Density of States in Fractal Silica Smoke-Particle Aggregates

Torsten Freltoft and Jørgen Kjems
Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

and

Dieter Richter
Institut Laue-Langevin, F-38042 Grenoble Cedex, France

(Received 27 April 1987)

The low-frequency vibrational density of states, $Z(\omega)$, in fractal silica aggregates has been measured by inelastic, incoherent neutron scattering. The samples were compressed powders of a hydroxylated, silica smoke-particle product, Cab-O-Sil. In the regime $\hbar\omega < 0.5$ meV, $Z(\omega)$ was found to be of the form ω^p with $p = 0.8 \pm 0.1$ at $T = 136$ K and $p = 1.1 \pm 0.05$ at $T = 265$ K. The values of p are larger than the current theoretical predictions for excitations on fractal networks. The observed temperature dependence of $Z(\omega)$ indicates an important role of anharmonicity.

PACS numbers: 63.50.+x, 61.40.+b

There has been considerable recent interest in the dynamical properties of random systems.[1] Alexander and Orbach[2] first pointed out that the thermal excitation spectra are strongly influenced by the fractal structure of such systems and they introduced a new dynamical exponent, d_s, to describe the vibrational density of states, $Z(\omega) \propto \omega^{d_s - 1}$ for the fracton modes. In normal, homogeneous systems, d_s corresponds to the Euclidean dimension. It was also shown[3] that an anomalous enhancement of the density of states, the so-called fracton edge, could be expected at the crossover between the homogeneous, long-wavelength phonon regime and the fracton regime at shorter wavelengths. Neutron-scattering experiments on epoxy resins[4,5] and vitrious silica[6] have been interpreted in these terms. In the analysis it is presumed that the fractal nature originates from the chemical bonding network rather than the mass distribution which is quite uniform on length scales that exceed the atomic distances. A recent Brillouin-scattering experiment[7] has shown the long-wavelength phonon excitations near the expected crossover to the fracton regime in aerogel samples of different densities. In a neutron-scattering experiment[8] on a dilute antiferromagnet, the similar magnetic excitations were followed through the crossover region.

In this Letter we present a spectroscopic determination of the vibrational density of states for ramified clusters with known fractal geometry on a length scale corresponding to the wavelength of the excitations that were probed. The clusters are formed as smoke-particle aggregates of small silica particles. The fractal nature of the geometrical structure has been established by small-angle neutron scattering[9] and it can be characterized by a fractal dimension $d_f = 2.5 \pm 0.1$ up to length scales of order 30 nm.

The thermal excitations consist of the internal modes in the SiO_2 spheres and the external modes of the cluster network. These modes correspond to different frequency and wavelength regimes since the internal modes have a low-frequency cutoff, ω_c, determined by the sphere radii and the elastic constants of amorphous SiO_2. Below ω_c the cluster modes are probed.

An amplitude-weighted, vibrational density of states can be measured directly by incoherent, inelastic neutron scattering and in the quasiharmonic approximation the cross section for isotropic systems is given by

$$\left(\frac{d^2\sigma}{d\Omega\, dE}\right)^{\mathrm{inel}}_{\mathrm{inc}} = \frac{\sigma_{\mathrm{inc}}}{4\pi}\frac{k'}{k}\frac{N}{4M} q^2 \exp[-\tfrac{1}{3} q^2 \langle u^2\rangle] \frac{Z(\omega)}{\omega}\left\{\coth\left(\frac{\hbar\omega}{2k_B T}\right) \pm 1\right\}$$

$$\propto \frac{k'}{k} q^2 \exp[-\tfrac{1}{3} q^2 \langle u^2\rangle] \frac{Z(\omega)}{\omega^2} k_B T, \quad k_B T \gg \hbar\omega, \qquad (1)$$

where σ_{inc} is the incoherent-scattering cross section, the scattering vector $\mathbf{q} \equiv \mathbf{k} - \mathbf{k}'$, N and M are the number and mass of the scatterers, $\exp[-\tfrac{1}{3} q^2 \langle u^2\rangle]$ is the Debye-Waller factor, $\hbar\omega$ is the energy transfer, T is the temperature, and the term in the curly braces is the population or Bose factor for neutron energy gain and loss, respectively.

This experiment was performed on SiO_2 aggregates commercially available under the trade names Cab-O-Sil and Alfasil.[10] They are produced by the process of flame hydrolysis in which $SiCl_4$ is burned to give a snowlike product where the basic small-particle units are amorphous SiO_2 spheres roughly 4 nm in diameter. The incoherent neutron scattering from this system can be dramatically enhanced by studying a hydroxylated sample. This technique was first applied by Richter and Passell[11,12] and may be used to obtain the density of states. They exploited the large incoherent cross section of hydrogen and enhanced the incoherent cross section of the sample by attaching H atoms to the SiO_2 surfaces. The idea is that the very light, but strongly bonded, hydrogen atoms will reflect the dynamics of the underlying silica spheres, and hence give direct information about their internal, as well as external, vibrational modes. The hydrogen covering of the SiO_2 surface is accomplished by soaking the aggregates in H_2O. During hydroxylation, a surface layer of adsorbed water also forms, but it was removed again by baking the sample at 110 °C. The OH groups are, however, much more tightly bound and will first be removed after extensive baking at 700–800 °C, as was done for a reference sample, for 24 h (to a residual vapor pressure below 10^{-3} mbar).[12] Both samples were prepared with equal amounts of silica aggregates compressed to 0.2 g/cm^3 before the heat treatments. Afterwards, they were loaded in He-gas atmosphere into indium-sealed cylindrical aluminum containers of 4.2 cm diameter and 100 cm^3 volume.

The measurements were performed with cold neutrons on a time-of-flight spectrometer IN5 at the Institut Laue-Langevin high-flux reactor in Grenoble. A chopper system supplied a pulsed monochromatic beam of $\lambda = 0.5$-nm (3 meV) incident neutrons, and detectors were placed at the fixed scattering angles $2\theta = 54°$, 67.5°, 88°, 107.3°, and 124° covering the q range from 11 to 22 nm^{-1} at zero energy transfer. For each detector, a neutron event was updated in a 500-channel array corresponding to flight times between 0.15 and 2.0 ms or energy transfers from -2 to $\simeq +100$ meV with an energy resolution of the order of 0.1 meV in the elastic channel. Note that the resolution function for a multichopper system is triangular, and has, therefore, no wings. A spectrum from vanadium foil imitating the sample geometry was used to normalize the data for detector efficiency and ensure a correct energy calibration. The scattering from the reference sample (baked at 700 °C) was typically around 50% lower than the scattering from the hydroxylated sample at 265 K (see Fig. 1), and background corrections due to sample container and SiO_2 were simply performed by subtracting the reference spectrum from the sample spectrum. This was done in the energy representation after normalization and energy calibration.

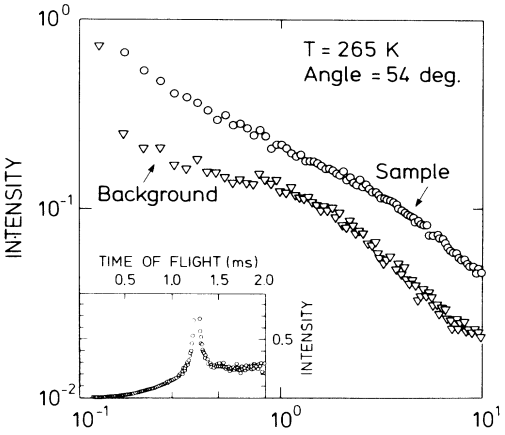

FIG. 1. Inelastic incoherent scattering from the hydroxylated silica sample together with background scattering from hydrogen-free aggregates plotted in double-log representation. The background is typically 50% lower than the scattering from the sample. Inset: The same data on linear scales before transformation from time of flight to energy.

The aim of the experiment was to obtain incoherent scattering curves $I(q,\omega)$ from the hydrogen atoms reflecting the dynamics of the underlying aggregate structure at different temperatures. The consistency of the measured spectra $I(q,\omega)$ with $\partial^2\sigma/\partial\omega\,\partial\Omega$ of Eq. (1) can be examined through their q and T variation. In order to test the q dependence of the measured intensities at a given temperature, $\ln[I(q,\omega)/q^2]$ is calculated for each scattering angle. This function is then plotted versus q^2 for each energy. Equation (1) predicts a linear relationship in such a plot. This is fulfilled by the data as can be seen from the inset in Fig. 2. Extrapolating to $q=0$, we obtain

$$\exp[\lim_{q\to 0} \ln\{I(q,\omega)/q^2\}] \propto (k'/k)[(Z(\omega)/\omega]\{\coth(\hbar\omega/2k_BT) \pm 1\}. \tag{2}$$

From Fig. 2 it is clear that $Z(\omega)$ strongly deviates from the normal Debye behavior, $Z(\omega) \sim \omega^2$. In the energy range from 0.2 to 2 meV, $Z(\omega)/\omega^2$ follows a power law with the exponent -0.9 ± 0.05 for $T = 265$ K, and for $T = 136$ K we find an exponent of -1.2 ± 0.1. There is no trend towards saturation in the low-energy limit indicating that the crossover to the long-wavelength phonon regime is not within the reach of the present experiment. In addition to the low-frequency power-law behavior, the 136-K data exhibit two broad peaks around 1.5 and 4 meV. Note that a remnant of these peaks in the form of a weak shoulder is still present in the 265-K data.

According to Eq. (2) the temperature dependence of the inelastic scattering should follow Bose-Einstein statistics and in our temperature range be proportional to T. The ratio of the inelastic intensities recorded at 265 and 136 K is thus expected to be about 2. Experimentally, such an intensity ratio is observed for energies above 3 meV. In the power-law regime below 1 meV, however, the observed ratio is about 4.5. Such a strong increase of the inelastic intensity is indicative of the presence of im-

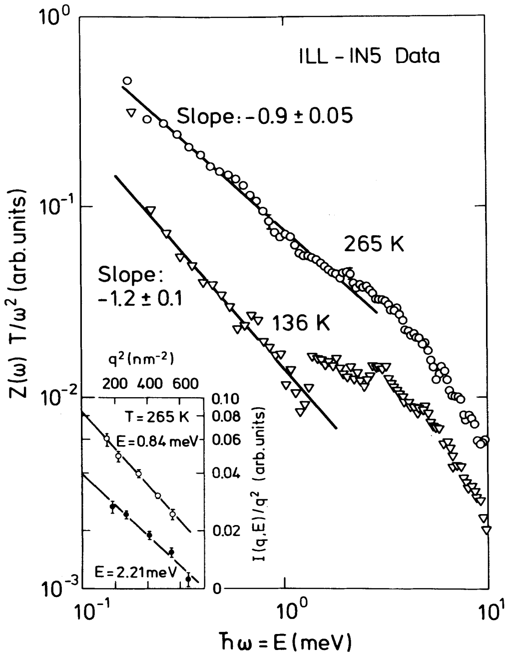

FIG. 2. Double-log plots of $Z(\omega)T/\omega^2$ extracted from extrapolation of the measured scattering curves to $q=0$ for $T=265$ K and $T=136$ K. Inset: Two typical extrapolations leading to the two points with error bars on the 265-K data. The slopes correspond to $Z(\omega)\propto\omega^p$; $p=1.10\pm0.05$ at 265 K and $p=0.8\pm0.1$ at 136 K.

portant anharmonic forces which, in the quasiharmonic approximation, lead to a renormalization of the force constants and, thus, to an effective softening of the network with increasing T. However, this approximation cannot explain the observed change in the spectral slope, i.e., the change of exponent, p.

In order to investigate further the consistency of our experimental results, we have compared the measured inelastic intensities with the Debye-Waller factor (DWF) that we obtained from the elastic scattering. The DWF, $\exp(-\frac{1}{3}q^2\langle u^2\rangle)$, represents the self-correlation function of the thermal fluctuations of the single-particle positions $\langle u^2\rangle$ and is directly related to the density of states by

$$\langle u^2\rangle \propto k_BT\int_0^{\omega_m}\frac{Z(\omega)}{\omega^2}d\omega,\quad k_BT\gg\hbar\omega. \tag{3}$$

Note that the integrand is proportional to the quantity plotted in Fig. 2. The ratio of $\langle u^2\rangle$ for the two temperatures may therefore be obtained by integration of the measured spectra. The DWF can also be obtained from the elastic peak intensities

$$(\partial\sigma/\partial\Omega)_{\text{inc}}=(N\sigma_{\text{inc}}/4\pi)\exp(-\tfrac{1}{3}q^2\langle u^2\rangle), \tag{4}$$

which were measured at four different temperatures, $T=265$, 136, 61, and 7 K, at the five fixed scattering angles. The prefactor in Eq. (4) and effects of the zero-point motion are taken out by our normalizing the intensities from the three highest temperatures by the 7-K data. The normalized peak intensities for the background-subtracted data are shown in Fig. 3 on a semilogarithmic scale versus q^2. From the slopes, $\frac{1}{3}\langle u^2\rangle$ may be determined and in Table I the results are listed together with the values obtained from integration of the data in Fig. 2 over the experimental range. The excellent agreement is a gratifying internal consistency check of the interpretation of our inelastic data in terms of a density of states.

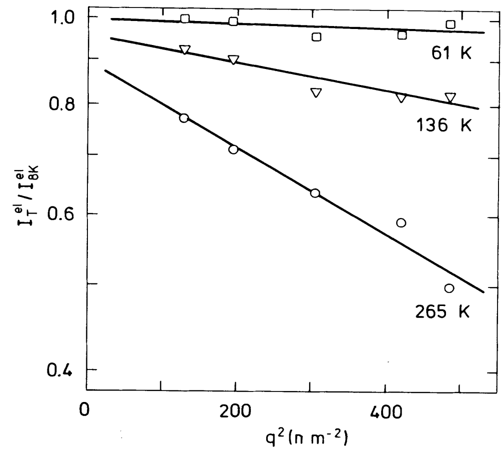

FIG. 3. Semilog plots vs q^2 of the incoherent elastic scattering from the hydroxylated sample with the background subtracted and normalized to the scattering at very low temperature (7 K) (Ref. 13). From the slopes the Debye-Waller factors have been determined. The results are listed in Table I.

We note in passing that Eq. (3) shows that the mean square displacements diverge at the low frequencies if the exponent for the density of states is equal to or less than 1, i.e., the spectral dimension equal to or less than 2. The divergence is removed by the crossover to the phonon modes, but it can still lead to considerable amplitudes at finite temperatures and, hence, generate unusual

TABLE I. Results for the Debye-Waller factor obtained from normalized elastic peak intensities (Fig. 3) and from integration of $[Z(\omega)/\omega]\coth(\frac{1}{2}\hbar\omega/k_BT)$ (Fig. 2). The ratios between the results at 136 and 265 K are seen to be in agreement.

T (K)	Elastic peak $\frac{1}{3}\langle u^2\rangle$ (10^{-2} nm^2)	Ratio	$Z(\omega)$ integration (arbitrary units)	Ratio
265	0.112	> 3.2	0.406	> 3.2
136	0.035		0.126	
61	0.004			

anharmonic effects.

After having established that the inelastic intensity observed in our scattering experiment originates from vibrational excitations, we now remark on the relevance for the fracton problem: We commence with the data taken at 136 K, where the peak observed at 1.5 meV corresponds to the lowest small-particle mode of a SiO_2 sphere of 2.5 nm radius. We estimate that $\hbar\omega_{\min} = \hbar c a_{10}/R = 1.65$ meV, where $c = 4200$ m/s is the average sound velocity in fused silica, a_{10} is the first zero of the derivative of the first-order spherical Bessel function, and R is the particle radius.[12] Excitations of frequency less than $\omega_{\min}$ must correspond to the network modes, and in this frequency range we measure the density of states of the network excitations. From the slope of $Z(\omega)/\omega^2$ vs ω of -1.2 we derive a spectral dimension $d_s = 1.8 \pm 0.1$ [see Eq. (1)]. At $T = 265$ K the slope decreases, or the spectral dimension increases to $d_s = 2.1 \pm 0.05$. It is surprising to find a significant temperature dependence of the exponents, and simple treatments of anharmonic effects cannot explain this. Furthermore, the high-temperature value of $d_s = 2.1$ is larger than the theoretical limit for localization and, taken at face value, this would indicate a profound temperature effect on the nature of the excitations.

To our knowledge, these measurements constitute the first direct observations of fracton densities of states that exhibit strong deviations from the normal Debye spectrum. The experimental results of $d_s = 1.8$ and $d_s = 2.1$ are both considerably larger than the value $d_s = \frac{4}{3}$ postulated as universal for percolation clusters by Alexander and Orbach.[2] It also exceeds the value of 1.56 which can be calculated for a Sierpinsky gasket.[1] Our results indicate that there is considerable scope for further investigations, both experimental and theoretical, to establish the nature of the vibrational modes in random networks and to understand their dynamic stability, the role of anharmonicity, and their thermodynamic properties, in general.

The authors wish to acknowledge the competent assistance of Dr. Herma Blank (Institut Laue-Langevin) during the performance of the experiment.

---

[1] *Scaling Phenomena in Disordered Systems,* edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985).

[2] S. Alexander and R. Orbach, J. Phys. (Paris), Lett. **43**, L625 (1983).

[3] A. Aharony, S. Alexander, O. Entin-Wohlman, and R. Orbach, Phys. Rev. B **31**, 2565 (1985).

[4] H. M. Rosenberg, Phys. Rev. Lett. **54**, 704 (1985).

[5] R. Orbach, in Ref. 1, pp. 335–359.

[6] U. Buchenau, N. Nücker, and A. J. Dianoux, Phys. Rev. Lett. **53**, 2316 (1984); A. J. Dianoux, J. N. Page, and H. M. Rosenberg, Phys. Rev. Lett. **58**, 886 (1987).

[7] Eric Courtens, Phys. Rev. Lett. **58**, 128 (1987).

[8] Y. J. Uemura and R. J. Birgeneau, Phys. Rev. Lett. **57**, 1947 (1986).

[9] T. Freltoft, J. K. Kjems, and S. K. Sinha, Phys. Rev. B **33**, 269 (1986).

[10] Cab-O-Sil (grade M5) is a trademark of Cabot Corporation; Alfasil was Stock No. D 89376 (Alfa Products 1981 catalog).

[11] D. Richter and L. Passell, Phys. Rev. Lett. **44**, 1593 (1980).

[12] D. Richter and L. Passell, Phys. Rev. B **26**, 4078 (1982).

[13] As may be noted, the extrapolations of the fitted lines do not approach 1.0 for $q \to 0$ as expected from Eq. (4). This may be interpreted in terms of a temperature-dependent transmission due to the high incoherent inelastic cross section at high temperatures which vanishes as the temperature approaches zero.