STRUCTURE OF GLASSFORMING LIQUIDS CONFINED IN MESOPOROUS MATERIALS

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Viscosity and structural (α)-relaxation times in supercooled liquids can vary over 14 orders of magnitude when changing temperature by a mere factor of 2 at atmospheric pressure leading to the glass formation. The dramatic increase of relaxation times and the manifestation of heterogeneous dynamics close to the calorimetric glass transition temperature T_g are most naturally interpreted as resulting from collective and cooperative behavior. Several experiments showing dynamical heterogeneity have been developed during the last decade (multidimensional NMR, dielectric hole burning, light scattering). They provide a new supermolecular length scale of few molecular diameters whose lifetime is somewhat larger than the α-relaxation time just above T_g. The possible existence of this mesoscopic characteristic length in deeply supercooled liquids has constantly won attention and the notions of cooperativity, correlation length, heterogeneities or domains have been introduced in many theoretical models[1]. However no structural indication of these clusters has been found so far[2].

When confined within a pore of a few molecular diameters the properties of a liquid are strongly modified. The cooperative length postulated above will not be able to extend to distances greater than the pore diameter thus leading to a different dynamical regime and then to indirect information on this length scale. Moreover changing the system size from a few molecular diameters to the macroscopic limit largely affects the phase diagram and the occurrence of long range ordered phases; as a consequence freezing can be avoided which may give rise to a glass transition at lower temperature for very simple model liquids that always crystallize in bulk conditions.

Most experiments have been performed with Controlled Porous Glasses (CPGs) or Vycor[3] as a confinement matrix. These mesoporous materials present a rather irregular porous geometry due to a broad distribution of size and shape of the interconnected cavities leading to a complex interplay of various effects. However recent advances in the synthesis of mesostructured porous silicates[4] of the MCM-41 series and SBA-15 offer a unique possibility to study confined phases in highly regular structure made of a hcp array of non-connected cylindrical pores (with 1.8 to 14 nm pores). Their structural parameters are obtained from nitrogen adsorption and neutron scattering. The structure factor of MCM-41 exhibit Bragg peaks at low Q due to the hcp structure. At higher Q, the structure factor of amorphous silica that formed the walls is restored as presented in Fig.1.

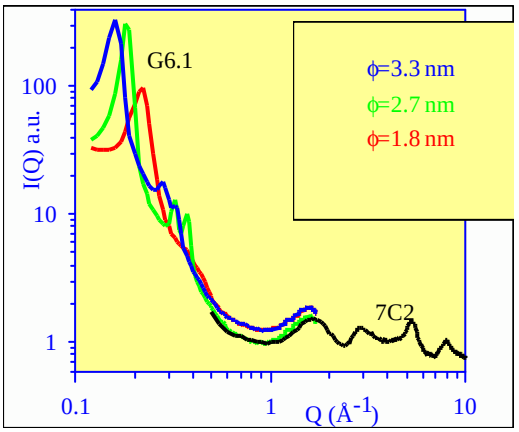

Figure 1 : Structure factor of empty MCM-41, over a wide Q-range, taking advantage of the two spectrometers G6.1 and 7C2 at the L.L.B

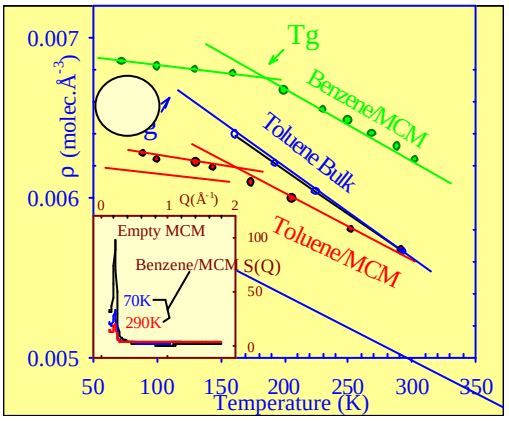

Figure 2 : Density of confined liquids estimated from contrast effects at the MCM-41 (100) Bragg peak (see insert)

Surprisingly the dynamical experiments of confined liquids performed so far do not give a clear answer as to the cooperative dynamics of supercooled liquids. It was not yet possible to distinguish between the influence of the fluid wall interaction and pure confinement effects on one hand, and, on the other hand, no thermodynamic and structural properties were available to describe properly the conditions (isochoric, isobaric,..) under which the glass is obtained and compared to the bulk system. In order to elucidate these points, we focus on weakly interacting model molecules (benzene and toluene) confined in monodisperse cylindrical pores.

The static structure factors of bulk and confined toluene and benzene in MCM-41 have been measured at the L.L.B. on the two double-axis spectrometers G6.1 and 7C2 encompassing an extended Q-range from 0.13 $Å^{-1}$ to 10 $Å^{-1}$ over a wide temperature range from the liquid at 290K down to the glass at 70K. The samples are prepared from a mixture of empty outgased MCM-41 with a proper amount of liquid in order to completely fill the pores. The density changes of the confined liquid can be controlled in an unique and consistent way by taking advantage of the regular hcp structure and from contrast effects considerations at the (100) Bragg peak of the matrix (Fig. 2). For the first time, we observe that the macroscopic density of a liquid in a small pore does not follow the density of the bulk, with a thermal expansivity of the half. This leads to much smaller value of the density of the glass obtained at a higher Tg than the bulk.

A complete discussion on the shape of the structure factor of bulk toluene is provided in [2]. Most of the possible changes of the intermolecular short range order may be illustrated by changes of the shape of the main diffraction peak in the Q range from 1 to 2 $Å^{-1}$. For the small pore size presented on Fig.3, confinement (and surface presumably) induces noticeable changes of the local order in the fluid, which is consistent with the density measurements. This affects the overall properties of the liquid such as dynamics giving rise to a toluene glassy state at lower density and higher temperature than the bulk. Its also affects possible crystallization of benzene. For the first time, it gives access to a description of the structure of benzene in the vitreous state.

The investigation of the heterogeneities of supercooled bulk liquid through confinement would hopefully benefit from the combination of highly regular novel mesopores and microscopic description of confinement effects.

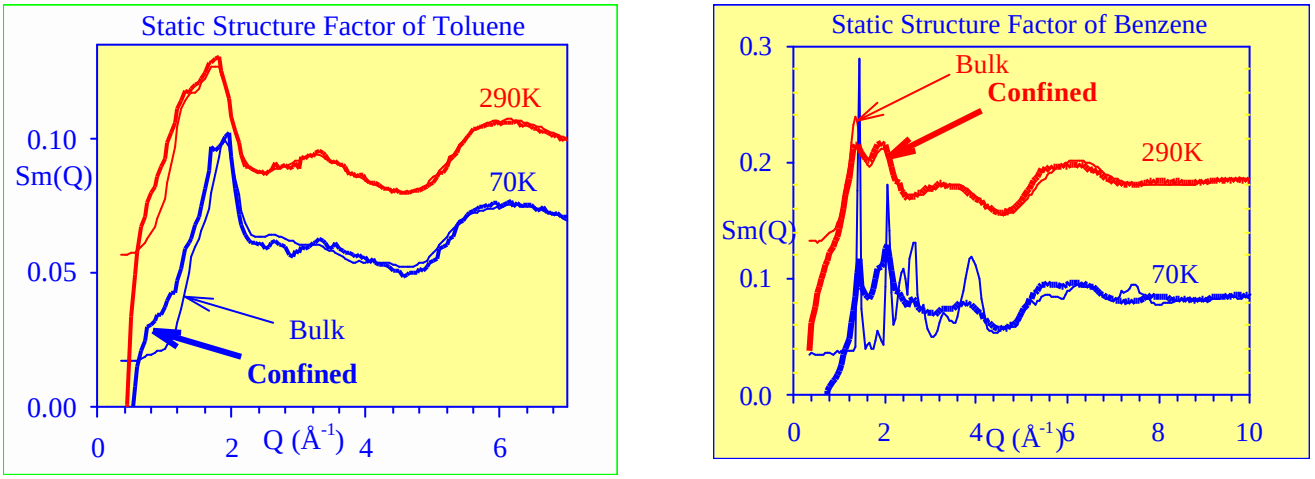

Figure 3 : Static Structure Factor of bulk liquid and confined liquid in MCM-41 with pore diameter ϕ=1.8nm, above their melting point (290K), and below their glass transition (70K) : (a) toluene, (b) benzene.

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