Temperature and frequency dependence of the sound velocity in vitreous silica due to scattering off localized modes

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The behavior of the sound velocity in vitreous silica is investigated in a range of temperatures around that of the plateau in the thermal conductivity. Localized vibrational modes play an important role in thermal transport and inelastic phonon scattering in this temperature regime. A model based on the idea of a crossover from phonon to fracton vibrational dynamics at frequencies of the order of the plateau temperature has been developed, and is used to calculate the expected temperature and frequency dependence of the velocity of sound. The result can be expressed in terms of experimentally measurable quantities, and contains no arbitrary parameters. Good agreement is obtained with available experimental data.

I. INTRODUCTION

The velocity of sound in a number of amorphous materials exhibits a temperature dependence that is very different from that of crystals. The change in the sound velocity is decidedly nonmonotonic at low temperatures (see Fig. 1) in contrast to the crystalline case. The initial temperature dependence of the sound velocity in conventional glasses at very low temperatures is rather successfully accounted for in terms of two-level systems (TLS's).[1] Thus, below 1 K or so, the temperature dependence of the velocity of sound arises from resonant scattering of the phonons off TLS's.[2] In the vicinity of 1 K and above, relaxational scattering is said to come into play, leading to a decrease in the sound velocity with increasing temperature. The temperature dependence is predicted to be logarithmic (with the sign reversed with respect to the resonant scattering regime) and is observed experimentally.[3] With continuing increase in temperature, the sound velocity exhibits a stronger temperature dependence. It is in this regime, above 10 K or so, that we suggest effects due to scattering from localized vibrational modes become dominant. The temperature scale for this regime is set by the experimental observation of a "plateau" in the thermal conductivity of glasses. This sets the energy scale for the onset of localized vibrational excitations, or fractons in the model that we shall use for the calculations. In our discussion, we shall use the measured thermal properties of glasses along with theoretical expressions for the various vibrational scattering lifetimes in the problem[4,5] to obtain an expression for the sound velocity from the temperature of the plateau of the thermal conductivity ~ 10 K to temperatures ~ 60 K.

Referring again to Fig. 1, the sound velocity decreases to a minimum at about 60 K, then increases with increasing temperature. The linear increase at high temperature is linked to a similar increase in the elastic constants. It has been speculated[6] that this increase is caused by density fluctuations, a view supported by the observation that the slope of the linear region appears to scale with the melting temperatures of the glasses studied. However, this linear region is outside the scope of our present model. Here we shall consider the additional temperature dependence of the velocity of sound that results from the scattering of phonons from the localized excitations. The characteristic energy scales correspond to a range of temperature from about 10 to 60 K or so, where the sound velocity, v_s decreases with increasing temperature. We use the fracton model developed to treat the thermal transport in this regime of temperature and find that the change in the sound velocity in this regime can be expressed in terms of measured quantities (e.g., the thermal conductivity κ). Thus, in addition to the temperature

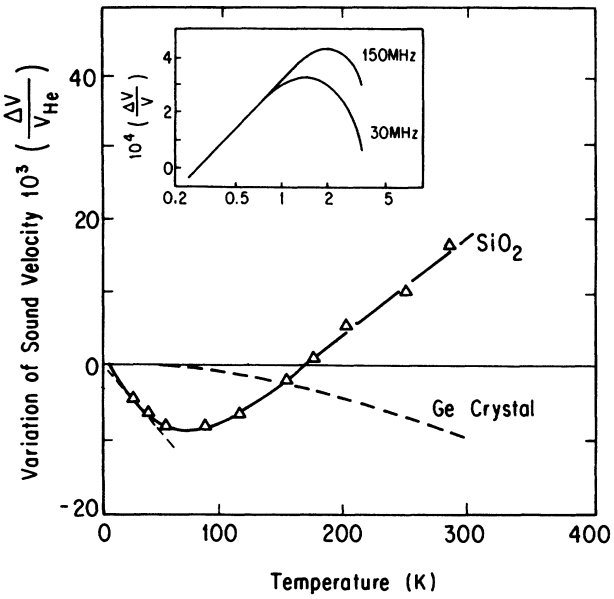

FIG. 1. Plot of the fractional change in sound velocity for vitreous silica as a function of temperature and, for purposes of comparison, for crystalline germanium (from Ref. 2). The inset shows an enlarged plot of the typical behavior at small T for three different frequencies. The dashed line is an estimate of the slope of the linear region, as discussed in the text.

dependence of v_s, which we find to be linear, we provide a quantitative estimate of the change in v_s using the measured thermal conductivity. A brief outline of our model now follows.

At the lowest temperatures, phonons are scattered predominantly by TLS's resulting with a characteristic $\tanh(\beta\omega)$ dependence of the mean free path for phonon scattering, where $\beta=(k_\beta T)^{-1}$. We assume a different scattering process at "intermediate" temperatures (our reference being the plateau temperature). Thermal phonons now scatter from localized vibrational modes which are increasingly excited as the temperature approaches that of the plateau. We consider here the change in the velocity of phonon propagation arising from phonon scattering by fracton modes. These modes are assumed to couple to the phonon via a third-order anharmonic coupling term in the elastic Hamiltonian.

Our model assumes the existence of a crossover in the density of states from extended to localized regimes. The crossover occurs at a frequency corresponding to the temperature of saturation of the phonon contribution to the heat conductivity (the "plateau" temperature). The energy scale for this crossover is set by a length scale of the structural disorder in the glass. More specifically, one assumes that the glass may be considered to be structurally homogeneous at large length scales, but fractally connected at a microscopic length scale. The crossover length scale in our model is that at which the elastic force-constant connectivity crosses over from three dimensional (3D) to fractal. The vibrational modes at short length scales (high frequency) are termed fractons. They are taken here to be superlocalized objects characterized by wave functions which decay faster than exponentially in distance.[7] The consequences of third-order anharmonic interaction between phonon and fracton modes can be calculated in terms of this model and compared with a variety of experimental data.

One such successful application of this model to glasses, proposed by Alexander *et al.*,[8] has been the computation of the contribution to heat transport arising from fracton modes. At sufficiently high temperature, it was suggested[4] that anharmonic interactions allow for heat transport by localized vibrational-mode diffusion via phonon-assisted fracton hopping. This has been shown recently to generate a quantitative prediction for the increase in the hopping conductivity above the value at the plateau, in good agreement with measured values.[5] Our consideration of the associated changes in the sound velocity in this paper will be restricted, similarly, to temperatures high enough that scattering processes between phonons and fractons dominate. This is expected to occur in a range of temperatures starting somewhat below the plateau in the thermal conductivity up to a temperature beyond which the model is not applicable (see Ref. 5 for details). In the case of vitreous silica, this corresponds to a range of temperatures from 10 to 60 K or so.

Anharmonic-interaction-induced phonon scattering from fracton states gives rise to a temperature-dependent decrease of the sound velocity. Above the temperature of the plateau, the decrease will be shown to be linear in the temperature. Furthermore, we will show that the mechanism responsible for the change in sound velocity is the same as that responsible for thermal conductivity. Therefore, the sound velocity can be expressed directly in terms of the hopping contribution to the thermal conductivity, reducing the number of adjustable parameters. Expressed in such a manner, the theoretical value for the decrease in sound velocity with increasing temperature is found to be close to values measured by experiment.[2]

As noted above, the anharmonic-interaction-induced phonon-fracton interaction has several observable consequences, one of which is the proposed contribution to heat conduction in glass.[5] Thus, the same processes that couple phonons to fractons and give rise to thermal transport generate an inelastic phonon lifetime. This would contribute to a diminution of the phonon mean free path. The temperature and frequency dependence of the phonon mean free path caused by phonon-fracton scattering has been calculated, and used in Ref. 5 to estimate the magnitude of the fracton-hopping contribution to the thermal conductivity. Our approach here is similar. We express the change in the velocity of sound in terms of the phonon mean free path, and then use measurements of the latter to determine the former.

We calculate the change in the velocity of sound within this model in Sec. II, and compare it with experiment in Sec. III. Section IV contains our summary.

II. COMPUTATION OF THE CHANGE IN VELOCITY OF SOUND

We make use of a Kramers-Kronig relation between the real and imaginary parts of the phonon self-energy due to the processes shown schematically in Fig. 2 to compute the change in the velocity of sound. The two-phonon one-fracton process [Fig. 2(a)] has been shown to result in a phonon scattering rate that is smaller by a factor ω/ω_c than that of Fig. 2(b), recalling that $\omega \ll \omega_c$ for the phonons typically studied in experiment. We will therefore begin by considering the contribution of the process pictured in Fig. 2(b), the one responsible for the hopping contribution to thermal conductivity, $\kappa(T)$.

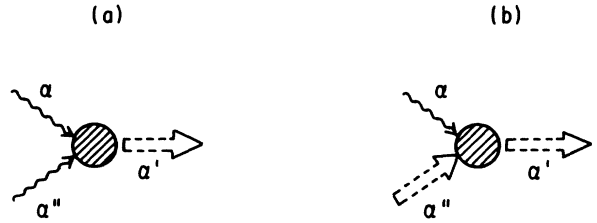

FIG. 2. Schematic illustration of the processes contributing to phonon scattering at intermediate temperatures (i.e., in the vicinity of the plateau temperature). Extended phonon states are denoted by wavy lines, localized fracton states by double-dashed lines. Process (*a*) corresponds to two phonons combining into a fracton; process (*b*) corresponds to a phonon combining with a fracton to form a fracton. Process (*b*) is responsible for the phonon-induced fracton-hopping contribution to the thermal conductivity.

The interaction between phonon and fracton modes proceeds by virtue of the lattice anharmonicity which we express by the form

$$\mathcal{H}_{\rm int}=C_{\rm eff}\sum_{i,j,k}A_{ijk}B_i^{\dagger}b_j^{\dagger}b_k+\text{H.c.}\ , \tag{1}$$

where the $b^{\dagger}$ and b operators create and destroy modes that are either extended (phonons) or localized (fractons) depending on the mode frequency, denoted here by the subscript i or j. The factor A_{ijk} is a matrix element that can be computed from the wave functions of the modes involved in the scattering process. The anharmonic coupling $C_{\rm eff}$ is an important unknown parameter. It can be determined by comparison of our results with experiment, but we shall eliminate it by substitution of experimentally measurable quantities.

The matrix elements A_{ijk} for the two most important scattering processes, pictured in Fig. 2, have been computed in Ref. 5. The partial lifetime of a phonon of frequency ω ($\omega \ll \omega_c$) caused by the interaction process pictured in Fig. 2(b) has been calculated to lowest order in $C_{\rm eff}^2$ to be[5]

$$\tau_b^{-1}(\omega,T)=C_b\omega^2T \tag{2}$$

at temperatures satisfying the condition $k_BT>\hbar\omega_c$. The constant C_b is known in terms of the coupling $C_{\rm eff}$ and various numerical coefficients.[5] It was pointed out in Ref. 5 that the matrix elements and the parameters are not known precisely, leading to the possibility of large errors because of the high powers which enter into the estimation of C_b in Eq. (2). One can minimize these errors by eliminating the matrix element A_{ijk} using the expression for the fracton-hopping contribution to $\kappa(T)$, which arises from precisely the same process [i.e., that pictured in Fig. 2(b)]. Doing so enables us to express the contribution to the phonon lifetime from Eq. (2) in terms of an experimentally measurable quantity, with some remaining dependence on the exponents characterizing the fractal network at short length scales. These are not known, but as they enter our equations as simple multiplicative constants, and there are physical grounds for believing these exponents to be small and of order unity for any real system, their precise numerical value is not necessary. It suffices for our purpose here to use values that have been found in numerical experiments on three-dimensional percolating networks (although it must be understood that the small-scale force-constant structure of vitreous silica, even if fractal, is not that of a percolating network).

Using the results of Ref. 5, the phonon scattering rate for process (b) is

$$\tau_b^{-1}(\omega,T)=0.09(\omega/\omega_c)^2\xi k_B^{-1}\kappa(T)\ , \tag{3}$$

where the numerical prefactor is evaluated using values of the various exponents in the problem appropriate to a 3D percolating network. This expression is accurate up to factors of order unity. The crossover length ξ is related to the crossover frequency ω_c by $\omega_c=2\pi v_s/\xi$. The value of the crossover frequency is such that the phonon mean free path is about equal to its wavelength.[9] Equation (3) gives us the phonon lifetime caused by the scattering process pictured in Fig. 2(b) in terms of measurable quantities, ξ and $\kappa(T)$. One caveat to be noted is that Eq. (3) is not valid at all temperatures. Our calculations hold only in the range from slightly below the plateau temperature to an upper limiting temperature determined by the breakdown of the perturbation expansion in $(\omega_c\tau_{\rm hop})^{-1}$, where $\tau_{\rm hop}$ is the fracton-hopping lifetime.

In fact, if one examines the sound attenuation in glasses (see Fig. 3), a universal behavior is observed when the inverse scattering rate [equivalently, the scattering rate given in Eq. (3)] rises[2] linearly with the temperature (as we calculate) in the temperature range that we consider here. At the upper end of this range, the observed scattering rate peaks, and then falls to lower values. This "absorption peak" has been attributed to relaxation by thermally activated processes.[10] This is supported by the observation that the shifts of the peak temperature with changes in the frequency are in good accord with an Arrhenius-type law. However, to explain the experimental data it is necessary to allow for a distribution of activation energies. Fitting the attenuation of phonons in the range from 20 to 1000 MHz, Hunklinger[11] found a fairly broad Gaussian spectrum with a mean activation energy of 410 K, and a half-width of about 550 K, with a cutoff for the lower end of the distribution. We suggest in this paper that there are additional scattering processes which contribute to the attenuation, Figs. 2(a) and 2(b), which should be taken into account when fitting the data. Presumably, this might merely serve to alter the phenomenological fitting parameters of Hunklinger.[11] The contribution from the scattering processes we consider is expected to be quenched at temperatures very much above the plateau temperature. We shall take Eq. (3) to be applicable immediately above the plateau temperature.

Using the Kramers-Kronig relation to obtain the change in the sound velocity corresponding to the

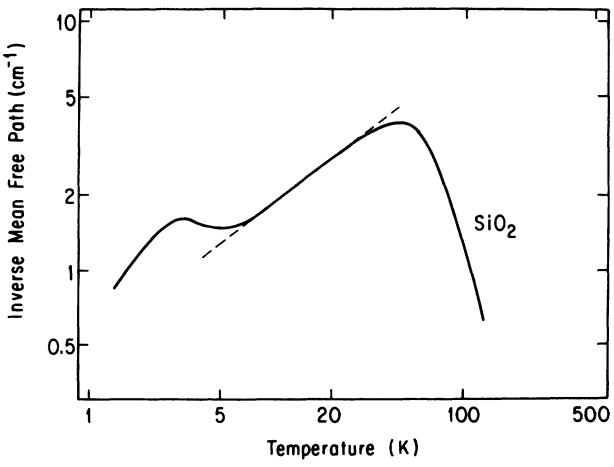

FIG. 3. Plot of the inverse mean free path vs temperature for longitudinal phonons of frequency 20 MHz for vitreous silica (from Ref. 2). The dashed line represents the linear dependence expected in the fracton-scattering regime.

scattering process (b), it is quite straightforward to find

$$\left.\frac{\delta v_s}{v_s}\right|_{(b)} = -(C_b T\omega_c/\pi) \times\{1+\tfrac{1}{2}(\omega/\omega_c)\ln[(\omega_c-\omega)/(\omega_c+\omega)]\} . \quad (4)$$

Expanding the logarithm, to lowest order in ω/ω_c, this becomes

$$\left.\frac{\delta v_s}{v_s}\right|_{(b)} = -(C_b T\omega_c/\pi)[1-(\omega/\omega_c)^2] . \quad (5)$$

In this expression, $\delta v_s/v_s$ varies linearly with T and is independent of the phonon frequency for low-frequency phonons. This is expected to be valid at temperatures $\sim\hbar\omega_c/k_B$, where fracton scattering becomes important. There is, as well, an upper cutoff determined by the temperature at which the fracton lifetimes become extremely short so that the phonon-fracton scattering process is quenched.[5]

We now turn to the second process for phonon scattering, pictured in Fig. 2(a), involving two phonons and one fracton. This process, (a), has been shown to result in a scattering rate given by[4,5]

$$1/\tau_a = C_a\omega^3 T , \quad (6)$$

where the constant C_a depends on a set of parameters similar to C_b. We can express C_a in terms of C_b using the values of the various exponents appropriate to a 3D percolating network. This is not as reliable as the procedure which led to Eq. (3) because C_a and C_b depend upon different matrix elements. The Kramers-Kronig formula for process (a) then yields

$$\left.\frac{\delta v_s}{v_s}\right|_{(a)} = -0.14(C_b T\omega_c/\pi)[1-(\omega^2/\omega_c^2)\ln(\omega_c^2/\omega^2)] . \quad (7)$$

Combining Eqs. (4) and (7), the total change in sound velocity is thus

$$\left.\frac{\delta v_s}{v_s}\right|_{(b)} = -(C_b T\omega_c/\pi) \times\{1.14-(\omega/\omega_c)^2/[1+0.14\ln(\omega_c^2/\omega^2)]\} \quad (8)$$

to leading order (note that the phonon frequencies typically used are around 20 MHz, far smaller than the crossover frequency, $\omega_c\sim 10^{12}$ s^{-1}).

III. COMPARISON WITH EXPERIMENT

We now make use of the observation that the hopping contribution to the thermal conductivity, $\kappa_{\rm hop}(T)$, is rather simply related to the phonon lifetime:[5] $\kappa_{\rm hop}(T)=\text{const}\times(k_B\omega_c^2\xi^{-1}/\omega^2\tau^{(b)})$. In this relation, ω is any phonon frequency, as in our model the product $\omega^2\tau^{(b)}$ is frequency independent for process (b), and depends only on the temperature [see Eq. (2)]. Eliminating C_b in terms of thermal conductivity, we find the leading term from Eq. (8) to equal

$$\left.\frac{\delta v_s}{v_s}\right|_{(b)} = -0.1(\xi^2/2\pi^2 v_s)[\kappa(T)/T]k_B^{-1}T . \quad (9)$$

The slope of this linear region can be found using Eq. (6) given the slope of the straight-line region of $\kappa(T)$, just beyond the plateau temperature. From the data of Cahill and Phol,[12] the slope of the linear region above the plateau is $\kappa(T)/T=8\times10^{-3}$ W/mK^2. From Ref. 9, the value of ξ is 15 Å. Using the velocity of sound in vitreous silica at the reference temperature to be $v_s=5.8\times10^3$ m/s at 0.28 K,[13] we find

$$\left.\frac{\delta v_s}{v_s}\right|_{(b)} = -(1.0\times10^{-3}\ \text{K}^{-1})T \quad (10)$$

valid for temperatures from 10 to 50 K or so (after which deviations from this simple linear behavior may be expected for the reasons explained in Ref. 5).

Referring to Fig. 1, experimentally one finds that $\delta v_s/v_s$ decreases with increasing temperature above liquid helium, with a minimum around 70 K, after which there is an increase with increasing temperature. We concentrate on the region below 50 K or so, where we expect our theory to work reasonably well. In this temperature regime, the experimental plot of sound velocity versus temperature exhibits curvature, while Eq. (9) accounts for a linear temperature dependence. If one interprets the experimental results in terms of a linear region sandwiched between crossover regions at either end, a value for the slope can be extracted. We extract a value of $\delta v_s/v_s$ for vitreous silica of $-(0.15\times10^{-3}\ \text{K}^{-1})T$. We must subtract from this slope a positive slope contribution of approximately $(0.12\times10^{-3}\ \text{K}^{-1})T$, which represents the increase attributed to density fluctuations (the dominant effect at higher temperatures, as shown in Fig. 1). The experimental value for the slope of the linear decrease is thus approximately -0.3×10^{-3} K^{-1}. Our calculated value [Eq. (10)] somewhat overestimates the slope. However, the numerical prefactors which led to Eq. (10) were only approximate, and so the agreement with experiment can be considered quite reasonable under the circumstances.

Above $\sim$50 K, we estimate that there will be substantial deviation from the simple perturbative results used here. At higher temperatures, moreover, phonon-fracton scattering becomes less effective because of fracton-lifetime effects.[5] This in turn implies that the phonon-fracton scattering contribution to $\delta v_s/v_s$ will diminish so that the increase due to coupling with density inhomogeneities will become dominant. This would then account for the minimum in $\delta v_s/v_s$ observed around 60 K, and its subsequent linear rise up to the highest temperatures measured.

A second prediction is the frequency dependence of $\delta v_s/v_s$, as given by Eq. (8). The leading term is independent of phonon frequency. The first correction is quadratic in phonon frequency, but down by $(\omega/\omega_c)^2$ in magnitude.

IV. SUMMARY

We have presented results on the effects of phonon-fracton scattering on the velocity of sound in glass. It is hoped that these will provide stimulus for further experiments. In particular, we note that the basic assumption is that of localized modes which scatter phonons, analogously to the TLS's, at lower temperatures. These localized modes also contribute to thermal transport by phonon-mediated diffusion. A relationship between these processes is established and used to estimate the changes in the sound velocity as a function of temperature. This yields results that compare favorably with experiment. Within the general context outlined here, our discussion may be applicable to a variety of disordered materials, independent of the particular assumption of fractal structure at short range, but requiring extended-localized vibrational state interactions.

Note added in proof. The model presented here facilitates explicit calculations within the context of the idea that thermal transport in a disordered solid can occur by diffusion of localized modes. This idea has existed for some time, and we note a recent calculation by Cahill *et al.*[14] fitting the thermal properties at high temperatures in terms of a model using diffusion of localized oscillators. It is to be noted that as the temperature is raised, our localized fracton excitations evolve into single-particle excitations, approaching in this limit the description proposed by those authors. In the oscillators model it is found that at sufficiently high temperature, the thermal conductivity becomes essentially independent of the temperature. This is consistent with our expectation here that the velocity of sound also ceases to exhibit temperature dependence due to the mechanism outlined in this paper at sufficiently high temperature.

ACKNOWLEDGMENTS

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