omega)/\omega^2$ in place of the reduced density of states has been followed as the number of chemical bonds between the molecules increases. Figure 1(a) shows the evolution of this quantity. If changes of $g(\omega)$ only reflect a transformation in the properties of the elastic medium, as quantified by the Debye frequency, then these changes disappear upon scaling ω by the Debye frequency, *i.e.*, $g(\omega)d\omega = g(\omega/\omega_{\mathrm{D}})d(\omega/\omega_{\mathrm{D}})$ is valid for each value of ω_D. Accordingly, by setting $\Omega = \omega/\omega_{\mathrm{D}}$, the function $g(\Omega)/\Omega^2 = \omega_{\mathrm{D}}^{1mathrm3} g(\omega)/\omega^2$ is the same for each value of ω_{D}. The same scaling property should be obeyed by $g_{Raman}(\Omega)$, *i.e.*, $g_{Raman}(\Omega)/\Omega^2 = \omega_{\mathrm{D}}^3 g_{Raman}(\omega)/\omega^2$ is a universal function of Ω, which we express by saying that $g_{Raman}(\omega)/\omega^2$ scales with the factor $1/\omega_{\mathrm{D}}^3$ when the frequency is scaled by ω_{D}. The time variation of ω_{D}, calculated using THz-frequency values of the longitudinal and transverse sound velocities v_{L} and v_{T}, is reported in the inset panel of Fig. 1(b). Using these data, the main panel shows that an excellent master curve is indeed generated, and therefore, the polymerization-induced modification of $g_{\mathrm{Raman}}(\omega)$ can be rationalized as an elastic-medium transformation. Also, it is interesting to observe that the position of the

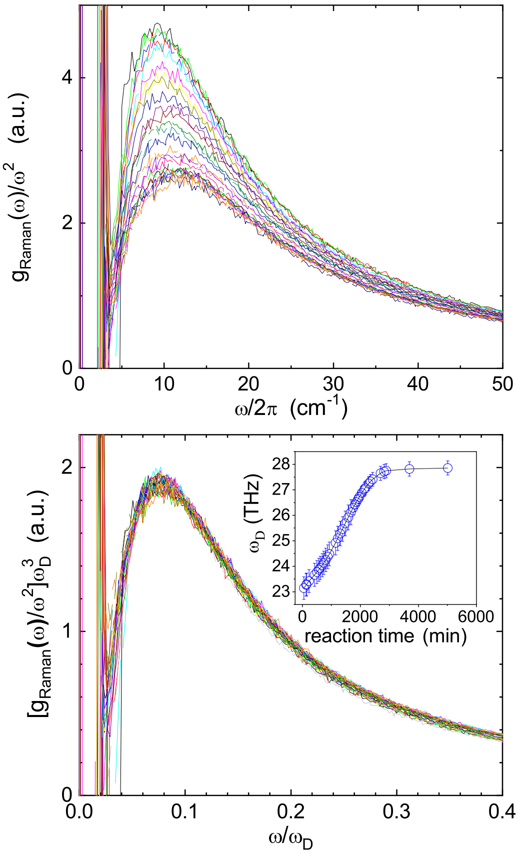

FIGURE 1. (a) Evolution of the quantity $g_{\mathrm{Raman}}(\omega)/\omega^2$ during the isothermal polymerization of the epoxy resin. (b) The same quantity represented in a Debye-frequency normalized way, *i.e.*, by scaling, for each spectrum, the frequency by the Debye frequency, ω_D, and the intensity by $1/\omega_D^3$.

peak in Fig. 1(b) well corresponds to the relative value of ω_{BP} to ω_D reported in literature, typically about one tenth.

This approach only represents an indirect way to check the scaling properties of the vibrational spectrum, as the data reduction relies on two approximate assumptions, both of which merit some discussion. First, it is assumed that the function $C(\omega)$ is not changed by the external parameter (here the number of chemical bonds between the molecules), and can be considered $\propto \omega$. The latter assumption is certainly rather crude and needs to be carefully checked. In this respect, it is worth noting that the available experimental data and the theoretical prediction of model calculations indicate that the deviation from proportionality, if any, is not pronounced in the low-frequency region. Moreover, $C(\omega)$ is found to scale with the BP position, so that using $C(\omega) \propto \omega$ will alter the shape of the density of states in the same manner for all the spectra, preserving the scaling properties of the function. As a

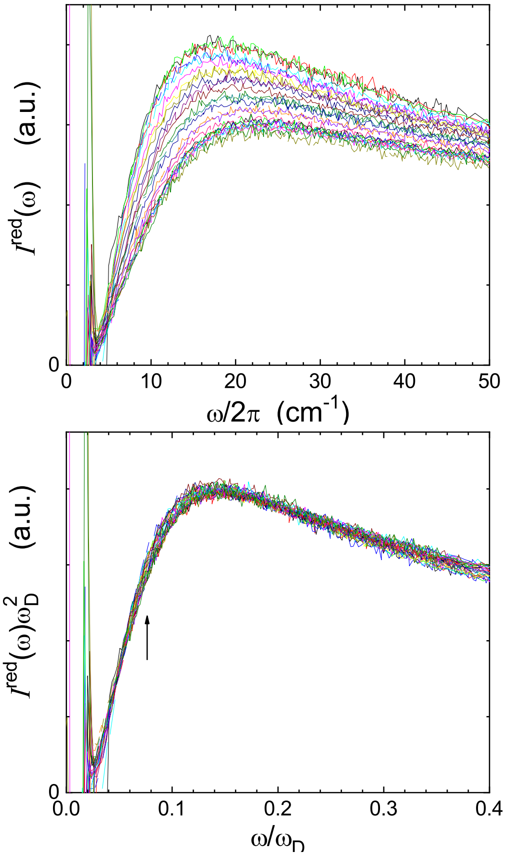

FIGURE 2. (a) Evolution of the reduced Raman intensity $I^{red}(\omega) = I(\omega)/[n(\omega)+1]\omega$ during the isothermal polymerization of the epoxy resin. (b) Master curve of the data obtained by scaling, for each spectrum, the frequency by the Debye frequency, ω_{D}, and the intensity by $1/\omega_{\mathrm{D}}^2$.

second approximation, it is assumed that the Raman intensity is itself proportional to the vibrational density of states. Despite the theory of elastic heterogeneity, as mentioned above, does not support this assumption, in the light of the same theory it is however expected that the Debye scaling holds during polymerization, since no change in the state of disorder reasonably occurs as the fluid mixture spontaneously evolves towards the glassy phase. This strongly favors an interpretation of the scaling behavior of $g_{\mathrm{Raman}}(\omega)$, independently of the relationship of this quantity to the experimentally measurable density of states, as a reflection of the scaling behavior of the vibrational spectrum in the BP region. In the next section we show the implications of this conclusion for the Raman intensity.

Scaling properties of the Raman intensity. In Fig. 2(a) the Raman intensity is represented in the common reduced form, $I^{\mathrm{red}}(\omega) = I(\omega)/[n(\omega)+1]\omega$. It has to be noted that, mathematically, $I^{\mathrm{red}}(\omega) = g_{\mathrm{Raman}}(\omega)/\omega$. As a consequence, since the function $g_{\mathrm{Raman}}(\omega)/\omega^2$

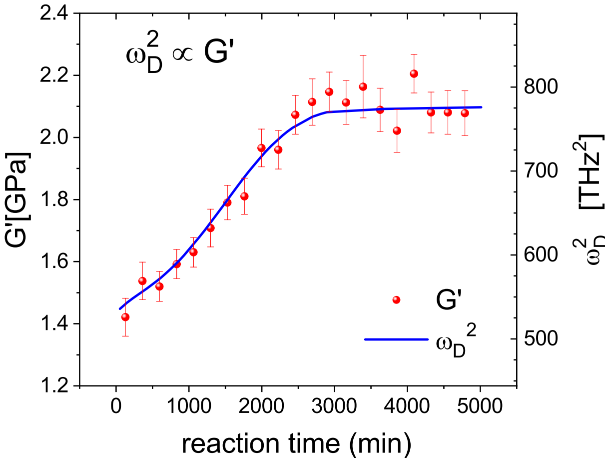

FIGURE 3. Real part of the shear modulus, G', determined in the THz frequency range by IXS, and Debye frequency squared, ω_{D}^2, at different times during the isothermal polymerization. The right and left y-scales differ by a multiplication factor.

scales with $1/\omega_{\mathrm{D}}^3$ when the frequency is scaled by ω_{D}, then $I^{\mathrm{red}}(\omega)$ has to scale with $1/\omega_{\mathrm{D}}^2$. A direct confirmation is given by the master curve shown in Fig. 2(b), where the arrow indicates the position of the pronounced peak observed in the representation of Fig. 1(b).

We now compare the factor that scales the reduced Raman intensity with the changes undergone by the elastic properties of the material, in particular the shear modulus. To this end, in Fig. 3, the shear modulus G' (solid circles), and the Debye frequency squared, ω_{D}^2 (solid line), are plotted in the same graph by using y-scales differing by a multiplication factor. It can be seen that the time evolution of ω_{D}^2 is in close agreement with the time evolution of G' throughout the polymerization process, with their numerical values directly proportional. This demonstrates that the reduced Raman intensity essentially scales with $1/G'$. This finding can be rationalized by considering the relationship between the shear modulus G' and the Debye frequency ω_{D}, both of which can be expressed in terms of the longitudinal v_{L} and transverse v_{T} sound velocities. According to its definition, the variation of ω_{D} is due to changes in the sample density ρ and in the sound velocities, through the relation $\omega_{\mathrm{D}}^3 \propto \rho v_{\mathrm{D}}^3$, where v_{D} is the Debye sound velocity defined as $v_{\mathrm{D}}^{-3} = (v_{\mathrm{L}}^{-3} + 2v_{\mathrm{T}}^{-3})/3$. During the reaction, the longitudinal, $M' = \rho v_{\mathrm{L}}^2$, and the shear, $G' = \rho v_{\mathrm{T}}^2$, elastic moduli are connected by a simple Cauchy-like relation $M' = 3G' + a$, with a a relatively small constant (Fioretto *et al.* 2008). For approximate estimates, one can neglect this constant and write $v_{\mathrm{L}} \approx \sqrt{3} v_{\mathrm{T}}$, from which $v_{\mathrm{D}}^3 \approx v_{\mathrm{T}}^3/0.86$. By using this expression, it results $\omega_{\mathrm{D}}^2 \propto \rho^{\frac{2}{3}} v_{\mathrm{D}}^2 \approx \rho^{\frac{2}{3}} v_{\mathrm{T}}^2/0.9$. For the density values measured during the polymerization reaction one has $\rho^{\frac{2}{3}}/0.9 \approx \rho$, and then, $\omega_D^2 \propto \rho^{\frac{2}{3}} v_{\mathrm{D}}^2 \approx \rho v_{\mathrm{T}}^2 = G'$.

From the scaling property of $I_{\mathrm{red}}(\omega)$, which is essentially the Raman susceptibility $\chi''(\omega)$ divided by the frequency, it follows that $\chi''(\omega)$ scales with $1/\omega_{\mathrm{D}}$. On this point, the theory of elastic heterogeneity has something to offer to reflection. In fact, within the theory, $\chi''(\omega)$ is given by an integral, in the wavevector space $\mathbf{k}$, of a function in which the frequency dependence only appears within the expression $2\chi''_{\mathrm{L}}(k,\omega)+3\chi''_{\mathrm{T}}(k,\omega)$, where $\chi''_{\mathrm{L,T}}(k,\omega)$ are the imaginary part of the longitudinal and transverse dynamic susceptibilities $\chi_{\mathrm{L,T}}(k,\omega)$ – for mathematical details the reader is referred to Schmid and Schirmacher (2004). These latter, at low frequency, approximate as $\chi_{\mathrm{L,T}}(k,\omega)\approx 1/v^2_{\mathrm{L,T}}(\omega)$ and become inversely proportional to the longitudinal, $M(\omega)=\rho v^2_{\mathrm{L}}(\omega)=M'(\omega)+iM''(\omega)$, and shear, $G(\omega)=\rho v^2_{\mathrm{T}}(\omega)=G'(\omega)+iG''(\omega)$, elastic modulus. For the imaginary part one has

$$\begin{aligned}\chi''_{\mathrm{L}}(k,\omega)\propto\left(\frac{1}{M}\right)'' &= \frac{M''}{M'^2+M''^2}=\frac{1}{M'}\frac{\Gamma_{\mathrm{L}}/\omega}{1+(\Gamma_{\mathrm{L}}/\omega)^2}\\ \chi''_{\mathrm{T}}(k,\omega)\propto\left(\frac{1}{G}\right)'' &= \frac{G''}{G'^2+G''^2}=\frac{1}{G'}\frac{\Gamma_{\mathrm{T}}/\omega}{1+(\Gamma_{\mathrm{T}}/\omega)^2}\end{aligned}$$

where $\Gamma_{\mathrm{L}}=\omega M''/M'$ and $\Gamma_{\mathrm{T}}=\omega G''/G'$ are the longitudinal and transverse acoustic attenuation coefficients. By inserting these expressions and using the Cauchy-like relation $M'\approx 3G'$, the frequency dependence in the formula for the Raman susceptibility is given by a non-trivial expression

$$2\chi''_{\mathrm{L}}(k,\omega)+3\chi''_{\mathrm{T}}(k,\omega)\propto\frac{1}{G'}\left[\frac{2/3\Gamma_{\mathrm{L}}/\omega}{1+(\Gamma_{\mathrm{L}}/\omega)^2}+\frac{3\Gamma_{\mathrm{T}}/\omega}{1+(\Gamma_{\mathrm{T}}/\omega)^2}\right].$$

We note that if the frequency dependence of the term in square brackets were negligible, then the Raman susceptibility $\chi''(\omega)$ would scale with $1/G'\approx 1/\omega_{\mathrm{D}}^2$; only if this non-trivial frequency dependence comes out to be of the order of ω in the BP region, then $\chi''(\omega)$ scales with $\omega_{\mathrm{D}}/G'\approx 1/\omega_{\mathrm{D}}$, as expected on the basis of the experimental observation.

3. Conclusions

In summary, in this contribution we have revisited the Raman data acquired during the isothermal vitrification process of an epoxy resin induced by the progressive polymerization of the molecules in the system, by focusing on the BP scaling behavior in connection with elastic heterogeneities. The theory of heterogeneous elasticity provides a physical basis to the expectation that changes of the vibrational density of states by increasing the number of chemical bonds can be described by an elastic-medium transformation, the same behavior that is found experimentally for the phenomenological quantity $g_{\mathrm{Raman}}(\omega)$. This strongly supports the idea that the scaling properties of $g_{\mathrm{Raman}}(\omega)$ correctly reflect the scaling properties of $g(\omega)$, independently of the relationship existing between these quantities. By examining how the Debye-scaling properties of $g_{\mathrm{Raman}}(\omega)$ impact on other quantities, we have established a direct connection between the behavior of the reduced Raman intensity $I^{\mathrm{red}}(\omega)$ and the macroscopic elasticity of the material, demonstrating that $I^{\mathrm{red}}(\omega)$ inversely scales with the shear modulus, G', when the frequency is scaled by ω_{D}. Finally, we have found that the observed scaling properties of the Raman susceptibility $\chi''(\omega)$ crucially require, in the framework of the theory of heterogeneous elasticity, that an approximate linear frequency dependence of $\chi''(\omega)$ holds in the BP region.

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