Brillouin scattering from bulk polybutadiene: distribution of relaxation times *versus* single relaxation time approach

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Two different approaches are usually employed to analyse hypersonic data: a non-exponential density relaxation function $g(t)$ with a non-Arrhenius $\tau(T)$ *versus* an exponential $g(t)$ with an Arrhenius temperature dependence of the longitudinal relaxation time $\tau(T)$. In this report we provide strong evidence that spontaneous Brillouin scattering alone cannot discriminate between the two approaches. The knowledge of $\tau(T)$, which is of primary importance for this problem, results from complementary ultrasonic and photon correlation experiments on the same sample. We report evidence that the distribution of relaxation times in polybutadiene becomes narrower with increasing T in agreement with experiments and theoretical predictions.

(Keywords: polybutadiene; structural relaxation; distribution of relaxation times; light scattering; ultrasonic techniques; Brillouin scattering)

INTRODUCTION

The density time autocorrelation function $C(q, t)$ (at wavenumber q) plays a central role in the study of dynamic structural rearrangements in dense materials. It has recently been the main focus of interest in new microscopic theories of the glass transition[1-3]. At low temperatures, near the conventional glass transition temperature T_g, the structural relaxation time τ can be longer than 10^{-6} s and $C(q, t)$ is best studied by photon correlation spectroscopy (p.c.s.)[4], a dynamic light scattering technique in the time domain 10^{-6} to 10^2 s. The shape of $C(q, t)$ is definitely non-exponential and usually described by the Kohlrausch–Williams–Watts (KWW) function:

$$g(t) = \exp(-(t/\tau)^{\beta}) \tag{1}$$

where the parameter β is a measure of the distribution of relaxation times and the normalized $g(t) \equiv C(t)/\langle|\rho_q(0)|^2\rangle$, with $\langle|\rho_q(0)|^2\rangle$ being the mean square density fluctuations. In most known cases, the exponent β exhibits no significant dependence on temperature T when examined by p.c.s. However, if β does show temperature dependence then it invariably increases with temperature.

At high temperatures, far above T_g, the dynamics of the density fluctuations in the gigahertz frequency range can in principle be investigated by polarized Brillouin scattering (BS). The Brillouin spectrum at a scattering angle θ is determined[5] by the qth mode of the Fourier transform of the $C(q, t)$. In practice, the Brillouin experiment measures the longitudinal modulus M^* ($\equiv M' + iM''$) related to the density relaxation function $g(t)$ by[6]:

$$M' - M_0 = M_r\omega \int_0^{\infty} \sin \omega t \, g(t) \, dt \tag{2}$$

$$M'' = M_r\omega \int_0^{\infty} \cos \omega t \, g(t) \, dt \tag{3}$$

where the relaxation strength M_r ($= M_{\infty} - M_0$) is the difference between the high and low frequency limiting M' values. Although the relevant correlation function is the same in both light scattering techniques, different relaxation processes could affect $g(t)$ at low and high temperatures. P.c.s. measures $g(t)$ directly in an isothermal experiment, whereas in BS the experimental quantities $M'(T)$ and $M''(T)$ are usually obtained as a function of T at a frequency w_B which also varies with T. To extract $g(t)$, it is therefore of crucial importance to know $\tau(T)$, as well as $M_r(T)$, which is hard to obtain from BS experiment alone. Alternatively, if the only available information on structural relaxation originates from BS, then the description of $M^*(T)$ is somewhat model-dependent. Hence, use of the two different approaches employed to analyse hypersonic data is now debated[5,7-15]. A non-exponential $g(t)$ and a non-Arrhenius $\tau(T)$ or an exponential $g(t)$ and an Arrhenius $\tau(T)$ are used in equations (2) and (3). Other potential contributions[16] to hypersonic sound propagation and attenuation are ignored.

In this short report, we provide a thorough review of the two major hypotheses, mainly through additional information on structural relaxation extracted from complementary p.c.s. and ultrasonic measurements on the same bulk polybutadiene (PB) sample. Ultrasonic measurements usually yield $M^*(T)$ values at megahertz frequencies and hence cover the intermediate temperature range between p.c.s. and BS measurements.

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EXPERIMENTAL

The Rayleigh–Brillouin spectra were mainly obtained at a scattering angle of $\theta = 90°$ in the so-called VV scattering configuration over a temperature range 20–140°C. The excitation source was an argon ion single-mode laser (Spectra Physics 2020), operating at $\lambda = 4880$ Å, with a stabilized power of about 200 mW. The scattered light was spectrally analysed using a piezoelectrically scanned Fabry-Perot interferometer, stabilized with a Burleigh DAS-10 system. Spectra were taken at a free spectral range of 20.3 GHz with an accuracy better than 60.

The storage modulus M' is associated with the hypersonic velocity u, whereas the loss modulus M'' is related with the Brillouin full-width Γ_B according to $(f_B \gg \Gamma_B)$.

$$M' = \rho u^2, \qquad M'' = \frac{\Gamma_B}{f_B} M' = \frac{2u\alpha}{\omega_B} M' \qquad (4)$$

where ρ is the density whose temperature dependence is given by: ρ(in kg m^{-3}) $= 896 - 0.75\Delta T$(in K), $\Delta T = T - 20$(in °C); α $(= \pi\Gamma_B/u)$ is the sound attenuation and f_B $(= \omega_B/2\pi)$ is the Brillouin shift (in GHz). The hypersonic velocity u $(= \omega_B/q)$ is computed from the Brillouin shift and the amplitude of the wavevector $q = (4\pi/\lambda)n \sin(\theta/2)$, with n being the refractive index of the medium whose temperature dependence is given by: $n = 1.5229 - 0.366X10^{-3}T$.

The material properties M' and M'' at ultrasonic[17–19] (1 MHz) and hypersonic (5–9 GHz) frequencies are plotted *versus* T in *Figure 1*. The low frequency limiting M_0 $(= \rho u_0^2)$ is obtained from the ultrasonic velocity data at high T where the linear temperature dependence u_0(in m s^{-1}) $= 2360 - 3.1T$(in K) is used. At high T, there is no dispersion in M' and both ultrasonic and hypersonic values of M' approach M_0. In order to determine the relaxation strength $M_\tau(T)$ (equations (2) and (3)), $M_\infty(T)$ is needed. Different approaches have been used for the determination of M_∞: (i) one can extrapolate the velocities[13] at low T, provided that dispersion occurs at much higher T; (ii) one can use the velocity value at lowest measurement temperature along with the u_∞ obtained at the temperature of peak absorption utilizing the peak condition $\omega\tau = 1$ and equation (6) below[14]; (iii) a more precise procedure is the combination of a velocity value at low T (not affected by dispersion, as is evident from *Figure 1* (symbol ▲): $\Theta = 150°$C) with the two additional u_∞ values obtained from the hypersonic and ultrasonic absorption peak, whenever ultrasonic absorption data are available. It is reported that rather than M_∞ itself, its inverse (i.e. adiabatic compressibility) varies linearly with T and this dependence of M_∞ in PB is seen in *Figure 1*.

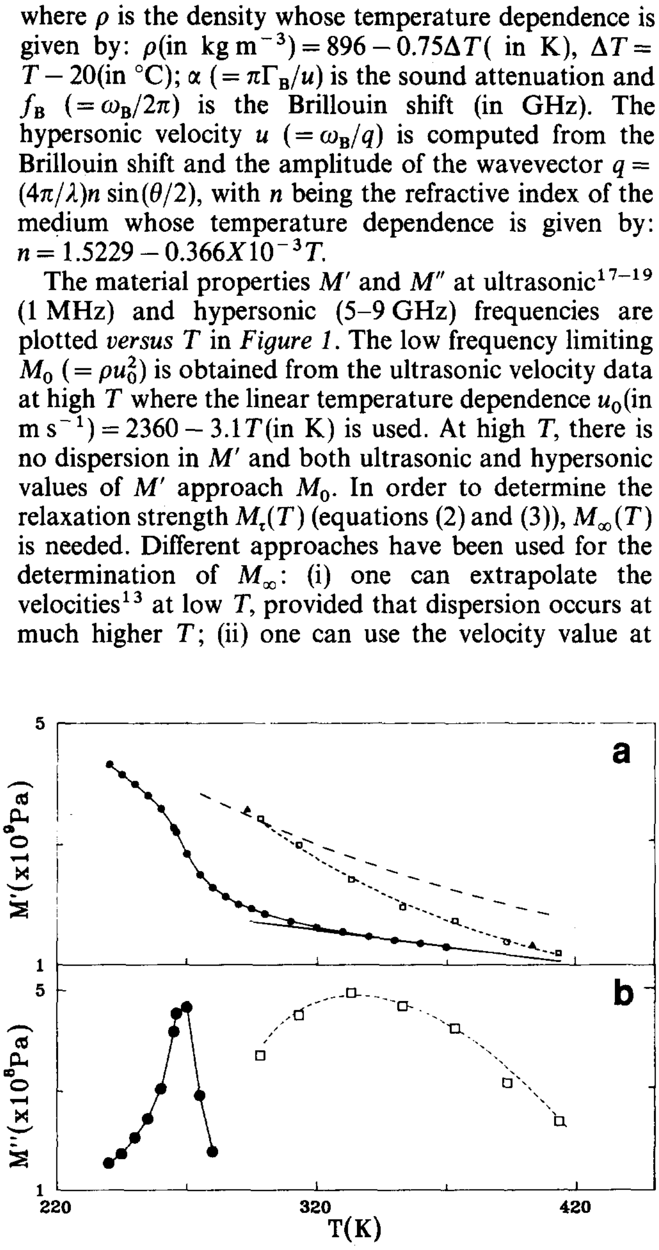

Figure 1 The real (a) and imaginary (b) part of the longitudinal modulus M in bulk PB ($T_g = 222$ K) *versus* temperature. ●, Ultrasonic experiments at 1 MHz; □, Brillouin scattering experiment at 5–9 GHz. ——, Temperature dependence of M_0; – – –, temperature dependence of M_∞, the low and high limiting values of M' respectively

DISCUSSION

Distribution of relaxation times

The width of the $M''(T)$ peak exhibits a large increase at high T (gigahertz frequencies) compared to that at low T (1 MHz) as depicted in *Figure 1*. This disparity arises to a large degree from the different temperature rate of τ at low and high T. The variation of $\tau(T)$ with T is therefore needed to describe the $M''(T)$ experimental curves with a limiting number of adjustable parameters. The $\tau(T)$ can be deduced from the fit of the longitudinal relaxation times τ_M at low T near T_g (p.c.s.)[17–19] at intermediate T (ultrasonic) and high T (BS) to the well known Vogel–Fulcher–Hesse–Tammann (VFHT) free volume equation:

$$\tau = \tau_0 \exp[B/(T - T_0)] \qquad (5)$$

The experimental values of τ used in the fitting procedure were consistently defined as $\tau_M = 1/\omega_B^*$ at T^* at which M'' assumes its maximum value $M''_{\max}$ (*Figure 1*). For the time domain p.c.s. experiment[17], which measures the time-dependent longitudinal compliance $D(t)$[20,21], the necessary transformations should be carried through. For PB, the relaxation function $g(t)$ is well represented by equation (1) with $\beta = 0.36 \pm 0.03$ and τ in this equation is converted to τ_M by a factor of 1.5. The fit of equation (5) to the times τ_M over the temperature range 230–360 K yields $\tau_0 = (3.4 \pm 1) \times 10^{-14}$ s, $B = 1130 \pm 70$ K and $T_0 = 192.9 \pm 1$ K. Using these parameters in equation (5) along with the KWW decay function (equation (1)) the reduced loss $N'' \equiv M''/M_\tau$ can be computed from equation (3) for different values of the distribution parameter β and then compared to the experimental $M''(T)$ curves.

Figure 2 presents the outcome of this comparison. Apparently, the BS loss is broader than the single relaxation time ($\beta = 1$) prediction (solid lines) and better represented by a distribution characterized by $\beta = 0.4$. The same value was reported for the Brillouin data of poly(propylene glycol) and its complexes with various salts[13,14] assuming, however, the values of the three parameters in equation (5). This is a strong assumption that exerts a large influence on the β value and hence renders the peak analysis ambiguous. In fact, *Figure 2* provides strong evidence that for PB this value of β is physically less meaningful. We first observe, in contrast to the picture of a single structural relaxation process, that the experimental hypersonic M'' value at low T is not similar but well above the corresponding ultrasonic value. This hypersonic value should not be confused with the residual Brillouin width at low $T(\omega_B\tau \gg 1)$ which in the case of PB was found to be quite low[22]. Second, the

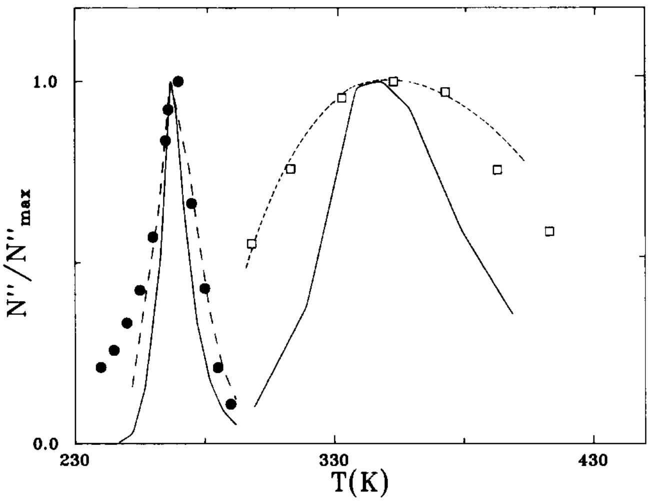

Figure 2 Normalized longitudinal loss peaks for PB *versus* temperature: ●, ultrasonic experiments at 1 MHz; □, Brillouin scattering experiments at 5–9 GHz. ———, Single relaxation time ($\beta = 1$) curves; $\beta = 0.4$; - - -, $\beta = 0.6$; calculated from equation (3)

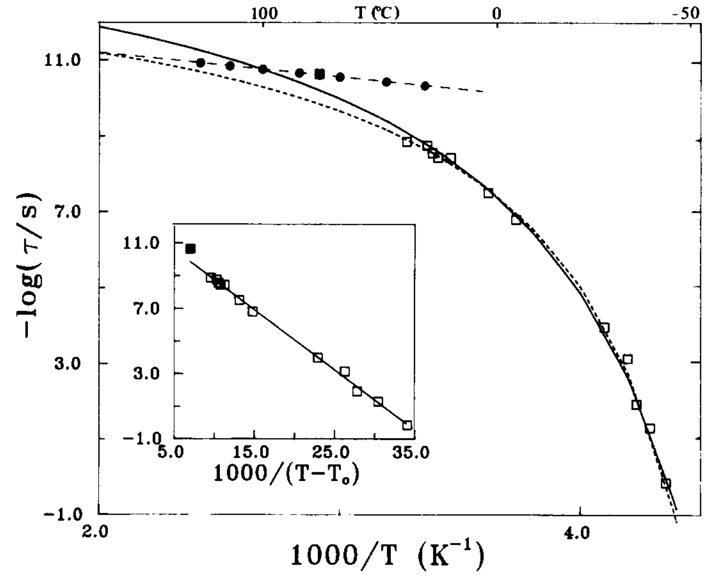

Figure 3 Temperature dependence of the longitudinal relaxation time τ in PB obtained from different complementary techniques. ●, Times τ_s obtained from single relaxation time fit of Brillouin data; □, time $1/w_B^*$ from maximum hypersonic attenuation. The solid line indicates the VFHT fit (equation (5)) to times obtained from ultrasonics, p.c.s. and BS; - - -, VFHT fit to ultrasonics and p.c.s. data. The insert represents a VFHT plot for the p.c.s. and ultrasonics relaxation times at $T_0 = 200.2$ K

ultrasonic loss is represented by equation (3) using a narrower KWW relaxation function ($\beta = 0.6$) than for the BS peak. To obtain an unbiased VFHT fit, we have used the $\tau(T)$ obtained from the fit of the times from p.c.s. and ultrasonic measurements which already cover a broad time range, i.e. $\tau_0 = (3.9 \pm 2) \times 10^{-13}$ s, $B = (845 \pm 100)$ K and $T_0 = 200 + 3$ K. These values are at variance with the previous values for reasons discussed below with regard to *Figure 3*.

From the p.c.s. experiment in the relatively narrow temperature range 230–246 K, we obtained a constant $\beta = 0.36 \pm 0.03$ and from the ultrasonic peak in *Figure 2* the higher value $\beta = 0.6$. If the experiments encompass a wide temperature range, then invariably β increases with T (refs 23–27) in agreement with the predictions of the coupling model of relaxation[28] and the glass transition models[29,30]. Thus the description of the BS peak in *Figure 2* with $\beta = 0.4$ is inconsistent with the experimental findings and theoretical predictions. Finally the $M''_{\max}$ at gigahertz frequencies and hence high T appears to exceed the corresponding ultrasonic value at low T. This may signal the narrowing of the relaxation time distribution with increasing T.

Single relaxation time

The second approach assumes a single relaxation time ($\beta = 1$) for which equations (2) and (3) read:

$$M' - M_0 = M_\tau \omega^2 \tau_s^2/(1 + \omega^2 \tau_s^2) \tag{6}$$

$$M'' = M_\tau \omega \tau_s/(1 + \omega^2 \tau_s^2) \tag{7}$$

Since M_0 is known with better precision than M_τ or equivalently M_∞, we have chosen to compute τ_s by the simple relation $\tau_s = (M' - M_0)/(\omega M'')$ using only experimental quantities. The $\tau_s(T)$ thus obtained is depicted in *Figure 3* along with τ_M from p.c.s., ultrasonics and the value $1/\omega_B^*$ at T^*. An Arrhenius fit to τ_s yields $\tau_s = (3.5 \pm 1) \times 10^{-13} \exp[(1464 \pm 95)/T]$ (in s) which exhibits a significantly weaker temperature-dependence compared to that of times τ_M represented by a VFHT equation. The values of the VFHT parameters given in the preceding section depend on the inclusion or exclusion of $1/\omega_B^*$ in the fitting procedure and describe respectively the solid and dashed lines in *Figure 3*. All available τ_M times do not conform to a single VFHT dependence and the hypersonic data point is faster than the predicted VFHT value. This is still the case even if we choose the $1/\omega_B^*$ value within $T^* \pm 10$ K. Similar behaviour is displayed by polyisoprene (PIP)[28,29] when p.c.s. dielectric relaxation and BS data are interrelated by the ionic $2Ca(NO_3)_2 3KNO_3$ mixed salt[23–27], and other molecular glass formers[9]*. The Arrhenius and VFHT (dashed line) dependencies in *Figure 3* suggest the presence of two different relaxation processes in PB which tend to merge at very high T. In the context of the coupling theory of relaxation, the crossover from a KWW to a single relaxation time decay function seems to occur in the lower gigahertz frequencies[28]. Furthermore, in the case of rotational relaxation, the bifurcation into slow and faster relaxation well above T_g is theoretically supported[33].

The single time τ_s and its weak temperature-dependence is in accord with the observation that the hypersonic attenuation at low T exceeds the corresponding ultrasonic value (*Figure 2*). The calculated $M''(\omega)$ from equation (7) using the Arrhenius $\tau_s(T)$ adequately describes the experimental $M''(\omega)$. This comparison is depicted in the plot of $N''/N''_{\max}$ *versus* the normalized frequency $\omega\tau$ in *Figure 4*. We have also plotted in this format the ultrasonic attenuation from *Figure 2* and the isothermal $M''(\omega)$ computed from equation (3) using the KWW equation from the p.c.s. experiment ($\beta = 0.36$ over the range 230–246 K). The distribution of relaxation times becomes narrow with increasing T in agreement with some experimental findings[23–27] so far and theoretical predictions[30,32,33].

Provided that the VFHT form adequately describes the $\tau(T)$ over an extended temperature range[34], the

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* We observe similar behaviour for the molecular glass formers aroclor (A1248) and dioctyl phthalate (DOP) (unpublished data)

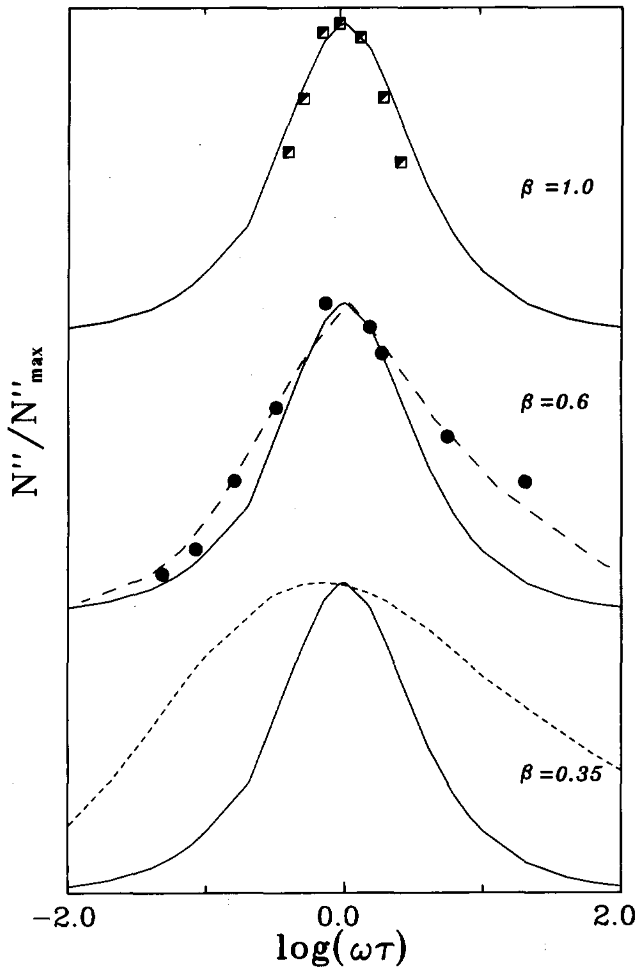

Figure 4 Normalized $N''(\omega)$ *versus* normalized frequencies $\omega\tau$ for bulk PB investigated by p.c.s. ($\beta = 0.35$); ultrasonics ($\beta = 0.6$); BS ($\beta = 1.0$) at low, intermediate and high temperatures, respectively

dynamics of the exponential density–density correlation function $g(t)$ obtained from the Brillouin experiment at high T appears to contradict two pertinent experimental findings. First, at low T near T_g, both density and orientational correlation function have the same non-exponential KWW shape and roughly the same relaxation time τ and τ_{or}, probably due to the strong coupling between translational and rotational motions near T_g[35]. It is also known that volume and shear relaxation time are very similar near T_g. For the sample under consideration this is true up to 70°C above T_g[36]. On the other hand, at high T, τ_s determined from BS is faster than τ_{or} by at least a factor of 10 (ref. 9). Secondly, the non-exponential shape of the orientation correlation function persists at high T, as shown by recent dielectric relaxation (DR) measurements on bulk poly(phenyl methyl siloxane) (PPMS)[37] and PIP[31,32]. It is evident that for these systems, DR at high T probes slow dynamics associated with the primary glass–rubber relaxation and hence τ_{or} follows the VFHT form. In fact the frequency-domain depolarized Rayleigh spectra[32] of PPMS and PIP are clearly not single Lorentzian lines. Alternatively, at gigahertz frequencies the temperature variation of the Brillouin spectra seems to reflect the relaxation of the bulk modulus (K) rather than the relaxation of the shear modulus G, ($M^* = K^* + \frac{4}{3}G^*$). The reorientation of polymer segments is not essential in causing hypersonic dispersion because the condition $\omega_B\tau_{or} \gg 1$ holds (see equations (6) and (7)). Moreover, at high T, the bulk modulus is much larger than G_∞. Finally, in the context of the 'hierarchically constrained dynamics'[38], the τ_s may be associated with the fast degrees of freedom whereas in the picture of the coupling model of relaxation[28] τ_s is the primitive relaxation time.

To conclude, conventional Brillouin scattering alone cannot discriminate between an exponential and KWW decay function $g(t)$. The inclusion, however, of the complementary ultrasonic and photon correlation experiments performed on the same sample turns out to be very helpful in determining the appropriate form of $g(t)$ responsible for the hypersonic dispersion in bulk polybutadiene. The present data favour a quasi-exponential $g(t)$. In this context, an alternative promising approach would be the performance of ultrasonic time-dependent impulsive-stimulated Brillouin scattering and frequency-domain spontaneous Brillouin scattering experiments on the same sample.

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