

## Tracer Self-Diffusion in Porous Silica. A Dynamical Probe of the Structure.

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**Abstract.** – We have studied the diffusion of a fluorescent molecule in porous silica of various porosities. The measured diffusion coefficient depends on the length scale. At small scales we observe free diffusion; at large scales the diffusion is slowed down because of the obstruction effects created by the porous structure. The crossover region begins at scales comparable to the pore size. This is to our knowledge the first measurement of scale-dependent diffusion where the limits of free diffusion and large-scale diffusion are clearly evidenced. The analysis of the data leads to an original description of the structure of the porous media.

Transport of matter in heterogeneous media is a problem of great technological importance in a variety of different fields: hydrogeology, oil recovery, chromatography and filtration. We will be concerned here with one of the simplest transport processes: diffusion of a tracer particle in solution in a porous medium. Recent studies of the structure of several porous media have shown the relevance of new concepts developed in disordered matter physics: fractal objects, percolation structures... [1]. It must be noted, however, that even if the solid matrix is fractal, the solvent subspace, in which in our case diffusion takes place, is not. Diffusion in the solvent subspace is nevertheless expected to be scale dependent. For scales much smaller than the smallest pore size, the diffusion coefficient will be the same as in the pure solvent  $D_0$ . For scales much larger than the largest pore size, the diffusive motion will be averaged over the different paths, and the effective diffusion coefficient becomes scale independent:

$$D_\infty = D_0/\tau, \quad (1)$$

where  $\tau$  is the tortuosity of the medium [2].

Studies of molecular diffusion in porous media were recently performed [3, 4]. Dozier *et al.* [3] have studied tracer diffusion in porous Vycor glass. But they have measured diffusion over lengths  $L$  much larger than the pore sizes. They have found, as expected, an effective

diffusion coefficient which is independent of  $L$ . Furthermore, they did not perform any systematic investigation of the influence of the porosity.

Bishop *et al.* [4] have studied the diffusion of polystyrene in porous silica. They observed a scale variation of the effective diffusion coefficient, but they were not able to reach the limit of free diffusion. More importantly, the size of the tracer particles was not small compared to the mean pore size and the transition regime was complex because of the hydrodynamic polymer-wall interactions, forbidding direct interpretation in terms of the medium's structure.

*The experiment.* – In order to overcome these difficulties, we have chosen a system with small tracer particles and large pore size (dilute silica gels). We have used a fringe pattern photobleaching technique to measure tracer diffusion: the length scales of the technique ( $5 \div 100$ )  $\mu\text{m}$ , are well suited to cover the whole range of pore sizes. Samples were made of variable amounts of colloidal silica mixed with an index matching solvent, mixture of ethanol and ethanol amine. The solvent contains fluorescein isothiocyanate tracer molecules (FITC, molecular probes, size  $\sim 20$  Å) the concentration of which was 100  $\mu\text{M}$ . The silica (Aerosil R972) was generously provided by Degussa Co., Frankfurt, RFA. It is made of hydrophobic spherical silica particles (18 nm diameter): the OH groups at particle surface have been chemically replaced by  $\text{CH}_3$  groups. During this operation, partial aggregation of the silica particles occurs; the elementary objects of the silica powder are rather large ramified aggregates [5]. The hydrophobicity of the silica is particularly important to prevent adsorption of the tracer particles. As is known that the above surface treatment does not suppress all the OH groups, we have checked that the tracer adsorption was nevertheless negligible: a mixture of silica powder (about 1.5% by volume), solvent and tracer was stirred overnight; the powder and the solvent were then separated by centrifugation and the tracer concentration in the solvent measured with a differential spectrophotometer. The difference between initial and final concentration was only about one per cent.

The porous samples were made as follows, in order to ensure macroscopic homogeneity: a mixture of silica powder and solvent with the fluorescent tracer was first prepared; after a rest of about one hour, the mixture was slowly compressed, the solvent excess being removed via a passage through a filter which retains the silica particles. The sample was then kept overnight under pressure and was finally sealed with optical windows in order to avoid solvent evaporation and shape changes. The final silica volume fraction  $\phi$  in the different samples ranges from 1.4 to 5.5%.

The tracer diffusion coefficient was measured using fluorescence recovery after fringe pattern photobleaching. When strongly illuminated the FITC molecules irreversibly lose their fluorescence property. After the illumination, the fluorescence intensity is measured with a low-intensity light beam: the signal increases as new tracer molecules diffuse into the studied volume. For a normal diffusion process, the fluorescence recovery curves are exponential with a characteristic time  $\tau$ . The method we have used is improved with a modulated fringe pattern. The diffusion coefficient is given by:  $D = L^2/(4\pi^2 \tau)$ , where  $L$  is the fringe spacing. We have performed the experiments for different fringe spacings ranging from 5  $\mu\text{m}$  to 100  $\mu\text{m}$ . The experimental set-up is described in more detail in ref. [6].

The fluorescence recovery curves recorded with the porous samples are pure exponential (fig. 1). The corresponding uncertainty on  $D$  is less than 3%, at small fringe spacing. It increases to about 10% at the largest fringe spacing, due to limited accuracy in the measurements of the largest spacings.

The results of the measurements of  $D$  are shown in fig. 2. We observe clearly two regimes where  $D$  is constant. At small scales  $L$ , the  $D$  value is the same for all the porous samples. It is also identical to the  $D$  value measured for the tracer in the pure solvent  $D = D_0$ . At large

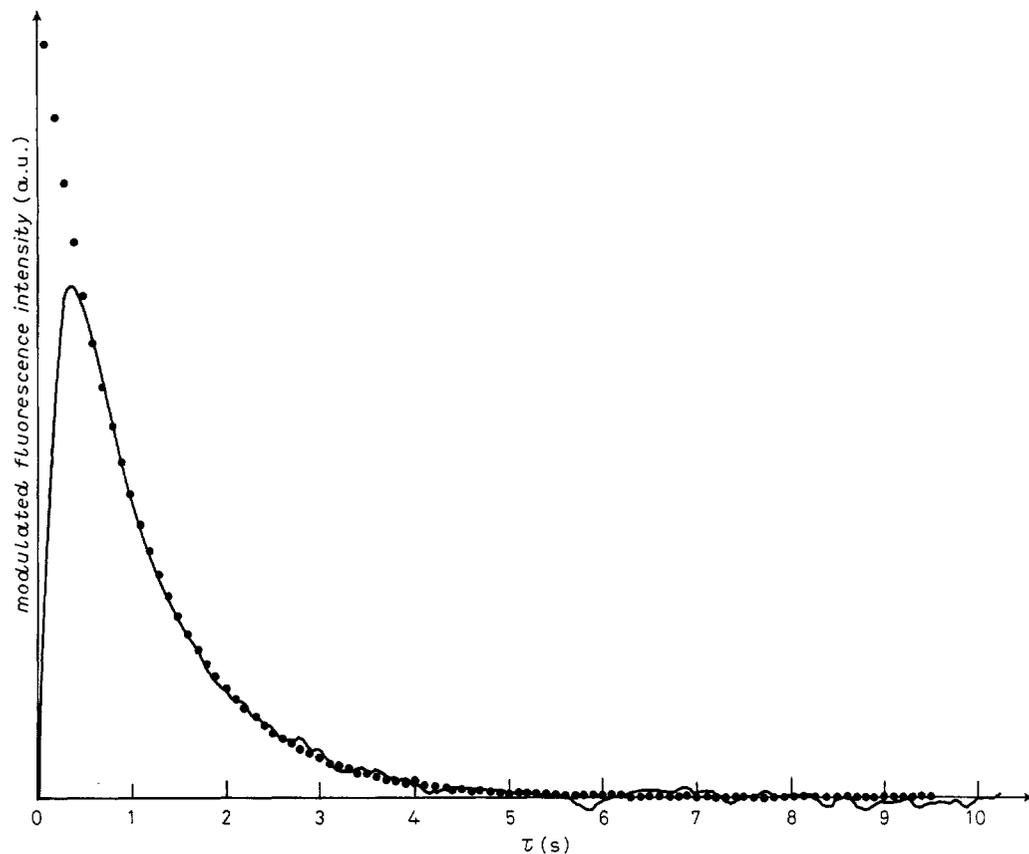


Fig. 1. – Decrease of the modulated fluorescence intensity (in a.u.) vs. time in a typical experiment. The full line is experimental, the dots are the best exponential fit. The deviation to the fit at short times is due to the finite time constant of the lock-in detection.  $\varphi = 3.5\%$ ,  $L = 30 \mu\text{m}$ .

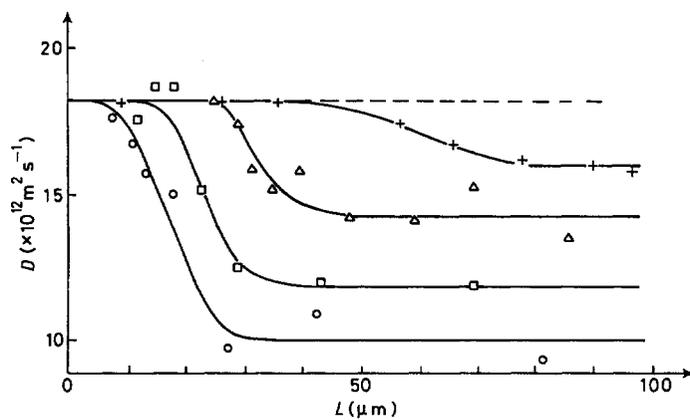


Fig. 2. – Self-diffusion coefficient vs. the fringe spacing  $L$  at different silica concentration; +  $\varphi = 1.4\%$ ;  $\Delta$   $\varphi = 2.8\%$ ;  $\square$   $\varphi = 4.1\%$ ;  $\circ$   $\varphi = 5.5\%$ . The dashed line is the  $D$  value in the pure solvent.

scales  $L$ ,  $D$  is again constant but decreases with the porosity  $\Phi = 1 - \varphi$ ,  $\varphi$  being the silica volume fraction. In an intermediate range of scales, again depending upon  $\varphi$ , we observe a variation of  $D$ , although the recovery curves remain exponential: this means that, in each time region explored, the diffusion is normal  $L^2 \sim D$ , but  $D$  is  $L$ -dependent.

*Interpretation.* – We shall now try to understand the whole of our data within a simple picture of the porous media. We *hypothesize* that this structure is characterized by (at least) three length scales (see fig. 3). The first one is simply the size of the silica spheres:

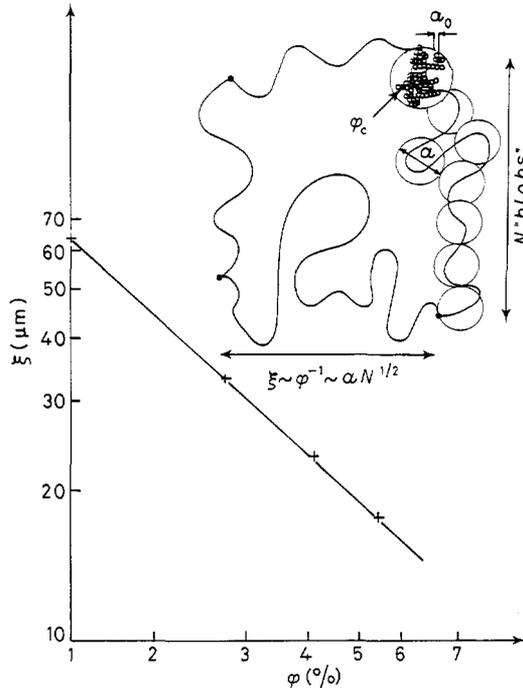


Fig. 3. – Log-log plot of  $\xi$  vs.  $\varphi$ . The line corresponds to  $\xi = 1.2\varphi^{-0.98}$ . Insert: sketch of the proposed structure of these silica gels.

$a_0 = 18$  nm. Those spheres are known to aggregate during the chemical treatment of the silica, forming porous (possibly fractal) clusters of size  $a$  and mean internal volume fraction  $\varphi_c$ . We suppose that  $a$  and  $\varphi_c$  weakly depend on the overall volume fraction  $\varphi$ . Finally, those clusters organize in mostly linear structures, forming the analog of a semi-dilute polymer solution ([7] and see fig. 3) with a mesh size  $\xi$  which plays the role of the *pore size* of the porous medium at the length scale of interest. For lengths larger than  $\xi$  the gel is *homogeneous*. If  $N$  denotes the number of clusters involved in the mesh size, one expects:  $\xi \sim aN^\nu$ . The volume fraction  $\varphi$  is related to  $\xi$  by:  $\varphi = N(a/\xi)^3 \varphi_c$ , which allows to obtain  $\xi$  as

$$\xi \sim a(\varphi/\varphi_c)^{\nu/(1-3\nu)}.$$

Experimentally,  $\xi$  is extracted from the position of, say, the inflexion point of the curves  $D(L)$ . The variation of  $\xi$  with the silica volume fraction is shown in fig. 3. We find

$$\xi = 1.2\varphi^{-0.98 \pm 0.010}, \quad (\xi \text{ in } \mu\text{m}).$$

Comparing with the above expression we get:  $\nu = 0.52 \pm 0.03$ . This exponent is characteristic of an ideal random walk structure, frequently found in colloidal silica aggregates [8]. The structure is thus a fractal of dimension  $d_f \sim 2$  for lengths  $l$  such that  $a \ll l \ll \xi$ . Note that fractal structure of different types silica gels has been observed by other methods but for *much smaller length scales* ( $(10 \div 100) \text{ \AA}$ ) [9]. Assuming  $\nu = 0.5$ , we obtain:  $a\varphi_c \sim 1.2 \mu\text{m}$ .

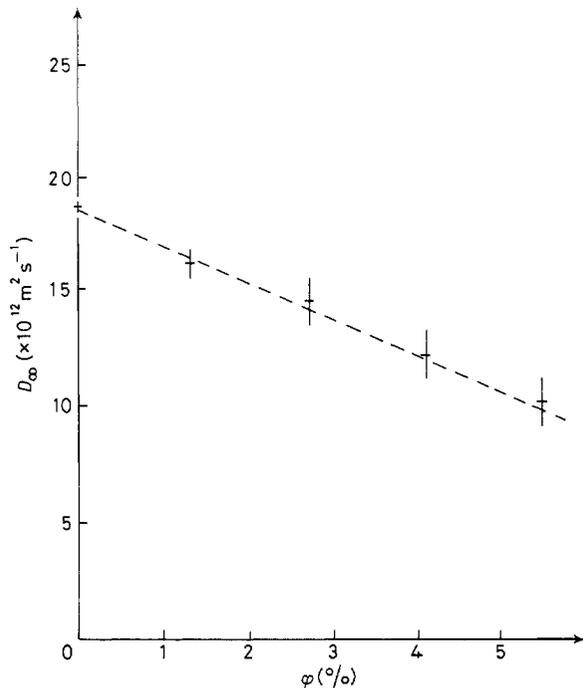


Fig. 4. — Large-scale diffusion coefficient *vs.* silica volume fraction. The dashed line is a fit with  $D_\infty = D_0(1 - 9\varphi)$ .

Figure 4 shows the behaviour of  $D_\infty$  *vs.*  $\varphi$ . The initial behaviour is linear with a very large slope equal to  $-9D_0$ . The slowing down of diffusion due to the silica particles is quite a drastic effect since a nominal volume fraction as low as 6% divides the diffusion constant by a factor 2. This strongly suggests that the structure is indeed tenuous, so that, as is the case for polymers, very little matter occupies a large region of space within which Laplacian fields (here the probability distribution) are strongly screened by the fractal boundary [10]. We thus propose that the local diffusion constant *within* the clusters  $D_c$  is much smaller than  $D_0$ . We model the medium as a cubic lattice of lattice size  $a$  and random local diffusion constant taking the values  $D_0$  with probability  $1 - \varphi/\varphi_c$  and  $D$  with probability  $\varphi/\varphi_c$ . A naive effective medium treatment [11] (neglecting the blob-blob spatial correlations—which in fact are present since they organize as a random walk) leads to

$$D_\infty = D_0 \left( 1 - \frac{3(D_0 - D_c)}{2D_0 + D_c} \varphi/\varphi_c \right).$$

We then have three unknowns ( $a$ ,  $\varphi_c$ ,  $D$ ) and only two experiments to determine them.

We really lack a direct structural information on  $a$  and  $\varphi_c$  which could be reached through, *e.g.*, electron microscopy. Those three parameters cannot, however, take wild values (one must have in particular, for the consistency of the model:  $a < \xi$ ,  $\varphi < \varphi_c$  and  $D_c \ll D_0$ ), and can be sensibly chosen to reproduce the data as:  $a \sim 10 \mu\text{m}$ ;  $\varphi_c \sim 0.1$ ;  $D_0/D_c \sim 4$ ; but these figures are surely only indicative and could be a factor 2 off.

Note that for interfringe separation much less than  $a$ , one should observe recovery curves which are the sum of two exponentials, with characteristic times governed by  $D_0$  and  $D_c$  separately. However, the time scales involved are too small to be observed with our apparatus.

*Conclusion.* – In conclusion, we have observed scale-dependent diffusion of a tracer particle in a porous silica gel with clear evidence of two extreme regimes. At small scales we observe free diffusion, at large scales diffusion slowed by obstruction effects. The crossover behaviour takes place in the region where the scales are comparable to the mesh size of the silica gels. From the data obtained at different porosities, we have been able to describe the medium as a random walk association of tenuous, «opaque» to the tracer, subunits made up themselves of an association of spherical elementary particles. The analysis of the data gives therefore in an original manner a subtle description of the structure of the porous medium: it should be mentioned that a «double scale» structure has also been very recently evidenced in the electron microscope experiments of Bourret [12] on other silica gels, which exhibit a well-defined length scale around  $1 \mu\text{m}$ .

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