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Quasielastic neutron scattering on glycerol

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We have done a quasielastic incoherent neutron scattering (QENS) study on the glass-forming glycerol system $C_3H_5(OH)_3$ in the equilibrium liguid phase, in order to determine the temperature and wavenumber dependence of the quasielastic line width. QENS spectra are analyzed in terms of the mode-coupling theory, by convoluting the resolution function with three different models, namely one-Lorentzian, non-lorentzian and two-Lorentzians. We have found that both the non – Lorentzian and the two – Lorentzian models deliver good description of the experimental data that can be qualitatively interpreted in terms of mode coupling theories,but the experimental results show no clear distinction between them.

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1. Introduction

Neutron scattering is a powerful experimental tool for studying the structure and dynamics of atoms and molecules in condensed matter systems [1, 2, 3]. This is possible as neutron has a wavelength matching with the inter-atomic spacings in solids and also its energy is comparable to that of the excitations in solids. It is suited for studying the dynamics of protons because of its large scattering cross-section of the latter compared to other elements ($\sigma_H \approx 81$ barns, $\sigma_{other-elements} \approx 4-5$ barns). Inelastic neutron scattering (INS) is a technique dedicated to study of dynamical processes such as the elementary excitations of phonons in solid, and vibrational and rotational motions of molecules in molecular solid and liquid systems. It offers a unique possibility of analysing spatial dimensions of atomic or molecular processes and their development over time. Glasses are uniform amorphous solid materials usually produced when ~~a~~ viscous molten materials are cooled very rapidly, thereby not giving enough time for a regular crystal lattice to form. The dynamic of glass-forming systems is a subject of high interest in connections with the still not understood phenomena relating to the transition to a glassy state. Considerable progress in the understanding of the liquid-glass transition has been made and various aspects have been elucidated using the mode coupling theory (MCT). MCT provides a framework that allows one to calculate the time evolution corelations from nonlinear microscopic equations of motions [4, 5]. MCT, in its simplified form, predicts an ergodic to non ergodic phase transition when the liquid-glass transition occurs. For atomic supercooled simple liquids the theory predicts the existence of a dynamic instability at a temperature T_c above the glass transition temperature T_g. Two dynamical processes are usually taking place: (i) the α relaxation, which can be studied by relaxation techniques, photon correlation spectroscopy and quasielastic neutron scattering on a time scale from 10^{-7} s to 10^{-11} s, and (ii) the β relaxation, a faster dynamical process (time scale ~ 10^{-12} s) that can be observed by time-of-flight neutron scattering in glass forming systems at temperatures around the glass transition temperature T_g. Between T_g and T_c temperatures, only β processes occur. The α relaxation process occurs above T_c and involves the diffusive motion. The α and β process have different scaling frequencies [6].

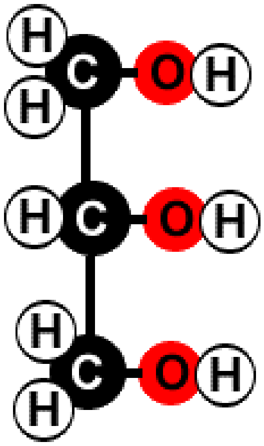

Fig. 1 The glycerol diagram.

The glycerol [$C_3H_5(OH)_3$] is a viscous liquid, a hydrogen-bonded system called an intermediate between fragile and strong glasses [7] with a glass transition temperature T_g = 188 K, a melting temperature T_m = 290 K. The glycerol molecule is schematically shown in Fig. 1. The aim of the present work is to study the dynamic behavior of glycerol by time-of-flight QENS. The experimental results offering information about the α relaxation process in the equilibrium liguid phase of glycerol are discussed in terms of the MCT theory.

2. Experimental method

The experiments have been performed at NEAT time-of-flight spectrometer of the Berlin Neutron Scatering Center, Helmholtz – Zentrum, Germany. The spectrometer has a system of seven choppers that produces a pulsed monochromatic (monoenergetic) neutron beam. The neutrons scattered by the sample change their energy and direction according to scattering laws implying annihilation or production of excitations with characteristic frequencies and wavevectors in the sample compounds. The scattered neutrons are recorded on detectors placed at a certain distance (flying path) over a wide angular range. The time the scattered neutrons need for reaching the detectors (time-of-flight) is proportional with their final energy after the scattering process, while the angle under they are recorded with respect to the incoming beam gives information about the momentum transfer during the scattering process. The measured energy and momentum trasfer of neutrons in the scattering event is proportional with the energy and wavevector of characteristic excitations in the investigated systems.

We have used at NEAT an incoming neutron beam with a 5.1 Å wavelength corresponding to an energy E_0 = 3.145 meV. The energy resolution (FWHM) of about 98 μeV was determined by using a vanadium standard sample. The trasmission of the glycerol sample in a flat aluminium container was about 95%. No special multiple scattering corrections were thus necessary. The data were collected in a large continuous angular range, between 15.41° and 134.5° and grouped and summed up in twenty-seven groups of detectors. This range corresponding to a kinematic space delimited by the elastic wave vector Q_0 = 0.33 Å – 2.31 Å and an energy transfer in the range 0 meV – 21.74 meV. The sample was investigated at eight temperatures 50 K, 100 K, 188 K, 240 K, 290 K, 320 K and 400 K following the transitions from the amorphous to glassy to liquid state. After applying all usual corrections, data were normalized to the elastic scattering of vanadium and transformed into the double differential scattering cross section $d^2\sigma/d\Omega dE$. In this work, we will focus on the data taken in the equilibrium liquid phase at temperatures 320 K and 400 K.

3. Data analysis

The revealed signal in INS experiments is essentially due to hydrogen atoms whose cross section is almost exclusively incoherent and much higher than the coherent and incoherent cross sections of any other element. The incoherent scattering process reflects the properties of a single atom since no interference of the scattered neutron waves takes place. The experimental time-of-flight spectra were processed using the standard fitting program written for NEAT spectrometer and DAVE program. Using the vanadium runs for the normalization and for determining the resolution function the program allows converting the experimental data from the time of flight scale to the energy scale and obtaining the scattering law:

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \left(\frac{\sigma}{4\pi}\right)\left(\frac{k}{k_0}\right)S_{inc}(Q,\omega) \qquad (1)$$

When neutrons are scattered by matter, the process can alter both the momentum and the energy transfer of the neutrons and the matter. The conservation laws of the momentum and energy during the scattering are:

$$\hbar\vec{Q} = \hbar\left(\vec{k} - \vec{k}_0\right) \qquad (2)$$
$$\hbar\omega = E - E_0$$

where k_0 is the wave vector of the incident neutron and k is that of the scattered neutrons and E_0, E are the neutron energies before and after scattering. The quantity $Q = k - k_0$ is known as the scattering vector. The incoherent scattering law $S_{inc}(Q,\omega)$, which is the quantity containing the full information about the time and space development of a dynamical process, was determined in the kinematic space. The experimental spectra were converted from the constant angle in constant Q representation.

4. Results and discussion

4.1 Time-of-flight spectra

The inelastic neutron scattering spectra are show in Fig. 2 at the constant Q_0 = 2.14 $Å^{-1}$. In the supercooled liquid phase, with increasing the temperature above T_g=188 K, the quasielastic line centred at zero energy transfer broadens continuously, while the spectral component centered around 4meV becomes weaker and eventually vanishes from the spectrum. The low energy peak-like feature denotes the "β relaxation" process while the broadening of the quasielastic line is referred to as "α relaxation".

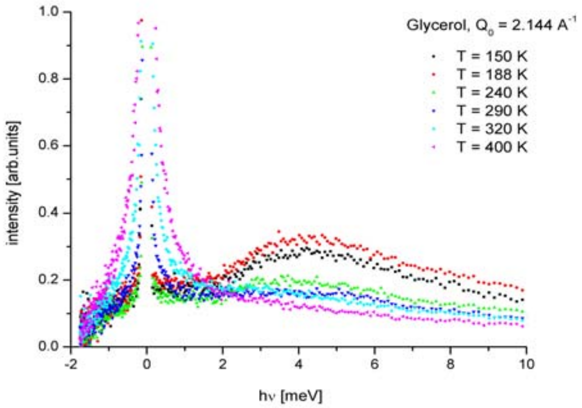

Fig. 2. Inelastic time-of-flight scattering spectra on Glycerol at Q_0 = 2.144 $Å^{-1}$

4.2 The quasielastic line

The form, the width and integral intensity of quasielastic line for incoherent scattering molecular compounds gives information about the diffusion processes of the molecular groups in the compound investigated.

The models which describe such types of motions imply an elastic contribution in the theoretical form of the incoherent quasielastic scattering law [1]

$$S_{inc}^{th}(Q,\omega) = A_0(Q)\delta(\omega) + \sum_l A_l(Q)L(\omega,\Gamma_l(Q)) \tag{3}$$

The first term A_0 is the elastic incoherent structure factor known as EISF while the second term from Eq. 3 gives the real quasielastic contribution. In the majority of the rotational diffusion systems only the first lorentzian is retained. The experimental scattering law is given by the convolution of theoretical function, Eq. 3, with the resolution function $R(Q,\omega)$ of the neutron spectrometer. It consists of the sum of two terms: the first term contains the convolution of the delta-function with the resolution function while the second term is given by the convolution of the first lorentzian with the resolution function. In the present studies, in the approximation used in the DAVE fitting program [8], three different models have been proposed for the quasielastic scattering of liquid glycerol: a simple Lorentz, a Lorentz raised to the power 2/3 and two-Lorentzian.

4.2.1 Lorentzian model

The quaielastic scattering function is normally described in terms of the Lorentzian function, for the liquid. The broadening of the quasielastic line in the liquid phase is due to the increased diffusive motion. The Lorentzian form is

$$S_l(Q,\omega) = S(Q)\frac{\Gamma(Q)}{\Gamma^2(Q)+\omega^2} \tag{4}$$

where $\Gamma(Q)$ is the energy line width. The diffusion constant, D, can be determined by analysing the width of the quasielastic spectra. In the incoherent approximation $\Gamma(Q) = DQ^2$. As shown in Fig. 3, the fitted results obtained with Lorentzian form are not describing well the experimental results.

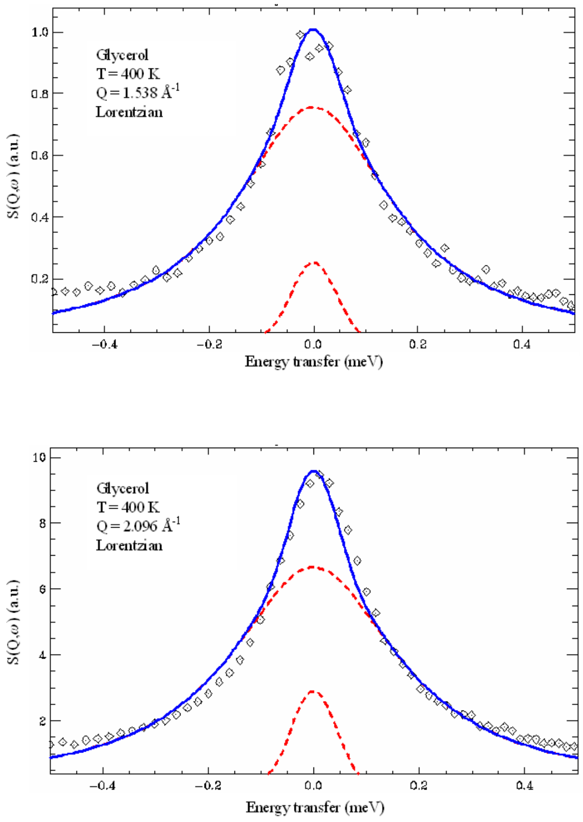

Fig. 3. The quasielastic fits of Lorentzian model (solid line) at 400 K for different Q_0 values.

4.2.2 Non - Lorentzian model

A non-Lorentzian form can be written like

$$S_{nl}(Q,\omega) = S(Q)\left[\frac{\Gamma(Q)}{\Gamma^2(Q)+\omega^2}\right]^{2/3} \tag{5}$$

This model is based on jump-relaxation processes [9,10] and predicts that forward-backward hopping sequences cause a dispersive conductivity as well as broad components in the quasielastic neutron scattering spectra.

The fits of this non-Lorentzian model are compatible with the neutron scattering data as shown in Fig. 4.

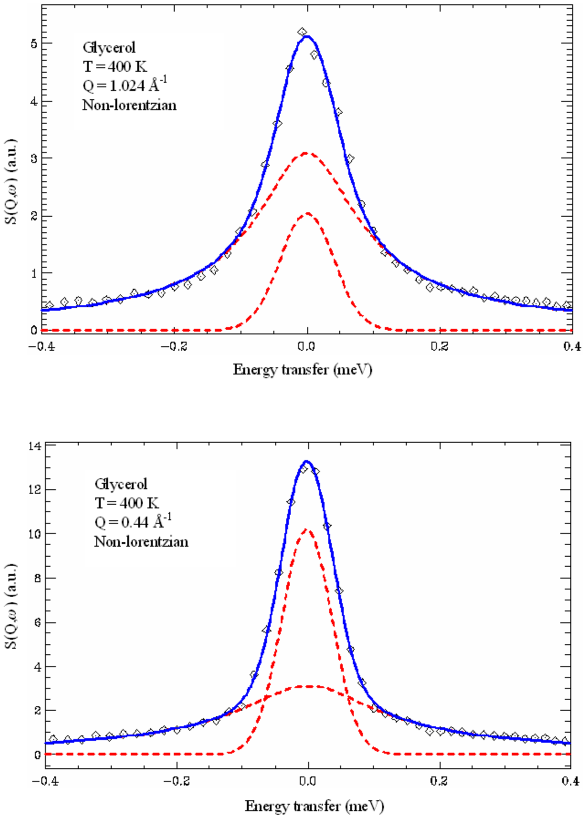

Fig. 4. The quasielastic fits of non-Lorentzian model (solid line) at 400 K for different Q_0 *values.*

4.2.3. Two Lorentzian model

In almost all experiments, as predicted by theory, two dynamical processes were observed above the characteristic temperature T_c in addition to the elementary phononlike microscopic excitations: a fast local relaxational process – the β process, and a slower, strongly temperature dependent process – the α relaxation, which is identified as the structural relaxation.

This possible mixing of relaxations in the equilibrium liquid phase invited us to test a "two Lorentzian model":

$$S_{2l}(Q,\omega)=S(Q)\left(\frac{A\Gamma_\alpha(Q)}{\Gamma_\alpha^2(Q)+\omega^2}+\frac{B\Gamma_\beta(Q)}{\Gamma_\beta^2(Q)+\omega^2}\right) \qquad (6)$$

where A, B, $\Gamma_\alpha(Q)$, $\Gamma_\beta(Q)$ are amplitudes and line widhts of the α and β relaxations. The fits obtained are also in a good agreement with the measured data.

4.2.4 Q dependence of the quasielastic line width

We have determined the quasielastic line width at different Q_0 from the non Lorentzian model, as shown in Fig. 5. Here, the Q dependence of the line width is calculated from 0.33 Å^{-1} to 2.273 Å^{-1} at temperatures 320 K si 400 K. The behavior of $\Gamma(Q)$ is rather similar at both temperatures: the line width show almost no variation or varies slowly with Q. It is observed that $\Gamma(Q)$ does not vary as DQ^2 as expected in the incoherent approximation.

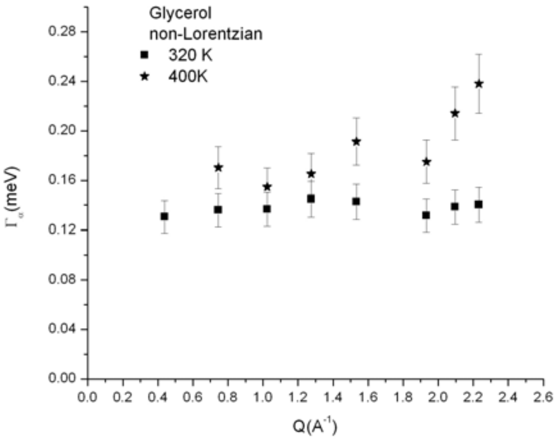

Fig. 5. The Q *dependence of the quasielastic line width of the non Lorentz model.*

A comparison between the line width of the non Lorentz and the line width $\Gamma_\alpha(Q)$ of the two Lorentz models as a function of Q is shown in Fig. 6. Both line width parameters display the same Q dependence and do not vary as Q^2.

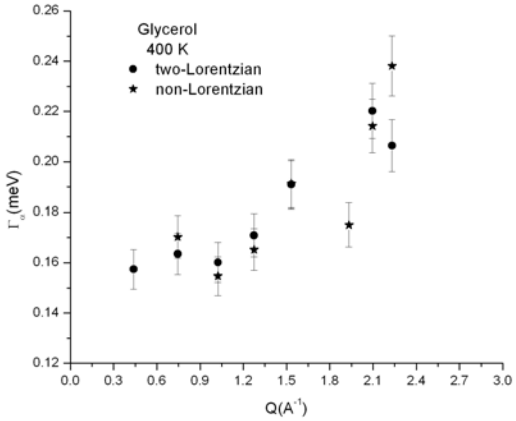

Fig. 6 The Q *dependence of the quasielastic line width of the non Lorentz model and for the α relaxation process in a two Lorentz model.*

5. Conclusions

In this work time-of-flight neutron scattering on glycerol (hydrogen-bonded network) was applied for the investigation of the dynamical processes in this glass-forming material (including α process, fast β process, and microscopic response – the boson peak). The dynamics relating to the appearance of the boson peak in the scattering spectra was elsewhere analysed [11]. The results reported here can be summarized as follows.

The increase of the spectral density observed in the inelastic time-of-fligt spectra above the conventional glass transition temperature T_g corresponds to additional vibrational modes or the structural relaxation as implied by mode coupling theories. This has also been observed in other types of glasses [12, 13, 14, 15]. A simple Lorentzian description of the α relaxation process in glycerol is not adequate in the echilibrium liquid state. Both the non – Lorentzian and the two – Lorentzian models deliver good description of the experimental data that can be qualitatively interpreted in terms of mode coupling theories,but the experimental results show no clear distinction between them. The good fits obtained from the possible mixing of relaxations in the equilibrium liguid phase leads us to interpret the fast local relaxational process as occuring in the liquid state.

Acknowledgments

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