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Experimental setup for simultaneous measurements of neutron diffraction and dielectric spectroscopy during crystallization of liquids

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Here we present an experimental setup to obtain information on structural and dynamical changes in liquids during crystallization. This setup consists in a sample cell that allows performing simultaneous measurements of neutron diffraction and dielectric spectroscopy experiments. The capabilities of the technique have been probed by following in real time the crystallization process of a model liquid: the isopropanol. By performing the simultaneous experiment information can be obtained from both phases, amorphous and crystalline, and therefore it can provide a complete description of the changes occurring during a crystallization process. The use of this setup allowed us to demonstrate that a breakage of the hydrogen-bond network is a precursor step for the crystallization of isopropanol. © 2005 American Institute of Physics. [DOI: 10.1063/1.1876992]

I. INTRODUCTION

Glass formers liquids are a class of materials which can be maintained out of the equilibrium, in the amorphous state, without crystallizing. Below the equilibrium melting temperature, the supercooled liquid is thermodynamically unstable due to its higher free energy as compared with that of the crystal. Consequently, above the glass transition temperature $T_g$, the supercooled liquid tends to reduce its free energy undergoing a first order phase transition. By means of this transition, referred to as crystallization, molecules self-assemble forming crystals. The nature of the crystals and the overall fraction of crystalline phase can be estimated experimentally by neutron diffraction (ND) measurements. In order to obtain precise information about the changes occurring in a supercooled liquid during crystallization, a real time experimental setup may be crucial. Nowadays, as far as crystalline phase development is concerned, neutron sources offer the possibility to perform real time diffraction experiments. Scattering techniques can also be used to extract structural information in amorphous materials. However, due to the fact that crystals provoke strong diffraction phenomena, superimposed over a relatively weak contribution of the amorphous phase, mainly information about the crystalline phase is obtained. Thus, undergoing processes in the amorphous fraction of the supercooled liquid are almost nondetectable for these techniques due to the absence of order. An improvement in the understanding of crystallization in terms of interrelation between crystalline and amorphous development is obtained when diffraction experiments are simultaneously accompanied by dielectric spectroscopy (DS). Regarding the amorphous phase, it has been shown that, upon crystallization, the segmental dynamics of glass formers is strongly affected by the progressive development of the crystalline phase. Therefore by monitoring simultaneously, in real time, both the crystal development and the dynamic changes occurring in the amorphous phase, a more complete picture of the crystallization process can be obtained. This approach has been successfully used to follow polymer crystallization in real time but, as far as we know, not to follow crystallization in liquids.

In this article we present the development of an experimental setup which allows one to perform simultaneous measurements of time resolved ND and DS. After a description of the experimental setup, the performance of the ND–DS technique will be illustrated with the results obtained during the crystallization process from the supercooled state of isopropanol which can be considered as a model crystallizable alcohol.

II. DESCRIPTION OF THE EXPERIMENTAL SETUP FOR SIMULTANEOUS MEASUREMENT OF NEUTRON DIFFRACTION AND DIELECTRIC SPECTROSCOPY

Dielectric spectroscopy measures the complex dielectric permittivity $\epsilon' = \epsilon - i\epsilon''$ as a function of frequency and temperature, where $\epsilon'$ is the dielectric constant and $\epsilon''$ is the dielectric loss. A schematic view of a dielectric spectroscopy experiment for liquids is shown in Fig. 1. The liquid is placed in a container between two metallic electrodes of area $A$ separated a distance $d$ and is subjected to an alternating electric field of angular frequency $\omega$. Through measurements of the complex impedance of the sample it is possible to experimentally determine $\epsilon'$. Dielectric spectroscopy is a very suitable method to study molecular dynamics in liquids above $T_g$. In this case, molecular motions give
rise to a main relaxation process, which can be observed as a maximum in $\varepsilon''$ and a step-like behavior in $\varepsilon'$ as a function of frequency.

A scheme of the ND–DS sample holder is illustrated in Fig. 2. The liquid is placed in a container (1) made from anodized aluminum (50 $\mu$m thick). Anodized aluminum was chosen for two reasons. First, aluminum is an appropriate material to obtain a weak neutron intensity absorption. Second, by anodization aluminum becomes insulating. Two standard aluminum pieces (2) acting as electrodes separated by a teflon spacer (3) and connected through the cap (4) to the dielectric are connected to a Stanford lock-in amplifier SR830 with a dielectric interphase and control unit from Novocontrol. Electrodes are glued to the cap by a cryogenics glue. The set formed by the cap, the electrodes and the spacers encloses the liquid by means of an indium ring (5) and four screws (6). The teflon spacer is the only exchangeable part (due to degradation with neutrons) and keeps the electrodes in place at a distance of 3 mm. Taking into account that the resolution of the dielectric spectroscopy equipment is of 0.1 pF, by changing the shape of the teflon spacer the volume of liquid can be varied if necessary in order to vary the capacity as well.

In order to test the performance of the ND–DS cell, different tests with both experimental techniques were performed. First, a test with neutrons were carried out using the diffractometer D1B at the ILL (Grenoble, France) by measuring isopropanol at room temperature. The ND–DS cell has been designed as simple and compact as possible to fit in the D1B cryostat ($\phi$=25 mm), but offering sufficiently good results. The capacitor inside covers an area nearly equal to the neutron beam size. An advantage is that it can be used in the rest of the cryostats (and instruments) which generally have a diameter $\phi$=50 mm. The test measurements were carried out using a wavelength of $\lambda$=2.52 Å and the results were normalized to the monitor (for accounting for fluctuations in the intensity of the beam). The results are shown in Fig. 3(a) for the diffraction spectra of the isopropanol using the ND–DS cell, where the contribution of the different materials of the sample container to the diffraction pattern can be observed.

Afterwards a dielectric spectroscopy test was performed on 1-propanol at $T$=138 K using both cells, the ND–DS and the standard dielectric one. At this temperature the sample is above its glass transition temperature and therefore exhibits a structural relaxation. $^{13}$ Complex dielectric permittivity $\varepsilon' = \varepsilon'' - i\varepsilon'$, was measured covering a frequency range $10^6$ Hz $< \nu < 10^9$ Hz. This assures the performance of dielectric measurements during crystallization in real time. Results obtained with a standard dielectric cell were compared to those obtained by the ND–DS cell and are shown in Fig. 3(b) for 1-propanol. In order to characterize the shape of the dielectric relaxation a Havriliak–Negami function was used $^{17}$

$$e'' = \Im \left[ \varepsilon'_{\infty} + \sum_{x=1,2} \frac{\Delta \varepsilon_x}{1 + (i\omega\tau_x)^{\beta_x}} + i \frac{\sigma}{\epsilon_{\text{vac}}\omega} \right],$$  

(1)

where $\Delta \varepsilon$ is the relaxation strength which corresponds to the area below the relaxation peak, $\tau_x$ is the central relaxation time of the relaxation time distribution, $c$ is the asymmetry parameter, $b$ is the broadening, the subscripts refer to the different relaxations, namely primary and secondary relaxations (I and II, respectively), $\sigma$ is the direct current electrical, $\epsilon_{\text{vac}}$ is the dielectric constant for the vacuum, and $s(0 < s < 1)$ depends on the conduction mechanism. $^{13}$ For the test only a single relaxation term ($\Delta \varepsilon_{\text{I}}=0$) was considered because the purpose was to compare the relaxation shape between both cells.

After fitting the broadening parameter, $b$ was 0.91 and 1.0 for the ND–DS cell and the standard dielectric cell, respectively. On the other hand, the asymmetry parameter $c$ was 0.88 and 0.89 for the ND–DS cell and the standard di-
electric cell, respectively. This indicates that the relaxation spectra as measured by both cells gives rather comparable results within the standard experimental error involved in the dielectric measurements.

III. SIMULTANEOUS NS AND DS MEASUREMENTS DURING CRYSTALLIZATION OF A MODEL ALCOHOL: ISOPROPANOL

In order to test the performance of the simultaneous measurement using the NS–DS cell, a deuterated isopropanol sample (2 propanol D8) was selected which can be considered as a model alcohol to follow crystallization. A glassy isopropanol specimen was obtained by deep quenching from room temperature to 50 K. Isopropanol, like many other glass forming liquids, can develop a certain degree of crystallinity provided it is heated at \( T > T_g = 115 \) K. For this first simultaneous experiment, the dielectric spectroscopy equipment was sent to the ILL in such a way that the DS data taken by the dielectric analyzer are collected by a IEEE-interface interconnected with a personal computer.

Figure 4 presents ND–DS data during a crystallization experiment at \( T_c = 134 \) K. The ND intensities are given as a function of the scattering angle 2\( \theta \). Every pattern was recorded with an acquisition time of 3 min. The \( \epsilon'' \) data from DS are presented as a function of frequency \( F = \omega/(2\pi) \) being \( \omega \) the angular frequency. The initial amorphous state is characterized by an amorphous halo in the ND diagram and by the primary relaxation process of isopropanol centered around a \( F_{\text{max}} \) value of \( 2 \times 10^3 \) Hz in the DS data. As time increases, the onset of crystallization is denoted by the incipient appearance of Bragg peaks in the ND pattern reflections of the monoclinic unit cell of isopropanol.\(^2\)

The dielectric losses can be described considering two relaxations: primary and secondary ones being Cole–Davidson processes in accordance with Eq. (1) with \( b = 1 \).\(^{12}\)

Figure 5 shows the area \( (\Delta \epsilon) \) below the primary and the secondary relaxation as a function of the crystallinity at \( T = 134 \) K. The crystallinity was estimated from the ND data as...
the ratio between the area below the crystalline peaks to the total diffracted intensity. As is shown in Fig. 5 the primary relaxation decreases dramatically in the first stages of the crystallization and the secondary relaxation follows the two-phase model phases that correspond to network and crystalline. The simultaneous experiment allowed us to confirm that a breakage of the hydrogen-bond network occurs as a first step previous to the formation of the crystals.

The results discussed in the present article have shown that in some processes, as is the crystallization, is crucial to have a direct relationship between structure and dynamics. Concerning the applicability of the ND–DS cell, it is worth it to mention that such a sample container could also be used for other neutron scattering experiments, as quasielastic neutron experiments, in order to obtain information during the crystallization of the dynamics at different time scales. The simplicity of the design concept will allow to construct another cell with similar characteristics to allow us to perform such experiments.

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FIG. 5. Area below every relaxation process for (top) the primary (Δε₁) and (bottom) the secondary (Δε₂) relaxation processes as a function of crystallinity. Crystallinity values were estimated from the ND patterns as the ratio between the area below the crystalline peaks to the total diffracted intensity.