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Thermal and acoustic experiments on polymorphic ethanol

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Abstract

We report calorimetric and acoustic experiments conducted on pure ethanol, in the temperature range around 80 – 180 K, where different solid \leftrightarrow solid and solid \leftrightarrow liquid transitions are observed. Using a versatile calorimetric experimental system, we have accurately measured the specific heat of the different phases, and also studied the phase transitions between them, the latter supported by complementary Brillouin-scattering experiments. The influence of several factors in the kinetics of crystallization vs vitrification is also shown and briefly discussed.

Keywords: Glass transition; Specific heat; Brillouin scattering; orientationally-disordered crystals; ethanol; crystallization kinetics

1 Introduction

Despite its simple chemical composition, pure ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) has been found to be a model system in order to study different kinds of disorder in condensed-matter phases. Indeed, ethanol exhibits [1-6] an interesting polymorphism, 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, and the ordinary, amorphous glass by quenching the supercooled liquid (SCL). Astonishingly, both the standard glass transition and that dynamical freezing of the PC into the ODC were found to occur exactly at the same temperature ($T_g \approx 97$ K) and with comparable discontinuities in the specific heat. Furthermore, the ODC of ethanol shows [3-6] 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. In last years, our knowledge about the different structural phases of ethanol has been improved mainly through x-ray diffraction and calorimetric experiments [7]. In particular, we found that there may exist at least 4 different monoclinic crystalline phases of ethanol, in addition to the cubic glassy crystal and to the truly amorphous glass. Moreover, we have also found that the obtained solid phase when cooling liquid ethanol does not depend exclusively on some critical cooling rate, but other factors such as the experimental cell employed, the thermal history followed, or some possible water-impurity content, can play a dominant role in the kinetics of either crystallization or vitrification. In this paper, we present new calorimetric and acoustic experiments performed between 77 and around 180 K, hence in the temperature range where all the relevant phase transitions take place. The former kind of experiments are conducted in a homemade low-temperature calorimetric set-up [8] and the latter using High Resolution Brillouin Spectroscopy (HRBS) [9]. After them, we discuss our current understanding of the rich phase diagram of pure ethanol.

2 Experimental

Pure ethanol (Merck, “dry”, max. 0.02% H₂O) without further purification was employed in these experiments, with care taken in its handling to minimize any possible contact with air moisture.

Both specific-heat measurements and calorimetric studies of the phase diagram of ethanol were conducted by employing a versatile calorimetric system, especially intended for glass-forming liquids. As described in more detail in Ref. [8], we have implemented a so-called continuous method that allows accurate heat-capacity determination after coherent cooling and heating runs, using liquid nitrogen as thermal sink. This experimental method somewhat resembles Differential Scanning Calorimetry (DSC), but contrary to commercial DSCs it can provide direct measurements of the heat capacity based upon simple physical equations, without any *ad hoc* calibrations. From the equation of heat transport, one can readily obtain [8] that the heat capacity C_p of the experimental cell is given by:

$$C_p = \frac{V_h I_h}{\left(\frac{dT}{dt} - \Theta(T) \right)} \quad (1)$$

where V_h and I_h are the voltage and current across the heater element attached to the cell, and $\Theta(T) \equiv (dT/dt)_{drift}$ is the intrinsic (negative) thermal drift of the system, which is directly measured as a function of temperature by standard cooling at $I_h = 0$, with the thermal reservoir fixed at 77 K. Within this experimental method, the heating runs are not performed at an exactly constant heating rate, but rather at a constant applied current or power, though the former will vary little within the studied temperature range. In order to obtain reliable and accurate results, typical heating rates are kept within +0.5 K/min and +5 K/min. On the other hand, a direct display of the measured dT/dt curve as a function of temperature T , for a constant applied power, is besides a useful thermogram to monitor first-order transitions such as melting and crystallization processes.

Three types of calorimetric cells, mostly made of copper, have been used. A first type of cell (C-1) was initially designed and used for measurements at low temperatures, essentially being a small (approximately, 20 mm diameter, 5 mm height, and thin walls of 0.2 mm) pan-shaped, vacuum-tight copper container [4–8]. In this case, the typical sample mass is 1.5 g, for an empty copper cell of around 3 g. A fine copper mesh is fitted inside this sample holder to allow a rapid achievement of thermal equilibrium. A second type of cell (It-3) employed was a copper cylindrical container (13 mm diameter, 25 mm height) with relatively thin walls (< 0.5 mm), and with an indium-sealed copper cover. Typical sample mass is here 2.5 g, for an empty copper cell of around 13 g. A photo of these two cells can be seen in figure 1 of [8]. Finally, we have also used a third kind of cell (F-2), similar to C-1, but thinner and flatter, and devoid of the internal copper mesh. In this case, sample mass is about 0.5 g, and the empty F-2 cell weights 1.1 g. A commercially-calibrated ceramic carbon resistor (CCS) was attached as only thermal sensor.

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 CF) was used. The temperature stabilization was obtained by means of an ITC-4 controller (Oxford Instruments). The ethanol samples were contained in rectangular optic cuvettes (Starna) with 1 mm optical

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3 paths (see [9] for more details). In this work, only backscattering geometry (180°) was
4 employed.
5

6 7 **3 Results and discussion**

8 9 **3.1 Critical cooling rate for vitrification of ethanol**

10
11 It is well known and accepted that whether a supercooled liquid becomes a glass below
12 T_g or crystallizes crucially depends upon the cooling rate. If it is cooled slow enough, it
13 will crystallize. Therefore, papers on glasses are plenty of critical cooling rate data,
14 above which the corresponding liquid can be vitrified. What is the critical cooling rate
15 for ethanol? The Osaka group that discovered in the 70's the difference between the real
16 (amorphous) glass and the "glassy crystal", claimed [1] that they needed a quench faster
17 than 30 K/min to get the glass. If slower, they obtained, at least partially, the plastic
18 crystalline phase, as deduced from their DTA measurements.
19

20
21 Nevertheless, there is some confusion in the literature about this point. In our
22 previous calorimetric experiments [4–6], we observed and reported a critical cooling
23 rate around 20 K/min. Other groups reported that 10 K/min [10] or even 6 K/min [2]
24 were enough. These discrepancies seem to be beyond those expected from different
25 experimental set-ups and thermometry. We have therefore conducted many experiments
26 under different conditions paying attention to this issue, and we have found that there
27 are at least three important factors involved:
28

29 (i) Small amounts of water [9,11] (even around 0.5%, by exposures to air
30 moisture for a few hours) enhance ethanol glass-forming ability.

31 (ii) By comparison of the three abovementioned calorimetric cells, we have
32 confirmed our previous claiming [7] that different experimental cells imply
33 different critical cooling rates. In particular, by employing "dry" ethanol we were
34 able to bypass the plastic crystallization at around 125 K, getting the glass phase
35 with cooling rates of 6 K/min with F-2 and It-3 cells, but were unable to do it with
36 the C-1 cell and quenching rates of almost 30 K/min. So, by using flat, smooth,
37 clean surfaces around the ethanol sample, nucleation centers are minimized and
38 the critical cooling rate of ethanol is very much reduced. In other words, we are
39 usually realizing *heterogeneous* crystallization, not a textbook, homogeneous one.

40 (iii) Finally, we have now found a more unexpected factor: the previous thermal
41 history of the sample can influence whether the thermodynamically stable liquid
42 solidify either into the glass or into the PC phase. Using cooling rates between 6
43 and 22 K/min, in consecutive experiments in the very same experimental
44 conditions with cell F-2 and dry ethanol, we obtained either phase independently
45 on the cooling rate. As a rule, when melting the crystal well above 160 K and then
46 quenching the liquid, the PC was obtained. If the liquid was heated close to room
47 temperature and then cooled, even rather slowly (6 K/min in the relevant range),
48 the glass was however obtained. We believe that these features could be related to
49 some kind of molecular order retained above its melting point in these relatively
50 complex molecular liquids. Further experiments are still needed to confirm this
51 idea and to understand its microscopic origin.
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57 58 **3.2 Specific heat measurements**

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60 Specific heat data for the different phases of ethanol, obtained with cell F-2 and
following the continuous method explained in section 2, are shown in figure 1. The heat
capacity of the emptied cell was measured afterwards and subtracted from the raw data

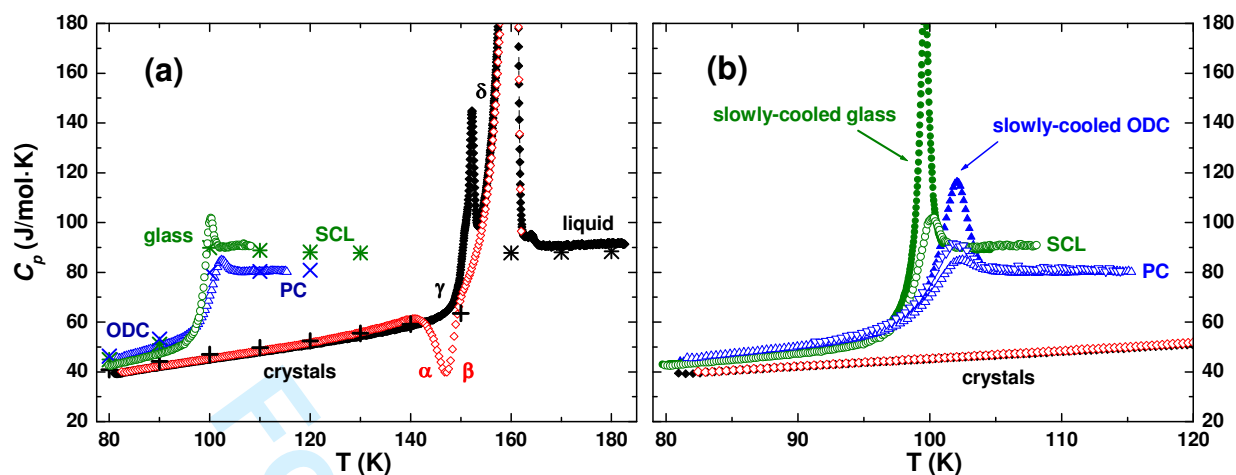


Figure 1. Specific heat measured for the different phases of ethanol, as indicated by the labels. The ordinary glass-SCL transition is represented by circles (green on-line), the ODC-PC transition by triangles (blue on-line), and lozenges correspond to specific-heat data of the monoclinic crystals: metastable α -crystal (open, red symbols) and stable γ -crystal (solid, black symbols). (a) Measurements in the whole studied temperature range. Earlier literature data [1] are also shown: glass/SCL/liquid (*), ODC/PC (\times) and crystal (+). (b) Specific heat measured for the different phases of ethanol focused around the glass-transformation temperature range. The ordinary glass-SCL transition (measured with an average heating rate of 1.1 K/min) is represented by green circles for a normally-quenched glass at about 15 K/min (open symbols) and for a slowly-cooled one (0.06 K/min, solid symbols). Blue triangles indicate three examples of the ODC-PC transition, heating at around 1.7 K/min ODC phases obtained at different cooling rates between 15 K/min and 0.06 K/min. Lozenges are specific-heat data of the monoclinic crystals measured with heating rates around 3 K/min: metastable α -crystal (open symbols) and stable γ -crystal (solid symbols).

in order to obtain the molar specific heat for each phase. As said above, the heating runs are not performed at a constant heating rate, but rather at a given constant Joule-heating current. Very well reproducibility of specific-heat curves has been observed [8] when using different heating rates, provided they are in the range mentioned in section 2. In particular, all shown glass measurements were conducted with an average heating rate of 1.1 K/min, shown ODC-PC measurements at around 1.7 K/min, and shown crystal curves at around 3 K/min.

As can be seen in figure 1(a), our data agree well with those from Haida et al. [1] for the corresponding phases. In figure 1(b), the temperature region around the glass transition has been amplified. The well-known effect of an overshoot in the enthalpy release at the glass transition, that increases with decreasing glass cooling rate (compared to the measuring heating rate) is very well observed. In this case, cooling rates were about 15 K/min (normally quenched glass) and around 0.06 K/min (slowly cooled glass) for a heating rate around 1.1 K/min. More interestingly, the *dynamic* “glassy” transition ODC-PC, between orientational and rotational disorder of a cubic crystal, exhibits the same phenomenon: by cooling the PC below 100 K at three different cooling rates (also ranging between 15 K/min and 0.06 K/min), the overshoot in the specific heat (measured at the same heating rate) is observed to clearly increase with decreasing cooling rate. On the other hand, the metastable, low-temperature monoclinic α -crystal exhibits a very slightly higher specific heat (almost within the experimental error) than that of the stable crystal at low temperature, the γ phase.

3.3 Different monoclinic crystalline phases

In figure 2, we show a representative collection of the many thermal cycles conducted by calorimetry –in fig. 2(a), where the recorded dT/dt curves are plotted as a function of temperature T – and HRBS –in fig. 2(b), where the backscattering phonon peak is also plotted as a function of T –, in order to check the existence of four different monoclinic crystalline phases, as previously observed by x-ray diffraction [7]. When the metastable α -crystal, obtained by heating the PC above 120 K, is heated, an exothermic transition into another metastable β phase is observed around 145 K, which eventually transforms into the stable δ phase at higher temperatures below the melting point T_m . This corresponds to the upper heating curve in fig. 2(a) and to the first heating run in fig. 2(b) (solid squares). When further cooling or heating crystalline ethanol, this metastable α -crystal is no longer observed, but one enters into a reversible cycle of $\gamma \leftrightarrow \delta$ transitions: endothermic peaks by heating at ≈ 150 K, exothermic peaks by cooling at ≈ 147 K, as shown in fig. 2(a), or by the upper curves with open symbols in fig. 2(b). If the stable γ -crystal is directly obtained by slowly cooling the liquid (the crystallization typically occurs at around 140 ± 5 K), the former features of the metastable phases are never observed, but the latter reversible cycle is directly and repeatedly reproduced (see the lower heating curve in fig. 2(a) and subsequent cycles). The first occurrences of these exothermic ($\alpha \rightarrow \beta$) and endothermic ($\gamma \rightarrow \delta$) solid-solid transitions, when heating the low-temperature crystals up to the melting point, can also be seen in the specific-heat curves of figure 1(a).

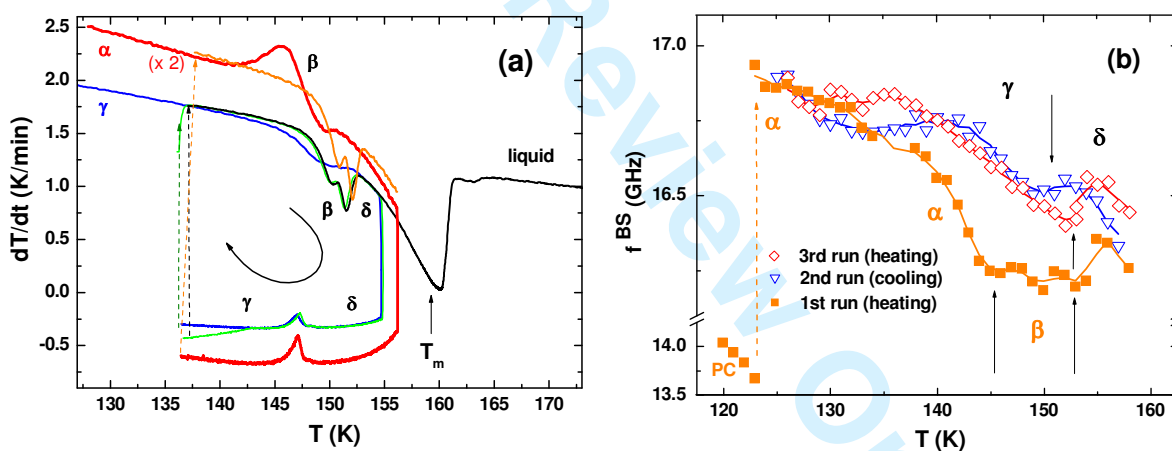


Figure 2. Different thermal cycles demonstrating the existence of four different (monoclinic) crystalline phases: α and β which are metastable, and γ and δ which are stable below and above ≈ 150 K, respectively. (a) Calorimetric thermograms: the upper thermal cycle (shown $\times 2$) starts from the metastable α phase, and the lower one from the stable γ phase obtained by slowly cooling the liquid; the former cycle falls into the latter cycle behaviour after the first heating run. (b) Brillouin-scattering cycles by depicting the measured phonon peak: the first heating run (solid squares) shows the transition from the plastic crystal (PC) phase into the α phase and then into the β phase above 145 K. Subsequent cooling and heating runs (open symbols) follow a different, reproducible curve ascribed to the stable γ and δ crystalline phases.

4 Conclusions

New specific-heat measurements and calorimetric studies of the phase diagram of pure ethanol have been conducted by means of a versatile calorimetric system, and using different experimental cells. The obtained results, also supported by complementary

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2
3 Brillouin-scattering experiments, confirm and deepen our previous knowledge about the
4 different glassy and crystalline phases of ethanol. In particular, it has been confirmed
5 that below 145 K, the usually obtained crystal by heating the PC (α phase) is
6 metastable, the γ phase obtained by slowly cooling the liquid being the stable one.
7

8 In addition, it is noteworthy that the typical “glassy phenomenon” of an
9 increasing enthalpy release about the glass-transition temperature with a decreasing
10 ratio of glass-formation cooling rate over the heating rate used in the calorimetric
11 measurement, is equally observed for the dynamic ODC-PC transition, which once
12 again shows up as a proper “glass transition”.
13

14 Furthermore, we have found that there are at least three important factors
15 influencing the glass-forming ability of liquid ethanol, which account for the
16 discrepancies about critical cooling rates found in the literature: (i) possible water
17 content; (ii) mechanical details of the experimental cell which may drive heterogeneous
18 crystallization; (iii) previous thermal history of ethanol, so that some memory of
19 orientational or positional order may unexpectedly persist in the liquid state! As a rule,
20 ethanol-glass formation is improved by: (i) a small amount of water impurity; (ii) a
21 smooth, flat and clean experimental environment, devoid of nucleation centers; (iii)
22 heating the liquid ethanol above 250 K.
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