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Relative variation in the sound velocity in polymethyl methacrylate at intermediate low temperatures

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Abstract

We have measured the relative variation in the sound velocity in amorphous polymethyl methacrylate (PMMA) from 4 to 77 K in the frequency range from 3 to 30 MHz. Our experimental results on the temperature and frequency dependence of the velocity shift at intermediate low temperatures (4–30 K) cannot be described by thermally activated motions of defect states. We also find that the temperature coefficient $\beta = \partial(\Delta v/v_0)/\partial T$ of the velocity shift in PMMA appears to be frequency independent in a broad frequency range.

1. Introduction

A common feature of glasses above helium temperatures, which has been called the Bellessa effect [1], is the linear temperature-dependent decrease in the fractional change in the velocity of sound or velocity shift, $\Delta v/v_0$. The phenomenon has been extensively studied, mainly by Bellessa and collaborators, in many inorganic [2–7] and polymeric [8–10] glasses. Bellessa found that his results in soda–silica and PdSiCu [2], for more than a decade of ultrasonic frequencies, are well described by the relation

$$\frac{\Delta v}{v_0} = -AT + B \ln \omega \qquad (1)$$

where A and B are constants and ω is the angular ultrasonic frequency. Bellessa suggests that the first term in eqn. (1) is due to the strong anharmonicity of the disordered lattice. The magnitude of B, however, was found to be in agreement with predictions from the standard tunnelling model [9, 11].

The observed temperature and frequency variation in the velocity shift in soda–silica and PdSiCu could not be described [2] by thermally activated relaxations of broadly distributed structural defects which predict a velocity shift proportional to $T \ln(\omega\tau_0)$, where τ_0 is a minimum relaxation time. More recently, Tielbürger *et al.* [12] report that velocity shifts for a variety of silica-based glasses, for an impressive eight decades of frequencies, are well described by their formulation of thermally activated relaxations of tunnelling states which yield approximately also a $T \ln(\omega\tau_0)$ law. This apparent contradiction between Bellessa's and Tielbürger *et al.*'s interpretation of the data for silica-based glasses prompted us to review the matter experimentally for the polymeric glass polymethyl methacrylate (PMMA). The material is convenient since the range of linear temperature dependence of $\Delta v/v_0$ extends well above helium temperatures, and also because there exist published sound velocity data in a broad frequency range.

2. Experimental methods and results

The velocity shift for longitudinal waves was measured by means of the pulse echo overlap method to an accuracy of better than 10^{-4}. The samples were cut from stock polished sheet of polymethyl methacrylate (commercial grade). The temperature was determined by germanium- and platinum-calibrated thermometers in an He-gas-filled cryostat.

The experimental fractional velocity change relative to its 4 K value v_0 is shown in Fig. 1 as a function of temperature. (The change in slope at around 40 K passed undetected in previous measurements [10].) In Fig. 2 the behaviour at intermediate low temperatures (roughly defined here by the extent of the thermal conductivity plateau) is shown for two well-separated frequencies in the experimental range. A mean value of $B = (3 \pm 0.5) \times 10^{-4}$ is found from this graph. Our

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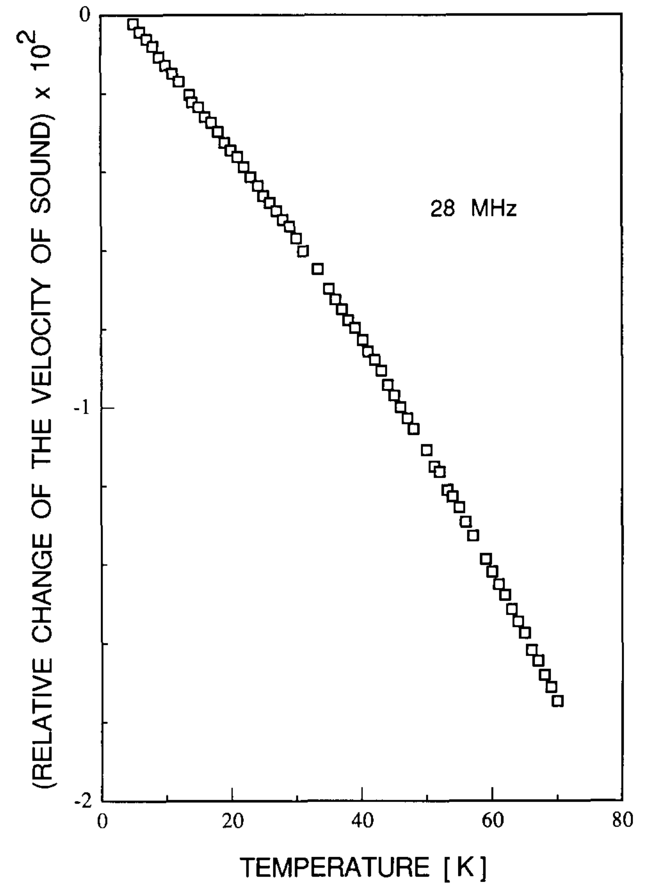

Fig. 1. Relative variation in the velocity of longitudinal sound waves as a function of temperature in amorphous commercial PMMA. Reference velocity at 4 K is 3.16 km s^{-1}.

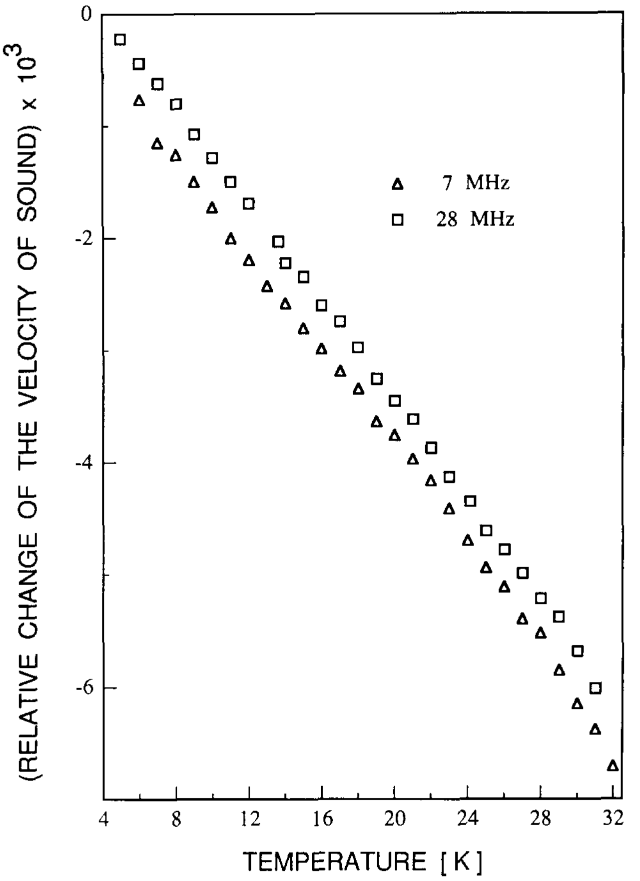

Fig. 2. Relative variation in the velocity of longitudinal sound waves as a function of temperature in amorphous commercial PMMA for two frequencies.

complete ultrasonic data set from 7 to 25 K is well represented by eqn. (1) with a mean value for A of 2.2 ± 0.1 in units of 10^{-4} K^{-1}. Thus, within our experimental precision, A and B for PMMA appear to be constants at ultrasonic frequencies.

3. Discussion

For the temperature regime where $\omega\tau_0 < 1$ the tunnelling model predicts [9] a value of B given by $P\gamma^2_e/2\rho v^2$, where P is the density of states and γ^2_e is the deformation potential. Using the published (attenuation) tunnelling parameters for PMMA [13], we calculate $B \approx 2 \times 10^{-4}$, which compares well with the experimental value quoted above. (Owing to experimental uncertainties in the absolute determination of the reference velocity v_0 previously reported [10], estimates of B were in excess by a factor of about 8.) Our value of A is within 3% of that deduced from published results for commercial PMMA at 18 GHz [14]. This agreement is shown more clearly in Fig. 3, where the magnitude of β for this frequency and for other published ultrasonic studies [15, 16] is plotted as a function of frequency together with the present results. It is evident from this graph that the relaxation formulation [12] leading to $\beta \approx \ln(\omega\tau_0)$ cannot be extended to PMMA.

While the logarithmic frequency dependence of the velocity shift in PMMA appears to follow the predictions of the standard tunnelling model, there remains the question of the origin of its linear temperature decrease at intermediate low temperatures. In this respect it is interesting to point out that crystals with low-lying Einstein-like anharmonic phonon branches such as quartz and rutile show an anomalous linear velocity shift [17, 18] in a temperature range well below their Debye temperatures. By extension from these cases the Bellessa effect in PMMA, and perhaps also in soda–silica and PdSiCu, could conceivably arise from the coupling, via the medium anharmonicity, of the sound waves with low energy vibrational modes at temperatures comparable with or greater than their characteristic temperature. Indeed, calculations within the fracton model [19] do predict a linear decrease in the velocity shift with temperature due to anharmonic interactions between phonons and localized vibrational modes. Finally,

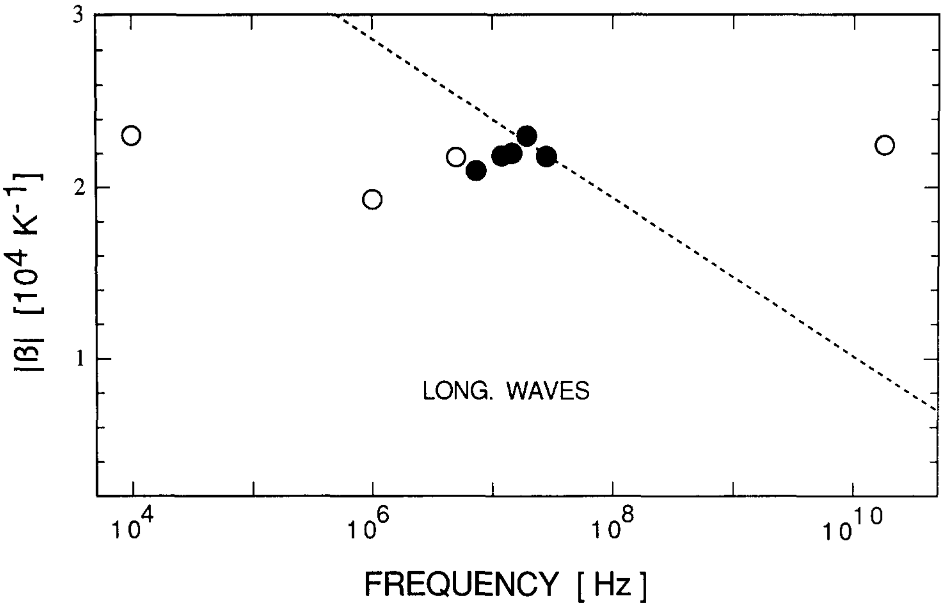

Fig. 3. Temperature coefficient $|\beta|$ of the relative variation in the velocity of longitudinal sound waves as a function of frequency at intermediate low temperatures in amorphous PMMA. The unfilled data points are taken from refs. 14–16. The datum at 10 kHz is for purified PMMA. Filled data points are from this work. The dashed line is an $\ln(\omega\tau_0)$ dependence approximately observed for silica glasses between 5 and 15 K.

we remark that anharmonicity may have some bearing on the apparent controversy [2, 12] about the velocity shift in sodium silicate and silica glasses mentioned in Section 1. It is known that increasing concentrations of Na_2O in silica significantly alter the magnitude and even the sign of the average thermal anharmonic parameter γ below 100 K, with the pressure derivatives of the sound velocities showing a parallel trend [20]. The implications of these changes for the temperature and frequency dependence of the velocity shift at intermediate low temperatures are not clear at present, but it might be that a common interpretation of the velocity shift for sodium silicate and pure silica glasses is untenable.

From the preceding discussion we conclude that lattice or network anharmonicity should be further investigated as a possible origin of the Bellessa effect in some glasses and disordered solids. Work on a simple lattice anharmonic phenomenology that may account for the Bellessa effect in some amorphous and disordered solids is in progress.

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