



Experiment title:
Non-exponentiality of slow glass dynamics in confined geometry investigated by nuclear resonant scattering

Experiment number:
SC-1008

Beamline:
ID18

Date of experiment:
from: 11/04/2002 to: 16/04/2002

Date of report:
28/02/2003

Shifts:
15

Local contact(s):
E. Schreier

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

T. Asthalter*¹, I. Sergueev*^{2,3}, H. Franz*⁴, G. Wellenreuther*⁴

¹ Universität Stuttgart, D-70569 Stuttgart, Germany

² Technische Universität München, D-85747 Garching, Germany

³ ESRF, F-38043 Grenoble, France

⁴ Hasylab, D-22603 Hamburg, Germany

Report:

The aim of this project was to check the influence of confined geometry on the slow dynamics of a glass in confined geometries, using quasielastic nuclear forward scattering (QNFS), over a more extended time window as compared with a previous study [1]. Our aim was both to obtain a higher accuracy of quadrupole splittings, Lamb-Mössbauer factors, and relaxation times and to assess the influence of confinement on the Kohlrausch stretching parameter β , since molecular-dynamics simulations [2] and dielectric spectroscopy on glasses in confinement [3,4] have given evidence for a broadening of the distribution of relaxation times.

The experiment was carried out in single-bunch mode using a three-bounce high-resolution monochromator with 2 meV resolution on two samples of ferrocene/dibutyl phthalate (where the ferrocene was enriched to 95.3 % in ⁵⁷Fe) loaded into nanoporous silica matrices with 50 and 25 Å pore size. The temperature was varied in the range between 15 and 205 K using a closed-cycle cryostat.

The data treatment was carried out in a similar way as described in [1], but instead of the delayed rocking curve, an extrapolation formula for the Lamb-Mössbauer factor (LMF) was used to obtain the relaxation time and the LMF separately from the slope of the time spectra. Comparison was made with data on bulk ferrocene/dibutyl phthalate as described in [5].

Fig. 1 shows the quadrupole splitting of the ferrocene molecule for bulk and nanopores. For low temperatures, the T dependence of the quadrupole splitting clearly differs from the bulk. The reason for this phenomenon is still unclear.

Fig. 2 shows the Lamb-Mössbauer factor for bulk and nanopores. For low temperatures, all samples exhibit roughly the same LMF, whereas above the glass transition temperature for the bulk (180 K), it decreases less strongly for the confined samples (both of them having the same LMF within experimental accuracy) than for the bulk. Hence, it seems that the fast dynamics sets in somewhat later than in the bulk when T increases.

Fig. 3 shows the relaxation rate (in units of the natural lifetime of the ⁵⁷Fe nucleus, $\tau_0 = 141$ ns) of the confined samples in comparison with the total (translational plus rotational) relaxation rate for the bulk, as determined by classical Mössbauer spectroscopy [6], and the pure rotation rate for the bulk as determined by SRPAC [7]. The total relaxation rate in pores seems to approach the purely rotational one of the bulk. This might be a hint that whereas in the confined liquid the ease of molecular rotation

remains largely unchanged, the translational motion is strongly hindered.

Fig. 4 finally shows a master plot of the square of the self-correlation function, together with the shape for a Kohlrausch parameter $\beta = 1$ (dotted curve) and $\beta = 0.5$ (solid curve). The latter value clearly gives a better description of the experimental data. Within the experimental accuracy we can not give a precise value of β , however a comparison of the χ^2 values of the fits for different β enable us to state that β seems to decrease slightly owing to geometrical confinement. This is in accord with the theoretical predictions [2] and experimental observations [3,4], since a smaller value for β corresponds to a broadening of the distribution of relaxation times for an ensemble of Debye relaxators.

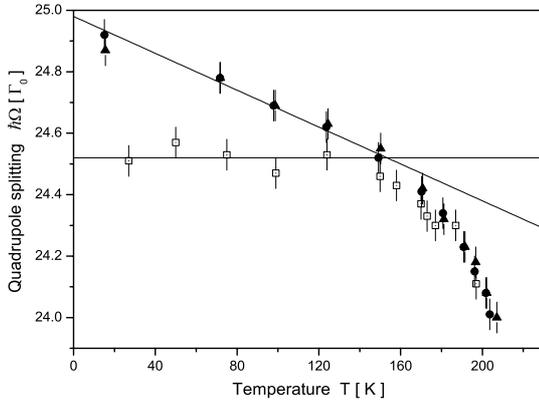


Fig. 1: Quadrupole splitting for bulk (open squares) and confined (50 Å pores: triangles, 25 Å pores: full circles) ferrocene/dibutyl phthalate

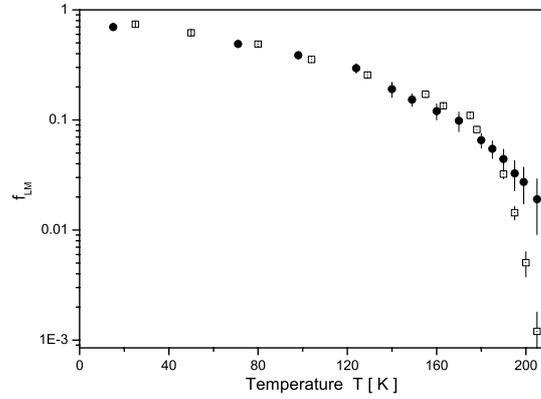


Fig. 2: Lamb-Mössbauer factor for bulk (open squares) and confined (full circles) ferrocene/dibutyl phthalate

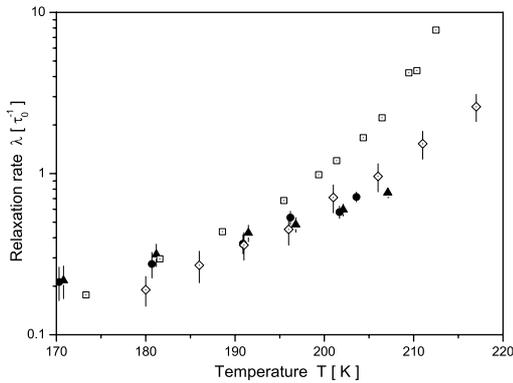


Fig. 3: Total relaxation rate for bulk and confined ferrocene/dibutyl phthalate (symbols as in Fig. 1) and rotational relaxation rate for the bulk (open diamonds)

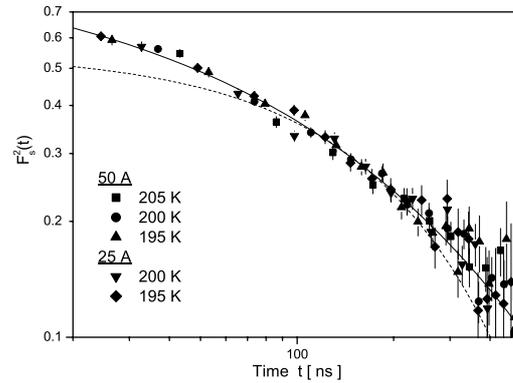


Fig. 4: Master curve for the self-correlation function for confined ferrocene/dibutyl phthalate, scaled to (50 Å, $T = 200$ K); solid curve: $\beta = 0.5$, dotted curve: $\beta = 1$ (Debye relaxation)

- [1] T. Asthalter, I. Sergueev, H. Franz, R. Ruffer, W. Petry, P. Härter, and A. Huwe, *Eur. J. Phys. B* **22**, 301 (2001)
- [2] P. Scheidler, W. Kob, K. Binder, *Europhys. Lett.* **52**, 277 (2000)
- [3] M. Arndt, R. Stannarius, H. Grootjes, E. Hempel, F. Kremer, *Phys. Rev. Lett.* **79**, 2077 (1997)
- [4] J. Schüller, Yu. B. Mel'nichenko, R. Richert, F. W. Fischer, *Phys. Rev. Lett.* **73**, 2224 (1997)
- [5] I. Sergueev, H. Franz, T. Asthalter, W. Petry, U. van Bürck, G. V. Smirnov, *Phys. Rev. B* **66**, 184210 (2002)
- [6] S. L. Ruby, B. J. Zabransky, P. A. Flinn, *J. Phys.* **6**, C6-745 (1976)
- [7] I. Sergueev, U. van Bürck, A. I. Chumakov, T. Asthalter, G. V. Smirnov, H. Franz, R. Ruffer, W. Petry, ESRF Highlights 2002 p.61