Comparison of the structural and orientational glass-transition dynamics in ethanol

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The dynamics of glass-forming liquids has been extensively studied during recent years from both the theoretical and experimental points of view. The dominant dynamical process governing the behavior of a glass-forming material is referred to as the $\alpha$ relaxation, and is identified as a structural relaxation. From an experimental point of view, the $\alpha$ relaxation displays some universal features: a departure from Debye-like behavior and a rapid increase in the relaxation time with decreasing temperature. The relaxation times of the two phases are very close and appear to cross at 96 K, the temperature corresponding both to the structural glass transition of the supercooled liquid and to the orientational glass transition of the rotator phase. Above 96 K, the relaxation time of the supercooled liquid decreases faster than that of the rotator phase, presumably due to the liberation of additional translational degrees of freedom in the former. The dielectric results, coupled with recent specific-heat measurements of the two phases, suggest that the rotational degrees of freedom provide the dominant contribution to structural relaxation near the glass transition, while flow processes provide a smaller contribution.

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It has been known for two decades that ethanol ($\text{C}_2\text{H}_5\text{OH}$) exhibits interesting phase polymorphism, and appears to be quite unique in that it can be made to assume a variety of phases simply by varying the temperature in a controlled manner. The fully disordered liquid phase transforms into a structural glass (SG) upon rapid cooling. The orientationally disordered crystalline phase transforms from a rotator phase (RP) to an orientational glass (OG) upon cooling at a moderate rate. Finally, the stable, orientationally ordered crystal is produced either by very slow cooling of the liquid or by annealing the RP or supercooled liquid. Recent x-ray, neutron-diffraction, and Raman-spectroscopic studies have confirmed the existence of an orientational glasslike transition in the RP crystal at nearly the same temperature ($T_g = 97$ K) observed for the supercooled liquid-tostructural glass transition. The close similarity of high-frequency dynamical behavior in the orientational-glass and structural-glass phases has been established by neutron time-of-flight spectroscopy and low-temperature specific-heat measurements. These properties, combined with the fact that the RP crystal can be readily prepared from the structural glass, suggest that ethanol provides a unique opportunity to investigate and compare the relaxation dynamics of both phases near their respective glass transitions. Such a comparison may help to clarify the role of translational and rotational degrees of freedom in the dynamical response of a material approaching the glass transition.

We have measured the complex dielectric susceptibility ($\varepsilon = \varepsilon' + i\varepsilon''$) of the supercooled-liquid and rotator-crystal
phases of ethanol near their respective glass transitions. We find that the dielectric relaxation in both the supercooled-liquid (SCL) and RP crystal is nonexponential, and that parameters characterizing the relaxation (e.g., degree of non-Debyeness and average relaxation time) can be approximated using a Cole-Davidson fitting function. For a given temperature, comparison of the dielectric response in each phase indicates a steeper temperature dependence of the average relaxation time in the SCL relative to that of the RP crystal, and the relaxation times of both phases are nearly equal at $T = 96 \text{ K}$.

Preparing ethanol in the supercooled-liquid and rotator-crystal phase follows an established protocol. Rapid cooling of the liquid at a rate greater than 6 K/min bypasses crystallization at $T_M = 159 \text{ K}$, and allows entry into the supercooled-liquid regime. Continuing to cool at the prescribed rate leads to the structural-glass transition at $T_g = 97 \text{ K}$. The RP crystal (body-centered-cubic, lattice constant $a = 5.37 \text{ Å}$) is then formed by warming and annealing in the temperature range 102–110 K. The exact temperature and annealing time required for conversion to the RP crystal depends on the warming rate, as well as the initial cooling rate into the glassy state.

Measurement of the frequency- and temperature-dependent complex dielectric susceptibility was carried out using a sealed coaxial capacitor identical in design to that used in our previous work. Two different measurement schemes were employed depending on the frequency range under consideration. In the range 1 mHz to 10 kHz, the in-phase and out-of-phase currents through the capacitor were measured using a Stanford SR850 Dual Phase Lock-in Amplifier in conjunction with a Stanford SR570 Current-to-Voltage Amplifier. For frequencies of 1 kHz to 10 MHz, a Hewlett-Packard 4192A Impedance Analyzer was used in a standard four-terminal pair configuration to measure the capacitance and conductance of the sample. Data obtained from the two methods are in excellent agreement where they overlap.

Sample material consisted of 200-proof, dehydrated ethyl alcohol (ethanol) obtained from Quantum Chemical Company of Tuscola, Illinois. To avoid contamination with water vapor, filling of the capacitor was carried out at room temperature in a dry-nitrogen atmosphere. The sample cell was then frozen, evacuated of remaining nitrogen gas, and sealed. The sample cell was then mounted inside a nested cryocan assembly described elsewhere. Finally, the entire cryocan assembly was immersed in a double-walled glass Dewar. This design provided control of the sample temperature to within 0.05 K over the range 4–300 K, and minimized the occurrence of temperature gradients across the sample.

Figures 1(a) and 1(b) show our data for the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric susceptibility for the supercooled liquid as a function of frequency for temperatures of 96, 98, and 100 K. Figures 2(a) and 2(b) show the corresponding data taken in the RP crystal at temperatures of 96, 98, 100, 102, 104, 106, 108, and 110 K. Although the glass-transition temperature is usually quoted as $T_g = 97 \text{ K}$, we emphasize that all our data are taken in the metastable equilibrium SCL and RP, respectively. The data at 96 K, in particular, were observed not to change over more than 1 h, indicating that no structural relaxation was taking place. Obtaining data over a broad temperature range in the SCL phase was hindered by the fact that time-dependent transitions to the RP crystal occur above 102 K. Thus, in order to broaden the range of liquid-phase data, additional measurements were
made in the temperature range 164–181 K. Figures 3(a) and 3(b) show the high-temperature liquid-phase data, where the contribution of dc conductivity to the response at low frequencies is readily apparent.

The solid lines passing through the data in Figs. 1–3 are fits to the Cole-Davidson fitting form given by

\[ \varepsilon^\prime(\omega) = \varepsilon_{\infty} + \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 - i\omega/\omega_p^{CD})^\alpha}, \]

where \( \omega = 2\pi f \). It is well known that fitting relaxation data with empirical forms such as the Cole-Davidson or Kohlraush-Williams-Watts function does not accurately describe the relaxation at all frequencies. In particular, at frequencies higher than two decades or so above the peak, the data typically obey a shallow power-law dependence extending to very high frequency. Nevertheless, the Cole-Davidson form can be used in the main peak region to provide estimates of parameters characterizing the dynamical response such as the mean relaxation time \( \tau \approx 1/\omega_p^{CD} \), and \( \alpha \), the degree of departure from a Debye-governed relaxation process \( (\alpha = 1) \).

Figure 4 shows the temperature dependence of the width parameter \( \alpha \) for both the SCL and RP crystal. Both phases display a characteristic feature common to many glass-forming materials, namely, a decrease of \( \alpha \) with temperature indicating deviation from idealized Debye behavior.

\[ \tau = \tau_0 \exp\left[\frac{A}{(T - T_0)}\right]. \]

Here, \( \tau_0 \) is an attempt time and \( T_0 \) is the Vogel temperature at which the relaxation time diverges. Results of the VTF

FIG. 3. (a) \( \varepsilon^\prime \) and (b) \( \varepsilon^\prime\prime \) vs frequency for temperatures of 164 ( ), 173 ( ), and 181 K ( ) in the liquid phase of ethanol. Solid lines are fits to the Cole-Davidson function plus a term of the form \( \sigma_{dc}/\omega \) in \( \varepsilon^\prime\prime \) due to dc conductivity.

FIG. 4. Plot of the Cole-Davidson exponent \( \alpha \) vs temperature for both the supercooled-liquid ( ) and rotator-crystal ( ) phases. Both phases exhibit increasingly non-Debye behavior as the glass transition is approached, a common characteristic of many glass-forming materials.

FIG. 5. The mean relaxation time \( \tau \) vs inverse temperature for the liquid and supercooled-liquid ( ) and rotator-crystal ( ) phases of ethanol. The relaxation times cross at 96 K, near the glass-transition temperature.
increase in the specific heat of approximately 31 J mol\(^{-1}\) K\(^{-1}\). Presumably the extra 9 J mol\(^{-1}\) K\(^{-1}\) in the SCL specific heat not present in the RP crystal corresponds to translational degrees of freedom. These results suggest that the rotational degrees of freedom are the dominant contributor to structural relaxation processes near the glass transition in both the RP crystal and SCL, and that flow processes such as mass diffusion associated with translational degrees of freedom in the SCL contribute to a lesser extent.

In conclusion, we have used dielectric spectroscopy to compare the dynamical response of the SCL and RP crystal phases of ethanol. We find that the orientational-glass transition in RP crystal exhibits all the characteristics observed in the structural-glass transition: an increasingly non-Debye relaxation and faster-than-Arrhenius behavior in the relaxation time as the glass transition is approached. Comparison of the relaxation time behavior above 96 K displays the effect of the additional translational freedom available to the liquid resulting in faster molecular reorientation in the SCL relative to the RP crystal for a given temperature. The dielectric data indicate that rotational motion is the dominant dynamical process governing the glass transition in both SCL and RP crystal ethanol. Thus, the construction of a minimal model utilizing restricted degrees of freedom now appears relevant to the behavior of real materials. A model such as that explored by Renner, Lowen, and Barrat\(^{15}\) involving hard needles on an fcc lattice, should be simple enough to allow a detailed numerical and analytical treatment.

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10 A typographical error in Ref. 5 giving \(T_m\) as 169 K has been propagated in some papers, e.g., Refs. 6 and 7.