Solvation dynamics in the plastic crystal and supercooled liquid state of ethanol

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Abstract

The dynamics of ethanol in its plastic crystalline and supercooled liquid state has been measured using triplet state solvation dynamics techniques. This study focuses on temperatures near the respective glass transitions T_g of the two distinct phases, where the structural relaxation times are between 1 ms and 10 s. In the plastic crystal, the correlation times of the Stokes shift dynamics match the longitudinal time constants of the system as derived from dielectric relaxation data. Additionally, a maximum of the time resolved optical linewidths is indicative of heterogeneous dynamics in the plastic crystal. The supercooled liquid state is obtained after quenching the liquid from room temperature to below T_g and displays relaxation times that are a factor of 100 faster compared with the plastic crystal at the same temperature. The results do not reveal different translational contributions to solvation for the two phases.

1. Introduction

The orientational motions of molecules in liquids exhibit complex behaviour regarding the shape of their relaxation functions and the temperature dependence of their average correlation time. This is particularly obvious in the viscous or supercooled regime of glass forming liquids. Provided that crystallization can be avoided, cooling a liquid below the melting temperature T_m leads to a gradual slowing down of the dynamics until larger scale molecular motion becomes arrested at the glass transition temperature T_g [1]. The dynamics of a typical glass forming liquid is characterized by non-exponential patterns of the correlation functions and non-Arrhenius temperature dependences of the timescale of structural relaxation [2]. Orientational molecular motion is an important aspect of many techniques targeted at measuring liquid dynamics. Examples are nuclear magnetic resonance, dielectric relaxation, dipolar solvation dynamics, optical Kerr effect and luminescence depolarization experiments [3, 4].

Several glass forming liquids also form a plastic crystalline phase, in which the molecular centres of mass are arranged on a regular lattice structure, while the system remains disordered regarding molecular orientation [5]. Materials that exhibit such a plastic crystal state are,

among others, 1-cyanoadamantane, adamantanone, pentachloronitrobenzene, cyclo-hexanol, ethanol and meta-carborane. As demonstrated by a recent in-depth dielectric relaxation study of the above systems by Brand *et al* [6], the molecular orientation in plastic crystal phases is not only disordered but exhibits dynamics reminiscent of that observed in the supercooled liquid state. This similarity includes the occurrence of the glass transition phenomenon in plastic crystals, where the times required for molecular reorientation exceed a typical experimental time window, say 100 s. Ethanol is one of the few cases in which both the supercooled liquid and the plastic phase can be studied, where the thermal history determines which metastable state is obtained. For the case of ethanol, Benkhof *et al* [7] have employed dielectric relaxation experiments to show that the two phases have a common value of $T_g = 97$ K but different apparent activation energies at T_g and thus different fragilities m. The interesting feature of such a liquid is the prospect of comparing the dynamics of a single chemical compound with and without the translational modes of molecular motion.

In this work, triplet state solvation dynamics experiments are used in order to study the dynamics of the plastic crystal and supercooled liquid phases of ethanol in the regime of sluggish orientational dynamics. This technique monitors the response of a solvent to the laser induced change in dipole moment of a probe molecule in terms of the time resolved dynamic Stokes shift [8, 9]. Because dipolar interactions dominate in the present case, the orientational motion of ethanol is the main source of shifting the emission energy of the probe molecule. The key quantities observed in this experiment are the average energy $\langle \bar{\nu} \rangle$ and width σ of the optical $S_0 \leftarrow T_1$ (0–0) transition as a function of time and temperature [10]. While $\langle \bar{\nu} \rangle(t)$ characterizes the dynamics in terms of the Stokes shift correlation function, $\sigma(t)$ allows us to discriminate between the heterogeneous and homogeneous nature of a dispersive (i.e., non-exponential) relaxation process [11–13]. Here, heterogeneity refers to a spatial variation of relaxation times being at the origin of the non-exponentiality regarding the overall relaxation pattern, whereas homogeneous dynamics is associated with the situation in which all relaxing units contribute with a common intrinsically non-exponential process [14]. Heterogeneity has been identified as the source of non-exponential relaxations in a number of experimental studies on supercooled liquids [15–17]. The question of whether the orientational dynamics in a plastic crystal are also heterogeneous has not yet been addressed by experiment.

The scope of this work is to compare the dynamics of solvation in a plastic crystal (with orientational disorder only) to that in the liquid (with both orientational and positional disorder). In particular, the interest focuses on identifying the nature of dispersive dynamics in the plastic crystal phase, homogeneous versus heterogeneous, and on comparing solvation dynamics data for the plastic crystal phase with predictions from solvation theories for the situation of a positionally ordered dipolar system.

2. Experiments

The solvent ethanol is purchased from Aldrich (99.5 + % purity, anhydrous) and used as received. The liquid is doped with the chromophore quinoxaline (QX, distilled) or naphthalene (NA, zone-refined) at a concentration level of 2×10^{-4} mol mol^{-1}. At the standard cooling rate $dT/dt \approx -2$ K min^{-1} of the cryostat, ethanol would crystallize instead of forming one of the phases of current interest. In order to circumvent this problem, the empty copper cell (inner volume 1 ml, heat capacity $C \approx 40$ J K^{-1}) equipped with quartz windows is mounted on the cold stage of a closed cycle He refrigerator (Leybold, RDK 10–320, RW 3) and cooled in vacuum to either 60 or 95 K. After reaching the respective target temperature, the cryostat is filled with argon gas (99.999% purity) to $p = 1$ atm, a 3 mm diameter hole at the top of the cryostat is opened and 1 ml of the room temperature liquid is injected into the cold cell using

a syringe guided by a stainless steel funnel. The state of the sample is determined by visual inspection. Injecting into the 60 K cell cools the sample quickly to near 90 K and leads to a clear and entirely transparent sample, corresponding to the supercooled liquid or glassy state. Injection into the 95 K cell generates the plastic crystal, which is moderately transparent and not entirely clear. In this latter case, the sample cools initially to approximately 115 K and then slowly to 90 K. In both procedures any motion of the liquid ceases ≈ 4 s after the injection, and the cooling rate is thus estimated as $dT/dt \approx -50$ K s^{-1}. The final temperature stability within ± 30 mK was achieved by a temperature controller (Lake Shore, LS 330) equipped with calibrated diode sensors.

An excimer laser (GAM Laser, EXC-200/100) operated at $\lambda_{ex} = 308$ nm with a repetition rate of 1 Hz and attenuated to irradiate the sample at ≈ 15 mJ/pulse served for the electronic excitation of the QX probe molecules. The emission from the triplet state is coupled into a monochromator (EG&G, 1235) and registered by an MCP intensified diode array camera (EG&G, 1455B-700-HQ) with controller (EG&G, 1471A), gating options (EG&G, 1304) and synchronization facilities (SRS, DG-535). The spectra consist of 730 channels with a resolution of 0.14 nm/channel. Because the spectral response function of the camera is practically flat over the spectral range of interest, no intensity calibration is used. Every final spectrum is obtained by averaging over the signals from 300 excitation pulses. In order to measure the Stokes shift dynamics without interference of possible probe rotation effects, the polarization angles of the excitation and detection are set to the magic angle at 54.74° [18].

With the above technique, time resolved emission spectra of QX in ethanol have been recorded for wavenumbers in the range $18\,850$ cm$^{-1} \leqslant \bar{\nu} \leqslant 23\,100$ cm^{-1}. The highest energy $S_0 \leftarrow T_1$ (0–0) transition is subject to a Gaussian fit in order to obtain the mean energy $\langle \bar{\nu} \rangle (t, T)$ and standard deviation $\sigma(t, T)$ of the optical line of interest. Following common practice [19], the solvent response is characterized by the Stokes shift correlation function $C(t)$ as derived from the time dependent average emission energy by normalizing according to

$$C(t) = \frac{\langle \bar{\nu} \rangle(t) - \langle \bar{\nu} \rangle(\infty)}{\langle \bar{\nu} \rangle(0) - \langle \bar{\nu} \rangle(\infty)}. \tag{1}$$

The total emission redshift $\Delta = \langle \bar{\nu} \rangle(0) - \langle \bar{\nu} \rangle(\infty)$ in dipolar solvation depends upon factors such as the dipole moment change $\Delta \mu$ of the chromophore and the polarity of the solvent. The chromophore NA with $\Delta \mu = 0$ is an exception to this rule because this non-polar probe displays mechanical solvation only [20, 21], i.e., time resolved solvation is associated with the shear modulus relaxation in this case [22]. The non-exponential time dependence of $C(t)$ is largely determined by the distribution of orientational relaxation times in the liquid.

3. Results

Quenching ethanol from 300 to 115 K leads to the plastic crystal state without an intermediate formation of the highly viscous liquid phase. The sample obtained this way is only moderately transparent and thus visibly distinct from the clear liquid or glassy phase and from the structural crystal. The sample is then cooled slowly to 90 K and the dynamics of solvation is measured between 95.7 and 111.4 K upon reheating in steps of 2 K. During the measurement no change in the appearance of the sample could be observed. Time and temperature dependent energies are observed within the limiting values $\langle \bar{\nu} \rangle(0) = 21\,295$ cm^{-1} and $\langle \bar{\nu} \rangle(\infty) = 20\,880$ cm^{-1}, resulting in a total red shift of $\Delta = 415$ cm^{-1}. The correlation decays $C(t)$ are well approximated by a stretched exponential or Kohlrausch–Williams–Watts behaviour,
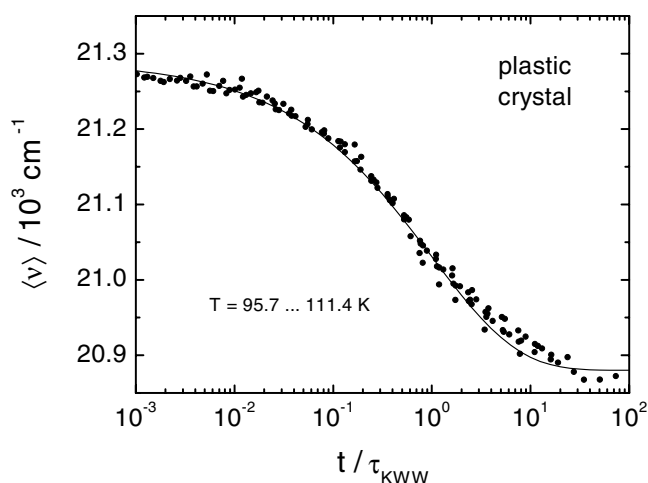
$$C(t) = \exp[-(t/\tau_{KWW})^\beta], \tag{2}$$

Figure 1. Time dependent average $S_0 \leftarrow T_1$ (0–0) energy for QX in the plastic crystal state of ethanol. Data are compiled from nine different temperatures in the range 95.7 K $\leqslant T \leqslant$ 111.4 K ($\Delta T = 2$ K), but shown in a master plot $\langle \bar{v} \rangle(t)$ versus t/τ_{KWW}. The solid curve fit is based upon the limiting values $\langle \bar{v} \rangle(0) = 21\,295$ cm^{-1} and $\langle \bar{v} \rangle(\infty) = 20\,880$ cm^{-1} and a decay following equation (2) with $\beta = 0.5$. In this range of temperatures, τ_{KWW} varies between 35 s and 1.3 ms.
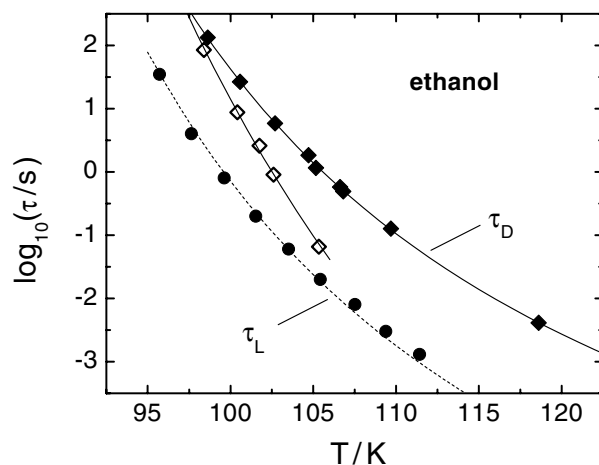

Figure 2. Characteristic relaxation times as a function of temperature in ethanol. Solid circles represent the solvation times τ_{KWW} for the plastic crystal state. Solid and open diamonds refer to dielectric relaxation times of the plastic crystal and liquid state, respectively. The dielectric data are taken from [7]. The line marked τ_D is a Vogel–Fulcher fit to the dielectric relaxation times in the plastic crystal; the line marked τ_L represents the longitudinal time constants derived from the τ_D curve.

with a temperature invariant exponent $\beta = 0.5$, but with some systematic deviations seen at long times. This is shown in figure 1 in terms of a master curve, $\langle \bar{v} \rangle(t)$ versus t/τ_{KWW}, including the fit based upon equation (2). The temperature dependence of the characteristic solvation times, τ_{KWW} (solid circles), is displayed in figure 2 along with the dielectric data for both the plastic crystal (solid diamonds) and the liquid (open diamonds) phase taken from the work of Benkhof *et al* [7]. The optical linewidth data, $\sigma(t)$, for this sample are compiled in figure 3, again using a master plot representation $\sigma(t)$ versus t/τ_{KWW}.
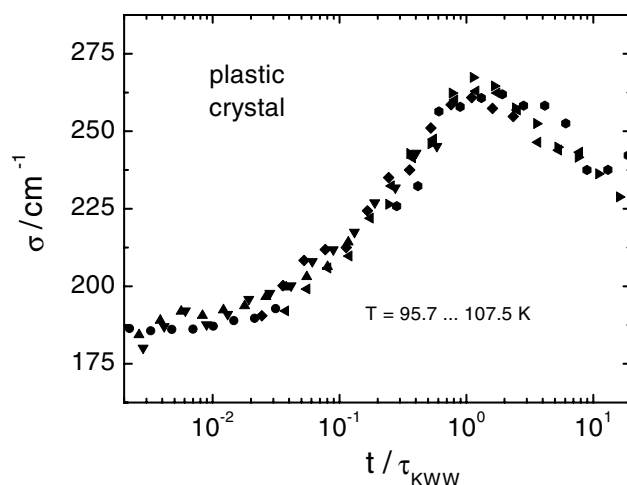
Figure 3. Time dependent linewidths of the $S_0 \leftarrow T_1$ (0–0) transition for QX in the plastic crystal state of ethanol. Data are compiled from seven different temperatures in the range 95.7 K $\leqslant T \leqslant$ 107.5 K ($\Delta T = 2$ K), but shown in a master plot $\sigma(t)$ versus t/τ_{KWW}. The observation of the $\sigma(t)$ data displaying a peak is indicative of heterogeneous dynamics in the ethanol plastic crystal.

We now turn to samples prepared by injecting the liquid into the cell precooled to 60 K, which results in a quench from 300 to 90 K, i.e., to near the glass transition temperature of the material. The samples resulting from this technique are entirely transparent after the initial quench and therefore associated with the liquid state. For this liquid phase the limiting energies $\langle\bar{\nu}\rangle(0)$ and $\langle\bar{\nu}\rangle(\infty)$ do not deviate systematically from those obtained for the plastic crystal case. Independent of the phase of ethanol, all total red shift results are represented by $\Delta = 415 \pm 20$ cm^{-1}. However, all Stokes shift correlation exponents β observed for the liquid phase, $\beta_{LQ} = 0.7$, indicate more exponential responses than those of the plastic crystal counterpart, $\beta_{PC} = 0.5$. The characteristic solvation times τ for both phases are shown in figure 4, where the dashed straight line separates the supercooled liquid data (lower left, open symbols) from the plastic crystal data (upper right, solid symbols). The liquid state data sets are both recorded upon stepwise heating, but different effective heating rates have been used. Both curves exhibit a transition into the plastic crystal phase in terms of an increase of the relaxation time by approximately two orders of magnitude, which is accompanied by a loss of the sample's transparency. That these transformations are irreversible is demonstrated by the $\tau(T)$ trace observed upon cooling (solid triangles). The solitary hexagonal symbol represents the relaxation time $\tau = 1$ s of a liquid sample before and after a 27 h waiting period at a constant temperature of 91.1 K.

All of the above mentioned results refer to dipolar solvation using QX as the probe molecule, which is subject to electrostatic coupling to the dipolar reorientation in the solvent. Additionally, the non-polar probe NA has been used in order to assess possible differences in the mechanical solvation response amplitudes of the two phases of ethanol, exploiting the absence of any coupling of the NA emission to dipolar reorientation. For both the plastic crystal and the supercooled liquid phase, the respective total red shifts of the NA emissions are very small, $\Delta = 24 \pm 3$ and 23 ± 3 cm^{-1}, with no indication of a significant difference. The average mechanical response times observed with the probe NA in the plastic crystal and supercooled liquid phase reflect the ratio of approximately 100 seen already for the orientational timescales of the dipolar solvation results obtained with QX.
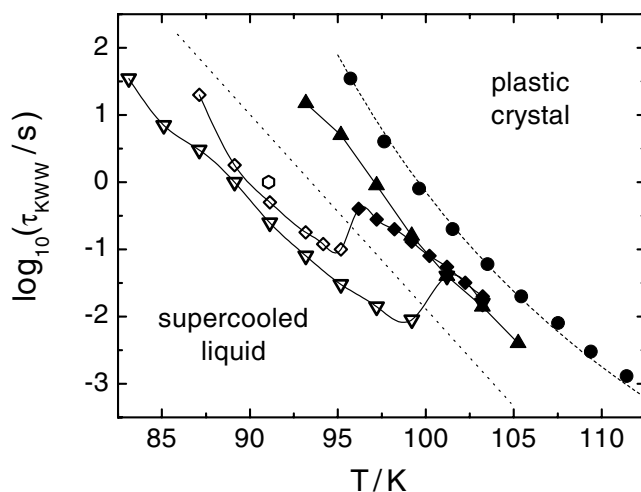
Figure 4. Temperature dependent solvation correlation times $\tau_{KWW}(T)$ in ethanol for the plastic crystal (solid symbols) and the liquid state (open symbols). The triangles pointing down and the diamonds are obtained upon stepwise heating a freshly quenched sample at the respective average rates of 40 and 10 mK min^{-1}. Triangles pointing up are obtained upon cooling the sample directly after recording the other triangles. The solitary hexagon represents $\tau = 1$ s and $T = 91.1$ K, where the liquid state persisted for a 27 h waiting period. The dotted straight line is a schematic separation of the two phases of ethanol in the τ–T-plane. Solid circles are for the annealed plastic crystal sample as in figure 2.

4. Discussion

Molecules forming the plastic crystalline phase are those with an aspect ratio not far away from unity so that reorientation can be accomplished without requiring significant translational displacements. In the present context, the important feature of this phase is the mobility and disorder regarding the molecular orientation in a system with long range positional order. With respect to improving our understanding of the dynamics in disordered materials, plastic crystals are ideal candidates for assessing the contribution of translational displacements to the complex dynamics of liquids and supercooled liquids. Ethanol is a particularly attractive example because both the plastic crystal and the supercooled liquid phase can be realized and compared. This has been exploited in dielectric studies of ethanol by Benkhof *et al* [7] and Brand *et al* [6], both demonstrating that the temperature dependences of the dielectric relaxation times τ_D differ for the two phases, but the $\tau_D(T)$ traces merge at $\tau_D \approx 500$ s to yield a common T_g. The $\tau_D(T)$ results of Benkhof *et al* [7] are shown by the diamonds in figure 2. In order to circumvent crystallization, a cooling rate of -50 K min^{-1} has been applied to enter the supercooled liquid state, followed by a slow (10 h) isothermal transformation into the plastic crystal at $T = 105$ K [7].

Of the two present cooling techniques, the injection into the cell that quenches to approximately 115 K and then cools much more slowly is more similar to what has been used in the above mentioned dielectric study. The Stokes shift correlation times $\tau_{KWW}(T)$ obtained for this sample are compared with the dielectric results $\tau_D(T)$ in figure 2. Although slope and curvature for the solvation and dielectric times in the plastic crystal are similar, the absolute values of τ are offset by as much as ≈ 1.8 decades. In a previous comparison of dielectric relaxation and solvation dynamics for the same solute, QX, but in a different supercooled liquid, 2-methyltetrahydrofuran (MTHF), the respective time constants were very similar [10, 23]. A quantitative comparison of the different correlation times requires solvation theories which

establish a link between the timescales [8, 9]. For supercooled liquids, a quantitatively adequate prediction of the Stokes shift correlation function $C(t)$ on the basis of dielectric data $\varepsilon^*(\omega)$ is not available. However, identifying the separate roles of solvent rotation and translation has been the subject of several theoretical solvation studies [24–28]. For dipolar solvation, the work of Chandra and Bagchi [26] suggests that the absence of translational motion shifts the time constant of the solvent response towards the longitudinal timescale τ_L. For a Debye type (exponential) dielectric relaxation, τ_L and τ_D are related by $\tau_L = \tau_D \varepsilon_\infty / \varepsilon_s$, where ε_∞ and ε_s are the dielectric permittivities in the limits of high and low frequencies, respectively. For the present case of a non-exponential dielectric relaxation, however, τ_L is largely determined by the correlation time of the dielectric modulus $M(t)$, whose frequency domain analogue is related to the dielectric function via $M^*(\omega) = 1/\varepsilon^*(\omega)$. Accordingly, the reciprocal of the empirical fit to the dielectric data supplied by Benkhof *et al* [7] was numerically transformed to the time domain and τ_L was determined as the '1/e'-time of the resulting $M(t)$ traces. In this manner, values for τ_L have been inferred from the dielectric data of the ethanol plastic crystal and are included as a dotted line in figure 2. The coincidence of the observed solvation times in the plastic crystal with the longitudinal timescale supports the above prediction for the solvation dynamics in the absence of translational degrees of freedom on a qualitative level. Of course, the degree to which solvent translation is suppressed in the immediate vicinity of the probe molecule QX will depend on how the probe is embedded in the crystal structure, and some distortion originating from structural incompatibility is expected. On the other hand, it is unlikely that such an impurity gives rise to significant translational motion in an otherwise positionally ordered material.

The above discussion has referred to the time dependence of the average emission energy and its sensitivity to the solvent response, irrespective of the linewidths σ. The results for $\sigma(t)$ in figure 3 show that the optical linewidth does not remain constant during the solvation process. Instead, the observations indicate a peak in $\sigma(t)$ for the plastic crystal phase of ethanol. Following previous experimental [29–31] as well as theoretical [32–34] scrutinies of linewidth peaks, a maximum in $\sigma(t)$ is indicative of the heterogeneous nature regarding the underlying dynamics. Note that approaches based upon homogeneous dynamics do not explain such a maximum in the time resolved linewidth [35, 36]. In qualitative terms, it is the spatial distribution of response times which allows some solute molecules to shift the emission energy much faster than others, thereby giving rise to broader optical lines at intermediate times. Because triplet quenching by efficient oxygen diffusion prevents the observation of the steady state limit $\sigma(t \rightarrow \infty)$ for the present samples, a quantitative analysis of the $\sigma(t)$ data in figure 3 is bound to remain ambiguous. However, the excess linewidth originating from heterogenity can be calculated on the basis of the total red-shift $\Delta = 415 \text{ cm}^{-1}$ and the stretching exponent $\beta = 0.5$ of the associated $C(t)$ curves using [32]

$$\sigma_{\text{het}}^2(t) = \sigma_\infty^2 + (\sigma_0^2 - \sigma_\infty^2)C(2t) + \Delta^2[C(2t) - C^2(t)]. \tag{3}$$

For $\sigma(0) = \sigma_0 = 175 \text{ cm}^{-1}$ and an estimated $\sigma(\infty) = \sigma_\infty = 235 \text{ cm}^{-1}$, the peak height should reach a value of 261 cm^{-1}, i.e., close to $\sigma_{\text{max}} = 265 \text{ cm}^{-1}$ observed in figure 3. We conclude that the solvation of QX in plastic crystalline ethanol is subject to heterogeneous dynamics, where the solvent response time is a spatially varying quantity [14, 15].

In order to compare the dynamics of solvation in the plastic crystal with that of the liquid phase, ethanol had to be quenched from room temperature to 90 K (near T_g) by injecting the liquid into a cell that was precooled to 60 K. In contrast to the plastic crystal state, the sample obtained with this -50 K s^{-1} quench is entirely transparent and thus associated with the supercooled liquid state. The red-shift $\Delta = 415 \pm 20 \text{ cm}^{-1}$ in the liquid is practically that of the plastic crystal case and represents a typical value for QX in supercooled

alcohols [37, 38]. The observation of similar red-shifts for the two phases implies that the translational contribution to the steady state solvation free energy is small compared with the rotational effects. In a recent simulation study, Milischuk and Matyushov [25] have shown that the relative contributions of translation and rotation depend strongly on the solvent polarity. For the present case of ethanol, this study predicts that only approximately 14% of the steady state shift Δ originates from translational motion.

In a non-polar solvation experiment using the probe NA, purely orientational motion of solvent dipoles does not contribute towards the solvation process [21]. Here, it is the excitation induced change in solute size which initiates a purely 'mechanical' solvent response [20, 22]. In this situation, translational aspects of the dynamics become important and one would thus expect the plastic crystal state to display a smaller response amplitude Δ compared with the liquid. However, the total red-shifts for both phases are found to be in the range $\Delta \approx 20$–25 cm^{-1}. Therefore, apart from the smaller amplitude Δ typical of non-polar solvation, the dipolar (QX) and non-polar (NA) probes experience the same differences regarding solvation in the plastic crystal and liquid state of ethanol.

The $C(t)$ curves measured for liquid ethanol are somewhat more exponential than those of the plastic crystal counterpart, $\beta_{LQ} = 0.7$ versus $\beta_{PC} = 0.5$. The relaxation timescales derived from the solvation experiment are compiled in figure 4. The solvation times in the liquid are measured upon heating the freshly quenched sample, which leads to an irreversible transition into the plastic crystal state at $T = 95$ or 99 K, depending on the effective heating rate. The transitions from open to solid symbols in figure 4 are accompanied by a change in the appearance of the sample from clear to moderately opaque. Measuring $\tau(T)$ from $T > 102$ K downward traces the relaxation time in the plastic crystal state. Unlike the dielectric results [6, 7], the temperature dependent solvation times in the two phases display similar slopes, but the relaxation times are offset by a factor of ≈ 100. A further unexpected observation is that the $\tau(T)$ data for the plastic crystal state formed from the supercooled liquid do not coincide with the results of figure 2 obtained for the annealed plastic crystal. Moreover, samples that were quenched directly into the glassy state always crystallized at $T > 105$ K, whereas the annealed plastic crystal remained stable up to $T = 112$ K. A possible explanation is the formation of a lower density sample by the fast quench to 90 K, with accordingly shorter relaxation times and with the tendency to crystallize before a denser disordered state is achieved. Because the present cooling technique does not allow for a systematic variation of the cooling rate, the above explanation cannot be tested and the solvation and dielectric results for supercooled ethanol are not directly comparable. As noted above, the solvation dynamics results for the sample which converts from the liquid to the plastic crystal phase may refer to the specific preparation technique using cooling rates estimated to be as high as -50 K s^{-1}. Nonetheless, the change in solvent response accompanying the transition indicates a substantial change in the dynamics in the vicinity of the probe molecules. From the solvation correlation times $\tau_{KWW}(T)$ obtained for the liquid and plastic crystal state the respective glass transition temperatures $T_g = 85$ and 92 K are extrapolated using the criterion $\tau_{KWW}(T_g) = 100$ s.

5. Summary and conclusions

The dynamics of ethanol has been studied in the regime of slow relaxations for the plastic crystalline and supercooled liquid phase using triplet state solvation dynamics techniques. It is found that the solvent response is slowed down significantly in the plastic crystal relative to the supercooled liquid state, a result that is qualitatively similar to previous observations based upon dielectric relaxation techniques. Time resolved optical linewidth data collected for plastic crystalline ethanol indicate dynamic heterogeneity in this positionally ordered state

of ethanol, i.e., the timescale of molecular reorientation is a spatially varying quantity. The solvent response times in the plastic crystal state coincide with the longitudinal dielectric relaxation times, which provides a hint towards the absence of translational solvent motion. On the other hand, the steady state data in terms of the response amplitude Δ for dipolar and mechanical solvation are the same in the two states, plastic crystal and supercooled liquid. Two explanations for these results can be offered: translational motion provides only a minor unresolved contribution to the steady state free energy of solvation, or alternatively the amplitudes of the relevant translational fluctuations in the plastic crystal are similar to those in the supercooled liquid. The latter notion implies relatively shallow potentials for the molecular positions in the plastic crystal state instead of assuming that the centres of mass are truly locked in a regular lattice structure. A more detailed investigation of the dynamics of solvation requires a simultaneous measurement of the dielectric relaxation data as a reference. Nonetheless, this study provides first steps towards an experimental assessment of the translational contributions to solvation processes.

Acknowledgments

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