Phonon localization in aggregates

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Experiments on the transport of thermal energy through aggregates of small particles at low temperature are discussed. A transition to a weakly-temperature-dependent thermal conductivity, or plateau, appears at the temperature at which the thermal phonon wavelength equals the particle size. This is interpreted as evidence of phonon localization on a length scale determined by the structural correlation length.

The concept of nonpropagating phonon modes occupying part of the phonon spectrum is implicit in several proposals for the vibrational properties of disordered materials. Computer simulations[1-3] of three-dimensional (3D) random networks show that a significant number of high-frequency modes may be localized, while a field-theoretical formulation[4] indicates a mobility edge separating low-frequency extended states from high-frequency localized states for dimensionality $d > 2$. Localized modes have been suggested[5] as scattering centers in an attempt to explain a long-standing puzzle in glasses—the temperature-independent thermal conductivity (the "plateau") in the range $\sim 1-30$ K, which is found universally in bulk glasses. More recently, glasses have been postulated[6-9] to be self-similar, and a band of (non-heat-carrying) localized modes ("fractons") has been invoked to explain the plateau.

In disordered structures, the wavelength of the localized phonons is expected to be intimately related to a characteristic length scale of the system.[10] In glasses, the nonpropagating character of vibrational energy transfer has been postulated[6] to occur at very short length scales on the order of 10—100 atomic distances. Because it is difficult to probe the phonon spectrum of glasses in this region, we have scaled the problem to longer lengths by examining heat transport in aggregates of small but macroscopic particles.[11] This has the advantage that the spatial arrangements on a micron or submicron scale can, in principle, be imaged directly. Such structures can be of low overall density, e.g., near the percolation threshold, can be highly ramified, and possibly self-similar over some range.

Measurements of thermal conductivity κ probe the structure with thermal phonons whose wavelength can be swept through the characteristic length scale of the structure by varying the temperature. Low-temperature measurements are particularly useful, as the accessible phonon wavelengths range from tens of angstroms to microns, the appropriate range for fine powder aggregates. We have examined the literature for low-temperature thermal-conductivity data of crystalline and amorphous aggregates and have measured κ for a fine silica soot. Our principal result is that the high-temperature edge of the plateau occurs at a temperature for which the thermal phonon wavelength *and* mean free path are comparable to the particle size.[12] Moreover, this condition occurs for a very wide range of characteristic lengths. We propose this observation as evidence for the onset of localization on a length scale determined by the particle size. This interpretation is independent of any particular theoretical model of localized vibrations, such as fractons.

Thermal-conductivity data for three substances are shown in Fig. 1. For reference,[13] we show κ for bulk a-SiO_2. Below 1 K, the T^2 dependence is due to conduction by long-wavelength propagating phonons with a mean free path limited by scattering from intrinsic tunneling systems. The weakly-temperature-dependent region from 5 to 20 K is the plateau. Neither the plateau nor the stronger temperature dependence of κ at higher temperatures is understood.[14] Also shown are new measurements of κ for an agglomerated powder of 800-Å-diam a-SiO_2. The sample was prepared by the high-temperature reaction of $SiCl_4$ and O_2 and subsequent precipitation onto the internal walls of a heated tube.[15] Electron micrographs show well-connected necks joining the particles, but the structure is very open, as demonstrated by its low average density $\rho = 0.18 \times \rho_{a\text{-}SiO_2}$, and its low Young's modulus $Y = 0.008 Y_{a\text{-}SiO_2}$ determined from beam-bending measurements. A rectangular sample was used ($2 \times 2 \times 8$ mm^3) with two arms of the material extending from one face to facilitate four-probe κ measurements.

Figure 1 also shows the thermal conductivity of Vycor,[16] a porous borosilicate glass. Vycor has a network of 60-Å-diam holes and an overall density $0.72 \times \rho_{a\text{-}SiO_2}$. The solid, connected portions of Vycor can be estimated from density and pore size to have typical dimensions of ~ 170 Å. Vycor and the soot aggregate ("anti-Vycor") are therefore the inverse of each other, on the basis of occupied volume, with a factor of 5 difference in correlation length. The thermal conductivity falls between κ(soot) and κ(bulk), with a well-developed plateau similar to the bulk but shifted to lower temperature. The upper edge of the plateau is marked with a vertical arrow for each material. The wavelength of the average thermal phonon (averaged over the Boltzmann distribution), $\lambda = 2.7hv/k_BT$, is given by the scale at the top of the graph, using the average sound velocity v of bulk a-SiO_2.

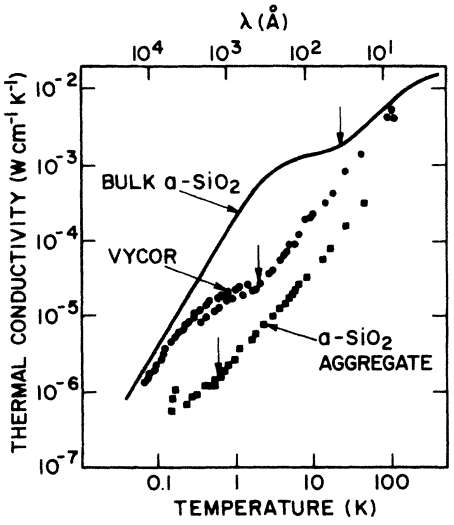

FIG. 1. Thermal conductivity of an aggregate of 800-Å-diam a-SiO_2 soot particles, Vycor glass with 60-Å channels (Ref. 13, two samples), and bulk a-SiO_2 (Ref. 10). The wavelength of the average thermal phonon λ is given in the upper scale for bulk a-SiO_2. The vertical arrows on each set of data mark the upper edge of the plateau.

(The average thermal phonon wavelength is expected to be close to the dominant thermal phonon wavelength because the mean free path does not vary much with frequency in this relatively-high-temperature range.)

It is instructive to compare these data with the conductivity of aggregates of *crystalline* powder. In Fig. 2 are shown some old but previously overlooked results[16] for a number of different aggregates of crystalline Al_2O_3: pressed Linde B ($L \approx 0.02\ \mu$m), sintered Linde B ($L \approx 0.3\ \mu$m), and a ceramic with grain size $\approx 3\ \mu$m. The high-temperature behavior of each sample approaches T^3, which is expected for crystalline materials with a phonon mean free path limited by the size of the grain or particle. In each case there is again a change between low- and high-temperature behavior (marked with a short vertical arrow) which occurs at successively lower temperatures for larger particle sizes.

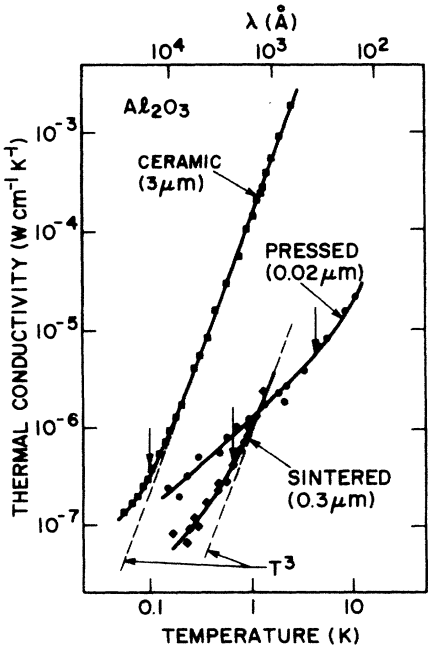

FIG. 2. Thermal conductivity of three different aggregates of Al_2O_3 (Ref. 13): pressed Linde B (0.02 μm), sintered Linde B (0.3 μm), and a ceramic with grain size $\approx 3\ \mu$m. The wavelength scale is calculated for bulk, crystalline Al_2O_3.

We shall assume that heat is conducted at high temperature by propagating modes. This is certainly true for short-wavelength modes in the individual *crystalline* particles.[17] The change to a more temperature-independent regime on cooling then represents a change of the thermally excited modes with energy $E \sim k_B T$ from propagating to localized. That is, the peak of the thermal spectrum moves from propagating phonons down to a band of localized modes, producing a relatively temperature-independent thermal conductivity. In the temperature-independent region, heat is carried primarily by long-wavelength propagating phonons of energy $E \ll k_B T$. It is important to note that previous investigations (thermal conductivity in glasses[14] and sound attenuation in sintered metal powder[18,19]) have approached this regime from the low-temperature or long-wavelength side. The present investigation using very short wavelengths allows us to probe the structural dynamics with wavelengths comparable to or shorter than the correlation length of the material.

In the above picture, the average phonon wavelength at the transition corresponds to the smallest characteristic dimension of the aggregate. To test this hypothesis, we plot in Fig. 3 the wavelength λ_c at the transition versus the particle or grain size L. The uncertainty in each quantity is based on available sample descriptions and scatter in the thermal-conductivity data. We find it remarkable that despite the uncertainties, there is general agreement not only in the linear dependence on L but also in the absolute magnitudes of λ_c and L. We note that the correlation length in all these materials is not significantly different from the particle size, since they are not particu-

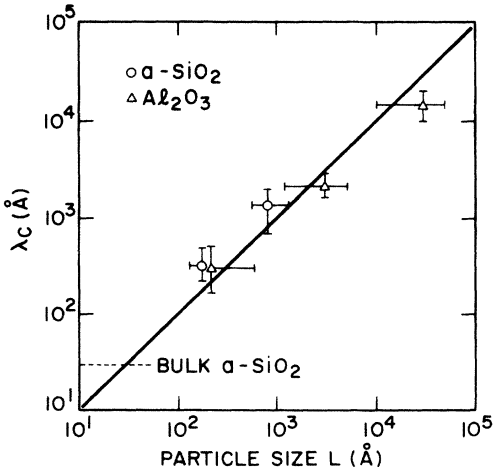

FIG. 3. The wavelength λ_c at the temperatures indicated by the vertical arrows in Figs. 1 and 2 versus the particle or grain size L. The line indicates $\lambda_c = L$.

larly close to the percolation threshold. The agreement extends over 2 orders of magnitude in either variable. This is strong evidence that phonon localization occurs in these aggregated materials on a length scale determined by the characteristic particle size.

A prediction of the present arguments is that the upper end of the plateau in bulk glasses arises from correlations on a length of ~ 30 Å (see Fig. 3). One must exercise caution in comparing such different materials as aggregates and bulk glasses. However, as we will present in a separate publication, there is evidence that phonon localization according to the Ioffe-Regel criterion $kl \approx 1$ occurs at the high-temperature edge of the plateau for all glasses.

This work presents the first experimental evidence that the long-studied thermal-conductivity plateau is a manifestation of disorder-induced phonon localization. The argument is very general and does not rely on the existence of any particular type of localized vibrational modes, such as fractons. The fact that the aggregates studied here are likely to be fractal over some length scale, however, implies that the correlation depicted in Fig. 3 supports a fracton model. While a convincing case must rely on a careful determination of the fractal properties of the samples, the present study of aggregates is not inconsistent with a fracton model.

It has been claimed[9] that the changes observed in the thermal-conductivity plateau of epoxy as the amount of hardener is increased shows support for a fracton model. The increased crosslinking with increased hardener-to-epoxy-resin ratio is thought to decrease the size of the structural units to some degree. A shift of the plateau toward higher temperature, by much less than a factor of 2, occurs as more hardener is added. Such a shift is qualitatively expected on the fracton model,[6] where a certain characteristic length of the structure determines the crossover between phonon and fracton excitations. We believe that these experiments and analysis are only suggestive, however, since the shift in temperature of the plateau is small and the change in characteristic length with hardener content is only assumed. The present experiments on aggregates, on the other hand, have the advantage that the length scale is directly accessible and can be varied over several orders of magnitude.

In conclusion, we have presented evidence for the localization of phonons in disordered aggregates which sets in at a length which scales with the particle size. In contrast to previous studies, which have approached the plateau from low temperatures and long wavelength, the present technique of rescaling the problem by using aggregates and thermal phonons enables one to investigate this difficult region from the opposite direction, i.e., lengths shorter than the characteristic length of the structure.

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