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Names and affiliations of applicants (* indicates experimentalists):
T. Asthalter*[1], M. Bauer*[1], U. van Bürck*[2], I. Sergueev*[2,3], H. Franz[4], A.I. Chumakov*[3]
[1] Universität Stuttgart, D-70569 Stuttgart, Germany
[2] Technische Universität München, D-85747 Garching, Germany
[3] ESRF, F-38043 Grenoble, France
[4] Hasylab/DESY, D-22603 Hamburg, Germany

Report:

The low-frequency vibrational properties of glasses and other disordered systems are a topic of long-term interest in condensed matter physics [1]. Especially the microscopic origin of the Boson peak is a recent matter of debate. We have applied nuclear inelastic absorption (NIA) to the molecular glass former dibutylphthalate/ferrocene, both in bulk and in nanoporous matrices having pore sizes of 50 and 25 Å, respectively.

Whereas it seems difficult to prove directly the validity of various theoretical models of the Boson peak, it might be a rewarding task to attempt an experimental study of the influence of geometrical confinement for two reasons. First, one might expect to see a cut-off of the DOS at very low energies / long wavelengths owing to the geometrical confinement. Second, the spectral position of the Boson peak itself may be shifted. Both a hardening originating from the interaction with a matrix having stiff walls and a softening owing to the increase of local free volume around molecules close to the pore wall are possible. Hence, conclusions about the microscopic nature of the softest lattice vibrations in disordered systems may be drawn.

NIA is a powerful tool for element-selective studies of the vibrational dynamics of crystalline solids and glasses [2]. It provides background-free measurements because only the resonant nuclei contribute to the delayed signal. This is especially advantageous in our case, where we introduce the glass former into a matrix whose dynamics are not of immediate interest to us.

The experiment was carried out at the Nuclear Resonance Beamline ID18, using a three-bounce high-resolution monochromator (HRM) with two highly asymmetrically cut Si (9 7 5) reflections and a Ge(3 3 1) symmetrically cut crystal that ensures an approximately horizontally outgoing beam. A new set of crystals providing an energy resolution of about 0.5 meV was used. Within this bandwidth, a high flux of $3{\cdot}10^8\,\mathrm{s}^{-1}$ was achieved by collimating the beam in front of the HRM by a compound refractive lens. The samples (whose preparation is described in [3]) were mounted into a copper holder sealed with Kapton windows in a closed-cycle cryostat. The extraction of the one-phonon contribution and the evaluation of the phonon DOS was carried out using DOS V2.1 [4].

Fig. 1 shows the total DOS of the bulk sample at 85 K, where the prominent features are the lattice modes ($E < 20$ meV) and the (intramolecular) optical modes of ferrocene at 22.0, 60.1 and 62.6 meV,

respectively. The difference between bulk and nanoporous samples becomes only noticeable when inspecting the reduced DOS $g(E)/E^2$, since low energies are emphasized by the $g(E)/E^2$ plot. This quantity is displayed in Fig. 2. For energies below 1.5 meV, the DOS is suppressed in the pores with respect to the bulk, whereas for higher energies the curves are almost identical. A shift of the Boson peak is not observed.

Qualitatively, the suppression at low energies can be explained by a cut-off of long-wavelength acoustic modes owing to the geometrical confinement. Quantitatively, however, we would expect that the cut-off energy is two times lower in 50 Å pores than in 25 Å pores. In contrast to this simplifying assumption, the position of the cut-off seems to be independent of the pore size within the accuracy of our energy resolution of 0.5 meV. Our finding may be compared with neutron time-of-flight results obtained on salol in nanopores, where a cut-off was observed as well [5], but the dependence on pore size was also smaller than expected. A possible explanation should consider the fact that the confinement of the glass former does not occur in three, but in two dimensions and that the channels in the sol-gel glass are interconnected in a highly irregular way.

On the basis of our data, it seems that the confinement does not introduce any discrete surface modes with respect to the bulk.

The interpretation of our results depends strongly on whether we apply the Debye model for the lowest energies or not. If we assume that $g(E)/E^2 = \text{const.}$ for small energies, which means that we treat our whole system as an infinite continuum having an average force constant, sound velocity etc., then the decrease of $g(E)/E^2$ of the Fe atom in confinement points to a hardening of long-range modes, which is consistent with the fact that the Debye temperature of silica (494 K) is much higher than the Debye temperature of dibutylphthalate (from the $g(E)/E^2$ value at 0.5 meV we obtain a value of 107 K). We therefore suggest that vibrational coupling between the glass former and the surrounding matrix is responsible for our observation. This conclusion is supported by first results from quasielastic nuclear forward scattering in confined geometries [6], where an increase of the Debye temperature from 89 K (bulk) to 122 K (50 Å pores) was found.

If, however, we assume that the interaction between glass former and matrix is negligible and only consider the confined glassy system, then the decrease of $g(E)/E^2$ could be attributed to a true cut-off of long-range vibrational modes. Depending on the change of density due to confinement, these modes might disappear or show up e.g. in the quasielastic range not accessible to NIA.

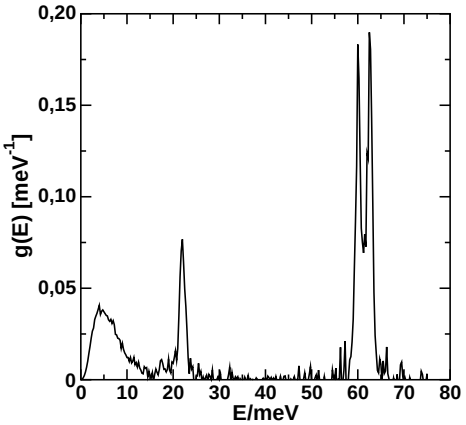

Fig. 1

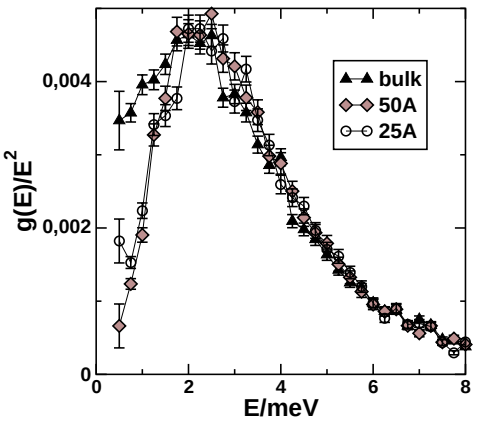

Fig. 2

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