



INVESTIGATION OF FRACTON DENSITY OF STATES IN AN AEROGEL BY RAMAN SCATTERING

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Raman scattering measurements on a silica aerogel have been used to investigate the density of states of acoustic vibrations in this disordered system. Above 27 cm^{-1} , we find that the reduced Raman scattering intensity $I(\omega)/[n(\omega)+1]$ shows a power law dependence on frequency, ω^v , that can be interpreted in terms of scattering from fracton excitations. From the analysis of Boukenter *et al.*, the exponent v is shown to be simply related to the fracton dimension $\tilde{d} = 3-v$, giving $\tilde{d} = 1.50 \pm 0.05$ for our aerogel sample. Whilst this value is not far from the Alexander-Orbach value $\tilde{d} = 4/3$, one should be cautious in interpreting data over the range of frequencies used here as evidence for the observation of fractons.

1. Introduction

The recognition of self-similarity, or invariance to scale transformation, has evolved rapidly in recent years since Mandelbrot's formulation¹ of the ideas of fractal geometry. Attempts have been made in various domains of natural sciences to use fractal dimensions to describe complex geometric environments and their processes. One example is the study by Rojanski *et al.*² of the surface of a mesoporous silica gel.

Alexander and Orbach³ were the first to suggest that "fractons" can describe the vibrational properties of disordered fractal systems. Alexander *et al.*⁴ derived the vibrational density of states for amorphous materials having fractal structures and they found that there is a cross-over length L_{c1} and corresponding cross-over frequency ω_{c1} , below which the appropriate vibrational density of states is of the normal phonon-like form and above which the vibrational modes are fractons with a corresponding fracton-like density of states brought about by the fractal geometry. Three dimensionalities are

used to describe the vibrational properties in a fractal system: the embedding (Euclidean space) dimensionality $d (=3)$, the fractal (Hausdorff) dimensionality D , and the fracton (spectral) dimensionality \tilde{d} . The fracton density of states $g(\omega)$ is expected to have a simple power-law dependence $\omega^{\tilde{d}-1}$ on frequency ω , and can be directly measured by Raman scattering.

In this paper, we describe Raman scattering measurements on a silica aerogel that is expected to have the properties of a fractal structure. We have been able to use these measurements to investigate some of the current ideas of the properties of fractons.

2. Light Scattering Intensity of Acoustic Vibrations in Non-Crystalline Solids.

In non-crystalline materials, the lack of translational symmetry brought about by the disorder causes the usual momentum selection rules in first order Raman scattering to be broken, with the result that

inelastic light scattering from acoustic vibrations can be observed at low frequencies. In the case of acoustic phonons, Shuker and Gammon⁵ showed that the Raman intensity at frequency shift $\omega/2\pi$ is given by

$$I(\omega) = C(\omega)g(\omega)[n(\omega)+1]/\omega \quad (1)$$

where $n(\omega)+1$ is the Bose factor for Stokes scattering, $g(\omega)$ the phonon density of states, and $C(\omega)$ the Raman coupling constant. At low frequencies, $C(\omega)$ has been shown by Martin and Brenig⁶ to be proportional to ω^2 , and $g(\omega)$ is given by the Debye form $g(\omega) \propto \omega^{d-1}$, so that

$$\frac{I(\omega)\omega}{n(\omega)+1} = C(\omega)g(\omega) \propto \omega^{d+1} \quad (2)$$

In 3 dimensions, the reduced intensity $I(\omega)\omega/[n(\omega)+1]$ is therefore predicted to depend on frequency as ω^4 . Such behaviour has been observed in several chalcogenide glasses⁷ and in amorphous silicon⁸.

Recently, Boukenter *et al.*⁹ showed that a different frequency dependence is expected for inelastic light scattering from the vibrational modes of a fractal system. The Raman tensor is now proportional to the local strains induced by the fracton excitations, these strains being in turn proportional to the gradient of the fracton wavefunctions. By making use of the form of the fracton wavefunctions proposed by Alexander *et al.*¹⁰, Boukenter *et al.* derive the expression

$$I(\omega) \propto \omega^{2q-1}g(\omega)[n(\omega)+1]. \quad (3)$$

Here, $q = \tilde{d}d_\phi/D$ is an index that describes the frequency dependence of the fracton wavefunctions $\phi(\mathbf{r})$ as defined by the relation $|\nabla\phi(\mathbf{r})|/\phi(\mathbf{r}) \propto \omega^q$. The exponent d_ϕ characterises the exponential localisation of the fracton wavefunctions by accounting for the distortion in Euclidean space of the assumed exponential decay on the fractal. Since the fracton vibrational density of states is of the form³

$$g(\omega) \propto \omega^{\tilde{d}-1} \quad (4)$$

the reduced Raman intensity is given by

$$\frac{I(\omega)\omega}{n(\omega)+1} \propto \omega^v \quad (5)$$

where

$$v = (\tilde{d}/D)(2d_\phi + D) - 1. \quad (6)$$

Equations (5) and (6) show that a graph of $\text{Log}\{I(\omega)\omega/[n(\omega)+1]\}$ versus $\text{Log}(\omega)$ for experimental Raman scattering data should reveal a straight line having a gradient v which, for the expected range of exponents D ,

\tilde{d} and d_ϕ for fractals (see below), is very different from the value $v=4$ typical of acoustic phonon scattering in disordered materials (cf. eqn. (2)).

The use of equations (5) and (6) to determine the fracton dimension \tilde{d} from experimental data is complicated by the need to know also the values of D and d_ϕ for the system under investigation. A considerable simplification of the analysis can be made through the use of a scaling argument due to Aharony *et al.*¹¹, who showed that the exponent d_ϕ that characterises the spatial decay of the fracton wavefunction is given by

$$d_\phi = (2-\tilde{d})D/\tilde{d} \quad (7)$$

Substituting this into eqn.(6) gives¹²

$$v = 3-\tilde{d} \quad (8)$$

so that under this model the reduced intensity scales with frequency as

$$\frac{I(\omega)\omega}{n(\omega)+1} \propto \omega^{3-\tilde{d}} \quad (9)$$

3. Experimental Results and Discussion

The silica aerogel sample¹³ used in this Raman scattering study was manufactured at DESY¹⁴. It is a very porous but transparent material, with a density of approximately 0.10 g cm^{-3} corresponding to a SiO_2 occupied volume fraction of 4.5%. The aerogel is believed to consist of a network of tiny spheres^{14,15} with radius $a \approx 2 \text{ nm}$, as estimated from the measured surface area of $700 \text{ m}^2 \text{ g}^{-1}$. The crossover from elastic continuum behaviour to that of fractal network modes of vibration is expected to occur when the wavelength approaches the structural correlation length ξ of the network^{16,17,18}. We estimate that this crossover in our aerogel sample should occur at a frequency $\omega_{c1}/2\pi \sim v_c/\xi \sim 0.005 \text{ cm}^{-1}$, well below the frequency range accessible to Raman scattering. These network modes extend in frequency from $\omega_{c1}/2\pi$ to $\omega_{c2}/2\pi \sim v_B/2a \sim 30 \text{ cm}^{-1}$, above which the vibrational modes are essentially confined to individual particles ($\lambda/2 < a$) and so are expected to be similar to those of bulk silica. (Here, v_c and v_B are the sound velocities in the low frequency continuum and in bulk silica respectively.) For an amorphous or glassy solid, these bulk modes will depend on the nature and characteristic length scales of the atomic disorder; they may either be phonon-like^{7,8} with a Debye density of states, or they

may show different behaviour which may be interpreted as evidence for fraxon-like excitations^{4,19,20} in the bulk material.

To investigate the density of states of the acoustic vibrations in aerogel, room temperature Raman scattering experiments were performed using a 90° scattering geometry with an argon ion laser exciting line of 514.5 nm at 200 mW power. Scattered light was collected from the flat surface of the sample. Figure 1 shows the Raman spectra of our silica aerogel sample taken at room temperature (in which the incident and scattered light polarizations are mutually parallel). The low frequency structure of the spectrum is very different from the Raman spectral of fused silica²¹ or vitreous silica²² in the sense that these latter both have boson peaks at around 60 cm⁻¹. The sample and spectra are also different from the measurements of Boukenter *et al.*⁹ on silica gel.

The perpendicularly-polarised spectrum is almost identical to that of Figure 1, so we have used only experimental data from the parallel spectrum in the following discussion.

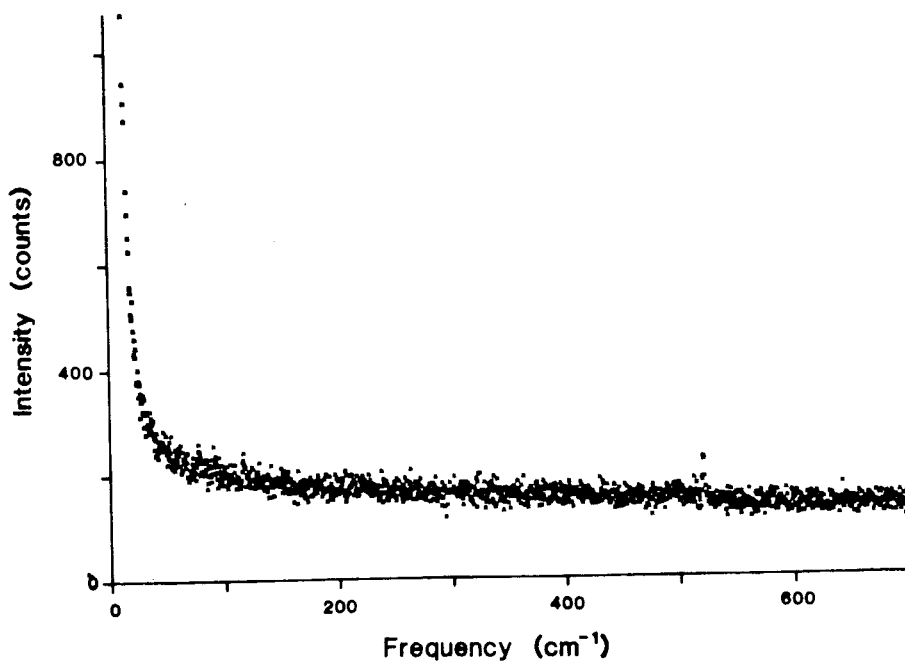


Figure 1. Raman scattering spectrum of silica aerogel at room temperature using 514.5 nm incident light, with parallel incident and scattered polarisation.

A plot of $\text{Log}\{I(\omega)\omega/[n(\omega)+1]\}$ versus $\text{Log}(\omega)$ is shown in Figure 2. The data can be well described by a straight line fit above about 27 cm⁻¹, with a slight decrease in gradient above about 300 cm⁻¹. The straight line with gradient $v=1.50\pm 0.05$ shown in Figure 2 represents the fit to the data in the range 27 to 250 cm⁻¹. Comparing the power-law behaviour of the reduced intensity in Figure 2 with eqn. (9), we obtain a value for the fraxon dimension of $\tilde{d} = 1.50\pm 0.05$. This value is not far from the the value $\tilde{d} = 4/3$ predicted by Alexander and Orbach³ and shown to be an almost exact result in some systems¹¹. The fact that the the two values are reasonably close suggests that scalar elasticity is the correct microscopic model for elasticity in the aerogel, at least for the inter-atomic elastic forces (as opposed to inter-particle forces) that are probed in the frequency range of the present experiments.

By contrast, the value $\tilde{d} = 0.9$ predicted for the bond-bending elasticity model²³ is apparently sufficiently different from our value to rule out this mechanism in our aerogel sample. It is of interest that our

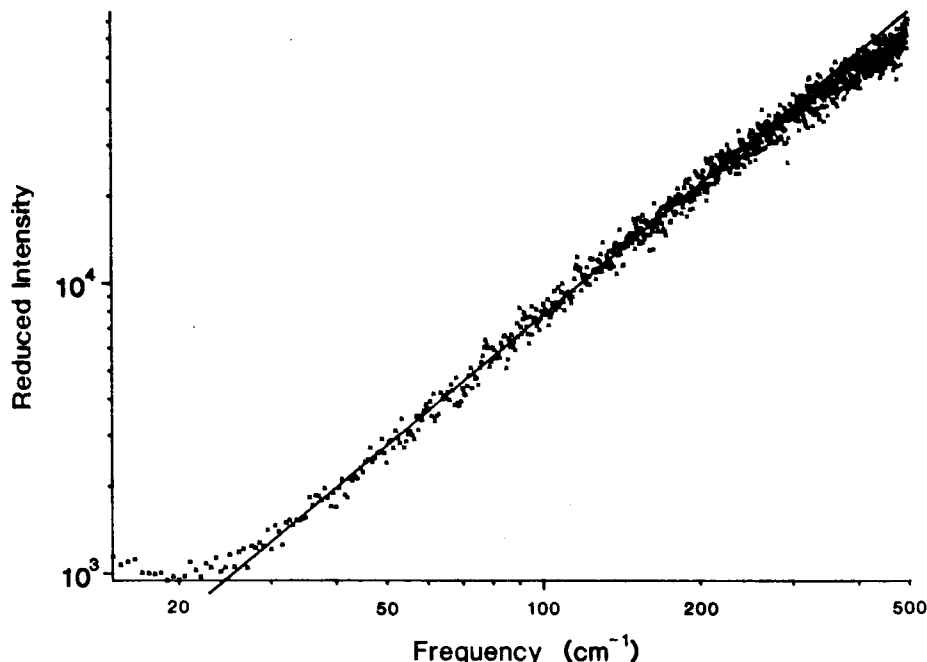


Figure 2. Log-Log plot of reduced intensity $I(\omega)\omega/[n(\omega)+1]$ vs. frequency $\omega/2\pi$ in cm^{-1} units for the Raman data of Figure 1. Straight line has a gradient $\nu=1.50$ on the Log-Log scale.

value for \tilde{d} is also fairly close to the value $\tilde{d} = 1.25 \pm 0.06$ determined by Courtens *et al.*¹⁷ from the scaling at lower frequencies of the sound velocity and Brillouin scattering linewidth in other aerogel samples.

The present experimental measurements do not lead to independent values for the fractal dimension D and the fracton localisation index d_ϕ , but if we take the percolation value $D=2.50$ then the corresponding value of d_ϕ from eqn. (7) is 0.83. Alternatively, if we take for d_ϕ its theoretical lower bound $d_\phi=1$, then $D=3.00$. Even without the use of (7) to simplify the analysis of the data, the range of probable values for \tilde{d} that is consistent with the data is rather narrow: for D between 1.75 and 3.00 as found experimentally in gels and porous silica^{2,22,24,25} and using $d_\phi=1$, eqn. (6) gives \tilde{d} between 1.17 and 1.50 when $\nu=1.60$. All these values are within the currently expected ranges.

We note that the power-law behaviour of the reduced scattering intensity has been observed only above 27 cm^{-1} in the present

experiments, indicating that the apparent fracton behaviour of the density of states applies to the intra-particle vibrational modes ($\omega > \omega_{c2}$) and not to the lower frequency network modes ($\omega < \omega_{c2}$) of the porous medium. The data thus support the idea^{4,19} that atomic disorder in amorphous materials leads to fractal behaviour of the vibrational excitations over a certain range of length scales, and are consistent with the fractal interpretation of the density of states measured by inelastic neutron scattering in bulk vitreous silica at frequencies above $\sim 20 \text{ cm}^{-1}$. Comparison with inelastic neutron scattering data in Cab-O-Sil, a small particle silica aggregate, is less clear, however; some of the data^{26,27} suggest that the vibrational density of states is Debye-like over the frequency range 10 cm^{-1} to 40 cm^{-1} , whilst recent time-of-flight data²⁸ show quite different behaviour.

Below 27 cm^{-1} , the inelastic light scattering intensity increases more rapidly with decreasing frequency shift than predicted by eqn. (9). This behaviour may be associated with increased scattering from

the lowest frequency vibrational Lamb modes of the individual spherical particles²¹, but it may also at least in part be due to the tail of the Rayleigh scattering peak. Further light scattering experiments are planned to investigate this point, and to investigate the crossover behaviour to the lower frequency network modes of the porous silica .

One would expect the vibrational modes studied in the frequency range of the present experiments to be relatively unaffected by the links between the particles that determine the long length-scale structure of the aerogel. To investigate this, we attempted to pulverise the silica aerogel into a structure closer to a dust by grinding it between a piece of metal and a glass dish. The resulting Raman spectrum is similar to that of Figure 1, and the $\text{Log}\{I(\omega)\omega/[n(\omega)+1]\}$ versus $\text{Log}(\omega)$ graph obtained from the powder spectrum can be fitted over the frequency range 50 to 300 cm^{-1} by a straight line of gradient $\nu=1.33\pm 0.05$ (as compared to 1.50 for the aerogel), implying somewhat unexpectedly an increase in \tilde{d} from 1.50 to 1.67 . Thus, even though the lower frequency modes of the network might become those of a "fractal dust" on pulverisation and be characterised by a value of \tilde{d} less than unity²⁹, it should be no surprise that such an effect is not observed in the frequency range of the present experiments. The cut-off frequency above which fracton behaviour occurs is increased from 27 cm^{-1} to 47 cm^{-1} on pulverisation. While this effect can be explained as being due to an increase in ω_{c2} so long as the effect of the pulverisation is

to lower the average size a of the silica particles, the possibility simply of an increase in the Rayleigh scattering from the powder as compared to the aerogel cannot be entirely ruled out at this stage.

In summary, low frequency Raman scattering from acoustic vibrations in aerogel shows a frequency dependence that cannot be explained in terms of Debye-like acoustic phonons, but can be interpreted in terms of localised fracton excitations using the analysis of Boukenter *et al.*⁹. However, some of the implications of this interpretation lead us to sound a note of caution in claiming unambiguous evidence for the existence of fracton effects, despite the clear power-law behaviour of the reduced Raman intensity. As noted above, the frequency range over which the reduced Raman intensity is observed to be proportional to ν does not correspond to the the frequency range of the inter-particle modes ($\omega_{c1} < \omega < \omega_{c2}$), so that the apparent fracton behaviour cannot be linked to mass fractal geometry. Also, the value $\tilde{d}=1.50 \pm 0.05$ that is obtained using this model is quite large, and even though it is close to the Alexander-Orbach value 4/3, it does appear to fall outside the range of most theoretical predictions. Finally we note that the analysis of Boukenter *et al.* assumes that the elasto-optic coupling constant is independent of frequency, and this may not be valid in the frequency range of the present data³⁰, which extends rather above the normal range of acoustic phonons in crystalline silica. If this assumption fails, the relationship (8) between ν and \tilde{d} would clearly be modified³¹.

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