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## Granular structure and fractal domains of silica aerogels

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**Abstract.** Observation of silica aerogels by scanning electron microscopy and transmission electron microscopy are presented. They are supplemented by information on pore volume and pore size distribution determined by thermoporometry. Comparison with small-angle neutron scattering allows precise characterization of the fractal domains. We identify three classes of structure. Primary chains, 30–50 Å in diameter, form the substructures of grains whose size varies from 100 to 500 Å depending on density. The grains form large-scale aggregates, leading to pores on scales exceeding 1000 Å. Since the system is demonstrated to be fractal between the chain and grain dimensions, we re-examine the phonon–fracton crossover and the fracton dimensionality determined by Brillouin scattering and Raman scattering.

### 1. Introduction

The structure of silica aerogels has been the subject of numerous investigations, mainly because of possible fractal aspects (Schaefer and Keefer 1986, Boukenter *et al* 1986, 1988, Courtens *et al* 1987, 1988, Calemczuk *et al* 1987, Vacher *et al* 1988, Bourret 1988, Tsujimi *et al* 1988, Reichenauer *et al* 1989). Small-angle neutron scattering (SANS) seems to show that such heterogeneous materials are fractal in a limited length domain. This remark is valid for aerogels prepared in basic or neutral conditions. In fact the different reactions (hydrolysis and polymerization) are strongly dependent on the pH which, consequently, determines the aerogel structure (Brinker and Scherer 1985).

SANS and small-angle x-ray scattering (SAXS) are sensitive to the geometrical distribution of the structural units. Brillouin scattering, low-frequency Raman scattering, inelastic neutron scattering and thermal measurements, on the other hand, are sensitive to vibrational modes called fractons in a fractal. A serious question arises when the frequency crossovers or length crossovers (which limit the fractal domain) determined by Brillouin scattering or low-frequency Raman scattering are compared with the length (or wavevector) crossovers determined by SANS. In particular, the large-scale crossover determined by Brillouin scattering is much greater than the same crossover determined by SANS.

This discrepancy remains, in spite of the numerous experiments. The structure of the silica aerogels remains in question. This discrepancy motivated us to make new observations, such as electron microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermoporometry. This latter technique provides information on the pore volume and the pore distribution. The aim of this work is to observe more directly the structure of aerogels. In this paper we present the results on neutrally reacted gels. Our observations are compared with measurements by SANS, Brillouin scattering and Raman scattering. This comparison allows clarification of the aerogel structure and leads us to discuss Raman scattering from a disordered fractal.

## 2. Experimental techniques

The silica aerogels were prepared at the Laboratoire des Matériaux Vitreux, Montpellier, by neutral hydrolysis and condensation of tetramethoxysilane in methanol. The solvent was removed under hypercritical conditions.

TEM observations were performed with a 200 CX microscope. Specimens were prepared by cutting and grinding small pieces which were ultrasonically dispersed in methanol. A droplet of the suspension was deposited on a 'holey' microgrid carbon film and dried.

The microstructure of the aerogels was observed by SEM with a Hitachi S800 scanning electron microscope. Aerogels were carefully broken at atmospheric pressure in a chamber. Then the pressure was slowly decreased to 0.1 Torr. A flash of gold was evaporated on the fractured surface. Other chemical techniques for biological specimens (Robinson *et al* 1987) were used. No dependence on sample preparation was observed.

TEM and SEM observations were supplemented by measurement of the porosity using the technique of thermoporometry. Details of this technique have been described elsewhere (Brun *et al* 1977).

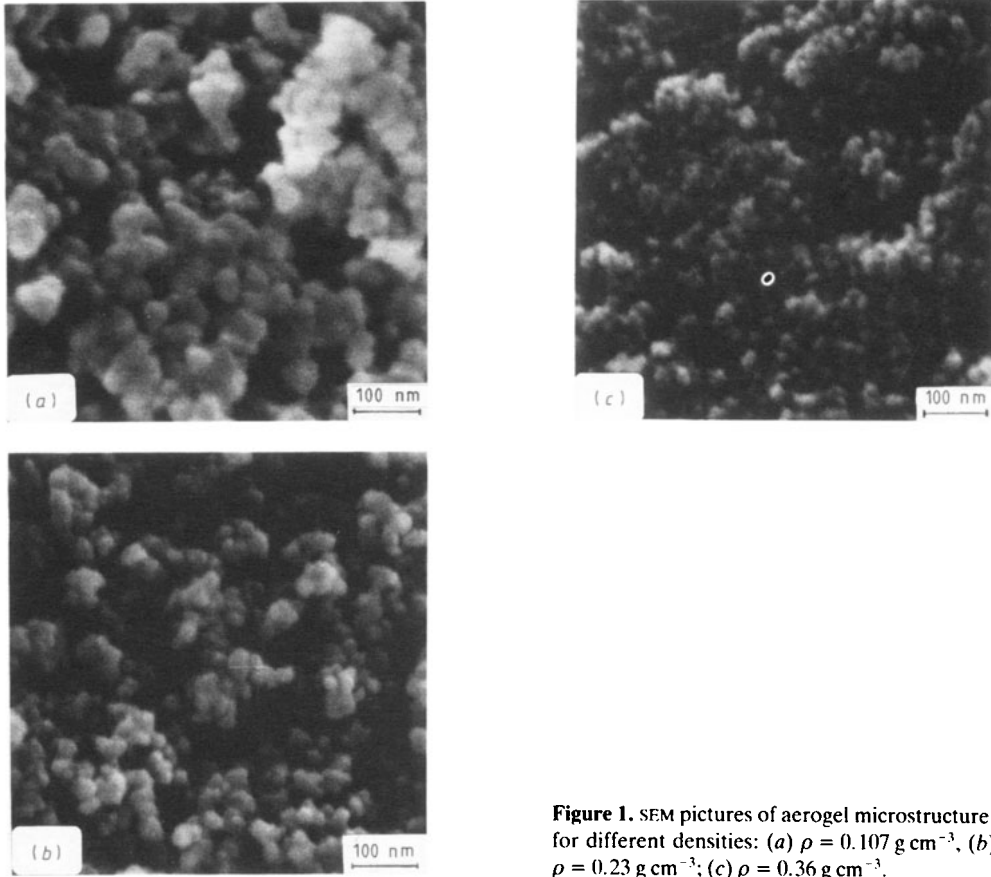
## 3. Experimental results

The SEM pictures in figure 1 show the granular structure of fractured surfaces of silica aerogels; the aerogel network appears to be constructed of clusters of spherical grains. The diameter of grains increases with decrease in aerogel density. The values given in table 1 correspond to an upper limit of the grain diameter.

The size distribution of the grains is narrow and can be considered as monodisperse. On the contrary the size distribution of clusters of grains and pores (macropores) separating these clusters is clearly polydisperse. The cluster polydispersity decreases with increasing aerogel density. The SEM pictures in figure 2 obtained at a lower magnification show the voluminous pores between the clusters. For the less dense sample ( $0.107 \text{ g cm}^{-3}$ ), the size distribution of macropores increases from about 1000 Å to about 10000 Å. For the two other more dense samples the macropore size is less than 5000 Å.

In addition to the polydisperse macroporosity, one observes, in particular in the less dense sample, large domains ( $1 \mu\text{m}$ ) that do not contain large pores. This inhomogeneity probably explains the milky aspect of the aerogels which increases rapidly when the density decreases.

TEM photographs (figure 3) show a network of intersecting chains with a diameter of 30–50 Å for the  $0.23 \text{ g cm}^{-3}$  aerogel. The length between two intersecting points is about



**Figure 1.** SEM pictures of aerogel microstructure, for different densities: (a)  $\rho = 0.107 \text{ g cm}^{-3}$ , (b)  $\rho = 0.23 \text{ g cm}^{-3}$ ; (c)  $\rho = 0.36 \text{ g cm}^{-3}$ .

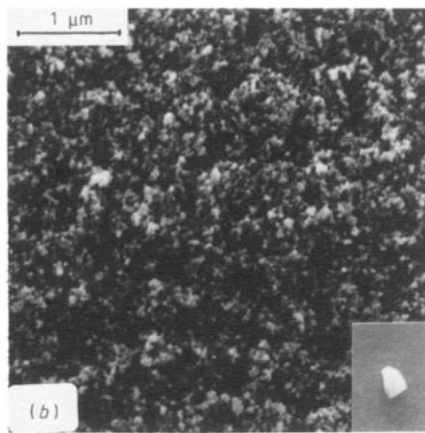
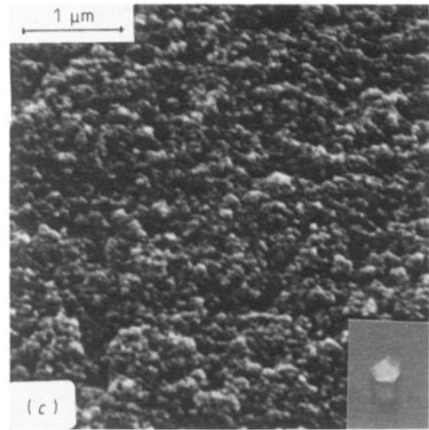
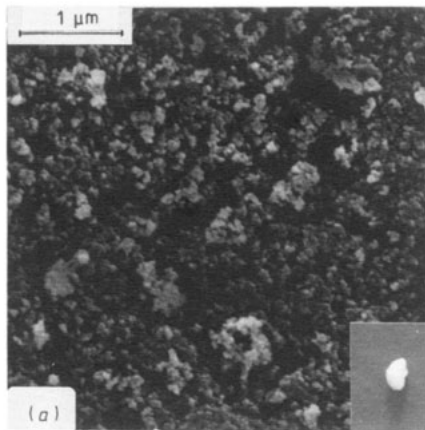
**Table 1.** Values of  $\rho(r)$  and the percentage of inter-grain porous volume.

Aerogel density ( $\text{g cm}^{-3}$ )	Density in grains ( $\text{g cm}^{-3}$ )	Diameter $2r$ of grain, SEM ( $\text{\AA}$ )	Diameter ( $2\sqrt{5}\xi$ ) of fractal grain, SANS ( $\text{\AA}$ )	Inter-grain porous volume (%)
0.36	0.89	130	179	75
0.23	0.60	270	360	67
0.107	0.395	500	1180	77

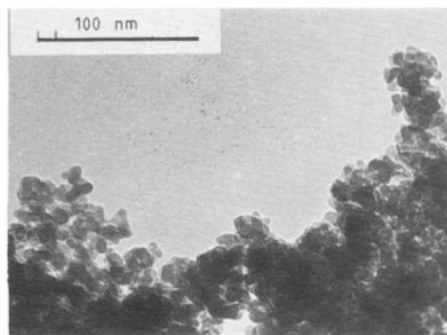
double the rod diameter. These observations are very similar to those of Bourret (1988). The structure of the intersecting chains corresponds to the internal structure of the spherical particles or grains observed by SEM.

A sketch of the aerogel structure deduced from SEM and TEM is proposed in figure 4.

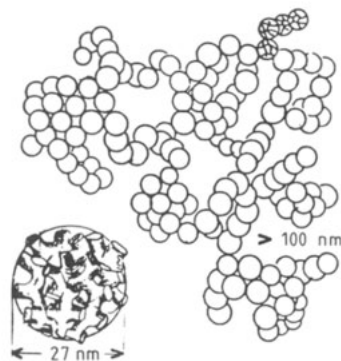
The technique of thermoporometry (Brun *et al* 1977) adds supplementary information on the aerogel texture. The total volume  $V(R)$  of pores of radius smaller than or equal to  $R$  is represented in figure 5.



**Figure 2.** Low-magnification SEM pictures of aerogels: (a)  $\rho = 0.107 \text{ g cm}^{-3}$ ; (b)  $\rho = 0.23 \text{ g cm}^{-3}$ ; (c)  $\rho = 0.36 \text{ g cm}^{-3}$ . The insets are photographs of the aerogel samples.

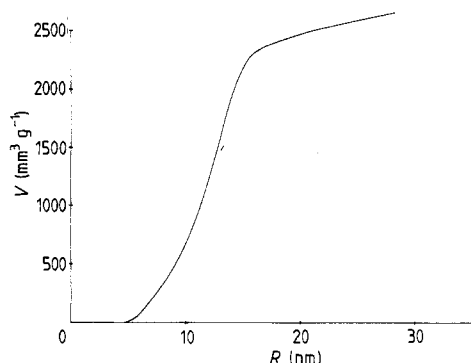


**Figure 3.** Transmission electron micrograph of the aerogel in figure 2(b) ( $\rho = 0.23 \text{ g cm}^{-3}$ ).



**Figure 4.** Sketch of the aerogel structure deduced from electron microscopy.

As is apparent in figure 5, the pore volume  $V(R)$  for  $R < 45 \text{ \AA}$  (the microporous volume) is negligible. The thermoporometry does not allow observation of pores with a radius  $R$  larger than  $400 \text{ \AA}$ . To be consistent with the measured density of  $0.23 \text{ g cm}^{-3}$ ,



**Figure 5.** Cumulated porous volume against the pore radius obtained from thermoporometry.

27% of the total pore volume must correspond to pores of radius larger than 350 Å. This amount of macroporous volume is close to that estimated from SEM pictures (figure 2).

Now it is interesting to compare the geometrical characteristics obtained by electron microscopy and thermoporometry with those deduced from SANS (Vacher *et al* 1988), Brillouin scattering (Courtens *et al* 1987) and low-frequency Raman scattering (Tsuji *et al* 1988).

## 4. Discussion

### 4.1. Electron microscopy and small-angle neutron scattering: fractal dimensionality and fractal domain

Vacher *et al* (1988) reported the neutron-scattered intensities  $I(q)$  against the magnitude of the scattering vector  $q$ , for silica aerogels prepared under same conditions and in the same laboratory as those described in this paper. Their curves were interpreted as scattering from a fractal in a  $q$ -domain, the upper cut-off of which depends on the density of the aerogel. The fractal dimension  $D$  was found to be equal to 2.4.

From the fitting of  $I(q)$ , Vacher *et al* deduced the variation in the correlation length  $\xi$  with the density. The relation between the Orstein-Zernike correlation length  $\xi$  and the diameter  $2r$  is  $2r = 2\sqrt{5}\xi$ . Using the values of  $\xi$  deduced from SANS by Vacher *et al*, we find values of  $2r$  larger than the diameter observed by SEM. However, taking into account the experimental errors and the imprecision in the determination of  $\xi$ , we conclude that the agreement is remarkable.

If we accept a fractal model, we are forced to conclude that the quasi-monodisperse grains observed by SEM have an internal fractal structure with  $D = 2.4$ . The aggregation of these grains is not necessarily fractal but does lead to large-scale polydisperse aggregates and pores as observed in SEM.

SANS is not sensitive to the large- $q$  limit of the fractal domains; the Porod regime ( $I(q) \propto q^{-4}$ ) is not observed with the aerogels prepared in neutral conditions because of the internal structure of grains.

If it is the branched chain structure seen in figure 3 that is fractal, then the lowest length limit of the fractal domains would equal the chain diameter  $2a \approx 40$  Å. The density  $\rho(r)$  of the fractal grains seen in figure 1 would then be

$$\rho(r) = \rho(a)(r/a)^{D-3} \quad (1)$$

where  $r$  is the grain size.

The density  $\rho(a)$  in the chains or in the aerogel skeleton (Woignier and Phalippou, 1987) is close to 1.8. The values of the density  $\rho(r)$  calculated using (1) are collected in table 1 along with the percentage of macroporous or inter-grain volume.

It has been proposed before (Tsujimi *et al* 1988) that the lowest length limit of the fractal domain is smaller than 20 Å, a size which would correspond to the diameter of approximately spherical species with a density close to 1.8. From this assumption the calculated density  $\rho(r)$  using (1) in fractal grains of the 0.23 g cm<sup>-3</sup> aerogel is found to be equal to 0.38 by taking  $\rho(a) = 1.8$  and  $a = 10$  Å. This corresponds to a porous volume in grains equal to 2100 mm<sup>3</sup> g<sup>-1</sup>.

From figure 5, which gives the cumulated volume for the pores which have a radius less or equal to  $R$ , the volume of 2100 mm<sup>3</sup> g<sup>-1</sup> includes pores with diameter up to 300 Å. This diameter is close to the grain diameter (table 1); it is difficult to imagine grains  $2r$  in diameter in which pores would exist with the same diameter. On the contrary with  $2a$  equal to 40 Å, i.e. the chain diameter, the porous volume in a grain is found to be a factor of about 2 smaller, and the maximum diameter of pores in grains deduced from figure 5 becomes smaller than the grain diameter. Therefore the hypothesis of a lowest length limit of the fractal domains greater than 20 Å and equal to 40 Å is more consistent.

#### 4.2. Electron microscopy and Brillouin scattering

Courtens *et al* (1987) determined a crossover frequency  $\omega_{co}$  and a correlation length  $\xi_B$  such that  $\xi_B = 1/k_{co}$ , where  $k_{co}$  is the magnitude of the wavevector at the crossover determined by Brillouin scattering. Assuming a fractal structure of the aerogels, these workers considered the crossover as a transition from phonons (weakly localized) to fractons (strongly localized). It is not obvious, however, that this transition corresponds to a phonon–fracton crossover. From electron microscopy and SANS we have deduced just above that the fractal structure probably describes the structure internal to the grains observed by SEM. Since voids in the structure exist on scales larger than the grains, however, strong localization could be expected on scales exceeding the grain size, in particular for the less dense aerogels. In conclusion, it is not at all evident that the crossover deduced from Brillouin measurements is a phonon–fracton crossover and probably the correlation length  $\xi_B$  is related to the pore size rather than to the grain size.

The same workers assume further a ‘mutual self-similarity’ which implies that the density in the fractal domains is the density of the aerogel samples. Clearly this assumption is not confirmed by SEM; there exists a polydisperse distribution of grain aggregates leading to large-scale inter-aggregate porosity; the density in the fractal grains therefore must be larger than the density of the sample, as we conclude above.

Courtens *et al* plotted the experimental crossover frequency  $\omega_{co}$  and the acoustic wave velocity  $v(\xi_B)$  at the crossover against the sample density  $\rho$ . They interpreted their data through power-law functions  $\omega_{co} \propto \rho^y$  and  $v(\xi_B) \propto \rho^x$ . In a fractal structure the parameters  $x$  and  $y$  are functions of the fractal dimensionality  $D$  and the fracton dimensionality  $\tilde{d}$ . From the two points emphasized just above, namely first that  $\omega_{co}$  and  $v(\xi_B)$  are not related to the real phonon–fracton crossover and secondly that the aerogel density  $\rho$  is not the density in the fractal, it is clear that the parameters  $D$  and  $\tilde{d}$  deduced from Brillouin measurements are not the fractal and the fracton dimensionalities in fractal grains. Certainly a correlation exists between the geometrical characteristics of the grains and the aggregates (of grains). Consequently a correlation between the Brillouin parameters and the true fractal dimensionality  $D$  and fracton dimensionality  $\tilde{d}$  might exist.

### 4.3. Electron microscopy and low-frequency Raman scattering

Like other workers (Tsuji *et al* 1988), we observed (for the most transparent silica aerogels described in this paper) a maximum of Raman scattering intensity divided by the Bose factor, situated between 25 and 30  $\text{cm}^{-1}$ . We assumed that this maximum corresponds to the scattering from surface vibration modes of quasi-spherical 40 Å blocks which form the chain network of the grains observed by TEM (Bourret 1988). It has been shown (Duval *et al* 1986) that the frequency  $\omega_0$  of the spheroidal surface vibration modes is related to the diameter  $2a$  of the particle and to the velocity  $v$  of sound in the particle:

$$\omega_0 \approx 0.8v/2a. \quad (2)$$

From TEM observations,  $2a$  varies between 30 and 50 Å (Bourret (1988) found a slightly smaller diameter, about 30 Å). The velocity of sound deduced from (2) varies between 3120 and 4220  $\text{m s}^{-1}$ . These values are a little smaller than the velocity in fused silica. This is not surprising, because the density in the chains internal to the grain network, as deduced from thermoporometry and other measurements (Woignier and Phalippou 1987) is slightly smaller (1.8–2) than the density in fused glass. Note that good agreement between electron microscopy and Raman scattering was obtained for the base-catalysed aerogels as well (Boukenter *et al* 1988).

Tsuji *et al* (1988) measured the low-frequency Raman scattering using a Fabry–Pérot interferometer. They observed the same maximum at about 30  $\text{cm}^{-1}$  for the silica aerogel with a density equal to 0.36, but they deduced (from equation (2)) a diameter  $2a$  of about 16 Å by taking the velocity  $v$  of sound equal to 2000  $\text{m s}^{-1}$ . It is not justified to choose such a small velocity with such small units which have a density close to the density of fused silica. Furthermore it has been shown before that a diameter  $2a$  smaller than 20 Å leads to a diameter of pores in grains close to the diameter of grain itself.

For the silica aerogel with a density equal to 0.36  $\text{g cm}^{-3}$ , Tsuji *et al* observed another Raman maximum at a lower frequency  $\omega_1$  of about 1  $\text{cm}^{-1}$ . From the SEM observations (figure 1) which show a relatively monodisperse distribution of grains with a diameter  $2r$ , it is reasonable to assign this lower-frequency maximum to surface vibrational modes of these grains. Furthermore from the interpretation of SANS measurements, which are in agreement with a fractal structure of grains,  $\omega_1$  corresponds to the lower frequency of the vibration modes in the fractal. Using equation (2) and taking  $2r = 130$  Å as determined by SEM, we find a sound velocity  $v(r) = 490$   $\text{m s}^{-1}$ . This value, as expected, is slightly higher than the velocity  $v(\xi_B)$  determined by Brillouin measurements which depends on the polydisperse aggregates of fractal grains.

As shown before, the lower size limit of the fractal domains is  $2a$ . Therefore the dispersion relation of the vibrational modes in a fractal (Alexander and Orbach 1982, Rammal and Toulouse 1983) gives

$$\omega_1/\omega_0 = (r/a)^{-D/\bar{d}}. \quad (3)$$

Taking the grain diameter  $2r = 130$  Å as determined from SEM and  $2a = 40$  Å which is the mean diameter determined by TEM,  $\omega_0 = 30$   $\text{cm}^{-1}$ ,  $\omega_1 = 1$   $\text{cm}^{-1}$  (Raman results) and  $D = 2.4$  (SANS), we find that  $\bar{d} = 0.83$ .

As shown by Boukenter *et al* (1986) in the fractal regime, the Raman scattering intensity  $I(\omega)$  divided by the Bose factor  $n(\omega) + 1$  depends on the fractal parameters  $D$ ,  $\bar{d}$  and  $d_\phi$ , the superlocalization exponent. We shall now review this relationship since it is still controversial.



The intensity  $I(\omega)$  of light scattered with a frequency shift  $\omega/2\pi$  is determined by the Raman tensor  $I_{ij}(\omega)$  defined as the Fourier transform of the correlation function of the space- and time-dependent fluctuations of the dielectric susceptibility  $\chi$  (Jackle 1981):

$$I_{ij}(\omega) = \frac{1}{2\pi\Omega} \int_{-\infty}^{+\infty} dt \exp(i\omega t) \int d^3r_1 d^3r_2 \exp[-ik(r_1 - r_2)] \langle \chi_i(r_1, t) \chi_j(r_2, 0) \rangle \quad (4)$$

where  $\Omega$  is the volume of the system. The dielectric susceptibilities  $\chi_i$  and  $\chi_j$  are linearly related to the elastic local strains  $e_k$  and  $e_l$  induced by the vibration

$$\chi_i \propto p_{ik} e_k \quad \chi_j \propto p_{jl} e_l \quad (5)$$

The local strain  $e(r, \omega)$  induced by the vibrational mode is assumed to be proportional to the gradient of the vibrational wavefunction. It is generally assumed that quantum states in fractals are superlocalized or damped along the fractal paths. The eigenfunction shape is written as (Alexander et al 1986)

$$\Psi(r) \propto \exp[-(r/l_\omega)^{d_\varphi}] \quad (6)$$

$l_\omega$ , the localization length, is related to the fracton frequency by the following dispersion law (Alexander and Orbach 1982, Rammal and Toulouse 1983):

$$l_\omega \propto \omega^{-\tilde{d}/D} \quad (7)$$

The gradient of  $\Psi(r)$  deduced from equations (5) and (6) gives only a mean value of the local strain  $e(r, \omega)$ :

$$e(r, \omega) \propto \omega^{d_\varphi(\tilde{d}/D)} \Psi(r) \quad (8)$$

Without specifying the relative polarization of the scattering and exciting lights which depends on the anisotropy, the Stokes Raman scattering intensity from superlocalized vibration modes, is from (4) and (8), using the golden rule,

$$I(\omega) \propto \frac{1}{\Omega} \omega^{2d_\varphi\tilde{d}/D} \omega^{-1} g(\omega) [n(\omega) + 1] \int d^3r_1 d^3r_2 \langle \Psi(r_1) \Psi(r_2) \rangle \quad (9)$$

where  $g(\omega)$  is the density of vibrational states and  $[n(\omega) + 1]$  is the Bose factor which gives the thermal population of the vibrational levels.

If  $\Psi(r_1)$  and  $\Psi(r_2)$  represent coherent vibrational states, the integral of the correlation function is proportional to the mass or the site number in the fracton localization volume:

$$\int d^3r_1 d^3r_2 \langle \Psi(r_1) \Psi(r_2) \rangle = l_\omega^D \quad (10)$$

From (7) and the expression for the density of vibrational states (Alexander and Orbach 1982, Rammal and Toulouse 1983),

$$g(\omega) \propto \omega^{\tilde{d}-1} \quad (11)$$

Then, we find that

$$I(\omega)/[n(\omega) + 1] \propto \omega^{2d_\varphi(\tilde{d}/D)-2} \quad (12)$$

However, in a silica aerogel a single fractal does not determine the structure down

to the  $\text{SiO}_2$  molecular unit or the  $\text{SiO}_4$  tetrahedron. As shown before, the lowest fractal length limit corresponds to the diameter of chains which is equal to about 40 Å from TEM. The limit given by Tsujimi *et al* (1988) is lower than 40 Å, approximately equal to 15 Å but larger than the size of the  $\text{SiO}_2$  molecular unit or the  $\text{SiO}_4$  tetrahedron. The disordered arrangement inside the structural units is different from the fractal inter-unit structure and is characterized by a correlation length.

The difference between the fractal and the internal unit structures brings about a random dephasing between the motions of atoms in different structural units. In consequence the coherence volume for the Raman scattering is not the fracton localization volume. It is determined by the correlation length of the arrangement inside the structural units and thus is smaller than the structural unit volume and independent of the fracton frequency. Therefore the Stokes Raman scattering intensity  $I(\omega)$  becomes

$$I(\omega) \propto \frac{1}{\Omega} \omega^{-1} g(\omega) [n(\omega) + 1] \int d^3r_1 d^3r_2 \langle e(r_1, \omega) e(r_2, \omega) \rangle. \quad (13)$$

Taking into account the fracton frequency independence of the coherence volume, we have

$$\frac{1}{\Omega} \int d^3r_1 d^3r_2 \langle e(r_1, \omega) e(r_2, \omega) \rangle \propto e^2(\omega) \quad (14)$$

with

$$e^2(\omega) \propto \omega^{2d_\varphi(\bar{d}/D)}. \quad (15)$$

Finally for a limited fractal as a silica aerogel the Raman scattering intensity is given by

$$I(\omega)/[n(\omega) + 1] \propto \omega^{2d_\varphi(\bar{d}/D) - 2 + \bar{d}}. \quad (16)$$

This expression for the Raman scattering intensity was given in previous papers (Boukenter *et al* 1986, 1988, 1989).

From the results of Tsujimi *et al* (1988) the slope of the reduced intensity  $I(\omega)/n(\omega) + 1$  against  $\omega$  in the log–log plot is equal to  $-0.36$ . Taking into account the random dephasing induced by the disordered arrangement in the structural units and then using equation (16), we obtain

$$2d_\varphi(\bar{d}/D) - 2 + \bar{d} = -0.36.$$

Taking  $D = 2.4$  (SANS) and  $\bar{d} = 0.83$  as found above from the dispersion relation (3), we obtain

$$d_\varphi = 1.17.$$

This value of the superlocalization exponent  $d_\varphi$  does not disagree with the theoretical estimations of Harris and Aharony (1987) who show that the upper limit of  $d_\varphi$  is  $D/d_l$ ,  $d_l$  being the chemical dimensionality. For the different types of fractal,  $D/d_l$  is close to 1.3.

Tsujimi *et al* (1988) neglected in their model of Raman scattering the random dephasing induced by the disordered arrangement in the structural units. They interpreted their experimental results by a frequency variation in the Raman intensity which is given by equation (12). Taking  $\bar{d} = 1.25$ , the result given by the interpretation of

Brillouin measurements (Courtens *et al* 1987), they found that  $d_{\text{q}} = 1.6$ . This value is larger than the theoretical upper limit of Harris and Aharony (1987).

## 5. Conclusion

Electron microscopy (SEM and TEM) was used to elucidate the structure of silica aerogels prepared in neutral (pH 7) conditions. For densities larger than 0.1 the gel is made up of aggregates of quasi-spherical grains. We observe a polydisperse distribution of both aggregates and macropores. The diameter of intra-aggregate grains and the size of aggregates themselves increase as the density decreases.

The network internal to the grains is an entanglement of intersecting chains. Comparison with SANS (Vacher *et al* 1988) indicates that the structure is fractal. The radius of grains determined by SEM is in excellent agreement with the lower cut-off of the fractal domain found in neutron scattering.

The comparison between electron microscopy observations and low-energy Raman scattering (Tsujimi *et al* 1988) allows us to correlate the crossover lengths and the crossover frequencies.

From electron microscopy and SANS it is obvious that the density of the aerogel sample is much smaller than the density in the fractal grains. Furthermore the frequency  $\omega_{\text{co}}$  and the velocity  $v(\xi_{\text{B}})$  of sound deduced from Brillouin measurements do not correspond to these quantities at the phonon–fracton crossover. In consequence, Brillouin scattering (Courtens *et al* 1987) does not fix the fractal and fracton dimensionalities.

When the dispersion relation of the vibrational modes in a fractal is taken into account, the low-frequency Raman scattering is consistent with the existence of a disordered arrangement in the structural units that is different from the fractal structure. In consequence the Raman scattering from the different scatterers in the fracton localization volume is incoherent. A very recent theoretical calculation of Raman scattering intensities from a disordered percolating system confirms this hypothesis of incoherent scattering (Viliani 1990).

Some electron microscopy observations are under way on the base-catalysed aerogels. Their structure is very different and much more homogeneous; the grains are smaller. A systematic comparison between the basic and neutral aerogels is in preparation.

## Acknowledgments

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