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ON THE FRACTAL STRUCTURE OF SILICA AEROGELS

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Résumé - Les mesures de diffusion élastique de neutrons aux petits angles montrent que les aérogels de silice, qu'ils soient préparés dans des conditions neutres ou en présence d'un catalyseur basique, peuvent présenter une géométrie fractale pour des échelles de longueur s'étendant sur plusieurs ordres de grandeur. Ces résultats fournissent une illustration du concept d'auto-similarité mutuelle. La discussion comporte également une analyse de l'influence de la catalyse sur la dimension de Hausdorff, la taille des particules, ainsi que sur la densification au cours de la transformation gel-verre.

Abstract - Both neutrally reacted and base catalyzed silica aerogels can be prepared which are fractals over several orders of magnitude in length. The concept of mutual self-similarity is explained in some details. The effects of catalysis on the Hausdorff dimension, particle size, and sintering are shown.

1 - INTRODUCTION

There is an increasing interest in the physical properties of aerogels /1/. Hence, it is of importance to determine accurately the structure of these materials. Following the first observation of a fractal structure over a restricted range of length in base catalyzed silica aerogels, it was suggested that fractality in solids could be present only in the very special case of extremely porous materials /2/. Simultaneously, from a small angle X-ray scattering study on aerogels prepared under various catalysis conditions, Craievich *et al.* /3/ concluded that their materials were not fractals. This position was reiterated by the same group several months later /4-5/. On the other hand, our Brillouin scattering study of acoustic excitations in a series of neutrally reacted silica aerogels /6/ indicated an unusual behavior, which could be interpreted in terms of a phonon-fracton crossover. From a scaling of the measurements of the characteristic crossover length in function of aerogel density ρ , we deduced a fractal (Hausdorff) dimension $D \approx 2.4$. To substantiate this interpretation, and to deepen the insight in the structure of these materials, we performed small angle neutron-scattering (SANS) measurements on the same series of samples used for the Brillouin experiments. This study was recently extended to another series of samples prepared under basic catalysis. We also investigated the structural evolution during the transformation of aerogels into glass *via* sintering at elevated temperatures. A number of results have already been published /7-8/. We summarize here the main features, and present new measurements on sintering of base catalyzed aerogels.

2 - SUMMARY OF PREVIOUS RESULTS

The SANS experiments were performed on the spectrometer PACE, at the Laboratoire Léon Brillouin (1) in Saclay, France. In that system, the wavelength of incident neutrons can be varied from $\approx 4 \text{ \AA}$ to $\approx 22 \text{ \AA}$. Elastically scattered neutrons are collected on a set of 30 annular detectors, whose radii range from 3 to 33 cm. The distance between sample and detectors can be varied from $\approx 1 \text{ m}$ to $\approx 5 \text{ m}$, allowing a range of momentum exchange q from $2 \times 10^{-3} \text{ \AA}^{-1}$ to 0.5 \AA^{-1} .

(1) Laboratoire mixte CNRS-Commissariat à l'Énergie Atomique.

Two series of samples were used, both prepared from tetramethoxysilane dissolved in methanol. In each series, different samples correspond to different densities. The first series was obtained under neutral conditions, while the second was prepared under basic catalysis. The upper three curves of Fig. 1 are examples of scattered intensities $I(q)$ obtained on samples prepared under neutral conditions. The most striking feature of these curves is the power law, $I(q) \propto q^{-D}$, observed for the lightest sample over about two orders of magnitude in q . A fractal dimension $D = 2.40 \pm 0.03$ is obtained from the fit of each individual curve to a theoretical expression for $I(q)$ /9/. For the lightest samples, fractal geometry extends down to the smallest length scale probed in this experiment. For aerogels with densities larger than 200 kg/m^3 , the departure of $I(q)$ from the $q^{-2.4}$ dependence at large q indicates the presence of particles with gyration radii of a few \AA . An expanded plot of the large- q range for the heaviest samples shows above $\approx 0.15 \text{ \AA}^{-1}$ a region where $I(q)$ is nearly proportional to q^{-3} . This power suggests fuzzy particles with a fractal surface /10/. The structure at that scale can be modified by oxidation at 500°C , a treatment which removes remaining $-\text{CH}_3$ groups and creates new siloxane bonds. After such a treatment, one observes $I(q) \propto q^{-4}$ at large q . This demonstrates that oxidation smoothens the surface of the particles.

From the upper three curves in Fig. 1 one also sees that ξ strongly decreases with increasing density. Using the values measured on the whole series of samples, one obtains $\rho \propto \xi^{-0.60 \pm 0.02}$ /7/. To interpret this

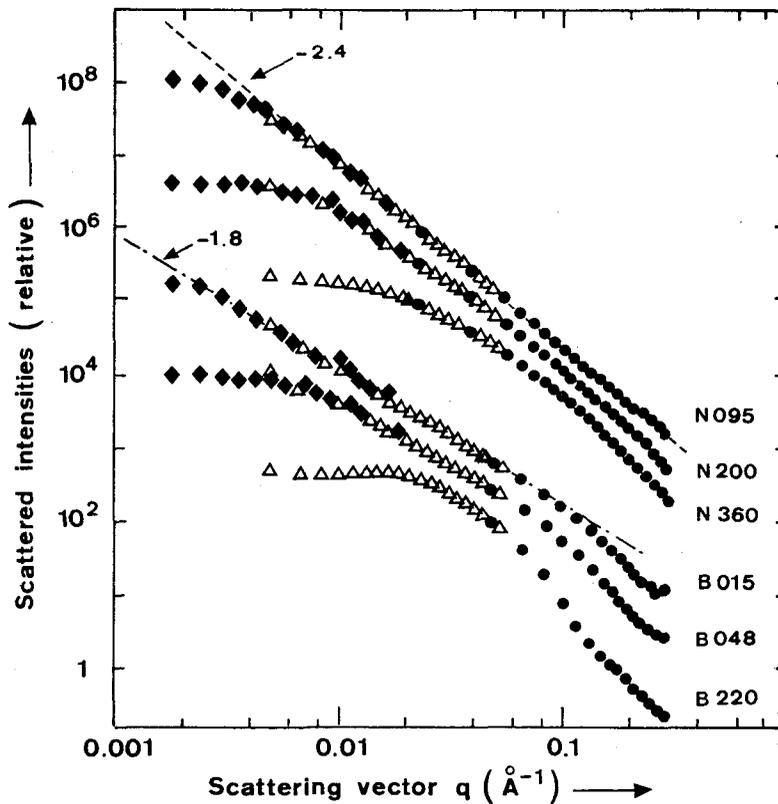


Figure 1. Small angle neutron-scattering results on three neutrally (N) reacted samples and three base (B) catalyzed ones. The numbers in the labels refer to the density in kg/m^3 . The straight lines are guides to the eye, indicating the large fractal range of light samples, and the effect of catalysis on the Hausdorff dimension D . The different symbols refer to different runs /7/.

scaling law, let us consider elementary fractal clusters assembled from homogeneous particles of size a . In 3-d Euclidean space, the density of such clusters at a length scale $L > a$ is $\rho(L) = \rho_a(L/a)^{D-3}$. Here, ρ_a is the density of the particles. Let ξ be the final average size of the clusters, and assume that the aerogel is built of an homogeneous assembly of such clusters. Hence, the bulk density of the aerogel is $\rho \equiv \rho(\xi)$. If we now construct another aerogel in exactly the same way, only changing the value of ξ , we obtain two materials of different bulk density, but which are identical at length scales at which they are fractal. We have named this property "mutual self-similarity" /7/. For these materials, the scaling law obeyed by ρ as a function of ξ on the whole series of samples is identical to the relation between $\rho(L)$ and L in the fractal region for any one sample. For our aerogels, $D = 2.4$ implies $\rho(L) \propto L^{-0.6}$ for each sample. Since an identical exponent is found for $\rho(\xi)$, the mutual self-similarity of our series of samples prepared under neutral conditions is established. Hence, a study of the dependence on ρ of macroscopic properties on such a series amounts to studying the scaling of those properties in function of the length scale on a single fractal.

The lower three curves in Fig. 1 are examples of $S(q)$ for samples prepared under basic catalysis /8/. They are very different from the upper three curves. First, they show that basic catalysis leads to the formation of large particles, with $10 \text{ \AA} \leq R \leq 20 \text{ \AA}$ weakly dependent on the aerogel density. Further, comparing N200 to B220, one notes that the extension of the power-law region is very different on these two curves. For this density, corresponding to a porosity of $\approx 90\%$, the sample prepared under basic conditions does not exhibit a clear fractal behavior /2/. To obtain in this case a fractal structure over two orders of magnitude, it is necessary to prepare materials of extremely low densities, as illustrated by curve B015. For the latter, the power-law behavior extends down to the smallest q -values accessible in this SANS experiment. Finally, a most striking effect of catalysis is found in the value of D . All curves from base catalyzed samples with an extended fractal range give $D = 1.8 \pm 0.1$.

These results demonstrate that aerogels can be prepared which are fractal over more than two orders of magnitude in length scale. Depending on catalysis, D varies between ≈ 1.8 and ≈ 2.4 . Furthermore, the elementary particles can be rough or smooth, and their size strongly depends on catalysis. This variation of the preparation is obviously sufficient to create vastly different aggregation conditions. In particular, in the case of base catalysis, it appears that diffusion-limited cluster-cluster aggregation /11/ may play a major role in the formation of the gel.

3 - SINTERING OF AEROGELS

The aerogel-to-glass transformation by sintering at elevated temperature (1050 °C) was investigated on samples taken from the above series. Four pieces of neutrally reacted aerogel of density $\rho = 310 \text{ kg/m}^3$ were sintered for increased durations. The SANS intensities multiplied by q^3 , to emphasize the changes in the particle-scattering region, are shown in Fig. 2. One immediately notices that particles grow with time, and apparently become fairly smooth, as indicated by the extended Porod region obtained after 20 min of sintering. The fractal dimension is practically unchanged during the early steps of densification, as long as a fractal description remains meaningful. Also in the early steps, the correlation range becomes progressively shorter, as the material shrinks. This is better seen in a presentation of $I(q)$ vs q /8/. The densification thus proceeds by coalescence of several small particles into larger ones. In this process, short range correlations can be expected to develop, and this probably explains the occurrence of "bumps" on the Porod slope.

Such features are more developed for base catalyzed samples, as illustrated in Fig. 3. The larger and more uniform particles of base catalyzed materials are more likely to develop short range correlations on coalescing. Thus, several oscillations are superimposed to the Porod slope, and their peaks move towards smaller q -values (longer lengths) with increased sintering time. Note that the fractal region, if any, is very small for these base catalyzed materials /2/ in spite of their relatively high porosity ($\approx 90\%$).

Comparing Figs. 2 and 3, one observes that after 20 min of sintering the curves are extremely similar, with nearly the same particle size, and practically no remaining fractal region. Also, after some sintering time, a structure starts to develop at the highest q -values, for both types of samples. This feature presumably belongs to the tail of the structure factor of dense silica /12/.

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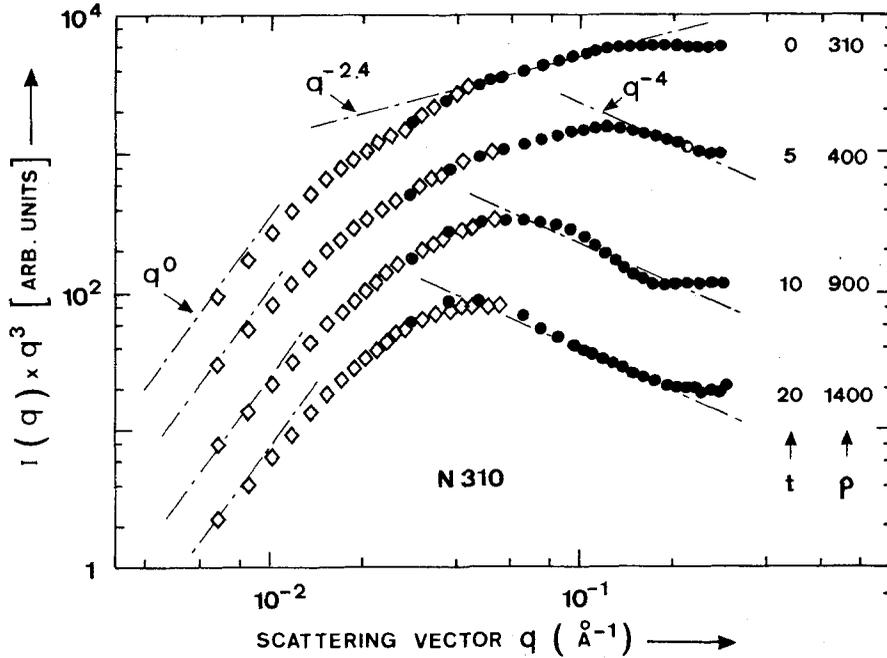


Figure 2. The effect of sintering on the neutrally reacted material N310. The sintering times t , and corresponding densities, are listed on the right hand side. Lines are traced to illustrate various power laws: $I(q) \propto q^0$ is the homogeneous limit, $I(q) \propto q^{-2.4}$ corresponds to the fractal region, rather narrow for this composition, and $I(q) \propto q^{-4}$ is the Porod region.

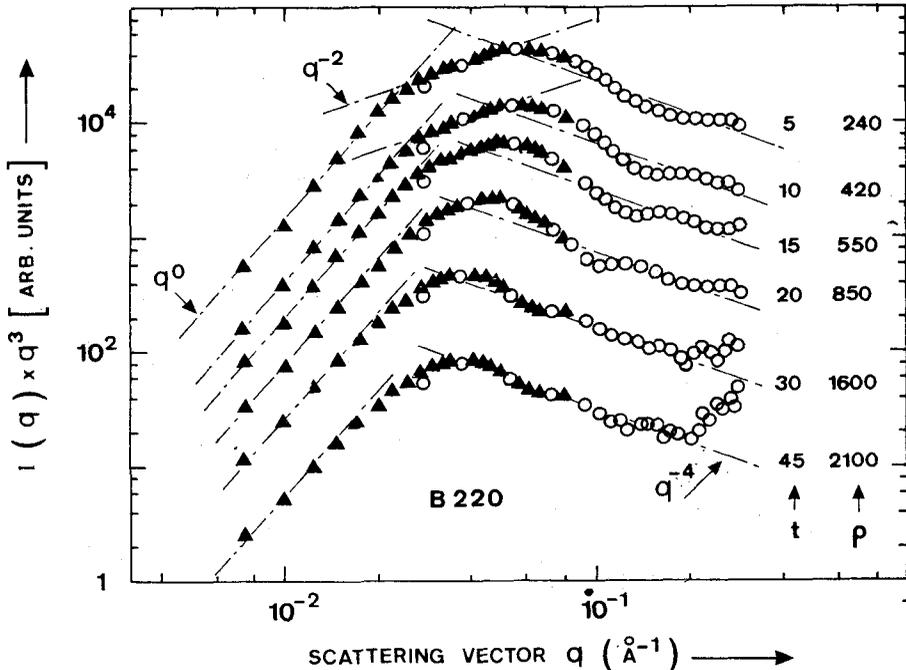


Figure 3. The effect of sintering on base catalyzed material B220. The labeling, and the relevant power laws, are shown as in Fig. 2.

REFERENCES

- /1/ see e.g., *Aerogels*, Fricke, J., Ed. (Springer Verlag, Berlin, 1985), and these Proceedings.
- /2/ Schaefer, D. W., and Keefer, K. D., Phys. Rev. Lett. **56** (1986) 2199.
- /3/ Craievich, A., Aegerter, M. A., dos Santos, D. I., Woignier, T., and Zarzycki, J., J. Non-Cryst. Solids **86** (1986) 394.
- /4/ Zarzycki, J., J. Non-Cryst. Solids **95 & 96** (1987) 173.
- /5/ Lours, T., Zarzycki, J., Craievich, A., dos Santos, D. I., and Aegerter, M. A., J. Non-Cryst. Solids **95 & 96** (1987) 1151.
- /6/ Courtens, E., Pelous, J., Phalippou, J., Vacher, R., and Woignier, T., Phys. Rev. Lett. **58** (1987) 128; Courtens, E., Vacher, R., Pelous, J., and Woignier, T., Europhys. Lett. **6** (1988) 245.
- /7/ Vacher, R., Woignier, T., Pelous, J., and Courtens, E., Phys. Rev. B **37** (1988) 6500.
- /8/ Vacher, R., Woignier, T., Phalippou, J., Pelous, J., and Courtens, E., J. Non-Cryst. Solids (in press).
- /9/ Teixeira, J., in *On Growth and Form* (ed. Stanley, H. E., and Ostrowski, N., Nijhoff, Dordrecht 1986) p. 145.
- /10/ Bale, H. D. and Schmidt, P. W., Phys. Rev. Lett. **53** (1984) 596.
- /11/ Meakin, P., Phys. Rev. Lett. **51** (1983) 1119; Kolb, M., Botet, R. and Jullien, R., Phys. Rev. Lett. **51** (1983) 1123.
- /12/ Mozzi, R. L. and Warren, B. E., J. Appl. Crystallogr. **2** (1969) 164.