THE POLARIZABILITY OF THE LOW FREQUENCY
EXCITATIONS IN DISORDERED SOLIDS*

MASTER

by

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The polarizability of the low frequency excitations in disordered solids

Richard B. Stephens

Abstract

We have attempted to determine whether an electric dipole moment, μ , is associated with the low frequency excitations observed in glasses at low temperatures. We have attacked the problem in two different ways by measuring 1) the temperature dependence of the dielectric constant of amorphous GeO_2 , Polymethylmethacrylate, and SiO_2 ($f \leq 140$ kHz), and 2) the electric field dependence of the thermal conductivity of fused quartz. In each case we obtained a null result.

In order to reconcile these measurements with dielectric measurements on vitreous silica ($f = 1$ GHz) by Schickfus et al., one must assume that only part of the low temperature excess in the specific heat, the component linear in T , is caused by tunneling systems.

The excess in the specific heat, C_{ex} , is generally quite non-linear, and a more reasonable a priori assumption would be that all of the low temperature excess is due to these systems. The non-linearity of C_{ex} is equivalent to a non-uniform distribution of tunneling states, $n(\Delta)$, over energy, Δ , and would greatly increase the effects of a given μ ; it would lead to an upper limit of .3 and .1 Debye respectively from our two measurements. This 2nd limit is much less than the .3 Debye calculated from Schickfus data. In order that our limit not conflict with Hunklinger's measurement, the distribution $n(\Delta)$ has to be constant to within $\sim 6\%$ over the range $1 \leq \Delta/k_B \leq 3$ K.

The polarizability of the low frequency excitations in disordered solids

1. Introduction

The mechanism which produces low frequency excitations and strong phonon scattering at low temperatures ($T < 1$ K) in all disordered materials is not at all understood.¹ This stands in marked contrast to our knowledge of the dynamics of crystalline materials. In pure dielectric crystals one observes only the phonon heat capacity and no bulk phonon scattering; even in doped materials, it is unusual to find strong phonon scattering for $T < 0.01 \theta_{\text{Deb}}$. Of the systems which are active at such low temperatures, atomic tunneling systems are the strongest phonon scatterers²; they usually also exhibit large electric dipole moments. Since the theoretical model popular at the time (Phillips³ and Anderson et al.⁴) attributed glasses' thermal properties to just such atomic tunneling states, we decided to search for a dipole moment associated with the glassy systems.

We looked for evidence of these dipole moments in two different low temperature experiments -- dielectric constant and thermal conductivity. They are described and the data analyzed in sections 2 and 3 respectively. We saw no evidence of an electric dipole moment in either experiment. The implications of those results are discussed in section 4.

2. Low temperature dielectric constant of amorphous GeO_2 , Polymethylmethacrylate (PMMA), and SiO_2 .

Although the tunneling model started as a specific mechanism -- a tunneling O^- atom⁵ -- the concept is very adaptable and the succeeding calculations are valid for any physical mechanism that can be described with an asymmetric multi-well potential. In practice, two well potentials are always

used since they are easier to work with than n wells ($n > 2$) and the calculations are rather insensitive to the actual value of n . A typical potential is shown in Fig. 1a and its accompanying energy levels in Fig. 1b. The energy level spacing is determined by two different aspects of the potential. The spacing marked $\hbar\omega_0$ is set by the shape of a single isolated potential well. The splitting of the ground state, Δ , is determined by the relationship between the two almost isolated potential wells. It is given by

$$\Delta = [\Delta_0^2 + (\Delta_A + \vec{\mu} \cdot \vec{E})^2]^{\frac{1}{2}} \quad (1)$$

where Δ_0 is the overlap integral which arises from the finiteness of the barrier, Δ_A is caused by the asymmetry of the well potentials, and $\vec{\mu} \cdot \vec{E}$ gives the effect of an external field on the asymmetry. For simplicity, one assumes that both Δ and kT are much less than $\hbar\omega_0$. With these conditions, one can always ignore the second excited state, and the problem reduces to evaluating a two level system. The polarizability of this system is calculated in appendix 1. One obtains:

$$\alpha(\theta) = (\mu \cos \theta)^2 \left[\frac{\beta}{4} \left(\frac{\Delta_A}{\Delta} \right)^2 \text{sech}^2 \left(\frac{\Delta \beta}{2} \right) + \frac{1}{2\Delta} \left(\frac{\Delta_0}{\Delta} \right)^2 \tanh \left(\frac{\Delta \beta}{2} \right) \right] \quad (2)$$

Since these systems are randomly placed, $\alpha(\theta)$ has to be averaged over all orientations. That replaces the $\cos^2 \theta$ factor with a $1/3$. From specific heat measurements one would assume a priori that these excitations are non-uniformly distributed in energy:

$$n(\Delta) = a + b \Delta^2, \quad (3)$$

so the total polarizability is calculated from

$$\alpha_T = \int_0^{\Delta_u} \alpha n(\Delta) d\Delta;$$

we have assumed that $n(\Delta)$ goes to zero at an arbitrary energy, Δ_u , in order to keep the number of systems finite.

It is assumed that $\Delta_u/k_B \gg 1$ K. Then one has:

$$\alpha_T = \frac{\mu^2}{6} \left(\frac{\Delta_A}{\Delta} \right)^2 \left[a \int_0^{\Delta_u} \text{sech}^2 x dx + \frac{4b}{\beta^2} \int_0^{\Delta_u} x^2 \text{sech}^2 x dx \right] + \frac{\mu^2}{6} \left(\frac{\Delta_0}{\Delta} \right)^2 \left[a \int_0^{\Delta_u} \frac{\tanh x dx}{x} + \frac{4b}{\beta^2} \int_0^{\Delta_u} x \tanh x dx \right] \quad (4)$$

where $x_u = \frac{\Delta_u \beta}{2}$ and the bar indicates an average value.

One generally assumes that the spread in the Δ 's is caused primarily by variation in the asymmetry of the wells; using that assumption one finds that for most of the systems $\Delta_A \gg \Delta_0$, so one has $(\frac{\Delta_A}{\Delta})^2 \sim 1$ and $(\frac{\Delta_0}{\Delta})^2 \ll 1$. It does not seem possible to measure the value of this last ratio. It appears in several other equations, but always in conjunction with an unknown coupling constant, M . From low temperature ultrasonics experiments, Pichè et al.⁶ have been able to calculate the product of $[(\frac{\Delta_0}{\Delta})^2]^{\frac{1}{2}}$ and M . For SiO_2 they found $[(\frac{\Delta_0}{\Delta})^2]^{\frac{1}{2}} M = .32 \text{ eV}$. This is similar to values of M measured in tunneling systems in crystals ($M \sim .5 \text{ eV}$ for NaBr:F^{7} and $\sim .25 \text{ eV}$ for KCl:Li^{2}), and implies that, contrary to the usual assumption $(\frac{\Delta_0}{\Delta})^2 \sim 1$. This corresponds to a set of tunneling systems in which the potentials are nearly symmetric ($V \sim 0$ in Fig. 1); the distribution of energies, $n(\Delta)$, is caused by variations in the barrier height, V_B .

Of course this is not a firm conclusion. M could be much larger in the amorphous systems. Since it is not clear which is the appropriate limit, we will analyze our data for both cases; we assume $\Delta_0 \ll \Delta_A$ in the immediately following section, 2.1, and $\Delta_0 \gg \Delta_A$ in section 2.2.

2.1 $\epsilon(T)$ for the case of asymmetric double well potentials -- $\Delta_0 \ll \Delta_A$

In this limit one can neglect the second half of Eqn. 4. The two remaining integrals are constants and one has:

$$\alpha = \frac{1}{15} [a + \pi^2 b (kT)^2]$$

One calculates the effect of this polarizability from the Clausius Mosetti equation:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} + \frac{4\pi}{3} \left[\frac{\mu^2 a}{6} + \frac{\pi^2 \mu^2 b (kT)^2}{90} \right]$$

Solving for ϵ one finds

$$\epsilon = \epsilon_0 \left[1 + \frac{2\pi b}{405} \frac{(\epsilon_0 + 2)^2}{\epsilon_0} (\mu \pi kT)^2 \right] \quad (5)$$

where a has been absorbed into ϵ_0 .

Note that the temperature dependence of ϵ is a direct consequence of the energy dependent density of tunneling systems (see Eqn. 3) determined from specific heat measurements. If in fact the distribution is energy independent, one would expect the $\ln(T)$ temperature dependence observed by Hunklinger *et al.*⁸. That would come from the second half of Eqn. 4, but is quite small and can be ignored in this limit because it contains the factor $(\frac{\Delta_0}{\Delta})^2$.

GeO_2 and Polymethylmethacrylate (PMMA)⁹ were used for our dielectric measurements. They were ground to ~ 0.3 mm thickness, and had $\sim 2 \text{ cm}^2$ gold electrodes. The capacitances of these samples were measured between 0.06 K and 0.35 K at 1.4, 14, and 140 kHz. In addition, unpublished data by T. Fiory was analyzed. He measured the capacitance of fused silica at 0.1, 1, 10, and 100kHz between 0.07 K and 0.4 K. In this range the effect of thermal expansion is completely negligible; the expansion coefficients for these materials at 1 K are in the range 10^{-7} to 10^{-8} K^{-1} . Least squares fits of the function $C_0(1 + \alpha T^2)$ to the measured capacitance, C ; the results are shown in Table 1.

One can see that although there is a significant temperature dependence at the lower frequencies, it disappears at the highest frequencies for SiO_2 , and nearly disappears for PMMA (see Fig. 2). Since one knows from Goubau's high speed heat capacity measurements¹⁰ that the systems responsible for the excess specific heat can equilibrate in considerably less than 10^{-5} seconds, one can conclude that the lower frequency temperature dependence is unrelated to the excess specific heat. The upper limit on μ is then given by the uncertainty in the T^2 coefficient for GeO_2 (8.2×10^{-4}) and SiO_2 (8.1×10^{-3}) and by the barely significant T^2 coefficient for the PMMA (8.6×10^{-4}). From Eqn 5, one has:

$$\delta > \frac{2\pi b}{405} \frac{(\epsilon_0 + 2)^4}{9\epsilon_0} (\mu \pi k_B T)^2$$

Solving for μ the inequality becomes:

$$\mu \leq \left(\frac{405}{2\pi} \frac{\delta \epsilon_0}{b} \right)^{1/2} \left[\pi k_B T (\epsilon_0 + 2) \right]^{-1/2}$$

The values used for b and ϵ_0 are shown in Table 2. Taking $T = 225$ K, the middle of our temperature range¹¹, one finds:

	GeO ₂	PMMA	SiO ₂	
$\mu \leq$	5.5	4.9	16.8	Debye

2.2 $\epsilon(T)$ for the case of symmetric double well potentials — $\Delta_o \gg \Delta_A$

There is no evidence that $\left(\frac{\Delta_o}{\Delta_A}\right)^2$ is small enough that the second half of equation 4 can be neglected. Indeed, from the scattering strength measured by Pichè, one might argue that it must be reasonably close to 1. In that case, one has $\left(\frac{\Delta_A}{\Delta_o}\right)^2 \ll 1$, can now ignore the first half of Eqn. 4, and gets:

$$\alpha_T = \frac{\mu^2}{6} \left(a \int_0^{x_u} \frac{\tanh x}{x} dx + \frac{4b}{3} \int_0^{x_u} x \tanh x dx \right) \quad (6)$$

We then split the integrals into two parts:

$$\int_0^1 \frac{\tanh x}{x} dx + \int_1^{x_u} \frac{dx}{x} \quad \text{and} \quad \int_0^1 x \tanh x dx + \int_1^{x_u} x dx$$

Where we have taken $\tanh(x) = 1$ for $x > 1$. The first integral of each pair can be numerically integrated to give a constant, and the second can be analytically analyzed. One obtains:

$$0.9088 + \ln\left(\frac{\Delta_u \beta}{2}\right) \quad \text{and} \quad 0.2850 + \frac{1}{2} \left(\frac{\Delta_u \beta}{2}\right)^2 - \frac{1}{2}$$

respectively. Plugging them back into Eqn 6, one finds two temperature dependent terms

$$\alpha(T) = \frac{\mu^2}{6} \left[a \ln\left(\frac{\Delta_u \beta}{2}\right) - \frac{0.86}{3} b \right] \quad (7)$$

which gives a temperature dependent dielectric constant of the form

$$\epsilon = \epsilon_0 \left\{ 1 + \frac{4\pi(\epsilon_0 + 2)^2}{9\epsilon_0} \frac{\mu^2}{6} \left[a \ln\left(\frac{\Delta_u}{2k_B T}\right) - 0.86 b (k_B T) \right] \right\} \quad (8)$$

Again, the constant terms have been absorbed into ϵ_0 .

Analyzing the contribution each term makes in our temperature range (.06 K < T < .35 K), one finds that the $\ln(T)$ term is completely dominant. Note that unlike the asymmetric case, in this limit the temperature dependence of ϵ is not a consequence of the nonuniform distribution of tunneling states.

We made least squares fits of the function $C_{\infty}[1+a \ln(1/T)]$ to the 140 kHz data. The results are shown in the bottom part of Table 1. One can see that there is no significant functional dependence. As before, the upper limit on μ is then given by the uncertainties in the $\ln(1/T)$ coefficient listed in Table 1. From Eqn. 8 one has:

$$\frac{S}{C_{\infty}} \geq \frac{4\pi}{3} \frac{(\epsilon_{\infty} + 2)^2}{3\epsilon_{\infty}} \frac{\mu^2}{6} a$$

Solving for μ the inequality becomes:

$$\mu \leq \frac{3}{(\epsilon_{\infty} + 2)} \left(\frac{3 S C_{\infty}}{2 \pi a} \right)^{1/2}$$

The values for a and ϵ_{∞} are shown in Table 2. One then finds:

GeO ₂	PMMA	SiO ₂	
$\mu \leq .062$	.16	.27	Debye

3. Electric field dependent thermal conductivity of SiO₂.

In the second set of experiments, we attempted to determine whether the "glassy" excitations had a significant dipole moment by using it to shift their distribution in energy via a large electric field. We assumed that the thermal conductivity at temperature T is determined by the density of systems with $\Delta = 3k_B T$ and with $\frac{\Delta_0}{\Delta} \sim 1^{15}$. Therefore, any shift in this distribution should result in a change in the thermal properties, i.e.

$$\frac{\Delta \Lambda(T)}{\Lambda(T)} \sim - \frac{\Delta n(\Delta)}{n(\Delta)}, \quad \Delta \sim 3k_B T \quad (9)$$

where the size of this effect is determined by the functional form of $n(\Delta)$ and by the shift in Δ caused by the electric field. One would assume, a priori that $n(\Delta)$ is determined by the observed excess in a glass's specific heat. In our temperature range, one can produce a reasonably accurate fit to the data using the function

$$n(\Delta) = a + b\Delta^2.$$

Values of a and b are given in Table 2.

An electric field affects the asymmetry of a double well potential so the energy levels are modified in the following way:

$$\Delta(\mathcal{E}) = [\Delta_0^2 + (\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}})^2]^{1/2} \quad (10)$$

where $\Delta(\mathcal{E})$ is the total difference between the lowest two levels, Δ_0 is the overlap integral, and arises from the finiteness of the barrier between the wells, Δ_A is caused by the asymmetry of the well potentials, and $\vec{\mu} \cdot \vec{\mathcal{E}}$ gives the effect of an external field on the asymmetry.

In the limit that $\vec{\mu} \cdot \vec{\mathcal{E}} \ll \Delta$, one can expand Eqn. 10 to get:

$$\Delta(\mathcal{E}) = \Delta(0) \left\{ 1 + \frac{\Delta_A}{\Delta} \frac{\vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} + \frac{(\vec{\mu} \cdot \vec{\mathcal{E}})^2}{2\Delta^2} - \frac{1}{2} \left(\frac{\Delta_A}{\Delta} \right)^2 \left(\frac{\vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} \right)^2 + \mathcal{O}[(\vec{\mu} \cdot \vec{\mathcal{E}})^3] \right\}. \quad (11)$$

Since the systems which strongly scatter the phonons are just those for which $\frac{\Delta_A}{\Delta} \sim 0$ (The scattering strength of these systems is proportional to $(\frac{\Delta_A}{\Delta})^2$; their strength is reduced by the extent to which the systems is localized in one of the wells by their asymmetry⁷), Eqn. 11 simplifies to;

$$\Delta(\mathcal{E}) = \Delta(0) \left[1 + \frac{1}{2} \left(\frac{\vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} \right)^2 \right] \quad (12)$$

Therefore, the new distribution, $n'[\Delta(\mathcal{E})]$ produced by turning on the electric field is given by:

$$\begin{aligned} n'[\Delta(\mathcal{E})] &= n[\Delta(0)] = n\left[\Delta(\mathcal{E}) \left[1 - \frac{1}{2} \left(\frac{\vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} \right)^2 \right] \right] \\ &= a + b\Delta^2(\mathcal{E}) \left[1 - \frac{1}{2} \left(\frac{\vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} \right)^2 \right] \\ &= n[\Delta(\mathcal{E})] - b(\vec{\mu} \cdot \vec{\mathcal{E}})^2. \end{aligned}$$

Since these systems are randomly placed, one has to also average over all orientations. This process yields:

$$n'[\Delta(\mathcal{E})] = n[\Delta(\mathcal{E})] - \frac{b}{3}(\mu\mathcal{E})^2. \quad (13)$$

Plugging Eqn. 13 into Eqn. 9, one predicts a change in the conductivity of the form:

$$\frac{\Delta \Lambda(\tau)}{\Lambda(\tau)} = -\frac{\Delta n'}{n'} = \frac{\frac{1}{3} b \mu^2 \mathcal{E}^2}{\alpha + b(3kT)^2} \quad (14)$$

Note that the expected effect in this case derives solely from the assumed non-uniform distribution of tunneling states. (The compression of the sample by the voltage on the electrodes will also affect the conductivity, but that effect is insignificant; one would expect a decrease in Λ of $\sim 10^{-4}\%$).

In order to detect this effect, the thermal conductivity of a piece of fused quartz in fields of 0 and 10^5 V/cm was measured between 0.15 and 1 K. A sketch of the experimental set up is shown in Fig. 3. It was constructed from a "Vitreosil" fused quartz microscope cover slip, $1" \times 1" \times 200 \mu^{15}$. Stripes of Indium (which will wet bare glass) was used for contacts for the heater, heat sink, and the two thermometers. Semi-transparent tin electrodes were evaporated on both sides. Because the electrodes are superconducting and very thin, they do not affect the conductivity of the sample.

The electrodes are big enough that most of the heat flows between them. This was checked by comparing the ℓ/A_{geom} calculated from the sample geometry (assuming all the heat flows directly between the tin stripes), to the ℓ/A_{exp} calculated by normalizing the thermal conductivity results to previous measurements on Vitreosil. It was found that $\ell/A_{\text{geom}} = 11.6 \text{ cm}^{-1}$, and $\ell/A_{\text{exp}} = 10.2 \text{ cm}^{-1}$. The rest of the sample serves to insulate the high voltage electrode from ground. In order to further protect against electric breakdown, all edges of the sample and electrode are coated with a thin layer of low temperature varnish (GE #7031).

The results are shown in Figures 4 and 5. In Fig. 4 the vertical scale was determined by comparison to previous thermal conductivity measurements¹³. The deviation below

0.2 K is due to the thermal resistance of an indium-glass interface which was included in the measurement; the cold thermometer was soldered to the heat sink rather than separately to the glass. The scatter in the data is shown in Figure 5 in which both sets of data are plotted as the deviation from a smooth fit to all the data points. The scatter increases below 0.4 K because of difficulty in reaching steady state conditions in such a spidery shaped sample at low temperatures.

It is clear that any field dependent changes are less than the 2% scatter in the data. A careful analysis shows a barely significant decrease of $0.4 \pm .3$ % in the conductivity when the field was turned on (the opposite direction from the predicted effect). Using this value, one can set an upper limit on μ . Solving Eqn. 14 for μ gives:

$$\mu \leq \left[\frac{3\Delta\Lambda}{\Lambda} \left(\frac{a/b + 9k_B T^2}{\epsilon^2} \right) \right]^{1/2}$$

The values of a and b are given in Table 2. We took $T = .5$ K, the middle of our temperature span. The applied field was 10^5 V/cm. To get the local field on the tunneling systems, one must calculate the Lorentz correction¹⁶; we used

$$\epsilon_{\text{local}} = \frac{5.78}{3} \times 10^5 \text{ V/cm. Then one finds } \mu \leq 0.10 \text{ Debye.}$$

A similar experiment had been done previously at 2.2 K by Challis and Hooker¹⁷. The barely significant change which they found corresponded to a $\mu = 0.5 \pm 0.3$ Debye.

4. Discussion

Neither of the above experiments yielded any solid evidence for the existence of an electric dipole moment, μ , associated with these glasses' low temperature properties. We therefore expressed our results as upper limits on the size of μ . However, in conjunction with the dielectric measurements on SiO_2 by Schickfus et al.⁸, these limits allow us to draw some new conclusions about the necessary characteristics of a tunneling systems model.

Schickfus et al. found a logarithmic temperature dependence for the SiO_2 dielectric constant. From our analysis in section 2, it is clear that therefore the potential must be nearly symmetric, i.e. $\Delta_o \gg \Delta_A$.¹⁸ The appropriate limits from our dielectric measurements then are those calculated in section 2.2: $\mu_{\text{GeO}_2} \leq .062 \text{ D}$, $\mu_{\text{PMMA}} \leq .16 \text{ D}$, and $\mu_{\text{SiO}_2} \leq .27 \text{ D}$. Our limit for SiO_2 does not conflict with Schickfus' value of 0.3 Debye. The limits for GeO_2 and PMMA are considerably smaller than that and reinforce Schickfus' conclusion that these tunneling systems must be formed from a relatively large atomic cluster in the glass. The dipole moment for a single atom system would be much larger.²

Our thermal conductivity experiment yielded an upper limit of $\mu_{\text{SiO}_2} \leq .10 \text{ Debye}$. This is considerably less than Schickfus' value of .3 Debye. In order to resolve this conflict, one must radically revise our ideas about the tunneling systems model.

Our experiment explicitly assumes that the low temperature phonon scattering and the excess in the heat capacity are caused by the same system. This assumption provides an elegance for the model since it need only invoke a single mechanism to explain all the low temperature phenomena,

but is not otherwise proven. Indeed, recent measurements by Stephens¹⁹ and Lasjaunias et al.²⁰ suggest that the relationship between the excess specific heat and the phonon lifetime, is not simple. They found the magnitude and temperature dependence of the excess specific heat and the phonon lifetime, if it exists at all, is not simple; the magnitude and temperature dependence of the excess specific heat is somewhat sample dependent though the thermal conductivity is not. At best this means that not all of the states seen in the specific heat are active phonon scatterers; at worst none of them are. The interpretation of the thermal conductivity change, however, depends on knowing the distribution of states; the expected effect comes about specifically because of the nonuniform distribution of states observed in the specific heat measurements, $n(\Delta)_C$.

A tunneling systems model has had great success in describing the thermal conductivity and the nonlinear phonon scattering,⁶ so our inclination is to make the best of the situation and assume that most of the specific heat is due to the tunneling systems (with that assumption, their phonon scattering strength is similar to that of other tunneling systems; see section 2). The residue of excitations are from sample dependent "dirt" systems, which do not scatter phonons as remarkably strongly as do tunneling systems. In this case one can make a statement about the distribution of tunneling states, $n(\Delta)_{\text{tun}}$. We use Schickfus et al.'s measurement of μ and work backwards to calculate the shape of the distribution $n(\Delta)_{\text{tun}}$. We find that in our range of measurements ($1 \text{ K} \leq \Delta/k_B \leq 3 \text{ K}$) the distribution must be flat to within 6%. That is $\sim 1/9$ the observed value.²¹

$n(\Delta)_{\text{tun}}$ cannot remain flat in the limit as one goes to lower temperatures. Lasjaunias²⁰ has shown that the specific heat of SiO_2 drops faster than linearly, and thus $n(\Delta)_C$ is diminishing, down to the lowest limit of his measurement (25 mK). At that temperature, $n(\Delta)_C$ is only p

1/2 that at 250 mK. It would be interesting to see if $n(\Delta)_{\text{tun}}$ remains flat at that lower temperature. If so, then, since $n(\Delta)_C \leq n(\Delta)_{\text{tun}}$, one would have to put a smaller upper bound on the magnitude of $n(\Delta)_{\text{tun}}$. This would mean that the tunnel systems' dipole moment and phonon coupling would be considerably larger than is presently calculated.

5. Summary

Our attempt to find manifestations of an electric dipole moment associated with the low temperature thermal properties of glasses has enabled us to set very low limits for GeO_2 and PMMA; .06 and .16 Debye respectively.

Our measurements of the temperature dependence of the dielectric constant and the electric field dependence of the thermal conductivity of SiO_2 in conjunction with dielectric measurements by Schickfus et al. has pinned down some of the features of a tunneling systems model. The potentials must be nearly symmetric ($\Delta_o \gg \Delta_A$) and the distribution of these states, $n(\Delta)_{\text{tun}}$, must be considerably more uniform than one would calculate from measurements of the specific heat of SiO_2 , $n(\Delta)_{C_p}$.

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Appendix 1

The Polarizability of an asymmetric double well potential

The polarizability of such a system is not simple, but its calculation is straight forward. One starts from the partition function

$$Z = \exp\left[-\left(\frac{\Delta}{2}\right)\beta\right] + \exp\left[-\left(-\frac{\Delta}{2}\right)\beta\right] = 2 \cosh\left(\frac{\Delta\beta}{2}\right). \quad (9)$$

From this one can determine the free energy

$$F = -\frac{1}{\beta} \ln Z$$

and finally the polarizability

$$\alpha = -\frac{\partial^2 F}{\partial \mathcal{E}^2}.$$

Therefore $\alpha = \frac{1}{\beta} \frac{\partial^2}{\partial \mathcal{E}^2} \ln Z = \frac{1}{\beta} \left[-\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \mathcal{E}} \right)^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial \mathcal{E}^2} \right]$, (10)
and one merely has to evaluate $\frac{\partial Z}{\partial \mathcal{E}}$ and $\frac{\partial^2 Z}{\partial \mathcal{E}^2}$ through eqns

1 and 9, and plug the results into equation 10. So

$$\begin{aligned} \frac{\partial Z}{\partial \mathcal{E}} &= \frac{\partial}{\partial \mathcal{E}} \cosh \frac{\Delta\beta}{2} = 2 \sinh \frac{\Delta\beta}{2} \left[\frac{1}{2} \frac{\Delta}{\Delta} (\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}}) \mu \cos \theta \right] \frac{\beta}{2} \\ &= 2 \sinh \frac{\Delta\beta}{2} \left(\frac{\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} \right) \frac{\mu\beta}{2} \cos \theta. \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 Z}{\partial \mathcal{E}^2} &= 2 \cosh \frac{\Delta\beta}{2} \left[\left(\frac{\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta} \right) \frac{\mu\beta}{2} \cos \theta \right]^2 \\ &\quad + 2 \sinh \frac{\Delta\beta}{2} \left[\left(\frac{\mu \cos \theta}{2 \Delta} \right)^2 \beta + \frac{\mu\beta \cos \theta}{2} \left(\frac{\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta^2} \right) \left(-\frac{1}{2} \right) \Delta (\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}}) \mu \cos \theta \right] \\ &= (\mu \cos \theta)^2 \beta \left[\cosh \frac{\Delta\beta}{2} \left(\frac{\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}}}{\Delta^2} \right)^2 \frac{\beta}{2} + \sinh \frac{\Delta\beta}{2} \left(\frac{1}{\Delta} - \frac{(\Delta_A + \vec{\mu} \cdot \vec{\mathcal{E}})^2}{\Delta^3} \right) \right]. \end{aligned}$$

In the limit of small fields

$$\left. \frac{\partial Z}{\partial \mathcal{E}} \right|_{\mathcal{E}=0} = \sinh \left(\frac{\Delta\beta}{2} \right) \frac{\Delta_A}{\Delta} \mu\beta \cos \theta$$

$$\left. \frac{\partial^2 Z}{\partial \mathcal{E}^2} \right|_{\mathcal{E}=0} = (\mu \cos \theta)^2 \beta \left[\cosh \left(\frac{\Delta\beta}{2} \right) \frac{\Delta_A^2}{\Delta^2} \frac{\beta}{2} + \sinh \left(\frac{\Delta\beta}{2} \right) \frac{1}{\Delta} \frac{\Delta_0^2}{\Delta^2} \right].$$

Then

$$\begin{aligned} \alpha(\theta) &= \frac{1}{\beta} \left[-\frac{1}{4 \cosh^2 \left(\frac{\Delta\beta}{2} \right)} \sinh^2 \frac{\Delta\beta}{2} \left(\frac{\Delta_A}{\Delta} \right)^2 (\mu\beta \cos \theta)^2 \right. \\ &\quad + \frac{1}{2 \cosh \left(\frac{\Delta\beta}{2} \right)} \cosh \frac{\Delta\beta}{2} \left(\frac{\Delta_A}{\Delta} \right)^2 (\mu\beta \cos \theta)^2 \frac{1}{2} \\ &\quad \left. + \frac{1}{2 \cosh \left(\frac{\Delta\beta}{2} \right)} \sinh \frac{\Delta\beta}{2} \left(\frac{\Delta_0}{\Delta} \right)^2 \frac{\beta}{\Delta} (\mu \cos \theta)^2 \right] \end{aligned}$$

$$\text{So: } \alpha = (\mu \cos \theta)^2 \left[\operatorname{sech}^2 \left(\frac{\Delta\beta}{2} \right) \frac{\beta}{4} \left(\frac{\Delta_A}{\Delta} \right)^2 + \tanh \left(\frac{\Delta\beta}{2} \right) \frac{1}{2\Delta} \left(\frac{\Delta_0}{\Delta} \right)^2 \right] \quad (11)$$

Footnotes

1. R. O. Pohl, W. F. Love and R. B. Stephens, Proc. of the 5th Int. Conf on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen, 1973, p.1121.
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5. The O^- ion has been suggested as a mechanism for producing low frequency excitations in SiO_2 for everything observed below 30 K; see R. E. Strakna, Phys. Rev. 123 2020 (1961), and A. F. Clark and R. E. Strakna, Phys. Chem Glass 3 121 (1962).
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8. M. von Schickfus, S. Hunklinger and L. Piche, Phys. Rev. Lett. 35 876 (1975).
9. Acrylic Plastic from Norcen Ind. Inc., 502 Railroad St., Jersey Shore, Penn. 17740.
10. W. M. Goubau and R. A. Tait, Phys. Rev. Lett. 34 1220 (1975).
11. We fit the data as a function of temperature squared; 0.25 K is the middle of our range on that scale.
12. R. B. Stephens, Phys. Rev. B 8 2896 (1973).

13. ϵ_0 was calculated for GeO_2 and PMMA from the geometry of the samples; ϵ_0 for fused quartz was taken from A. E. von Hippel, *Dielectric Materials and Applications* (New York: John Wiley and Sons, Inc., 1954).
14. J. Jäckle, *Z. Physik* 257 212 (1972).
15. The cover slip was obtained from the Thermal American Fused Quartz Co.
16. $\epsilon_{\text{applied}}$ is not the same as ϵ_{local} ; see C. Kittel, Introduction to Solid State Physics, 3rd ed. (New York: John Wiley and Sons, Inc., 1968) p. 381 for a derivation of the Lorentz correction. For cubic symmetry,

$$\epsilon_{\text{local}} = \frac{1}{3}(\epsilon + 2) \epsilon_{\text{applied}}.$$
17. L. H. Challis and C. N. Hooker, *J. Phys. C* 5 1153 (1972).
18. Schickfus et al. analyzed their data using the assumption that the potentials were symmetric, but did not mention it or its inevitability from the form of their data
19. R. B. Stephens, *Phys. Rev. B* (to be published 15 Dec 1975).
20. J. C. Lasjaunias, A. Ravex, M. Vandorpe and S. Hunklinger, *Proc. of the 2nd Int. Conf. on Phonon Scattering in Solids*, ed. L. J. Challis (New York: Plenum Pub. Corp.).
21. Piche et al. (ref 6) states that to get good agreement of theory with their sound velocity data, they use the distribution $n(\Delta)_C$. They do not state how bad the fit would be or how much it is improved over that for a uniform distribution.

Table 1: The temperature dependence of the dielectric constants of GeO_2 , PMMA, and SiO_2 between 0.07 and 0.4 K. The data for the SiO_2 is from unpublished work by A. T. Fiory. The dependence is described by the parameters, C_0 and a , of a least squares fit. The function $C(T) = C_0(1 + aT^2)$ was used for the upper section of the table, and $C(T) = C_0(1 + a\ln(1/T))$ for the bottom part.

$C(T) = C_0(1 + aT^2)$			
Material	$C_0(\text{pf})$	$a(\times 10^{-5})$	$f(\text{kHz})$
GeO_2	31.5253	$1.20 \pm .48$	1.4
	31.5213	$.139 \pm .19$	14.
	31.4420	$.031 \pm .19$	140.
PMMA	16.8176	$3.17 \pm .24$	1.4
	16.8155	$2.34 \pm .18$	14.
	16.7941	$.66 \pm .31$	140.
SiO_2	38.3722	$.85 \pm 1.9$	.1
	38.3612	1.1 ± 1.8	1.
	38.3526	$.54 \pm .87$	10.
	38.3768	$-.50 \pm 1.2$	100.
$C(T) = C_0(1 + a\ln(1/T))$			
Material	$C_0(\text{pf})$	$a(\times 10^{-4})$	$f(\text{kHz})$
GeO_2	31.4424	$-.064 \pm .19$	140.
PMMA	16.7962	$-.53 \pm .45$	140.
SiO_2	38.3747	$.19 \pm 1.3$	100.

Table 2: Values of materials parameters used in calculations for μ .

	GeO_2	PMMA	SiO_2	units
a^{12}	18.3	10.3	8.4	$10^{32} \text{erg}^{-1} \text{cm}^{-3}$
b^{12}	.29	1.7	.27	$10^{64} \text{erg}^{-3} \text{cm}^{-3}$
ϵ_0^{13}	8.0	2.8	3.78	

Figure Captions

1. a) An asymmetric two-well potential with barrier height V_B , asymmetry V , and well separation d .
b) Energy level spacing for a two-well potential with a finite and infinite barrier height.
2. Capacitance vs. temperature for GeO_2 , PMMA, and SiO_2 . The SiO_2 data is after unpublished data by T. Fiory. The dashed lines indicate the least squares fit of the function $C = C_0(1 + a \ln(1/T))$ to each of the sets of data.
3. Front and rear views of the sample used in measuring thermal conductivity in a large electric field. The high voltage electrode is isolated by a cover slip which is glued to the sample only along its edge. The heater, heat sink, and thermometers are soldered to the ground electrode with indium. All edges of the sample and electrode are coated with a thin layer of varnish. In spite of the unusual geometry, most of the heat flows directly from the heater to the heat sink between the electrodes; all other heat flow paths are much longer.
4. Thermal conductivity of Vitreosil high electric field sample. The vertical scale was determined by comparison to previous thermal conductivity measurements on the same material (solid line). The deviation below 0.2 K is due to the thermal resistance of an indium-glass interface, which was included in the measurement since the cold thermometer was soldered to the heat sink rather than separately to the glass.
5. Thermal conductivity of Vitreosil high electric field sample plotted as the percentage deviation from a polynomial fit. The filled circles are the data for $\mathcal{E} = 0$; the open circles are the data for $\mathcal{E} = 10^5$ V/cm.

a) Asymmetric Double Well Potential

b) Asymmetric Double Well Energy Levels