

Fracton interpretation of vibrational properties of cross-linked polymers, glasses, and irradiated quartz

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The density of states for thermal vibrations on a fractal is calculated with careful attention paid to the normalization condition. It is found that at the crossover between Debye-type excitations (long wavelength) and "fracton" excitations (short-length scale) the density of states is discontinuous. The size of the discontinuity is related to the ratio of the fracton dimensionality to the Euclidean dimensionality. Application is made to percolating structures. A set of missing modes is identified which may be the origin of the two-level systems hypothesized for amorphous structures. The specific heat of epoxy resin exhibits a crossover from a Debye-type region ($T < 8$ K) to a region (8–50 K) where the vibrational density of states depends linearly on the frequency. Over the same frequency regime, the thermal conductivity exhibits an effective phonon mean free path of the order of (or less than) a lattice constant. We interpret this behavior in terms of quantized fractons, with an energy range 8–50 K, and we suggest that these fracton states are localized. This is consistent with the usual interpretation of a precipitous drop in the phonon mean free path at the crossover energy of 8 K. Analogous behavior is argued for the thermal properties of glasses which exhibit a similar structure in the thermal conductivity. Recent neutron-irradiated quartz experiments tend to confirm this interpretation.

I. INTRODUCTION

Two of us have suggested that the concept of fractals¹ can be applied to the vibrational properties of macromolecules and have derived the vibrational density of states for fractal structures.² We found that the usual Debye-type density of states crosses over to a "fracton" density of states for length scales less than some characteristic length (L), corresponding to frequencies greater than a crossover frequency ω_{co} . We denote the Euclidean dimensionality by d , and call the density dimensionality of the fractal \bar{d} (the so-called Hausdorff dimensionality). (Thus the mass increases with increasing length r as $r^{\bar{d}}$). The exponent giving the dependence of the diffusion constant on distance is denoted by θ , such that

$$D(r) \propto r^{-\theta}. \quad (1)$$

Alexander and Orbach² show that the density of vibrational states in the regime of fractal behavior can be written as

$$N(\omega) \propto \omega^{\bar{d}-1} \quad (2)$$

where \bar{d} is the fracton dimensionality,

$$\bar{d} = 2\bar{d}/(2+\theta). \quad (3)$$

In Euclidean space, $N(\omega) \propto \omega^{d-1}$. The crossover frequency scales as

$$\omega_{co} \propto L^{-(2+\theta)/2}. \quad (4)$$

Recent experiments of Kelham and Rosenberg³ suggest that experiments involving the heat capacity and thermal transport of epoxy resins may be exhibiting behavior

relevant to the predictions of Ref. 2. We shall describe the relevance of these experiments to fractal behavior below, but first it is necessary to make explicit the crossover from phonon (long-length scales) to fracton (short-length scales) density of states. In particular, we need to derive the normalization coefficients which make the above Eqs. (1)–(4) quantitative.

II. PHONON AND FRACTON DENSITY OF STATES

We wish to normalize the long-wavelength phonon density of states to a volume L^d . This is because the phonon character of the elementary vibrational excitations terminates at the (minimum) length scale L . Thus we set

$$N_{ph}(\omega) = d(L/a)^d [(\omega)^{d-1}/(\omega_D)^d], \quad (5)$$

where a is an atomic distance which sets the shortest length scale in the problem (i.e., fracton behavior is obtained for length scales on a descending basis between L and a). Thus

$$\omega_{co} = (a/L)\omega_D, \quad (6)$$

where ω_D is the apparent Debye frequency as projected by the low-frequency velocity of sound. The integral of Eq. (5) from 0 to ω_{co} equals unity, indicating that there is one mode per volume L^d as required. Thus at the crossover frequency one finds

$$N_{ph}(\omega_{co}) = d/\omega_{co}. \quad (7)$$

The fracton regime is a little more complex. From the definition of the Hausdorff dimensionality there will be $(L/a)^{\bar{d}}$ atoms per molecule. This leads to an appropriate

fracton density of states,²

$$N_{\text{fr}}(\omega) = \bar{d}(L/a)^{\bar{d}}[(\omega)^{\bar{d}-1}/(\omega_{\text{FD}})^{\bar{d}}]. \quad (8)$$

We have introduced another quantity, the so-called fracton Debye frequency,

$$\omega_{\text{FD}} = \omega_D(L/a)^{\theta/2}. \quad (9)$$

This quantity sets the upper limit on the frequency regime of fracton behavior. Indeed, if we integrate Eq. (8) from ω_{co} to ω_{FD} we find $(L/a)^{\bar{d}} - 1$ modes as required. That is, there is one-phonon mode per volume L^d , and $(L/a)^{\bar{d}} - 1$ fracton modes, so that in total one finds $(L/a)^{\bar{d}}$ modes per volume a^d . At the crossover frequency, Eq. (8) reduces to

$$N_{\text{fr}}(\omega_{\text{co}}) = \bar{d}/\omega_{\text{co}}. \quad (10)$$

We therefore find the important relationship at crossover,

$$N_{\text{fr}}(\omega_{\text{co}})/N_{\text{ph}}(\omega_{\text{co}}) = \bar{d}/d. \quad (11)$$

Because we believe $\bar{d} < d$, we shall discover that the experiment appears to be in conflict with the ratio (11), even though the remainder of the spectrum appears to be consistent with the ideas of fractal behavior (see *Note added in proof*).

III. APPLICATION TO PERCOLATION

Though the experimental portions of this paper are certainly not described by percolating networks, it is of interest (and possibly of experimental importance) to carry through the ideas of the previous section to illustrate an example of fractal structure. It is necessary, however, to distinguish between the infinite cluster and finite clusters when calculating the full density of vibrational states for percolating networks.

As shown in Ref. 2, one can use the concept of fractals for percolating structures, with $(L/a)^{\bar{d}}$ atoms (sites) per molecule, where L is the percolation correlation length ξ_p . Denoting the infinite cluster by the superscripts IC, we find Eq. (8) becomes

$$N_{\text{fr}}^{\text{IC}}(\omega) = \bar{d}(L/a)^{\bar{d}}[(\omega)^{\bar{d}-1}/(\omega_{\text{FD}})^{\bar{d}}]. \quad (12)$$

The finite clusters need to be considered because the (specific-heat) density of states will be the sum of the infinite and finite cluster density of states. The probability per site, or atom, of belonging to a cluster of size $R < L$ is

$$[P(R)]_{\text{FC}} = (d - \bar{d})(R/a)^{-(1+d-\bar{d})}, \quad (13)$$

where the subscript FC means finite cluster. Equation (13) leads to

$$\int_a^L [P(R)]_{\text{FC}} dR = 1 - (a/L)^{(d-\bar{d})}, \quad (14)$$

the probability of belonging to a finite cluster. By defining

$$R(\omega)/a = (\omega/\omega_{\text{FD}})^{-2/(2+\theta)}, \quad (15)$$

only clusters with $R > R(\omega)$ contain modes of frequency ω . Next, the total number of sites (or atoms) in a volume L^d is, from Eq. (14),

$$(L/a)^d [1 - (a/L)^{(d-\bar{d})}]_{\text{FC}} + [(L/a)^{\bar{d}}]_{\text{IC}} = (L/a)^d, \quad (16)$$

and therefore not critical.

Equations (13) and (14) together enable us to calculate the total number of modes in the finite cluster. We have

$$\begin{aligned} N_{\text{fr}}^{\text{FC}}(\omega) &= (L/a)^d \int_{R(\omega)}^L (\bar{d}/\omega)(\omega/\omega_{\text{FD}})^{\bar{d}} P(R) dR \\ &= L^d (\bar{d}/\omega)(\omega/\omega_{\text{FD}})^{\bar{d}} \\ &\quad \times \{ [a/R(\omega)]^{(\bar{d}-d)} - (a/L)^{(\bar{d}-d)} \}. \end{aligned} \quad (17)$$

Adding $N_{\text{fr}}^{\text{IC}}(\omega)$ from Eq. (12) to Eq. (17), and using Eq. (15), we find the remarkable result that the total fracton density of states on a percolating network equals

$$N_{\text{fr}}(\omega) = \bar{d}(L/a)^d (1/\omega)(\omega/\omega_{\text{FD}})^{2d/(2+\theta)}. \quad (18)$$

Should we integrate Eq. (18) over the fracton frequencies, we would find,

$$\int_{\omega_{\text{co}}}^{\omega_{\text{FD}}} N_{\text{fr}}(\omega) d\omega = (\bar{d}/d)(L^d - 1), \quad (19)$$

or only $\bar{d}/d < 1$ modes per atom, and not one full mode. This reflects the missing center of mass modes of the finite clusters. The proof follows from the integration of Eq. (18) from $\omega(R)$, the smallest frequency allowed for a cluster size R , to the maximum fracton frequency ω_D ,

$$\begin{aligned} \int_{\omega(R)}^{\omega_{\text{FD}}} N_{\text{fr}}(\omega) d\omega &= R^{\bar{d}} \{ 1 - [\omega(R)/\omega_{\text{FD}}]^{\bar{d}} \} \\ &= R^{\bar{d}} [1 - (1/R)^{\bar{d}}] \\ &= R^{\bar{d}} - 1, \end{aligned} \quad (20)$$

which proves the statement for the normalization we have used. It is intriguing to speculate that this “missing mode” might be the analogous quantity for percolation systems that the two-level systems are for amorphous systems.

The total number of missing modes is $1 - (\bar{d}/d)$ per atom [see Eq. (19)]. Their frequencies are unknown, but their mass distribution can be calculated. There are $R^{-(1+d)}$ clusters between R and $R + dR$, leading to a mass distribution of mass $M^{-\tau}$ between $M (=R^{\bar{d}})$ and $M + dM$, with $\tau = (d/\bar{d}) + 1$. The missing mode frequencies Ω_{tl}^M (tl for “two-level” systems, and M for the mass of the cluster) must be less than [from Eq. (15)]

$$\Omega_{\text{tl}}^M < R_M^{-(2+\theta)/2} \propto M^{-1/\bar{d}}. \quad (21)$$

Summarizing the results of this section, Eq. (18) exhibits the fracton density of states for a vibrational network on a percolating structure. The fracton density of states at crossover remains that of the infinite cluster:

$$N_{\text{fr}}(\omega_{\text{co}}) = N_{\text{fr}}^{\text{IC}}(\omega_{\text{co}}) = \bar{d}/\omega_{\text{co}}, \quad (22)$$

but the slope for higher frequencies (i.e., within the fracton regime) is proportional to $\omega^{2d/(2+\theta)}$ instead of $\omega^{2\bar{d}/(2+\theta)}$ for the infinite cluster alone. This is because of the contribution of finite clusters to the fracton density of states. In addition, the integral over the finite-cluster den-

sity of states shows that one mode per cluster is missing. This mode can be attributed to the center of mass motion of the cluster, and may be analogous to the "two-level systems" attributed to amorphous systems.

We also note in closing that percolating structures can easily be achieved in magnetic systems by simple dilution. A previous paper⁴ showed that the diffusion equation not only maps on to the vibrational problem, but also on to the linearized spin-wave problem for ferromagnetic systems. Consequently, for randomly diluted ferromagnetic systems, the spin excitations would cross over from spin-wave-like at low energies to spin-fracton-like at higher energies, with a density of states proportional to $\omega^{\bar{d}/(2+\theta)-1}$ for the infinite cluster alone, and to $\omega^{d/(2+\theta)-1}$ for the sum of the infinite and finite clusters. Either specific heat or neutron-diffraction studies on randomly diluted ferromagnets would be interesting to compare with these forms.

IV. RELEVANCE OF FRACTON THEORY TO EXPERIMENT

We have already suggested that recent experiments on the specific heat and thermal conductivity of epoxy resins by Kelham and Rosenberg³ may have exhibited fracton properties. They have shown (from an analysis of their specific-heat measurements) that $N(\omega) \propto \omega^2$ for $\hbar\omega/k_B < 8$ K, but is proportional to ω for $8 \text{ K} < \hbar\omega/k_B < 50$ K. Their figure for $N(\omega)$ appears to exhibit a discontinuity between these two regimes, though the analytic form they have chosen does not. This change of slope is exactly what one would expect if the epoxy molecules were exhibiting fractal behavior. The "crossover frequency" is chosen to be 8 K, and corresponds to a length scale of 30 Å, about the length of the epoxy molecule (diglycidyl ether of bisphenol A). For stoichiometric hardening it is also the distance between cross links of hardeners. Use of the same number of hardener molecules, but of differing lengths, did not change the crossover frequency [Nicholls and Rosenberg (unpublished)] and the crossover length scale remained the distance between cross links. This is to be expected if the epoxy molecules alone are exhibiting fractal behavior. Preliminary evidence⁵ suggests that increasing the amount of hardener (i.e., reducing the distance between cross-links) tends to raise the crossover frequency. If one associates the length L in Eq. (4) with the distance between cross links, then this effect is in the correct direction. It suggests that the effect of the cross links is to restore the true Euclidean three-dimensional character of the lattice vibrations, and that the fractal behavior is to be associated with the behavior of the epoxy molecules between the connections with the hardener.

The observed power (linear) for the vibrational density of states above the hypothesized crossover frequency suggests $\bar{d}=2$. Unfortunately, at the present time we have no independent estimates for \bar{d} and θ for epoxy resin. We note, however, that the length scale can be changed for the epoxy, either by changing the amount of hardener, or by using different epoxy molecules, which allows the use of Eq. (4) to determine θ . Further, \bar{d} can be independently

determined from x-ray scattering (see the method of Stapleton *et al.*⁶). It would be of great interest to see if \bar{d} (now overdetermined) is consistent with such measurements.

There remains a problem between the analysis of the specific-heat data of Kelham and Rosenberg³ and the theory developed above [specifically, with Eq. (11)]. Because $\bar{d} < d$, and with θ positive, $\bar{d} < d$, so that the fracton density of states at crossover will always be less than the phonon density of states at crossover. Thus the density of states can only suffer a drop at crossover, whereas the experiments appear to exhibit a rapid rise at the frequency which we have interpreted to be crossover. We are at a loss to understand this difference in behavior. It is possible that there is an additional feature to the vibrational spectrum of epoxy resins in the fracton regime which adds a constant to the density of states, but we are unaware of its origin. As can be seen below, the analysis of the thermal conductivity is also consistent with fractal behavior above the frequency we have identified as crossover, so there is some compelling character to the evidence for fracton excitations above about 8 K in epoxy resins. However, the inconsistency with the direction of the discontinuity remains, and makes our hypothesis somewhat unsettled (see, however, the *Note added in proof*).

Perhaps a more extraordinary feature of the measurements of Kelham and Rosenberg is their finding that if one analyzes the thermal conductivity in the usual kinetic theory manner, the mean free path exhibits a precipitous drop to less than an atomic spacing above the frequency corresponding to 8 K (or the length of 30 Å). Such behavior for the effective mean free path was first noted for glasses by Zaitlin and Anderson.⁷ They used a nearly vanishing mean free path [region C of their Fig. (5)] as a method for analyzing the "plateau region" found for the temperature dependences of the thermal conductivity of almost all glasses.

A mean free path of less than a lattice constant certainly suggests localized states according to the Ioffe-Regel rule.⁸ We carry the fracton picture further and note that Domany *et al.* have recently shown⁹ that essentially all states are localized on a Sierpinski gasket (a well-known fractal geometry¹). In general, for fractal structures, Rammal and Toulouse¹⁰ have recently shown that the conductance $g(L)$ scales with length for fractals as

$$g(L) \propto L^{\bar{d}-2-\theta} . \quad (23)$$

With the use of the scaling relation of Abrahams *et al.*,¹¹ their quantity $\beta(g)$ becomes

$$\beta(g) = \frac{d \ln g(L)}{d \ln L} = \bar{d} - 2 - \theta , \quad (24)$$

or, in terms of the fracton dimensionality \bar{d} , using Eq. (3),

$$\beta(g) = \bar{d} [1 - (2/\bar{d})] . \quad (25)$$

The argument of Abrahams *et al.*¹¹ leads to localized states for $\beta \leq 0$. The specific-heat analysis of Kelham and Rosenberg³ suggests that $\bar{d}-1=1$, or $\bar{d}=2$. Use of this

value in Eq. (25) results in $\beta(L)=0$, so that the scaling factor of Abrahams *et al.* is consistent with localized behavior.

For localized fracton states one would not expect any contribution to the thermal conductivity, but rather only a scattering of the lower-energy extended phonon states, exactly as the lower-energy two-level systems¹² have been shown to do in amorphous systems.⁷ We are making a distinction here between the two-level systems which are also found in epoxy resin³ (and in nearly all amorphous materials^{7,13}) and the fracton modes. The density of states of the former are usually added to the extended phonon density of states, while the latter replace the phonons as the fundamental excitation above ω_{co} (but see our speculation concerning the origin of the “two-level systems” for percolating networks). Localized fractons would then manifest themselves by a sharp drop (vanishing) of the contribution to the thermal conductivity for excitations with $\omega > \omega_{co}$. A conventional thermal-conductivity analysis would result in a negligible mean free path in such an excitation region. The property of the epoxy resin which best maintains the correctness of our interpretation is that the frequency at which the “mean free path” becomes of the order of an atomic spacing is almost precisely the frequency at which the density of states suffers a discontinuity—crossover from a Debye-type to a fracton-like form.

At yet higher temperatures, the plateau in the thermal conductivity ends, and begins to increase (e.g., above ~ 10 K for epoxy resin). This could be caused by classical hopping-like transitions between localized fracton states, analogous to Mott’s variable range rate hopping¹⁴ for localized electronic states. We have not as yet carried through a detailed analysis for thermal transport in such a regime.

The fracton hypothesis suggests that materials exhibiting a significant temperature spread for the plateau regime, in the thermal conductivity, possess a characteristic length considerably larger than an atomic spacing between which vibrational excitations are localized (we hypothesize, fractonlike). For longer-length scales, one passes into the normal Debye-type regime. The width of the plateau region will increase as the crossover length L increases.

It is interesting to compare the results and analysis of Kelham and Rosenberg³ on epoxy resin with that of Zaitlin and Anderson⁷ on other noncrystalline materials (a borosilicate glass and a polycarbonate). As recognized by Kelham and Rosenberg, Zaitlin and Anderson were the first to associate the plateau in the thermal conductivity of almost all glasses (see Zeller and Pohl¹³) with a sudden drop in the phonon mean free path for frequencies above a minimum ω_0 (the crossover frequency?). This is clearly exhibited in their Fig. 5, region C. The similarity of their analysis for noncrystalline materials, and that of Kelham and Rosenberg for epoxy resin, where long-range correlations (~ 30 Å) are expected, is striking.

We admit that it is a little puzzling why ordinary glasses should exhibit such a length, roughly independent of the character of their constituents. However, our analysis would not be the first to argue for such extended

correlations. For example, Morgan and Smith¹⁵ have made similar arguments (even to lengths up to 1000 Å), though with a very different model in mind.

It is interesting to note that as pointed out by Morgan and Smith the plateau temperature width is much larger for amorphous Se than for most glasses (Zeller and Pohl¹³). It is known that the characteristic correlation length in amorphous Se is much longer than in most glasses. We have already noted this phenomenon above for epoxy resin. Finally, Phillips¹⁶ has also argued for extended correlations in amorphous systems.

Recent irradiation experiments on crystalline quartz also tend to confirm our interpretation of fractal behavior in glasses. Laermans *et al.*¹⁷ have shown that electron irradiation of crystalline quartz does not produce a plateau region in the thermal conductivity. However, neutron irradiation does generate a plateau regime with a width slightly larger for larger neutron doses.¹⁸ X-ray scattering by Grasse *et al.*¹⁹ shows that neutron irradiation causes amorphous regions of diameter 20 Å, while Grasse *et al.*²⁰ show that electron damage does not, hence the lack of a plateau region in the thermal conductivity for the latter. Finally, Grasse *et al.*²¹ point out that the size of the amorphous regime tends to grow slightly (20%) with increasing neutron irradiation. This is consistent with the slight increase in plateau length found by de Goer *et al.*¹⁸ as a function of increasing neutron dosage.

V. SUMMARY AND CONCLUSIONS

In summary, we contend that the thermal properties of epoxy resin and glasses can be understood on the basis of a crossover from Debye-type behavior at low frequencies to fracton behavior at higher frequencies. The density of states correspondingly changes the exponent of its power law from $d - 1$ to $\bar{d} - 1$ [Eq. (2)]. At this same crossover frequency, the vibrational states change their character from extended to localized, thereby profoundly affecting the thermal transport and serving as a possible explanation for the extremely small mean free path of phonons in this energy region as extracted from more conventional analyses. The crossover frequency is proportional to the inverse of the length scale, according to Eq. (4), fracton behavior expected for shorter lengths. Any increase in this length should therefore reduce the crossover energy and increase the width of the plateau region measured in thermal-conductivity experiments.

Note added in proof. The form we have used for the normalized fracton density of states assumed that the force constant and mass scaled smoothly through the crossover regime. Recent work of P. F. Tua, S. J. Putterman, and R. Orbach [Phys. Lett. (in press)] suggests an alternative picture: a drop in ω vs inverse length scale at the crossover length. This leads to a jump in the density of states (instead of a drop), going from the phonon to fracton regimes. Excellent agreement with the experimental results of Ref. 3 is obtained. Finally, an effective medium approximation for $N(\omega)$ has been obtained very recently for percolating networks by B. Derrida, R. Orbach, and Kin-Wah Yu (unpublished). It strongly supports the assumptions of Tua *et al.*, giving additional con-

confidence to a fracton interpretation for short-length scale vibrational excitations in amorphous materials.

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