



Dynamics of a glass-forming binary liquid confined in mesoporous silicon

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Report:

The dynamics of confined liquids is of interest for two reasons: First, diffusion in porous media is a key issue for the design of matrices for catalysts, and second, studies of confined liquid dynamics could yield valuable insights [1,2] in particular concerning the question of a diverging length scale at the glass-transition.

Much research has been performed implementing controlled pore glasses (CPG) with diameters ranging from 200 down to 25 Angstrom [3,4]. However, one-dimensional, channel like systems present a much better defined system. Scheidler et al [5] investigated the dynamics of a glass-forming liquid in a one-dimensional channel using molecular dynamic (MD) simulations and found a distinct change of the van- Hove self-correlation function and a dramatic change in the relaxation times.

Our experiment was carried out at the Nuclear Resonance Beamline ID18, using a high-resolution-monochromator with 0.5 meV bandwidth. We implemented mesoporous silicon with an estimated pore diameter of 5-8 nm as a confining matrix for the well known glass forming liquid 95% dibutyl-phthalate 5% ferrocene. The mesoporous matrix fixed in a copper sample-holder was mounted in a helium flow-cryostat.

The dynamics of the ferrocene-molecules was observed using quasi-elastic nuclear resonant forward scattering (QNFS). The forward-scattered signal was detected by a semi-transparent avalanche-photo-diode (APD). Behind the APD a ⁵⁷Fe-foil was used to monitor the number of the incident resonant quanta.

Due to the orientation of the pores we were able to observe different diffusional behaviour parallel and perpendicular to the channel axis. We were able to take data at 13 temperatures below and close to the glass transition temperature in both orientations.

For low temperatures the sample shows qualitative identical behaviour in both directions and in bulk [6]. At higher temperatures we observed two features: First, a shift of the glass transition temperature T_c of approximately 15-20 K compared to the bulk T_c , and second, differences in the time spectra depending on the orientation of the channels (illustrated in *Fig. 1*).

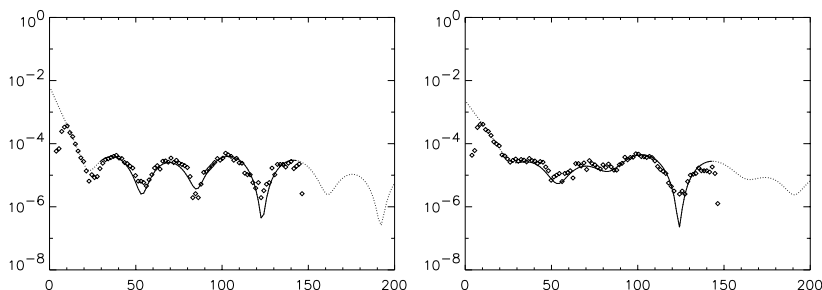


Fig. 1 **Time-spectra** (a.u. over nano-seconds): \diamond - data at 210 K, solid line - fit to the data

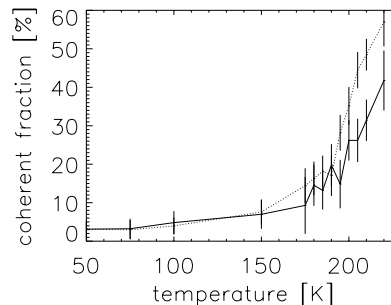


Fig. 2: **Coherent fraction of admixture of reduced QS**: Solid line - channel axis is parallel to the beam, dashed line - perpendicular

At low temperatures the data can be described very well using the quadrupole splitting (QS) of bulk ferrocene/dibutylphthalate ($\hbar\Omega/\Gamma = 24.4 \pm 0.1$). Starting approx. 10-15 K below the bulk T_c an additional QS of about 9 is observed. The fraction of admixture of this QS (see *Fig. 2*) rises steadily from a few percent up to 40% / 55% (parallel / perpendicular case). In principle this can be understood as motional narrowing due to fast rotation of the ferrocene-molecules. Gibb has shown [7] that anisotropic relaxation may lead to a splitting of the QS.

As can be seen in *Fig. 2* the data also differs depending on the orientation of the sample. The existing theory [8] only treats polycrystalline samples, and thus makes no prediction about angular dependencies. It will be necessary to extend the known theories in order to completely understand the present data.

References

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