*EXTENDED ABSTRACTS*

# FRACTAL ASPECTS OF MATERIALS: DISORDERED SYSTEMS

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# SAXS STUDIES OF THE SOL-GEL SILICA GLASS TRANSFORMATION

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## INTRODUCTION

Systematic SAXS studies have been performed at the LURE Synchrotron facilities using a beam of point-like cross-section at $\lambda = 1.55$ Å to obtain detailed informations about the kinetics and the effects of the different steps of the sol → humid gel → dry gel → $SiO_2$ glass transformation. The SAXS intensity at high angles have been analysed in term of power law in log-log plots: $I(Q) \sim AQ^{-\alpha}$ and the mean radius of gyration $R_G$ has been determined from the relation $I(Q) \sim A \exp(-1/3\ R_G^2 Q^2)$ using log I(Q) vs $Q^2$ plots. The kinetics of aggregation was studied in situ in Lindemann capillaries with samples prepared from TMOS - methanol solutions having 50 vol % TMOS; various amounts of bidistilled water, base (pH ≃ 9) or acid (pH ≃ 2) catalysed have been added in the molar ratio $[H_2O]/[TMOS]$ r = 1, 2, 4. Similar sols have been let to gel at 55°C in closed Pyrex tube and extensive measurements have been performed on humid gel (aged or not), aerogels dried by hypercritical solvent evacuation ($p_c \simeq 200$ bar, $T_c \simeq 300$°C) and aerogels sintered at fixed temperature between 530°C and 1080°C.

## RESULTS AND DISCUSSION

*a) Sol-gel kinetics* [1]

Figure 1 shows the sequence observed for acidic-catalysed sol. The curves tend progressively towards a limiting slope corresponding to $\alpha = 2.09$; 2.0 and 2.14 for r = 1, 2 and 4 respectively. For the basic series two linear regions are observed with a cross-over for $Q = 0.066$ Å$^{-1}$ for r = 1; for r = 2 and 4 the plots show a progressive curvature without well-defined linear portions; the average intermediate slope is ~ 2.2 while the limiting slopes at high Q exceed 3. In all cases the corresponding Guinier plots show a marked curvature with increase time.

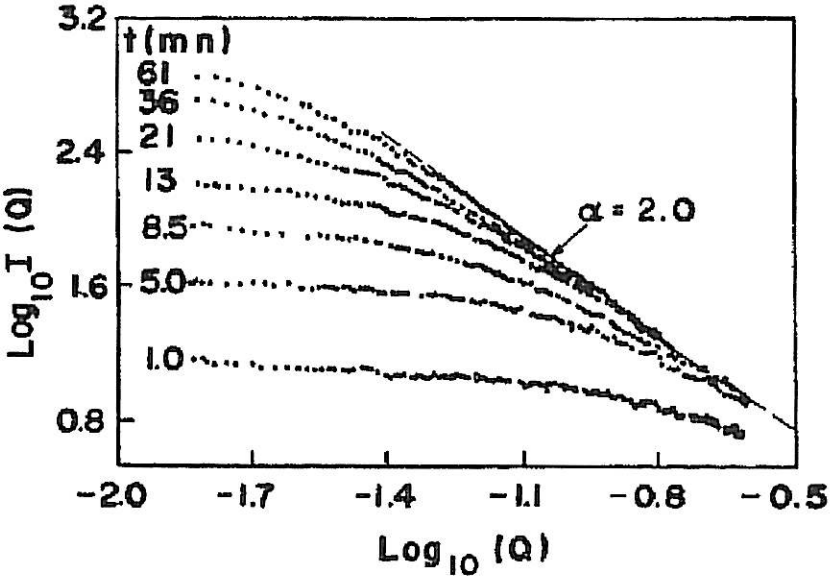


Fig. 1 - Log I(Q) vs log (Q) plot for an acid-catalysed sol with r = 2 and increasing time values t (minutes).

The variation of the average radius of gyration $R_G$ calculated from the limiting slopes indicate that agglomeration seems to be controlled in all cases by a diffusion process. If the fractal interpretation is adopted the results indicate that the particles are mass fractals for the acid series with fractal dimension $D = \alpha$. For the basic series a transition towards surface

fractals would have to be admitted for $\alpha > 3$. On the other hand an interpretation in terms of a polydisperse fractal solution [2] for which the exponent $\alpha = D(3-\tau)$, with $\tau$ being the classic scaling exponent of the mass distribution law $N(M) \sim M^{-\tau}$ is also plausible. Admitting the classic values $D = 2.5$ and $\tau = 2.2$ of the percolation theory we found for acid sols $\alpha = 2$ close to the experimental final slope and $\alpha = 2.2$ for basic sols.

*b) Humid gel* [3]. Acid catalysed gels exhibit a linear behavior over a large Q domain with no cross over, characteristic of mass fractal build up from small structural units (< 4 Å). The average fractal dimension is D = 2.3 and decreases as a function of TMOS concentration in samples with r = 1. For base catalysed gels (figure 2) the observation of two linear region indicates that the structures appear mass fractal at low Q values with $D \simeq 2.4$ almost independent of r and the TMOS concentration c. For high Q values the slopes $\alpha_2 = 2.8$ (r= 1), 3.3 for (r = 2) and 3.5 (r = 4) imply that the structural units are mass fractal at low water content and surface fractal at high water content. This behavior indicates the presence of hierarchical agglomeration of the clusters with an average radius of the structural primary units determined from the cross-over points of ~ 15 Å. Aging of basic gels was found to decrease their dimensionality (smoothing effect) and progressively to supress the fractal nature of the secondary particles structure. The process of gels formation in acidic sols is probably the same but involves much smaller structural units (< 4 Å).

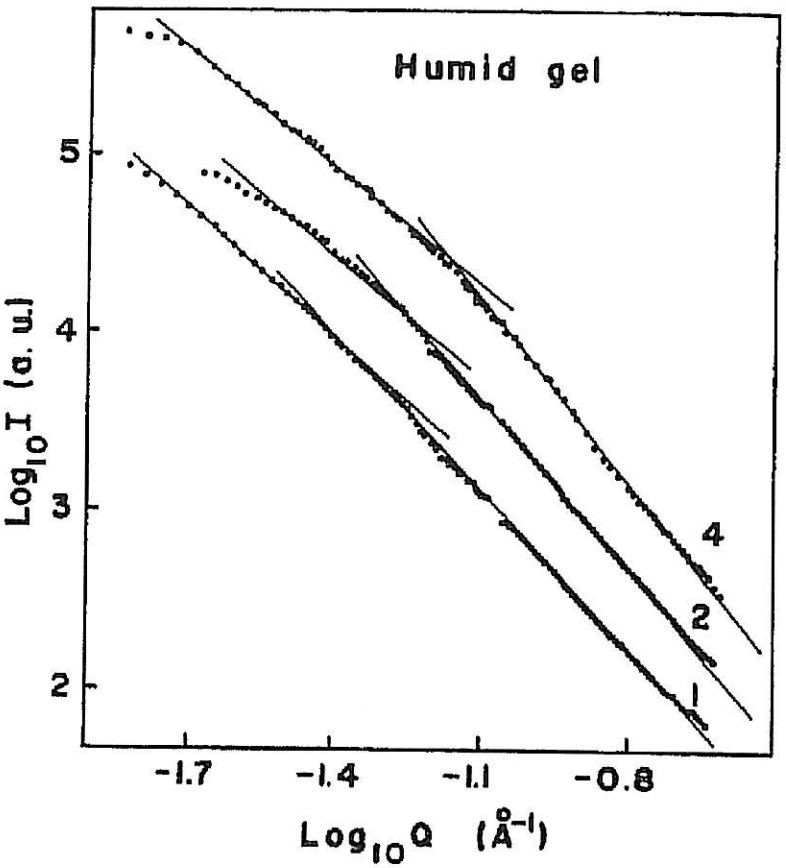


Fig. 2 - Log I vs log Q for basic - catalysed humid gels prepared with C = 50 vol % TMOS and molar ratio $[H_2O]/[TMOS]$ r = 1, 2 and 4.

*c) Aerogels* [4]. For low TMOS concentration (c < 60 vol %) two linear regions are observed with slopes $\alpha < 3$ at low Q and $\alpha = 4$ at high Q (figure 3), indicating that the structures are also build up by a hierarchical agglomeration of clusters consisting of small non fractal structural primary units of average radii (acid) 7Å ~ (neutral) 8Å < (basic) 12 Å and aggregated as a larger secondary mass fractal structure ($R_G$~ 80 - 200 Å) having a dimensionality which decreases as the TMOS concentration increases: $D \simeq 2.28 - 1.9$ (acid), D = 2.7 - 2.2 (neutral), D = 2.7 - 2.4 (basic) (figure 4). TEM pictures confirm this interpretation. Model calculations indicate that the matrix densities at length scale of ~ 20 Å are smaller than fused $SiO_2$ density (2.2 g/cm²) but slightly higher than the apparent aerogels densities. Aerogels prepared with higher TMOS concentration have sharp interfaces and exhibit the classical Porod's behavior ($\alpha = 4$).

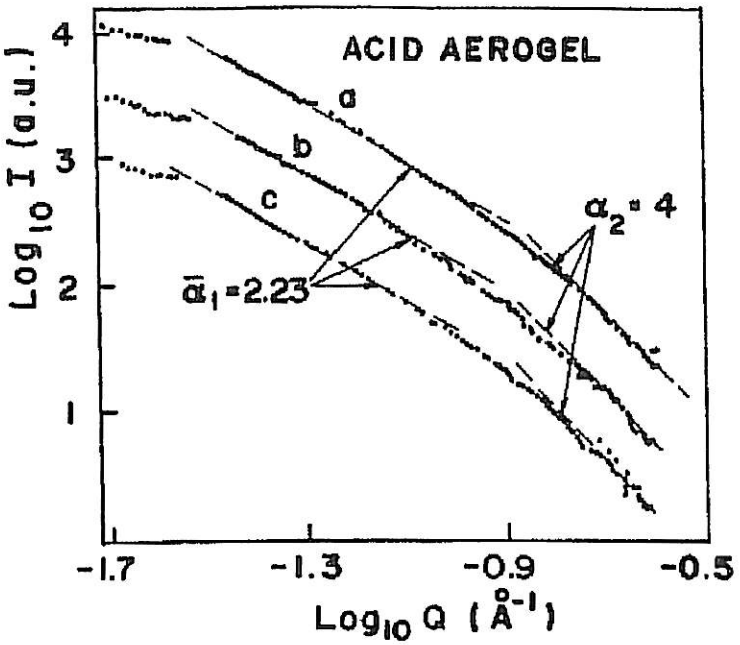


Fig. 3 - Log I vs log Q for aerogels prepared from acidic sols for TMOS concentrations a) 30 vol %, b) 40 vol %, c) 50 vol %; r =4.

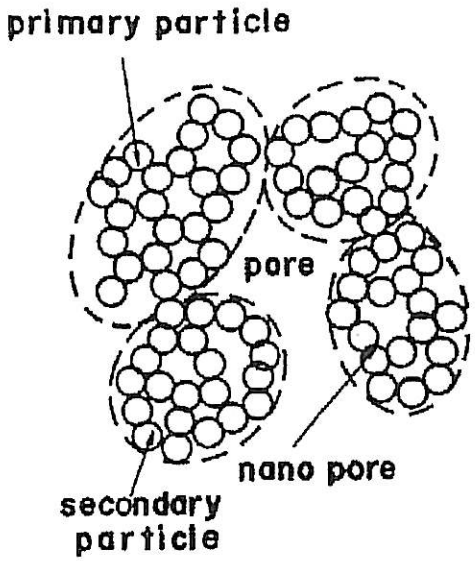


Fig. 4 - Model of aerogel structure showing the primary units and the secondary particles.

*d) Densification of aerogels* [5]. The classical Porod's behavior (well defined interfaces) is obeyed during sintering, and no fractal behavior is observed. This is due to a smoothing effect during the thermal treatment. For T < 810°C the average radius of gyration decreases linearly with time indicative of a diffusion-controlled shrinkage of the pores. Observation of an increase of $R_G$ at T > 912°C is probably due to a bloating process due to expansion of gases in closed pores.

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