Methyl group dynamics in a glass and its crystalline counterpart by neutron scattering

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Abstract. Methyl group dynamics in the same sample of sodium acetate trihydrate in crystalline and glassy states have been investigated by neutron scattering. Measurements have been carried out in the whole temperature range covering the crossover from rotational tunneling to classical hopping. The results in the crystalline sample have been analyzed according to the usual single-particle model, while those in the glass were analyzed in terms of a broad Gaussian distribution of single-particle potentials, with a standard deviation of 205 K. The average barrier in the glass (417 K) takes, within the experimental error, the same value as the unique barrier in the crystal.

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The dynamics of small rotors as ammonia, methane, ammine ions, and particularly, methyl groups, has been investigated mainly by neutron scattering [1]. In most of cases, the sum of the relevant interactions on these rotors can be modelized as an effective single-particle rotational potential. The drastic dependence of the rotational tunneling frequency on the potential barrier height allows an accurate determination of the latter by measuring the tunneling peaks. Due to the relatively simple character of their dynamics, these rotors are often used as internal dynamic probes to obtain information about characteristics of the environment [1].

Local disorder is reflected in distributions of rotational barriers [2]. When such distributions are sufficiently broad, as for methyl groups in glassy polymers, the corresponding distribution of tunneling frequencies has its maximum beneath the neutron scattering resolution, yielding a broad feature instead of well-defined tunneling peaks in the spectra even at liquid helium temperatures [3, 4]. This fact makes it difficult to determine the values of the barriers in the glass.

This problem has been tackled by a simple model (rotation rate distribution model, RRDM) for the temperature dependence of neutron scattering spectra for methyl group dynamics in glassy polymers [2–5], covering the crossover from rotational tunneling to classical hopping [5]. A series of neutron sacttering studies on polymers has confirmed the suitability of the RRDM for these systems [2–5], though in principle, its grounds are appliable to any disordered system.

In contrast to glassy polymers, which cannot be obtained in crystalline state, low molecular weight glasses allow a comparative study of the methyl group dynamics in a same sample in both states. In this way, some new insight may be obtained on the relevant interactions controlling the parameters of the distribution. For this purpose, we have selected sodium acetate trihydrate, a system thoroughly studied in the past in the crystalline state [6] and that can be easily obtained in the glassy state with moderate cooling rates. Moreover, a selective deuteration of the water molecules is possible, in order to attenuate their contribution to the spectra.

1 Theoretical aspects

Now we briefly summarize the usual model for methyl group dynamics in crystalline systems [1] and expose the grounds of the RRDM. At very low temperature ($T \sim 1$ K), the methyl group tunnels through a one-dimensional rotational potential $V(\Phi)$, which generally is approximated to the threefold term of its Fourier expansion: $V(\Phi) = V_3(1 - \cos 3\Phi)/2$. The tunneling frequency ω_t can be detected by neutron scattering as two inelastic peaks (for neutron energy gain and loss) for barriers V_3 below ≈ 700 K [1]. When increasing temperature, the coupling to the lattice phonons drives a crossover to the classical hopping regime [1]. As a consequence, the tunneling peaks broaden leading to Lorentzian lines and shift to the central elastic line [1]. At the same time, a quasielastic Lorentzian broadening appears around the elastic line [1]. The temperature dependence of the shift, $\Delta\omega_t$, and the half-width at half-maximum (HWHM), Γ_i and Γ_q, of the inelastic and quasielastic Lorentzians respectively, is well approximated by Arrhenius laws activated by the first librational energy [1]:

$$\hbar\Delta\omega_t = \gamma_{sh} \exp(-E_{01}/kT) \qquad (1)$$

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$$\Gamma_{i(q)} = \gamma_{i(q)} \exp(-E_{01}/kT) \tag{2}$$

γ_{sh}, γ_i and γ_q are temperature-independent preexponential factors. At temperatures typically about 50–70 K, the onset of the classical hopping regime is reflected in the merging of the three Lorentzians into a quasielastic Lorentzian, which broadens according to an Arrhenius law driven by the classical activation energy E_A [1]:

$$\Gamma = \Gamma_\infty \exp(-E_A/kT) \tag{3}$$

with Γ the HWHM of the Lorentzian. The preexponential factor Γ_∞ is temperature-independent. The merging occurs in a quite narrow temperature interval ($\Delta T \approx 5$–10 K) that will be approximated as a unique "crossover temperature" T_C. The corresponding incoherent scattering functions for the different regimes can be expressed as [1]:

$$\begin{aligned} S_{MG}^{inc}(Q, \omega) &= A\delta(\omega) \\ &\quad + B\left[\delta(\omega) + \delta(\omega - \omega_t) + \delta(\omega + \omega_t)\right] \end{aligned} \tag{4}$$

$$\begin{aligned} S_{MG}^{inc}(Q, \omega) &= A\delta(\omega) + B\Big[L\left(\omega; \Gamma_q\right) \\ &\quad + L(\omega - \omega_t + \Delta\omega_t; \Gamma_i) + L(\omega + \omega_t - \Delta\omega_t; \Gamma_i)\Big] \end{aligned} \tag{5}$$

$$S_{MG}^{inc}(Q, \omega) = A\delta(\omega) + 3BL(\omega; \Gamma) \tag{6}$$

for the tunneling, crossover and classical regime respectively. In these equations $A = [1 + 2j_0(Qr)]/3$ and $B = 2[1 - j_0(Qr)]/9$. j_0 is the zeroth-order spherical Bessel function and r the H−H distance in the methyl group. L is a normalized Lorentzian function.

These features are well established in crystalline systems [1]. However, in a glass the different local environments would yield a different barrier V_3 for each methyl group and therefore, a barrier distribution, $g(V_3)$, in the system [2–5]. As a consequence, the spectrum of the glass would result from the superposition of the crystal-like spectra of the individual methyl groups, weighted by $g(V_3)$. The incoherent scattering function for methyl group dynamics will therefore be calculated as:

$$S_{RRDM}^{inc}(Q, \omega) = \int dV_3 g(V_3) S_{MG}^{inc}(Q, \omega; V_3) \tag{7}$$

where each individual function $S_{MG}^{inc}(Q, \omega; V_3)$ will be given by one of the (4)–(6).

Due to the superposition of the individual spectra, the shift and broadening of the individual peaks and their merging when reaching the classical regime is not observable in a glass. For this reason, except in the tunneling limit at $T \sim 1$ K, it is not evident what physical description (the crossover picture below T_C, or the classical one above T_C) must be taken for each methyl group at the respective temperature. This problem is tackled by introducing a functional relationship $T_C = T_C(V_3)$, that can be obtained by assuming that the classical regime is reached when the rate for incoherent hopping equals the rate for coherent tunneling. Thus, we define the crossover temperature as that where $\Gamma = \hbar\omega_t$, or equivalently:

$$kT_C = E_A / \ln(\Gamma_\infty/\hbar\omega_t). \tag{8}$$

T_C defined in this way depends only on V_3, since E_A and ω_t are obtained as direct functions of V_3 [4], and it can be

seen that, for a given system, Γ_∞ can be taken as a barrier-independent quantity [2]. This definition allows to choose the functional form (5) or (6) for each individual function $S_{MG}^{inc}(Q, \omega)$. Moreover, we impose two constraints at the crossover temperature: i) the continuity condition $\Gamma_q(T_C) = \Gamma_i(T_C) = \Gamma(T_C)$ and ii) $\Delta\omega_t(T_C) = \omega_t$, as required by the disappearance of the inelastic processes in the classical onset. From these constraints, it is straightforward to see that the preexponential factors of (1), (2) can be calculated for each barrier V_3 as:

$$\gamma_{sh} = \gamma_i = \gamma_q = \Gamma_\infty \exp[(E_{01} - E_A)/kT_C] \tag{9}$$

After this procedure, all the quantities appearing in (1)–(6) are unambiguously determined if the values of V_3 and Γ_∞ are given, and the total incoherent scattering function $S_{RRDM}^{inc}(Q, \omega)$ can be calculated in terms of Γ_∞ and the parameters of the distribution $g(V_3)$. Finally, the total coherent contribution and the incoherent contribution of the other atoms in the molecule, both assumed to be elastic, are added, and the total function is convoluted with the instrumental resolution for comparison with the experimental scattering function $S_e(Q, \omega)$.

2 Experimental

Previous differential scanning calorimetric (DSC) measurements showed a glass transition temperature $T_g \approx 215$ K at a heating rate of 20 K/min. Neutron scattering measurements were carried out by means of the backscattering spectrometer IN16 at the Institute Laue-Langevin (Grenoble, France). An incident wavelength of 6.27 Å was selected, providing an energy- and Q-window from -15 to 15 μeV and from 0.2 to 1.9 Å^{-1} respectively. The instrumental resolution (HWHM $\approx$ 0.4 μeV) was calibrated by a vanadium sample of thickness 1 mm. A flat sample of thickness 0.7 mm was used to get a transmision close to 90%, allowing to neglect multiple scattering effects in the Q-range we restricted to in our analysis (1.3–1.9 Å^{-1}). Raw data were corrected from detector efficiency, sample container and absorption by means of the ILL standard programms.

Measurements were first taken in the crystaline state. In order to get the glassy state, the sample was heated a few degrees above its melting point (343 K), but far below the boiling point of water, in order to avoid dehydration. Thereafter it was quickly cooled down to 2 K. Once the measurements in the glassy sample were taken, the sample was recrystallized and measured again, recovering the crystalline spectra.

3 Results and discussion

Figure 1 shows the experimental spectrum at 2 K in the crystalline (black points) and glassy (white points) phases. In contrast to the crystal, the spectrum of the glassy phase does not show defined tunneling peaks, but a broad feature, that suggests the existence of a distribution of tunneling frequencies that would follow from $g(V_3)$. An excellent description of the experimental results (solid thick line) was achieved with a Gaussian distribution of pure threefold barriers:

$$g(V_3) = \left(1/\sqrt{2\pi}\sigma_V\right) \exp\left[-(V_3 - V_{30})^2/2\sigma_V^2\right] \tag{10}$$
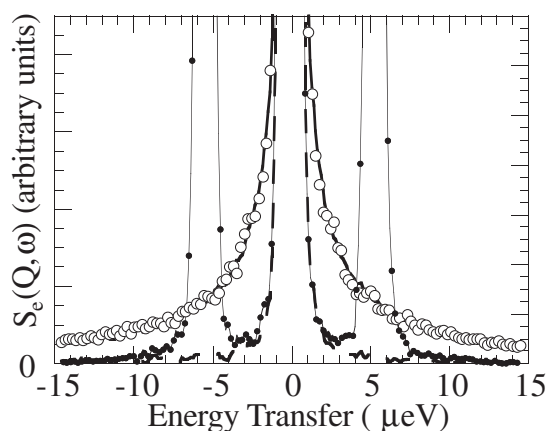
Fig. 1. Experimental IN16 spectra at 2 K (*white points*) and theoretical curve given by the RRDM (*solid thick line*) for glassy sodium acetate trihydrate. *Black points* correspond to the crystalline sample. The *solid thin line* is a guide for the eyes. The *dashed line* is the resolution function. $Q = 1.75\,\text{Å}^{-1}$. Scale: 5% of the maximum

Fig. 2. IN16 integrated intensities at $Q = 1.75\,\text{Å}^{-1}$ in the ranges 1–3 µeV (*circles*), 3–6.5 µeV (*squares*) and 6.5–10 µeV (*triangles*). *Solid lines* are the values predicted by the RRDM. *Dashed lines* correspond to a description exclusively in terms of classical hopping

with an average barrier $V_{3_0} = 417$ K and a standard deviation $\sigma_V = 205$ K. The value of the average barrier is, within the error bar (10%), equal to the unique one of the crystal [1]. The standard deviation takes a value similar to those found in the quite different structural glasses (polymers) studied up to now in terms of the RRDM [2–5]

The evolution of the spectra has been shown in Fig. 2 by depicting the temperature dependence of the integrated intensities in different inelastic windows of IN16. Solid lines in Fig. 2 are the theoretical curves given by the RRDM, with the parameters of $g(V_3)$ given above and a value of 4.8 meV for the preexponential factor Γ_∞. These curves were damped by a Debye-Waller factor as described elsewhere [3]. Dashed lines correspond to a description exclusively in terms of classical hopping. Such lines were constructed by assuming the classical equations (3), (6) for all the individual functions $S_{MG}^{inc}(Q, \omega)$ of the integrand in (7). The intensity excess respect to the classical prediction below ≈ 60 K is due to the fraction of

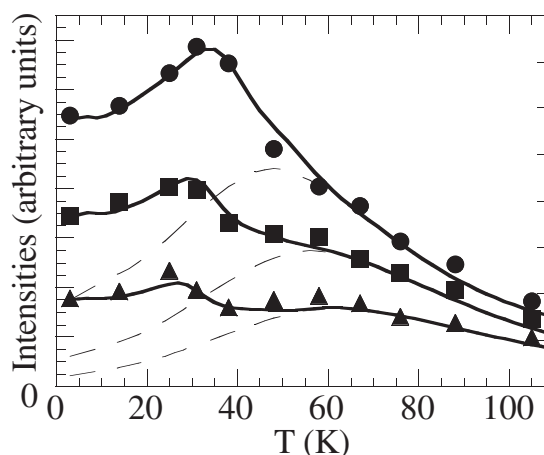methyl groups still having not reached their crossover temperature.

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