

Tracer Diffusion in a Soft Glassy Material

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Abstract. We have carried out Fluorescence Recovery After Photobleaching measurements of the diffusion of tracers of various sizes in a colloidal glass (a Laponite suspension). We have shown that the diffusion is only dependent on the ratio of the tracer size and the distance between Laponite disks. This suggests that the tracer diffusion hindrance in the glass stems from the hydrodynamical interactions between the tracer and the Laponite network, the physico-chemical Laponite-tracer interaction playing a negligible role.

Keywords: soft glass, tracer diffusion, confined diffusion, fluorescence recovery, porous medium

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INTRODUCTION

The diffusion of a brownian particle in a homogeneous medium is well described by Stokes-Einstein law: $D = kT/(6\pi\eta R)$ (with D and R the diffusion coefficient and radius of the particle, k the Boltzmann constant and T the temperature) where the particle is considered as migrating in a continuous medium of viscosity η . In heterogeneous media, steric and hydrodynamic interactions of the particle with the frozen part of the system (matrix in gel, frame in microporous medium, chain in polymers, ...) hinder diffusion, and diffusion of tracer with size similar to these heterogeneities is therefore often used as a tool to probe the dynamics of such complex systems [1, 2, 3].

It is our goal to study the dependance of the diffusion coefficient of a tracer in a heterogeneous medium on the relative size of the tracer and of the medium structure. Small tracers experience free diffusion in a quasi-infinite medium. When the tracer size approaches the characteristic dimension of the heterogeneities, long-range hydrodynamic interactions of the tracer with the medium induce a slowing down of diffusion. Finally large tracers are trapped by the structure. We aim particularly at investigating systematically the transition between the two extreme regimes.

The working system is a colloidal suspension of Laponite, a synthetic clay, in which the colloids are 30 nm-diameter charged disks separated by a roughly 50 nm distance. We used fluorescent spherical probes of sizes 1, 25, 37, 65 and 100 nm. Small ones are expected to diffuse freely in the solvent, large ones to be blocked by the Laponite patelets network, and the other ones to exhibit intermediate diffusion coefficient values. The structural details of the set Laponite suspension remain controversial, arguments existing in support of a gel and of a glass structure [4, 5]. But we want to emphasize that this uncertainty has no incidence on our conclusions, the tracer diffusion hindrance by the Laponite network being purely geometrical.

FLUORESCENCE RECOVERY MEASUREMENT OF THE DIFFUSION COEFFICIENT OF A PROBE IN A COLLOIDAL SUSPENSION

The investigating setup was a modified version of the classical Fluorescence Recovery After Photobleaching technique. In the course of an experiment, a sample of the Laponite suspension containing the fluorescent probes is bleached along a horizontal segment with a blue laser beam. Afterwards the fluorescent light intensity along the vertical axis, taking the form of a gaussian, is recorded as a function of time t . The redistribution of fluorophores by diffusion leads to a spreading of the gaussian, with decreasing height and growing diameter $w(t) = \sqrt{w_0^2 + 8Dt}$ (with w_0 the initial diameter of the gaussian). The best fit of the experimental intensity profile diameter with this law brings

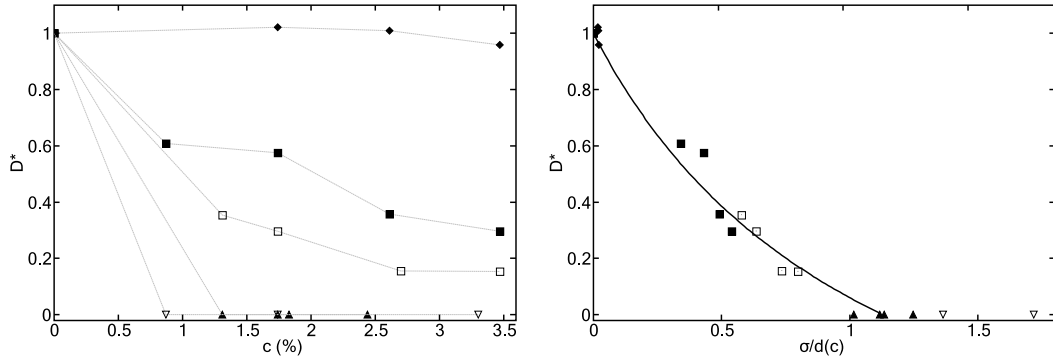


FIGURE 1. Left: Normalized diffusion coefficient $D^* = D(c)/D(c = 0)$ as a function of Laponite concentration c and tracer size σ . Right: Normalized diffusion coefficient $D^* = D(c)/D(c = 0)$ as a function of $\sigma/d(c)$, with σ the tracer size and $d(c)$ the inter-disk distance, and plot of Eq. 1 with $e = d(c)$ and $C = 0.9$. In both panels, plain diamond are for $\sigma = 1$ nm, plain squares for 25 nm, open squares for 37 nm, upward plain triangle for 65 nm and downward open triangle for 100 nm.

the tracer diffusion coefficient D . The Laponite suspension is a very sensitive system and numerous precautions have been taken to guarantee the diffusion measurements reliability:

- we have checked that the initial bleached zone extension corresponds, for a low laser intensity and small suspension volume, to the bleaching laser gaussian diameter.
- the diffusion coefficient can be also deduced from the gaussian height decrease but we have shown that this decrease stems also partially from a slow but significant photobleaching of the sample by the lightning beam, so the gaussian diameter method was preferred.
- the quantum yield of the fluorescent probes is roughly 1/2 so the photobleaching power may contribute to a temperature increase of the suspension inducing natural convection hiding the diffusing behaviour. This hydrodynamic disturbance is avoided by using narrow optical cells, delaying the instability threshold, and the lowest possible photobleaching intensity. If any convection arises, it is easily noticed, the bleached layer showing visible distortions and the $w(t)$ curve departing from linearity.
- histograms of 10 to 100 diffusion coefficients values are carried out for each system.
- Laponite suspensions are elaborated in dissolving 1 to 4% of pure clay, in the form of powder, in water. The setting time ranges from a few hours to a few days and care has always been taken to carry out the diffusion measurement once the suspension was in the gel state.
- the Laponite powder absorbs water so the Laponite concentration of the suspensions was measured by titrimetry, independantly of the elaborating protocole.
- we have checked that the filtering of the suspension just after elaboration has no influence on the diffusion measurements.

INFLUENCE OF PROBE AND PORE SIZE ON THE DIFFUSION COEFFICIENT

The evolution with concentration of the normalized diffusion coefficient D^* of the tracer, i.e., the ratio of its diffusion coefficient in the suspension to its diffusion coefficient in water, for the various tracer sizes, is shown in Fig. 1 (left panel). Overall D^* decrease when the Laponite concentration or tracer size increases. Small colloids (1 nm) have the same diffusion coefficient as in water ($D^* = 1$), showing no sensitivity to the existence of the Laponite network when diffusing in the inter-patelet space. Large colloids (65 and 100 nm) are trapped in the gel and exhibit no measurable diffusion ($D^* = 0$). Medium size colloids (25 and 37 nm) show values of D^* between 0 and 1, their motion being more and more hindered by the disk skeleton. This size range points the existence of a characteristic laponite structure dimension of a few tens of nanometers, which is likely to be the inter-disk distance. Concentration increase leads to a progressive reduction of this inter-disk distance, thereby enhancing the steric hindrance of the probes diffusive motion.

More quantitatively, if diffusion hindrance has a geometrical origin, the probe migration should compare to the diffusion of a tracer in an open porous medium. Hydrodynamic interactions with the colloidal platelets strongly hinder the diffusion of the probe when the probe size is of the order of magnitude of the inter-platelets distance. For a spherical tracer confined between two parallel plates, the diffusion coefficient varies with the interplate distance e like [6]:

$$\frac{D_{\parallel}}{D_0} = \frac{1}{\frac{2}{1-C\frac{\sigma}{e}} - 1} \quad (1)$$

where C is a numerical constant, σ the diameter of the sphere and e the inter-plate distance. Following this, we have plotted D^* as a function of $\sigma/d(c)$, with $d(c)$ the inter-platelet distance. σ has been taken as the probe diameter measured with our FRAP apparatus. To evaluate $d(c)$, which evolves with the Laponite concentration c , recalling that the Laponite structure is still controversial, we have assumed a homogeneous spatial repartition of Laponite disks, leading to $d(c) = (\rho_{\text{lap}}v/\rho_{\text{gel}})^{1/3}c^{-1/3}$ (with v the disk volume, ρ_{lap} and ρ_{gel} the laponite disk and gel density). Then the curve was fitted with Eq. 1 taking $e = d(c)$.

Fig. 1 (right panel) shows the experimental results and resulting fitted curve. Two major features arise. First, whatever the Laponite concentration and tracer size, all diffusion values collapse on a master curve, validating our assumption of the geometrical nature of diffusion hindrance, physicochemical interactions playing a negligible role. Secondly, D^* vanishes for $\sigma \sim d(c)$ as expected and it increases towards its bulk value like $\sigma/d(c)$ for small confinements ($\sigma/d(c) \rightarrow 0$), the scaling of which is characteristic of hydrodynamic interactions. While the picture leading to Eq. 1 is expected to provide only a qualitative sketch for the tracer dynamics in the platelets network, this expression proves to fit very well the experimental data for the diffusion coefficient, as shown in Fig. 1. Besides, the role of the well defined inter-disk distance $d(c)$ promotes the picture of a homogeneous glass for the Laponite suspension, rather than a gel.

CONCLUSION

We have performed Fluorescence Recovery After Photobleaching measurements of the diffusion coefficient of tracers of size 1 to 100 nm in a set Laponite suspension. The diffusion coefficient is shown to decrease with increasing Laponite concentration. Small tracers behave in the suspension as if in pure water. Large ones show no measurable diffusion. Tracers of intermediate sizes show average diffusion coefficient, with values between 0 and the value of their diffusion coefficient in water. The transition size is roughly 30 nm, revealing a characteristic structural length of the Laponite suspension. This result suggests that diffusion is hindered mainly by hydrodynamical interaction between the network and the tracers. The use of a model of diffusion in a slit pore enables to gather all the experimental points on a master curve and permits to identify this characteristic length with the distance between the disks of Laponite.

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