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Brillouin-spectroscopy experiments on polymorphic ethanol

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Abstract

We report Brillouin-spectroscopy experiments conducted on ethanol, in the liquid and glass states, as well as in the stable crystal, plastic crystal and orientationally-disordered crystal (“glassy crystal”) phases. Both the canonical supercooled liquid \leftrightarrow glass transition and the dynamical plastic crystal \leftrightarrow glassy crystal transition are observed as a kink in the sound velocity at 96 K. We have also studied the influence of small amounts of water on the crystallization kinetics for the stable and the plastic crystal phases, which are slowed down in favour of glass formation even with less than 0.5% water impurity.

Keywords: Glass transition; sound velocity; Brillouin scattering; orientationally-disordered crystals, crystallization kinetics

1 Introduction

The complexity of the phase diagram of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is one of the most interesting features of this material. It is now well established [1–6] that ethanol is polymorphic, presenting different solid phases: a fully-ordered (monoclinic) crystal, a (bcc) plastic crystal (PC) which by quenching becomes an orientationally-disordered crystal (ODC) with glassy properties (hence sometimes named “*glassy crystal*” or even orientational glass), and the ordinary, amorphous glass. Very strikingly, the conventional supercooled liquid \leftrightarrow glass transition and the dynamical-freezing transition PC \leftrightarrow ODC occur at the same temperature $T_g = 95\text{--}97$ K [1–6]. Moreover, the ODC of ethanol exhibits [3–5] the same universal behaviour in low-temperature properties and low-frequency dynamics as the conventional glass, hence the alternative use of the names *glassy crystal* or *orientational glass*. Traditionally, the glass of ethanol has been obtained by a fast quench from the liquid above its melting temperature $T_m = 159$ K to below T_g . Reported quenching rates range between -30 K min^{-1} [1] and -6 K min^{-1} [2,3]. Moderate cooling rates would lead to the PC phase, whose rotational disorder is quenched into an orientational one, at the same temperature T_g observed for the glass transition. Alternatively, the PC is obtained when heating the glass above T_g up to 110–115 K. On the other hand, the stable, monoclinic crystal is usually obtained by heating the PC above 120 K, though it may also be obtained by slow cooling and thermal stabilization of the supercooled liquid below T_m [7].

As it has been depicted above, the possibility of studying the structural changes occurring in ethanol in the temperature range ~ 100 K, as well as the elastic properties of both glassy phases at lower temperatures, is of great interest. One of the most sensitive experimental techniques to accomplish these goals is High Resolution Brillouin

Spectroscopy (HRBS). HRBS provides direct information about the propagation velocity of acoustic modes at hypersonic frequencies, acoustic dispersion and refractive index of the studied sample. In the present work, we focus on such acoustic properties of the different phases of ethanol in a wide temperature range and on the transformations observed between those phases. Furthermore, we also address the possible influence of small amounts of water on the kinetics of crystallization of ethanol, or on its acoustic properties.

2 Experimental

The HRBS spectra were recorded using a Sandercock 3+3 Tandem spectrometer. The light source was an Ar⁺ laser, and in order to change the temperature a continuous flow cryostat of Oxford Instruments (Optistat) was used. The temperature stabilization was granted by an ITC-4 controller (Oxford Instruments). The ethanol samples were contained in rectangular optic cuvettes (Starna) with 0.5 or 1mm optical paths. In this way, it was possible to simultaneously perform experiments in two different scattering geometries [8] (180° and 90°A). The backscattering geometry (180°) implies a refractive-index dependent acoustic wave vector and the 90°A scattering geometry is independent of the refractive index. The corresponding wave vectors are:

$$q^{90A} = \frac{4\pi\sqrt{2}}{\lambda_0}; \quad q^{180} = \frac{4\pi n_i}{\lambda_0} \quad (1)$$

λ_0 stands for the laser wavelength and n_i for the refractive index of the sample. The sound propagation velocity (v) results from the combination of the Brillouin frequency shift, f , and the corresponding acoustic wave vector:

$$v^{90A} = \frac{f^{90A} \lambda_0}{\sqrt{2}}; \quad v^{180} = \frac{f^{180} \lambda_0}{2n_i} \quad (2)$$

In the case of dispersion-free elastic, isotropic media, these velocities are identical.

Pure ethanol (Merck, “dry”, max. 0.02% H₂O) was employed in these experiments. However, since ethanol is hygroscopic, the real content of water impurity in published experiments (including ours) is uncertain. Therefore, in order to assess the possible amount of water present in the used ethanol and its influence on the results, we are currently measuring the index of refraction of the sample before and after the experiment. For this purpose, an optical Abbe refractometre (Krüss) is being used. The index of refraction n_D^{20} of the monochromatic D line of the sodium spectrum at 20°C can be compared with published data [9] for the binary mixture ethanol-water, and interpolated for the lowest water concentrations. For the corrections when measuring at temperatures not exactly 20°C, the found [10] linear rate $dn_i/dT = -(4.29 \pm 0.02) \times 10^{-4} \text{ K}^{-1}$ was considered. We estimate an absolute error of $\pm 0.25\%$ in the derived H₂O content, though the relative comparison among different cases is surely better.

[Insert figure 1 (a+b) here]

3 Results and discussion

The first approach to observe the glass transition in ethanol was performed by quenching an ethanol sample from room temperature to 40 K, with a cooling rate of roughly -5 to -6 K min^{-1} . Once the sample was stabilized at low temperature, it was slowly heated ($+0.05$ K min^{-1}). As far as the spectroscopic technique needs some time to accumulate the spectra, the temperature was changed stepwise. After a temperature step was produced, it was waited until the temperature was stabilized, and then the spectrum was recorded. It is in this way that the indicated cooling or heating rates have to be interpreted. Spectra in the 90°A and backscattering geometries were recorded simultaneously as far as it was possible. The typical kink-like anomaly at T_g (≈ 96 K) is clearly seen (figure 1a). At about 115 K a self-heating effect of the sample was observed (presumably, the plastic crystallization) and there are hence some points missing. At about 120 K a clear transition into the monoclinic crystalline phase occurs. The sample becomes translucent and only the backscattering mode is observed. Then, a second run with a much slower cooling procedure was conducted (-0.06 K/min). Starting from 170 K, the sample was slowly cooled and spectra were recorded. As can be seen in figure 1a, even at such a slow cooling rate both the monoclinic crystalline phase and the plastic crystalline phase were bypassed [7], and the conventional glass transition at $T_g = 96$ K was observed. It is worth remarking that the absolute values in the backscattering geometry perfectly coincide in both runs, and also agree with the values measured by Surotsev et al. [6]. There is also a reasonable agreement with the work by Ko and Kojima [9], though they give a slightly higher value for T_g and their ethanol sample had a purity of 99.5%. A very important point is to notice that in all the works mentioned above, the glassy phase was obtained by fast cooling (typically above -6 K min^{-1}) and then the experiment was performed always on heating. In the experiments presented in our work, the same results are obtained in different cooling and heating conditions. In addition, measured data for the ODC-PC phases are also shown in figure 1a. They exhibit the above-mentioned similarity between both *glassy* phases and transitions, and are also in agreement with the data by Surotsev et al. [6]. Figure 1b depicts the corresponding longitudinal sound-velocity data, which we are able to obtain without any unknown constant from the 90°A scattering geometry [see equation (2)].

[Insert figure 2 here]

As said above, there exists always an uncertainty in the water content of the experimental ethanol samples. Therefore, a new ethanol sample was carefully prepared and, in order to assess the real level of water content, the refractive index was measured. This “dry” ethanol sample had a refractive index at 20°C of $n_D^{20} = 1.3613$, very close to the values given in the literature [9] for 100% pure ethanol. From this we infer a water content of $0.06 \pm 0.25\%$. A very slow cooling rate (-0.2 K min^{-1}) was applied to this sample, from the liquid state at room temperature, and spectra were recorded in both scattering geometries. The experimental data (see figure 2) show no evidence of the monoclinic crystalline phase. On the other hand, it is clearly observed an abrupt change in the sound-velocity peak between 130 and 120 K. This is due to the transition from the supercooled liquid (SCL) to the plastic crystalline (PC) state.

In order to more precisely determine the transition temperature, the sample was heated up to 170 K, stabilized for some hours and then cooled down and measured to 130 K. Below 130 K the cooling rate used was always very slow (-0.033 K min^{-1}). As can be

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3 seen in figure 3, around 125 K a sudden increase in the sound-velocity signal features
4 the SCL→PC transition. Therefore, with typical slow cooling rates, “dry” ethanol
5 always transforms into the PC phase at $T_{pc} \approx 125$ K, in contrast with the “first” ethanol
6 used (see figure 1), where all the crystallization processes were avoided in favour of the
7 glass formation.
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10 [Insert figure 3 (a+b) here]
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14 In order to test whether some inadvertent water amount was responsible for the
15 suppression of the plastic crystalline phase in the first experiments, a new ethanol
16 sample was investigated. In this case, we kept the ethanol sample for three weeks in a
17 non-hermetic glass bottle with some air in it. The refractive index measured then was
18 $n_D^{20} = 1.3618$, that corresponds to a water content of $0.69 \pm 0.25\%$. When this
19 “moistened” sample was cooled down to 130 K (-1 K min^{-1}) and then very slowly down
20 to 114 K (-0.05 K min^{-1}) no hint of plastic crystalline phase was observed at all,
21 confirming the previous conclusion. It is also interesting to notice that the variable
22 content of water induces a change in the value of the Brillouin frequency shift.
23 Comparing the obtained frequency values at 130 K for the three samples (12.50, 12.56
24 and 12.71 GHz for the “dry”, “first” and “moistened” samples, respectively), it is
25 possible to give an estimation of the water content in the “first” ethanol sample of
26 $0.24 \pm 0.25\%$.
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31 4 Conclusions

32
33 We have conducted Brillouin-spectroscopy experiments, both in backscattering and
34 right-angle scattering, on polymorphic ethanol. This has allowed us to measure for the
35 first time the longitudinal sound velocity in a wide temperature range $20 \div 300$ K, for the
36 liquid, glass, plastic crystal and orientationally-disordered crystal phases. As observed
37 by calorimetry [1,3,4] or other techniques, acoustic data show that the dynamical-
38 freezing transition PC→ODC is very similar and occurs at the same temperature $T_g \approx 96$
39 K as the conventional or structural SCL→glass transition. We have also studied the
40 influence of small amounts of water on the crystallization kinetics and the acoustic
41 properties of ethanol. We have found that H_2O fractions in ethanol as low as 0.2 – 0.7%
42 are enough to hinder the plastic crystallization when cooling the SCL, and permits to
43 transform the SCL into the glass at very slow cooling rates.
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Figure captions

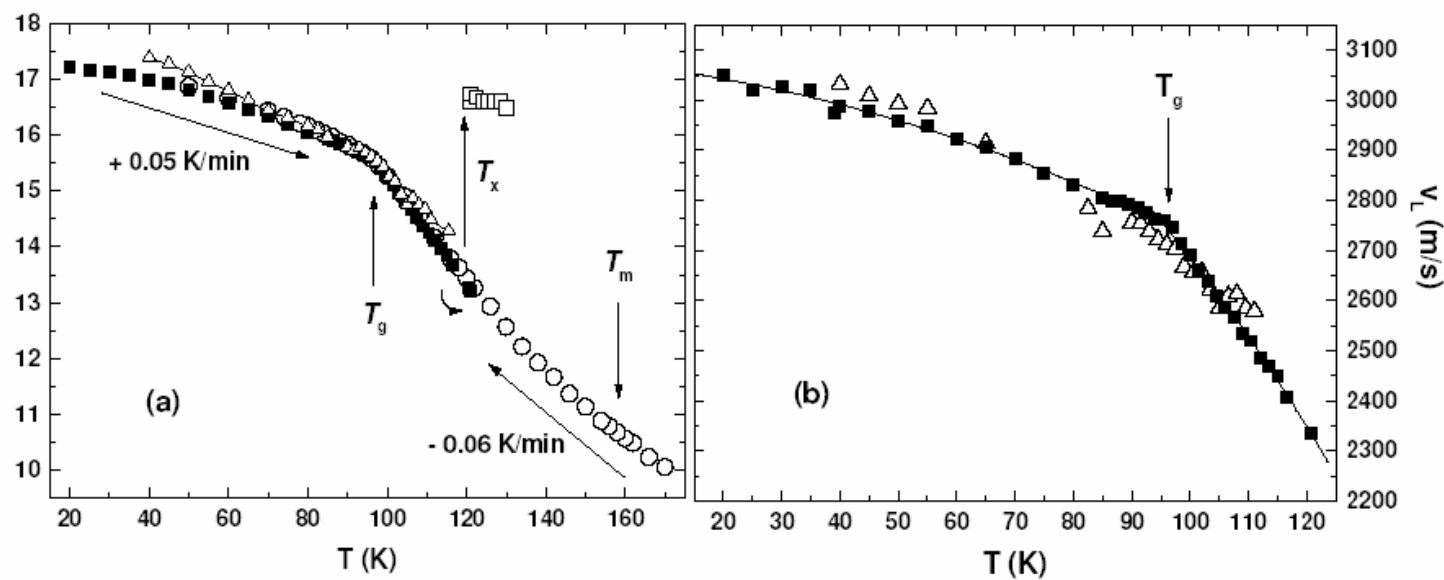
Figure 1: (a) Backscattering Brillouin frequency-shift measured during a heating run after quench (solid squares) and during a slow-cooling run (circles) of the liquid-glass transition of ethanol. Traingles are data for the PC-ODC phases and open squares for the monoclinic crystal. T_g , T_m and T_x indicate the glass-transition, melting and (monoclinic) temperatures, respectively. (b) Longitudinal sound velocities obtained from 90A scattering for the same heating experimental runs of (a). The solid line is an eyeguide for the glass curve.

Figure 2: Backscattering Brillouin frequency-shift measured during a slow-cooling curve of an ethanol “dry” sample. The bars separate three different temperature regions: The liquid region, the supercooled liquid region (SCL) and the plastic crystalline phase (PC). The dashed line is a guide for the eye.

Figure 3 (a): Data obtained in different cooling runs with backscattering geometry (a) and 90°A geometry (b) for “dry” samples of ethanol. Different solid symbols correspond to different cooling runs. **Below 130 K the cooling rate used was always very slow ($-0.033 \text{ K min}^{-1}$).** T_{pc} stands for the transition from supercooled liquid to plastic crystal. T_g stands for the glass-transition temperatures (either conventional or orientational). Open circles correspond to data **obtained** with the “first” ethanol of figure 1a, **by cooling at -0.06 K min^{-1}** which bypassed the plastic crystallization. Lines are only guides for the eye.

FIGURES

Figure 1 (a), (b):



Review Only

Figure 2:

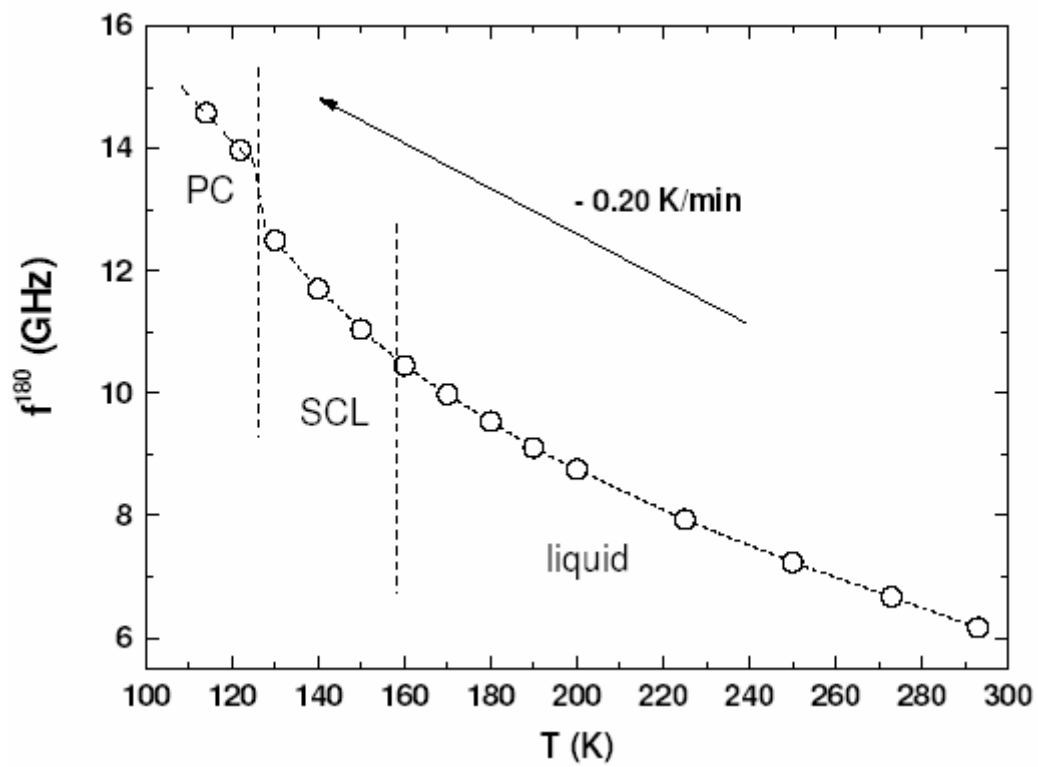


Figure 3 (a), (b):

