

4 - LIQUIDS AND DISORDERED SYSTEMS

Neutron scattering is an essential technique for the study of disordered systems in general and, more specifically for the investigation of structural and dynamic properties of molecular liquids and glasses. This is essentially due to the possibilities of isotopic substitution and of incoherent scattering.

One can realise that there is a very rich variety of experiments in the domain of liquids, glasses and critical mixtures either in bulk form or in confined volumes. They use regularly many of the neutron scattering instruments of LLB: the diffuse scattering diffractometer 7C2, the powder diffractometer G6.1, the small angle scattering instruments, the time-of-flight and spin echo spectrometers.

LIQUIDS: QUANTUM MODES, SUPERCOOLED STATE AND BINARY MIXTURES

Recent studies at LLB focus mostly on properties of liquids under extreme conditions (superfluid or supercooled state, pressure, temperature, critical conditions) or in confined volumes. Because of chemical affinities, in particular the formation of hydrogen bonds between liquids and solid substrates, the local structure of a liquid may be disturbed over distances of two or three molecular layers, inducing specific properties and important consequences in chemical processes. Most of the studies of confined liquids are achieved within a porous matrix and some ambiguity may occur from the superposition of effects due to the interface and due to the size of the pores. Some modern substrates such as carbon and metal nanotubes provide small volumes of diverse shapes where liquids can be confined under well-defined conditions.

Quantum liquid in confinement (“Highlight”)

Helium is the prototype of quantum fluid as it is the unique element that stays liquid in normal pressure conditions even at the lowest achievable temperatures. Below the Lambda transition temperature, $T_\lambda = 2.17$ K in bulk, Liquid Helium becomes superfluid with peculiar viscous and thermodynamic properties that have been related to Bose-Einstein Condensation (BEC) but the complex relation between superfluidity and BEC is far from being elucidated.

The confinement of Helium in porous media is expected to decouple the two transitions and may even lead to the inhibition of the Bose-Einstein Condensation due to the reduced dimensionality and disorder. Major efforts were devoted at the LLB to control the thermodynamic state of Helium ^4He confined in porous matrices to maximize the confined liquid volume and perform neutron scattering experiments without bulk liquid (Thesis F. Albergamo). Adsorption of Helium in several standard porous systems (carbon nanotubes, Vycor glass and MCM-41) was characterized by thorough isotherm experiments to compare the available porous media, study the capillary condensation and avoid bulk liquid.

Inelastic neutron scattering was performed on time-of flight machines to study the influence of confinement on the elementary excitations and their dispersion curve in the ‘Maxon’ and ‘Roton’ regime. The precise control of the adsorption process has even allowed to evidence the peculiar capillary waves, also called ‘Ripplons’, of the precursor wetting films (see the detailed “**Highlight**” thereafter). Modifications in the phonon and roton regime were evidenced and will help to understand the complex relation between the superfluid transition and the Bose-Einstein Condensation.

Supercooled liquid Selenium (“Highlight”)

Mode coupling theory (MCT), very successful in the interpretation of the dynamics of viscous liquids, is widely used, even out of its primary domain, probably because of its precise numerical aspects particularly adapted to neutron scattering. Sometimes, it represents simply a good mathematical model of complex systems with a broad relaxation spectrum. In such cases, MCT is used in a phenomenological way and important physical aspects may be bypassed. In some cases, the use of MCT is well adapted and then the information extracted from extensive experiments is very rich.

One of the following highlights details a remarkable study of the dynamics of liquid selenium at temperatures slightly above the glass transition (B. Rufflé and S. Longeville). The quantitative test of MCT



implies normally the analysis of a large time domain covering several orders of magnitude, which implies the use of different spectrometers, as well as a precise evaluation of the structure factor with a high-resolution powder diffractometer.

Binary liquid mixtures

A very innovative experiment concerns the local order in mixtures arsenic-sulphur (M.V. Coulet). The phase diagram of this mixture is particularly interesting and complex. Below a concentration in sulphur of the order of 25% and at high temperature (600°C) there is a miscibility gap.

The study of the structure of the mixture and of the two phases after separation has been done with an automatically driven diaphragm that allows independent measurements in situ from each side of the meniscus. One observes pair correlation functions similar to those of the mixture at 5% or 25% sulphur concentration. At a concentration of 5%, the pair correlation extend to the third neighbours as in As; at a concentration of 25%, it extend to the second neighbours as in Sulphur (Fig. 1).

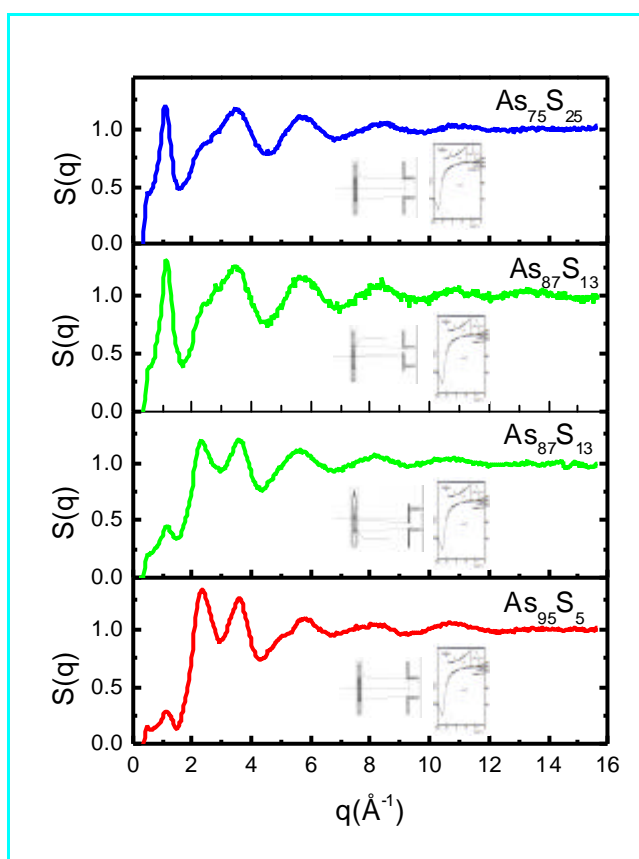


Figure 1. Structure factor of the $As_{1-x}S_x$ liquid on the borderline of the miscibility gap (bottom red curve $x=5$ and top blue curve $x=25$) and in the miscibility gap ($x=13$ bottom green curve in the dense phase and top green curve in the light phase). Note the similarities between the two top curves as well as between the two bottom curves.

Binary liquid mixtures in confinement (see also the related “Highlight”)

In porous media, most of the time, effects due to interfaces dominate those due to pore sizes, what is easily understood if one reminds that the oscillations of the pair correlation function of a molecular liquid extends over distances substantially smaller than the typical size of pores. However, one important exception is the case of mixtures of liquids that phase separate at given conditions of pressure and temperature. At such critical points, the correlation length of concentration fluctuations diverges, even if the extension of local order is not modified. One experiment of neutron scattered at small angles (F. Formisano and J. Teixeira) allowed the characterisation of the structure of two liquids confined in porous silica, at the critical point. The experiment allowed the discrimination between two proposed theoretical models and has interesting applications namely for the industry of oil extraction.



A more recent experiment on the same subject has been performed by S. Schemmel et al (see the detailed “**Highlight**” thereafter). The measurement of the diffusion coefficient by neutron spin echo shows that the microphase separation of the liquid mixture in the porous matrix extends over a large temperature range below the temperature of the phase separation in the bulk mixture.

Solid-liquid interfaces and hydrogen bond lifetime

In other cases, the main purpose is the study of the interactions liquid-solid substrate. In this context, water is by far the more studied liquid, because the interaction can be very different and yield major consequences in many different domains (see for example the Chapter on Life Science).

For example, in the case of silica, hydrogen bonds are formed with silanol groups; their lifetime is much longer than that of intermolecular bonds creating a relatively ordered and stable layer of water molecules at the surface of silica. In contrast, when the solid substrate is hydrophobic, the situation remains not well understood, despite many theoretical studies and computer simulations. The comparison of different hydrogenated liquids allows also the study of the effects due to hydrogen bonds (H. Farman, J.C. Dore and M.-C. Bellissent-Funel).

Always in the domain of structure, several experiments allow the precise evaluation of the molecular arrangement of a solvent around a macromolecule or an ion, as for example, the case of neodymium in diverse solvents (postdoctoral work of B. Belhorma).

Concerning dynamics, most of the experiments make use of the large incoherent cross section of hydrogen atoms to study different molecular motions (self-diffusion, rotations, vibrations). At LLB, the time-of-flight spectrometer Mibémol allows the study of relatively fast dynamics and has been extensively used for the study of the self-diffusion of liquids in confined volumes, already mentioned above.

A problem that remains open and controversial is that of the dynamics of hydrogen bonds. A priori, incoherent neutron scattering, together with NMR, are the best probes to enlighten this problem and establish comparisons with diverse, sometimes contradictory, numerical simulations. A study of the dynamics of the eutectic mixture water - dimethyl sulfoxide (DMSO) allows the separation of the bonds at the vicinity of the acceptor group from that near the hydrophobic methyl groups (J.T. Cabral, A. Luzar, J. Teixeira et M.-C. Bellissent-Funel).

With samples of fully deuterated DMSO, one avoids the large contribution due to the rotation of the two methyl groups and it is then possible to evaluate the diffusion of water molecules and the characteristic lifetime of the hydrogen bonds between water and the oxygen atom of DMSO. It is worth noting that, despite the large mass of the DMSO molecule, this last time is not much longer than that corresponding to bonds between water molecules. Because the study was performed with a eutectic mixture, measurements at very low temperature were possible and demonstrate that the hydrogen bond lifetime has small temperature dependence. This feature is a good argument against several theories of supercooled water that suppose a critical temperature dependence of the hydrogen bond lifetime.

In the same context, a study of the dynamics of water hydrating several polysaccharides (S. Magazù) showed a very rich variety of behaviours. Indirectly, one may understand why trehalose is the more frequent sugar in living organisms that, submitted to extremely low temperatures, can survive.

GLASSES AND DISORDERED SYSTEMS

Concentration modulation in complex silicate glasses

A case rather interesting, also for applications, is that of glasses of complex chemical composition (silicates containing aluminium, magnesium and nitrogen). A tiny change of the amount of additives has large effects on chemical bonding, then mechanical properties (Thesis of S. Deriano, Rennes). This result is important at least in two aspects (Fig.2). First, at the experimental level, the modulation of concentration plays the role of the isotopic substitutions currently used to evaluate the local environment of the atoms of the additives. Even if the method is not completely rigorous, the approximation is very good because the network of silica is only slightly disturbed by the presence of other compounds. Secondly, the determination of very precise distances through the pair correlation function allows their assignment to stable chemical bonds.

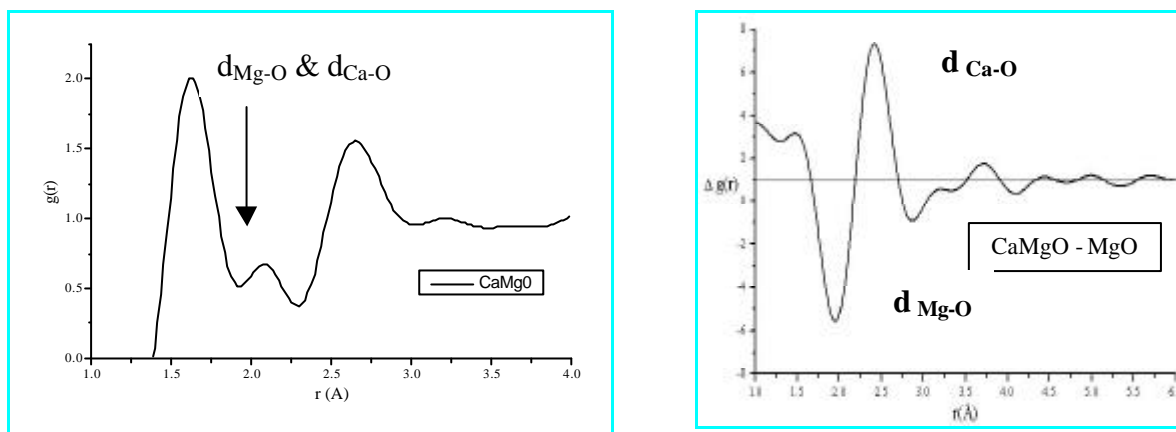


Figure 2. Pair correlation function of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ glass (left) and correlation difference (right) with the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ glass allowing to identify the Mg-O and Ca-O distances ($d_{\text{Mg-O}} \sim 1.99$ Å and $d_{\text{Ca-O}} \sim 2.37$ Å).

Small Angle Neutron Scattering (SANS) and complementary techniques (Raman and DSC) were used to characterize the microphase separation of Sulphur-rich glasses at nanometric scale and identify the role of sulphur chains and rings. The metastability of the chains leads to a complex ageing behaviour and changes in the glass transition (see the detailed “**Highlight**”, E. Bychkov et al, Université du littoral, Dunkerque).

Influence of a high pressure on the Glass transition (“Highlight”)

Finally, the studies of slower motions are achieved in spin echo spectrometers. Some experiments were devoted to the behaviour of viscous liquids, at the vicinity of a glass transition, of biologic macromolecules or at the vicinity of a demixtion point in a confined matrix, as mentioned above.

A particular situation is that of a glass transition of a confined liquid. Confinement changes both the temperature and the width of the transition (see the detailed “**Highlight**”, C. Alba-Simionesco et al, Université ParisXI-Orsay).

Polymeric liquids in confinement: anisotropic dynamics of Polypropylene Glycol

To introduce the next chapter on soft matter, let us mention that certainly, there will be in the near future an increasing number of studies of slow dynamics, namely in complex systems.

For example, an important domain, even for applications, concerns polymeric liquids in confined volumes. Polypropylene glycol with variable mass was included in a 2-dimensions porous medium, vermiculite, a clay that forms flat interfaces (J. Swenson and S. Longeville).

Orienting the clay, it is possible to measure the dynamics of the polymer chains either parallel or perpendicular to the interfaces. In the first case, one observes the classical dynamics of a liquid polymer in bulk form, while in the second situation, the dynamics is dramatically reduced. A complete study implies several experiments with polymer chains of different masses.