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Frequency and temperature dependence of dielectric and ultrasonic dispersion in amorphous materials at low temperatures

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Changes in ultrasonic velocity and dielectric constant with temperature and frequency in amorphous materials can be explained using the tunneling-states model in the temperature range 0.01 to 20 K, but it is necessary to include explicitly an energy-dependent density of states and a distribution of relaxation times for each tunneling-state energy.

The anomalous linear temperature dependence of the specific heat,[1,2] the T^2 dependence of the thermal conductivity,[1,2] and the temperature, frequency, and nonlinear effects[3,4] found in the ultrasonic properties of amorphous materials at low temperatures are most successfully explained by the tunneling-states model presented by Anderson, Halperin, and Varma[5] and by Phillips.[6] In this model, a broad spectrum of two-level excitations arises due to the quantum-mechanical tunneling of units of the glass residing in double-well potentials. Quantitative agreement has been reported[7,8] between the model and the measured variation of ultrasonic velocity with temperature (0.03–4 K) and with frequency (0.03–2 GHz). The explanation utilizes both a resonant and a relaxation mechanism of phonon absorption[3,9] by two-level states, the relaxation process becoming important only at the upper end of the temperature range investigated. It was reported[10] recently that at higher temperature (4–20 K), the relaxation absorption mechanism could not account for the observed temperature and frequency dependences of ultrasonic velocities measured between 10 and 500 MHz for vitreous soda silica and for glassy Pd-Si. It is the purpose of this paper to show that the relaxation process can, in fact, account for the temperature and frequency characteristics of the ultrasonic dispersion data above ≈4 K. The relaxation process also can account for the analogous dispersion of electromagnetic waves,[11-13] including an increase in the temperature dependence of the dielectric constant above ≈5 K which has not been reported previously.

The requirements these acoustic and dielectric data place on the parameters of the tunneling-states model make two important implications concerning those tunneling states. First, an energy-dependent density of tunneling states must be included in the calculations, as is necessary to explain several other[2,7-9,13-15] low-temperature properties of glassy materials. Second, it is also essential to include a spectrum[3,16] of thermal relaxation times τ of the tunneling states for each tunneling-state energy E. A broad spectrum of τ values is a distinguishing characteristic[17] of a tunneling-states model as opposed to other possible two-level models. The existence of such a broad spectrum of τ values has been called into question by the results of the short-time-scale specific-heat measurements of Kummer *et al.*[18]

Since the tunneling-states model predicts the same frequency and temperature dependences in the resonant and relaxation absorption for electromagnetic waves[11,12,19] as for acoustic waves, the analysis of the dispersion characteristics are reviewed in general. The results are then used to explain the ultrasonic data of Bellessa[10] and the dielectric behavior of a borosilicate glass.

The tunneling-states model[5,6] assumes a density of tunneling states that depends on both the double-well asymmetry energy ξ and the parameter λ, where λ depends on the height of the potential barrier, the distance separating the wells, and the mass of the tunneling unit. The tunneling overlap energy Δ is then proportional to $e^{-\lambda}$, and the total energy splitting of the ground state is $E=(\xi^2+\Delta^2)^{1/2}$. The thermal relaxation time[3,16] of a given state,

$$\tau^{-1}=\sum_i (2\pi\hbar^4\rho v_i^5)^{-1}(\gamma_i\Delta/E)^2E^3\coth(E/2kT)\,, \quad (1)$$

depends on the strength of the coupling of the state to phonon strains $\gamma\Delta/E$, the mass density ρ, the acoustic velocity v, and the three phonon polarizations i. Thus, for states of energy E, there is a spectrum of relaxation times due to the variation of Δ, with the fastest relaxation time $\tau_{\min}$ occurring for $\Delta=E$. The density of states $P(\xi,\lambda)$ was originally assumed to be a constant, but subsequent application of the model to data has generally required[2,7-9,13-15] an energy-dependent density $P(E)$. The density $P(\xi,\lambda)$ is then equivalent[15,20] to $P(E)$ $[2\tau(1-\tau_{\min}/\tau)^{1/2}]^{-1}$. (The form of this dependence on τ at any value of E is shown by the inset of Fig. 2.) To simplify certain integrals when calculating physical properties, the average value of $\gamma\Delta/E$ is often used.[3,7,9,10,12] However, this effectively reduces the spectrum of τ values at each tunneling-state energy to an average value, $\bar{\tau}$, at that energy.

The variation of ultrasonic velocity with frequency and temperature can be related[7] to phonon mean free paths by the Kramers-Kronig relation. Similarly, the variation of the dielectric constant ϵ is related[11] to the absorption α of electromagnetic waves of velocity c,

$$\frac{\Delta\epsilon}{\epsilon}=\frac{\epsilon(T,\omega_0)-\epsilon(T',\omega_0')}{\epsilon}=-2\frac{\Delta c}{c}=\frac{-2c}{\pi}\int_0^\infty d\omega\left(\frac{\alpha(T,\omega)}{\omega_0^2-\omega^2}-\frac{\alpha(T',\omega)}{\omega_0'^2-\omega^2}\right). \tag{2}$$

Two processes contribute to α which are analogous to the resonant and relaxation scattering mean free paths[3] of phonons. The resonant absorption[11] of electromagnetic waves with $\omega=E/\hbar$ is

$$\alpha_{\text{res}}=\pi^2(\epsilon+2)^2\mu_0^2(27\epsilon\hbar c)^{-1}E\tanh(E/2kT)P(E), \tag{3}$$

where μ_0 is the average microscopic dipole moment of the two-level states. Use has been made here of the Lorentz local-field approximation to relate the macroscopic dipole moment to μ_0, and it has been assumed[19] that the primary modulation of the state by the field is through the asymmetry energy ξ. The densities of states $P(E)$ may be different for the acoustic and electromagnetic cases. The absorption of electromagnetic waves analogous to the relaxation scattering of phonons is (see also Ref. 13)

$$\alpha_{\text{rel}}=\frac{\pi\mu_0^2(\epsilon+2)^2}{54\epsilon kTc}\int_0^{E_{\max}}\frac{dE\,P(E)}{\cosh^2(E/2kT)}\times\int_{\tau_{\min}}^{\tau_{\max}}\frac{d\tau\,(1-\tau_{\min}/\tau)^{1/2}\omega_0^2}{1+\omega_0^2\tau^2}. \tag{4}$$

Equation (4) displays explicitly the dependence of the relaxation process on the spectrum of τ values.

If we now let $B_v=\gamma^2/\rho v^2$, $B_\epsilon=(-2\pi/27)\mu_0^2(\epsilon+2)^2/\epsilon$, and $A=2\pi\hbar^4\rho v^2\gamma^{-2}(k^3\sum_i v_i^{-3})^{-1}\omega_0$, the acoustic and electromagnetic dispersions can be written in general form. We have, for z representing either ϵ or v, $\Delta z/z=(\Delta z/z)_{\text{res}}+(\Delta z/z)_{\text{rel}}$ with

$$\left(\frac{\Delta z}{z}\right)_{\text{res}}=B_z\int_0^{E_{\max}/kT}\frac{dx\,x\tanh(x/2)P(xkT)}{(\hbar\omega_0/kT)^2-x^2}-B_z\int_0^{E_{\max}/kT'}\frac{dx\,x\tanh(x/2)P(xkT')}{(\hbar\omega_0'/kT')^2-x^2} \tag{5}$$

and

$$\left(\frac{\Delta z}{z}\right)_{\text{rel}}=-\frac{B_z}{4}\int_0^{E_{\max}/kT}\frac{dx\,P(xkT)}{\cosh^2(x/2)}\int_0^{\ln(\tau_{\max}/\tau_{\min})}\frac{ds\,(1-e^{-s})^{1/2}}{1+A^2\tanh^2(x/2)e^{2s}(xT)^{-6}}-\left(-\frac{B_z}{4}\int_0^{E_{\max}/kT'}\frac{dx\,P(xkT')}{\cosh^2(x/2)}\int_0^{\ln(\tau_{\max}/\tau_{\min})}\frac{ds\,(1-e^{-s})^{1/2}}{1+(A\omega_0'/\omega_0)^2\tanh^2(x/2)e^{2s}(xT')^{-6}}\right). \tag{6}$$

For $\hbar\omega_0\ll kT$, Eq. (5) provides an approximately logarithmic increase of $\Delta v/v$ with T, while Eq. (6) reduces $\Delta v/v$ with increasing temperature. For $\Delta\epsilon/\epsilon$ the dependences are inverted, since B_ϵ is negative. Equation (5) has been evaluated analytically for a constant density of states for variations with temperature[3] and with frequency.[10] The latter showed that changes of $(\Delta z/z)_{\text{res}}$ with frequency are negligible for $\hbar\omega\ll kT$.

Figure 1 shows the results of numerical integrations of Eqs. (5) and (6). The dashed lines are calculated assuming an energy-independent density of states $P(E)=P_0$. The solid lines are calculated using the covenient quadratic form $P(E)=P_0(1+0.003E^2/k^2)$ with $P(E)=0$ above an energy of $E_{\max}/k=68$ K. In general, a stronger energy dependence of $P(E)$ results primarily in a more rapid decrease in $\Delta z/z$ with increasing temperature, at temperatures above the maximum in $\Delta z/z$.

The dashed and solid curves are calculated for a spectrum of τ values at each E, with $\tau_{\max}/\tau_{\min}\approx10^4$. A smaller ratio of $\tau_{\max}/\tau_{\min}$, i.e., a more narrow spectrum of τ, results primarily in a smaller dependence on frequency. Generally $\Delta z/z$ is only weakly affected by the magnitude of $\tau_{\max}/\tau_{\min}$. However, in the limit where a single or averaged value $\bar{\tau}$ is used[21] in place of the spectrum, the frequency dependence above the maximum in $\Delta z/z$ is absent as shown by the dotted line in Fig. 1. This dotted line is applicable to the frequency range 10^6–10^9 Hz. To force the dotted line to match the other curves near the maximum in $\Delta z/z$ required (for[12,21] $\mu=\mu'$) $P(E)=P_0(1+0.05E^2/k^2)$, resulting in a stronger temperature dependence at higher temperatures. Increasing $E_{\max}/k$ from 68 to 100 K would remove the minimum near

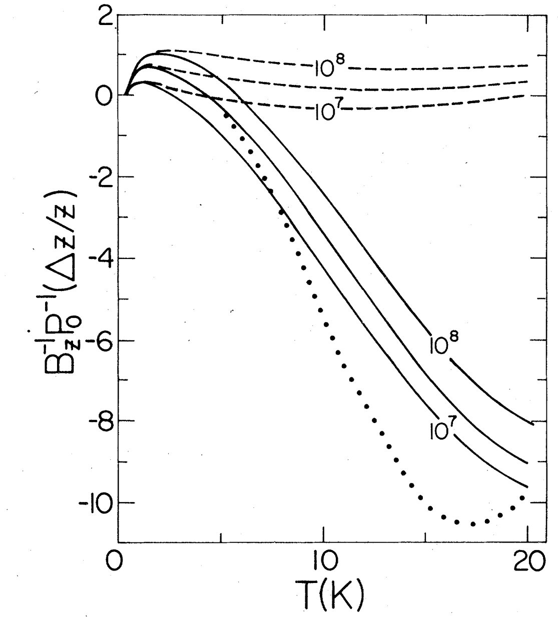

FIG. 1. Calculated changes of ultrasonic-velocity or (with B negative) dielectric constant vs temperature and frequency. The dashed lines assume a constant density of states, and the solid and dotted lines use a constant-plus-quadratic density. The dashed and solid lines are calculated with a spectrum of τ values for each energy, while the dotted line uses only an averaged $\bar{\tau}$ at each energy. The frequencies of 10^7, 3×10^7, and 10^8 Hz apply specifically to soda silica glass. The calculations have been normalized to $\Delta z/z = 0$ at 0.4 K for 10^7 Hz.

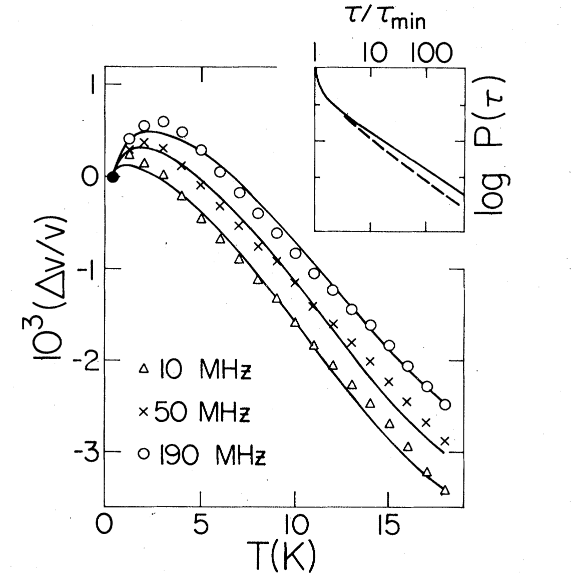

FIG. 2. Variation of ultrasonic velocity vs temperature and frequency for soda silica glass. The curves are calculated as discussed in the text. The data are from Ref. 10. The inset shows, by the solid line, the spectrum of relaxation times at each tunneling-state energy used in the original model and, by the dashed line, that used in Ref. 13.

17 K.

It may be concluded from Fig. 1 that, at temperatures above the maximum in $\Delta z/z$, the temperature dependence is dictated primarily by the energy dependence of $P(E)$, while the frequency dependence is determined by the spectrum of τ values at each E. Near and below the maximum in $\Delta z/z$, it is noted that a frequency dependence, although not a logarithmic dependence, is obtained even for a single or average value $\bar{\tau}$. Hence, as noted above, some low-temperature data ($T \lesssim 4$ K) can be fitted by the tunneling-states model without including explicitly the spectrum in τ values.[7] However, Fig. 1 also demonstrates that the apparent energy dependence of $P(E)$ is influenced by the choice of a single value $\bar{\tau}$ versus a broad spectrum of values.

To compare these general results to the acoustic velocity data of Bellessa,[10] we assume that the greatest part of the dispersion is caused by tunneling states. We recognize that other sources, such as thermal processes,[9] may be present. The measured mass density and acoustic velocities[14] of soda silica glass, a ratio of $\tau_{\max}/\tau_{\min} = 3\times10^4$, a γ_l of[22] 1.2 eV, and a density of states[23] given by $P(E) = (4\times10^{31})(1+0.003E^2/k^2)$ erg^{-1} cm^{-3} with $E_{\max}/k = 68$ K are substituted into Eqs. (5) and (6) for numerical integration. The results are compared with the ultrasonic data of Bellessa[10] in Fig. 2. The form of $P(E)$ used in this calculation is certainly not unique, nor is the abrupt cutoff at $E_{\max}$ realistic. But the calculation does serve to exhibit the necessity of including an energy-dependent density of states in the calculation to provide the observed temperature dependence. In addition, an explicit spectrum over τ is required. The frequency dependence of the data cannot be explained even qualitatively if use is made of a single or average value $\bar{\tau}$ as in the analysis of Bellessa,[10] nor can the frequency dependence be explained if the spectrum is much narrower than $\tau_{\max}/\tau_{\min} = 10^4$.

As another test of the theoretical model we have obtained dielectric constant data for the borosilicate glass BK7[24] from 0.02 to 40 K. The measurements were made on a $3.0\times1.4\times0.05$-cm^3 plate with 2.5-cm^2 vapor-deposited In electrodes using a three-terminal capacitance bridge. Measurements on sapphire using a similar geometry showed no frequency, temperature, or voltage variations. Measurements on BK7 from 10^2 to 10^4 Hz and from 0.02 to 40 K with measuring voltages of 0.03– 3 V showed *no* voltage dependence for ϵ, contrary to previous measurements on BK7 in which a voltage

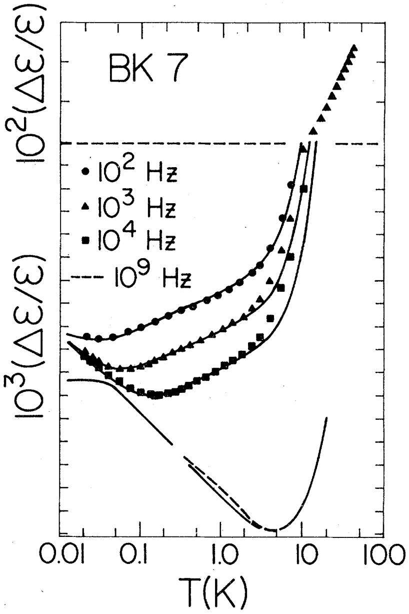

FIG. 3. Dielectric constant data for a borosilicate glass as a function of temperature for several frequencies. The microwave data are from Ref. 12 and have been adjusted vertically. The logarithmic frequency dependence shown at 10 K continues to 40 K. Solid lines are from the theory as described in the text. The maximum at low temperatures for 10^9 Hz is due to $(\Delta z/z)_{\text{res}}$ when $\hbar\omega \ll kT$ is not satisfied; see Ref. 8.

dependence was a dominant feature at low temperatures.[25]

Data[26] for three frequencies are plotted in Fig. 3 along with microwave data at 10^9 Hz from Ref. 12. Equations (5) and (6) are used with $P(E) = P_0(1 + 0.001E^2/k^2)$, $E_{\max}/k = 100$ K, $\gamma_t = 1.2$ eV, $\tau_{\max}/\tau_{\min} = 10^{10}$, and the mass density and acoustic velocities[3] for BK7 to produce the solid curves in Fig. 3. The large width of the τ spectrum reflects the need for relaxation times of $\approx 10^{-2}$ sec for thermal frequencies at 20 K. The minima, which scale[13] as ω/T^3 from 10^2 to 10^9 Hz, are accurately reproduced using these parameters. The roughly logarithmic increase with temperature of the low-frequency data below 3 K is related to the constant factor in $P(E)$, while the roughly linear temperature increase of $\Delta\epsilon/\epsilon$ above 4 K is produced by the quadratic portion. Using $\epsilon = 7$ and assuming[23] $P_0 = 6.4 \times 10^{31}$ $\text{erg}^{-1}\,\text{cm}^{-3}$ would give $\mu_0 = 3$ D. As in the case of $\Delta v/v$, the use of an averaged $\bar{\tau}$ in the theory for relaxation absorption does not give agreement with the higher-temperature dielectric constant data, producing a frequency independent behavior.

The temperature dependence of Fig. 3 is fit well through the use of essentially only two adjustable parameters, namely, the quadratic term in $P(E)$ and $E_{\max}$. Nevertheless, we do not wish to emphasize the quadratic form of $P(E)$, but rather that $P(E)$ is an increasing function of E. Also, the exact form of the spectrum of τ values used in this calculation is not critical. Frossati *et al.*[13] have observed similar variations in the dielectric behavior of vitreous silica below ≈ 1 K and have used a similar analysis to compare their dielectric absorption data with the capacitance data. They assumed a slightly different density of states $P(E) \propto \Delta^q = E^q \times (\tau_{\min}/\tau)^{q/2}$, with $q = 0.28$, which also changes the spectrum of relaxation times as indicated in the inset of Fig. 2. This spectrum provides reasonable agreement with their data. However, their analysis is limited to $T \lesssim 1$ K where the use of even a single value $\bar{\tau}$ provides satisfactory agreement in other investigations.

In summary, the observed high-temperature ($T \gtrsim 4$ K) behavior of ultrasonic and dielectric dispersion of glasses can be accounted for by the tunneling-states model of localized excitations. It is, however, necessary to assume a density of tunneling states which is energy dependent, as has been noted previously for a number of properties of glasses. It is also essential that a spectrum of relaxation times be associated with each tunneling-state energy. Whether there actually is a spectrum of τ values for each tunneling-state energy is a fundamental question since that is a distinguishing characteristic of a tunneling-states model. The short-time-scale heat-capacity experiment of Kummer *et al.*[18] casts doubt on the existence of a broad spectrum of values. However, the results presented here provide a strong indication that a broad spectrum of τ values does exist at each energy E in amorphous materials. Additional evidence for the existence of a broad spectrum of relaxation rates has been published since submission of the present paper. This includes data from acoustic hole-burning experiments[16,27] and from ultrasonic absorption and dispersion measurements in glassy metals.[28]

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[22] The only independent measurement of γ (from phonon echo experiments, Ref. 4) gave $\gamma_l = 1.5 \pm 0.4$ eV for one type of glass at 0.7 GHz. Good agreement of theory with the data of the present paper and of Ref. 15 was found for γ_l assumed constant for thermal frequencies and equal to 1.2 eV.

[23] The density of states P needed here is not that deduced from specific-heat measurements (n_s), but rather $P = 2n_s/\ln(4\tau_{\max}/\tau_{\min})$. Care also should be taken in using densities of states not measured on the same batch of glass. See Refs. 15 and 16.

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