Microscopic dynamics of glycerol: a QENS study

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Microscopic dynamics of glycerol: a QENS study

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Abstract. We report on a quasielastic incoherent neutron scattering (QENS) experiment on liquid glycerol. QENS data were collected at the temperature T=380 K and with a resolution (FWHM) R=55μeV. The analysis of the quasielastic signal enables us to draw a consistent picture of the diffusive mechanism on a picosecond time scale and to compare with most recent models for glycerol dynamics. Model selection, performed with the fitting algorithm FABADA, gives us a preliminary description about the motions of the glycerol molecules in its liquid state.

1. Introduction

Glycerol $C_3H_5(OH)_3$ is one of the weak hydrogen-bonded systems composed of small and highly flexible molecules. The presence of three hydroxyl groups in the molecule gives rise to a particularly rich and complex conformational and structural behaviour in condensed phases. As a consequence glycerol is an excellent glass former and the nature of its glass transition has been the object of several experimental investigations [1-3, 8-10]. The understanding of the microscopic structure and dynamical processes in highly viscous liquids such as glycerol, aimed at a unified theoretical description of the system, has been the focus of a great deal of attention for many decades [1-9]. Parallel to the computation advances [10-12], the recent developments in reliable experimental techniques provide high-quality data. Despite such a high scientific attention, it is not yet clear which is the theoretical model that better describes the microscopic dynamics. Many experiments were done using neutron scattering [13-19], but obtaining the diffusion coefficients from the measured quasielastic spectra requires high experimental care. The technical difficulties intrinsic to this kind of experiments can be sensibly reduced exploiting the high signal-to-noise ratio attained by the time-of-flight spectrometer TOFTOF at the Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II, Garching bei München, Germany) [20].

Here, we report on a QENS experiment carried out on TOFTOF with the aim of measuring the incoherent quasielastic response of liquid glycerol. We also propose two alternative models to describe the microscopic dynamics of glycerol: diffusion+3D Brownian oscillator and a more restrictive model such as diffusion+rotation.

2. Data analysis and results from QENS spectra

Experiments were performed at TOFTOF (FRM II, Garching) using an incoming neutron beam with a wavelength of 6.0 Å. The Q-range investigated was 0.4<Q(Å^{-1})<1.4. Data-reduction, including normalization and background subtraction was performed using the program FRIDA [21]. Spectra were obtained by regrouping the data into slices at constant Q [22]. The spectra were evaluated in the region of E = −0.5 meV to +0.5 meV where positive values for the energy transfer denote an energy gain of the neutron during the scattering process. The resolution was measured using a vanadium rod in the same instrumental configuration as the sample.

In order to analyze the data, the theoretical function must be convolved with the instrumental resolution R(Q,ω). When the width of the theoretical function Γ is close to the width of the energy bin ΔE, the theoretical function to be fitted can be reduced to a single point. In this case the broadening Γ obtained after the convolution process is greater than the real value [23]. This artefact is especially dangerous when fitting a diffusion process, since in this case Γ is proportional to the squared value of the momentum transfer Q. This causes that the value of Γ is bigger than the correct one in the low Q region. In other words, when using an energy bin ΔE too big related to the line broadening, a deviation from the Q^2 law is observed which is not related to any physical process, but to a numerical problem of the convolution. As stated in reference [24], in order to avoid this effect half the bin width must be smaller than the line width, i.e. Γ≥ΔE/2. In figure 1 we show the obtained values of Γ using a series of decreasing energy binnings (0.01, 0.005 and 0.001 meV). As it is clear in the figure using an energy bin too big could incorrectly lead to the conclusion that there is a level-off from the line broadening describing the diffusion at low momentum transfer. However, a fitting using smaller energy bins shows that, in fact, when the energy bin is small enough the Q^2 law is recovered, and the level-off at small Q is only a numerical artefact.

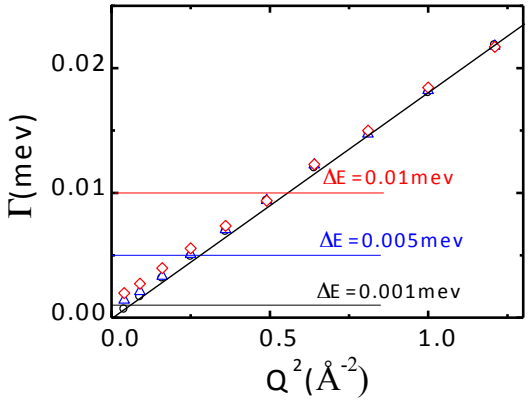

Figure 1.(colour online) Line broadening Γ as a function of the squared momentum transfer fitted using different energy binnings (diamonds for Δω=0.01 meV, triangles for Δω=0.005 meV and circles for Δω=0.001 meV). A series of lines showing the binning has been added for the sake of clarity.

In order to investigate which motions are taking place at a microscopic level, we have tested two models, both including a diffusion term and a confined motion at long times. First of all we checked a model where the particle executes a Brownian motion in an harmonic potential, the so called Brownian Oscillator (BO) [25]. The quasielastic scattering function is thus described in terms of a Lorentzian function related to the diffusion (D) with a broadening $\Gamma_D(Q)=DQ^2$, and the broadening related to the Brownian oscillator, Γ_{BO}. The scattering law can be written as:

$$S(Q,\omega) = L(\Gamma_D) \otimes \left(A_0(Q) + \sum_{m=1}^{\infty} A_m(Q) \frac{1}{\pi} \frac{m \cdot \Gamma_{BO}}{(m \cdot \Gamma_{BO})^2 + \omega^2} \right) \quad (1)$$

$$\text{with} \qquad A_0(Q) = e^{-Q^2\varepsilon^2} \quad \text{and} \qquad A_m(Q) = (Q^{2m}\varepsilon^{2m})/m!$$

For the second model a rotational motion has been assigned to the confined motion. We will call this model Diffusion + Rotational motion (D+R) and the scattering law can be expressed as:

$$S(Q,\omega) = L(\Gamma_D) \otimes \left(A_0(Q) + \sum_{l=1}^{\infty} A_l(Q) \frac{1}{\pi} \frac{\Gamma_{rot}}{(\Gamma_{rot})^2 + \omega^2} \right) \qquad (2)$$

$$\text{with} \qquad A_0(Q) = j_0^2(QR) \quad \text{and} \qquad A_l(Q) = (2l+1) j_l^2(QR)$$

where $\Gamma_{rot} = l(l+1)D_{Rot}$, and j_l are spherical Bessel function of l-th order.

Fittings were performed to the data at all Q-values simultaneously, in a way to fit, at once, both processes and avoid cumulative errors. In panels a and b in figure 2, we show two examples of the best fits to the data at two values of momentum transfer (Q=0.5 Å^{-1} and at Q=1.1 Å^{-1}). As it can be seen both models are able to fit the data reasonably well at a first glance. The parameters coming from the best fit are, for the D+BO model: diffusion coefficient of D=0.022·10^{-4} cm^{2}s^{-1}, Γ_m=0.05 meV and ε=0.7Å and for the D+R model D=0.025·10^{-4} cm^{2}s^{-1}, rotational diffusion coefficient D_{Rot}=0.054·10^{-4} cm^{2}s^{-1} and the radius of gyration is R=1.2 Å. The values for the diffusion coefficients appear to be compatible with the values obtained from NMR experiments (D=0.019·10^{-4} cm^{2}s^{-1}), as stated in reference [26].

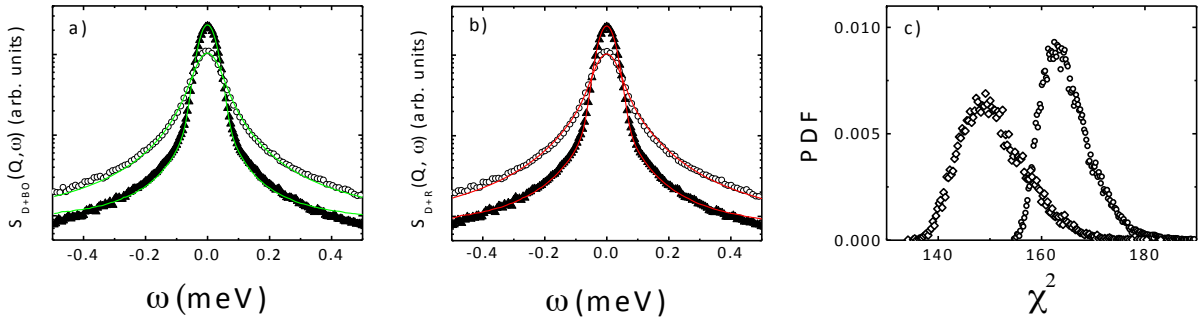

Figure 2. Experimental data together with the bests fit to two different models: Diffusion + Brownian oscillator (a) and Diffusion + Rotational motion (b) for Glycerol at T=380 K with a resolution of 55 μeV. For this two models we present two spectra and relative fits at the same Q values (triangles for Q=0.5 Å^{-1} and circles for Q=1.1 Å^{-1}). (c) Probability density function for the figure of merit χ^2 for the two models (diamonds D+BO, circles for D+R model).

In order to determine in a quantitative way which model fits better the data we show the Probability Distribution Function (PDF) of the figure of merit χ^2, for the two proposed models: the Diffusion + Brownian oscillator motion is clearly preferred since any combination of parameters leads to a better fit.

3. Conclusion

We present in this work a method to quantify which model is the best describing the data, beyond the "good looking fit" criterion. The analysis of the data for glycerol leads us to the conclusion that a Brownian oscillator describes better the data of the confined motion than a simple rotation of the whole molecule.

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