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## Analysis of the elastic behaviour of silica aerogels taken as a percolating system

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**Résumé.** — Des mesures de module d'Young par la méthode de flexion trois points pour des aérogels de silice sont présentées. Le comportement élastique est étudié en fonction de la densité apparente des matériaux. L'analyse de ces résultats expérimentaux est effectuée en utilisant l'analogie avec un système de percolation.

**Abstract.** — Measurements of the Young modulus of silica aerogels are performed using the three points flexural technique. The elastic behaviour is studied as a function of the apparent density of the materials. The analysis of the experimental results is made in terms of a percolating system.

### 1. Introduction.

The studies of the elastic properties of percolating systems are an active field of research. The purpose of these studies is to test the different models reported in the literature. As proposed first by De Gennes [1], assuming isotropic force constants, the elastic behaviour of a percolating system near the percolation threshold is identical to that of the conductivity  $\sigma$ . Thus the elastic moduli,  $K$ , are expected to scale as  $K \propto \sigma \alpha (P - P_c)^\tau$  with  $\tau \approx 1.8$ . As demonstrated by Alexander [2], a correct elastic description of the strong local strained medium is expected to give the same value of  $\tau$ .

A different approach takes into account the tensorial character of force constants which is the normal case in solids; analytical work and simulations on discrete lattice [3-5] have suggested that in this case (non isotropic forces), elasticity belongs to a different universality class than that of conductivity. The exponent of tensorial elasticity will be close to 3.6.

Finally, in a continuum percolation model, the so-called « Swiss cheese » model, another universality class of the elastic moduli has been proposed [6] with another exponent  $f$  higher than the tensorial elasticity exponent of the discrete lattice.

Experimental investigations refer to model systems (metal sheet in which holes are punched) [7-9] and real materials such as sintered powder of metal [10] or gels and polymers [11-13]. For the model

systems and sintered powder, the results support the tensorial elasticity. In contrast, for gels, the results suggest that scalar elasticity is significant. However the choice of the physical measurable parameter which can be identified with the percolation parameter is not obvious and this induces ambiguous conclusions. This point will be discussed later.

We present here the results of the elastic properties — Young's modulus determined from static measurement — for silica aerogels. These highly porous materials are obtained from a sol-gel process. Solvent is then eliminated under hypercritical conditions. The analysis of the elastic behaviour is made using two alternative approaches :

a) the materials are issued from gelation reaction : the same percolation descriptions as previously reported for other gels can be used [12].

b) These porous materials can be regarded as a « solid-holes » system using a volumic fraction of voids as percolation parameter. The latter assumption is identical to that used for the « Swiss cheese » model.

Moreover, the static modulus determination of silica aerogels gives complementary information on previous elastic dynamics investigations on the same materials using inelastic light scattering experiments [14]. So the relation of the static and the high frequency elastic behaviour can be analysed. Also a comparison with previous ultrasonic elastic properties of different aerogels [15, 16] will be given.

## 2. Experimental.

The gels are elaborated in neutral conditions by hydrolysis and polycondensation reactions of tetramethoxysilane (T.M.O.S.) diluted in methanol. The alcogels are transformed into aerogels by hypercritical evacuation of the solvent [17]. This procedure allows the monolithicity of the gel to be preserved. Drying under normal pressure produces mechanical stresses appearing in capillaries resulting in a collapse of the material texture. The apparent density is measured from the weight of samples whose dimensions are perfectly known. The volume fraction of pores  $q$  is calculated from apparent and skeletal densities, the later being close to 1.85 for aerogels and 2.2 for densified materials [19]. The apparent density of the aerogels increases ( $q$  decreases) with the T.M.O.S. concentration in the starting solution (Fig. 1). For concentrations higher than 50 % the various liquids are no longer miscible at room temperature. In order to obtain materials with a density higher than  $400 \text{ kg/m}^3$ , aerogels must be densified. The densification is carried out by a heat-treatment at a temperature of  $1\,050^\circ\text{C}$ . Depending on the duration of the treatment, the density of the material may become as high as that of the vitreous silica ( $2\,200 \text{ kg/m}^3$ ). Because the densification rate is very high, the duration of treatment must be precisely controlled [18].

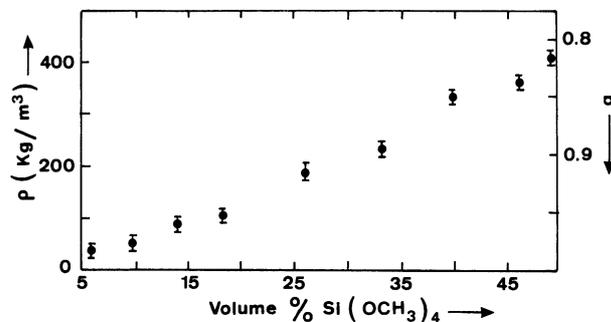


Fig. 1. — Evolution of the apparent density of the aerogels as a function of the T.M.O.S. concentration.

The three-point bend flexural experiments were performed on parallelepipedic samples according to a standard method,  $E$  is given by :

$$E = \frac{d^3 F}{4 e^3 l \delta} \quad (1)$$

$F$  is the applied load,  $e$  and  $l$  are the thickness and the width of the bar,  $d$  is span and  $\delta$  is the deformation produced by  $F$ .

Loading and unloading gave similar values for  $E$ . The given experimental values represent the average of at least three determinations. The Young modulus

of very light aerogels  $< 100 \text{ kg/m}^3$  could not be measured.

## 3. Results.

The evolution of the Young modulus as a function of the apparent density is plotted on log-log scales (Fig. 2). The values of  $E$  decrease by a factor  $10^5$  between the densified aerogels, whose densities are close to that of silica, and the most light weight ones ( $100 \text{ kg/m}^3$ ). Even for the lightest measured sample for which  $E$  is equal to 1 MPa, the stress-strain curve shows a perfect elastic behaviour and the « conchoidal » fracture morphology indicates that the material is as brittle as a conventional glass.

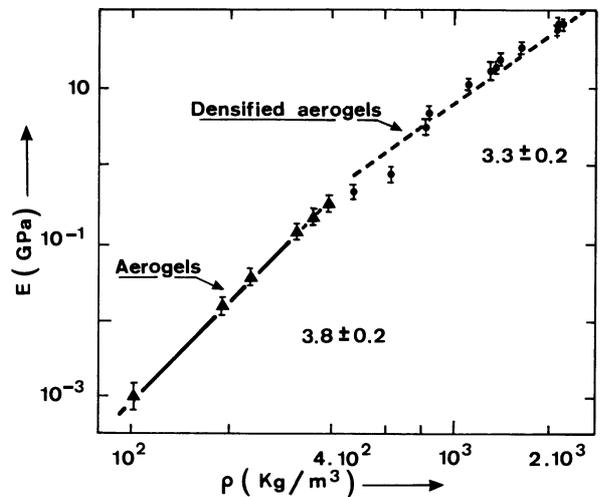


Fig. 2. — Evolution of the Young modulus as a function of the apparent density.

The sound velocity, ( $V = [E/\rho]^{1/2}$ ) may reach a value lower than the sound velocity in air. A similar behaviour was observed in the range of ultrasonic frequencies [15-16].

The variation of elastic modulus *versus* the density is quite similar to that obtained using ultrasonic technique [15-16]. However the ultrasound measurements show an important dispersion which must be attributed to the fact that the samples are coming from various origins [15]. In our case the sample preparation is well controlled and the elastic properties show a good reproducibility. (Furthermore, measurements carried out in the hypersound frequency range, on the same series of aerogels agree well with reported values [14].)

Aerogels and densified aerogels look to have different elastic behaviour, the slope corresponding to the densified aerogel is slightly lower than that for non treated aerogels. This result could not be pointed out in the previous measurements [15-16] due to the low number of studied samples. In fact, aerogel and densified aerogel are different materials

because the later has undergone an other heat-treatment to densify it. For these reasons, the analysis in terms of the percolation theory has been discussed for the set of aerogels only.

#### 4. Discussion.

In the following discussion, 3 types of analyses reported in the literature are proposed.

In the first analysis, the gelation process is compared to a site-bond percolation model with 2 probabilities [20]. In the case of the T.M.O.S. gelation, the probability of bond formation  $P_b$  is a function of several parameters such as :

- $H_2O$  concentration
- temperature of reaction
- duration of the polymerization reactions.

The probability of occupied sites  $P_s$  is proportional to the concentration of monomers in the solution. The completion of the gelation reaction (hydrolysis and polycondensation) transforms the site-bond percolation model in a simpler site percolation model where the  $P_s$  scale is replaced by the monomer concentration  $\phi$ . Then, the reaction was performed at high temperature ( $55^\circ C$ ), with 4 moles of  $H_2O$  per mole of T.M.O.S. and let to stand for a duration as long as 500 h to achieve the hydrolysis and polycondensation reactions.

For the solutions with a monomer concentration lower than 3 % the gel cannot be obtained. The gel does not occupy the whole volume of the container, it looks like isolated regions dispersed in the liquid. The range of concentration around 3 % corresponds to the critical concentration  $\phi_c$  necessary to obtain a gel. In term of percolating model, the isolated regions correspond to the finite clusters and  $\phi_c$  to the percolation threshold. The scaling exponent can be determined by applying the least-square method for the following relation :

$$E \propto (\phi - \phi_c)^\tau . \quad (2)$$

Taking  $\phi_c = 3 \% \pm 1$ , the scaling exponent  $\tau$  is equal to  $3.9 \pm 0.2$  (Fig. 3). This value is close to the value proposed by the models assuming a tensorial elasticity [4, 5].

The experimental determination of  $\tau$  is linked to a choice of the physical variable which can replace the unknown mathematical variables  $P - P_c$ . Various variables such as concentration in monomers [12, 20] or time [11, 13] were proposed assuming implicitly a proportionality between these variables and the  $P$  scale. This difficulty could be avoided if another scaling property is measured on the system leading to the elimination of the  $P - P_c$  factor.

The gelation-percolation analogy assumes that physical-chemical properties of the gel such as gel fraction, the number of macromolecules, the degree of polymerization scales with the  $P - P_c$  factor and

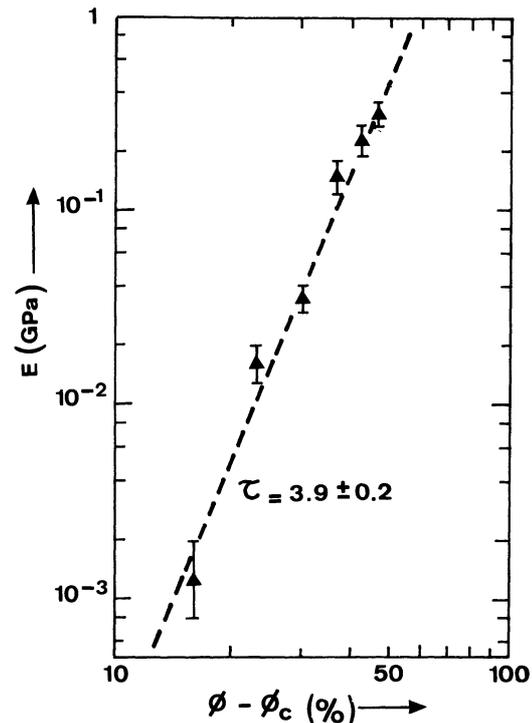


Fig. 3. — Evolution of the Young modulus as a function of the monomer concentration  $\phi - \phi_c$ .

critical exponents of the percolation theory [21]. For example the gel fraction is correlated to the percolation probability  $\mathfrak{F}(P)$ .  $\mathfrak{F}(P)$  is defined as the probability for a site to belong to the infinite cluster. In this gelation-percolation analogy, the gel fraction, and consequently the density of the gel, scales with the  $\beta$  exponent.

$$\rho \propto \mathfrak{F}(P) \propto (P - P_c)^\beta \quad (3)$$

$\rho$  is the density of the infinite cluster (gel network). Below  $P_c$  finite clusters (microgels) are present in the liquid and  $\rho$  is equal to zero. The following scaling relation can be derived.

$$E \propto \rho^{\tau/\beta} . \quad (4)$$

Experimental results give a  $\tau/\beta$  value of about 3.8 for the aerogel (Fig. 2). For a three-dimensional percolative model the  $\beta$  value is in the range 0.39-0.47 [22]. Then  $\tau$  would be in the range 1.5-1.8, and the scalar elasticity would be significant. This result is in a disagreement with the first analysis.

However, the assumption that  $\beta$  is close to 0.4 for the aerogel is not demonstrated. After the gelation of the organometallic solution, several structural modifications occur which increase the density of the material :

- the syneresis phenomenon favors the linkage of the « microgels » to the infinite cluster
- the autoclaving treatment induces a volumic shrinkage (10-15 %).

Consequently, the density of the aerogel is higher than the density of the infinite cluster of the alcogel just after the gelation. This phenomenon would induce a larger value of  $\beta$ .

In the third analysis, we identify the aerogels as a « Swiss cheese » continuum model [6]. In this case  $(P - P_c)$  is assumed to be directly linked to  $(q_c - q)$  where  $q$  is the volume fraction of voids, then :

$$E \propto (q_c - q)^f. \quad (5)$$

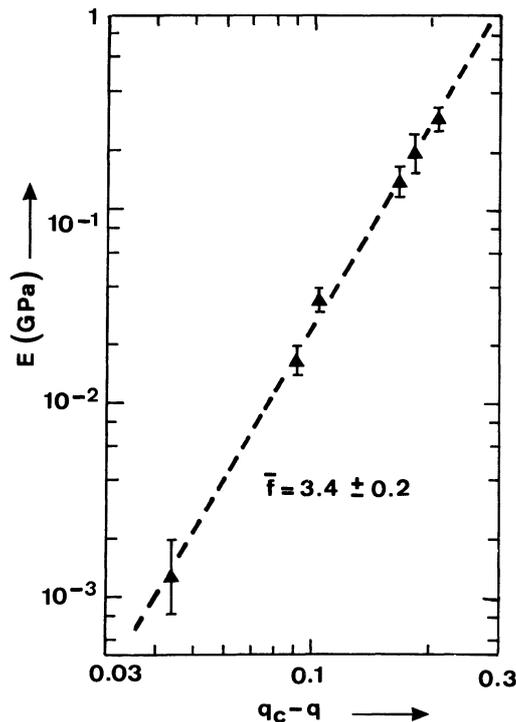


Fig. 4. — Evolution of the Young modulus as a function of the volume fraction of holes ( $q_c - q$ ).

The experimental results (Fig. 4) are analysed by least-squared fits and give  $q_c = 0.99 \pm 0.01$  and  $f = 3.4 \pm 0.2$ .

The predicted value (6) for tensorial elasticity is in the range  $3.6 \pm 0.2 < f \leq 6.2 \pm 0.2$ , which means that our experimental  $f$  value corresponds nearly to the lowest limit of the continuum percolation model.

Independently to the model used, the value of the fracton dimension  $\bar{d}$  calculated from the analysis of the dispersion curve [14] is closer to  $4/3$  [23] than to  $0.9$  [24] which indeed does give some support to scalar elasticity in these systems.

Finally it should be noted that the value of the fractal dimension  $D = 2.4$ , found by neutron scattering [25], is somewhat smaller than the fractal dimension of the infinite percolation cluster  $D = 2.5$  [21]. An identification of the aerogel with the infinite cluster of percolation models can only be an approximation.

### Conclusion.

The initial choice for the physical variable which is thought to correspond to  $P - P_c$  is highly important since different choices issued from the literature lead to contradictory conclusions. This result points out the difficulty to find the « good » physical variable to study a supposed percolating system.

The structure of an aerogel is due to the sequence of different processes : gelation, aging and shrinkage. Straightforward percolation is only an approximation which is certainly useful for a qualitative description but which might be too crude for quantitative results.

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