| ESRF | Experiment title: Glass dynamics in confined geometries using quasielastic nuclear forward scattering | Experiment number: SC-653 |
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Report:

The existence of a characteristic length scale near the glass transition remains an unsolved question up to date. Mode-coupling theory [1,2] implies no diverging correlation length; various theoretical models [3,4] attempt to incorporate the experimental observation that liquids are dynamically heterogeneous [5,6] into a coherent picture where the existence of cooperativity having a characteristic length scale plays an important rôle. If the interaction between particles is dominated by hard-potential forces (which is fairly well fulfilled by van der Waals liquids), the concept of cooperativity in the sense of [3] is meaningful and can be probed by introducing the glass former into a geometrically confined environment. Quasielastic nuclear forward scattering (QNFS) provides an inherently background-free probe of the slow dynamics (in the ns range) at a fixed scattering vector $q = 7.3\,\text{Å}^{-1}$.

Since the existence of hydrogen-bond networks might complicate the data interpretation, we have carried out quasielastic nuclear forward scattering investigations on dibutylphthalate doped with 5 atomic % of 95.3 % enriched ($^{57}$Fe) ferrocene rather than on the originally proposed substances 1,2-propylene glycol and glycerol, in nanoporous silica matrices (provided by Geltech Inc.) having pore sizes of 25, 75, and 200 Å, respectively. In order also to have mainly van der Waals interactions with the matrix, the pore walls were silylated using hexamethyldisilazane before loading the silica pellets with the glass former using a procedure described elsewhere [7].

The experiment was carried out at the new beamline ID22N at the European Synchrotron Radiation Facility [8], using two undulators, a standard Si(111) high-heat load monochromator with $LN_2$ cooling and a 6 meV four-bounce high-resolution monochromator. Time spectra were recorded in a temperature range between 70 and 200 K, using a closed-cycle Helium cryostat. Delayed quanta were detected simultaneously in forward direction and within $\sim \pi$ solid angle. Forward count rates were in the range of 120 Hz ($T$ =70 K) down to 0.5 Hz ($T$ =200 K).

Assuming a small effective sample thickness, a simple exponential diffusion law and the essential coverage of the inelastic spectrum by the high-resolution monochromator, we were able to separate the contribution of the onset of glassy relaxation (which enhances the decay of the coherent forward delayed signal) from the decrease of multiple scattering (which leads to just the opposite effect). Fig. 1 shows an Arrhenius plot of the relaxation times obtained. Obviously, the dynamics is not influenced considerably in large pores, but dramatical changes occur in 25 Å pores: relaxation sets in at much lower temperatures than in the bulk; assuming Arrhenius behaviour for the diffusion, the activation energy appears to be lower in confinement. Investigations of 50 Å pores could not be carried out due to vacuum problems in the storage ring; this will hopefully be done with the help of compensation shifts allocated in March 2000.
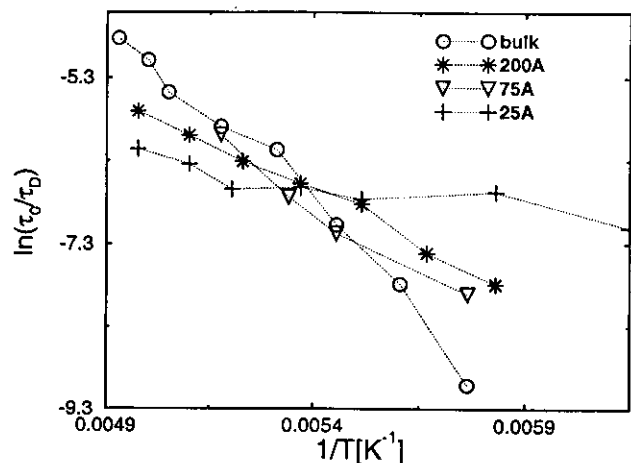


Arrhenius plot of the relaxation times $\tau_D$ in bulk [7] and confined dibutylphthalate/ferrocene as obtained up to date. $\tau_0$ = 141 ns is the natural lifetime of $^{57}$Fe. In order to check the presence of an activated process, obviously a denser temperature grid is essential.

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