Connecting thermodynamics and dynamics in a supercooled liquid: Cresolphthalein-dimethylether

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A B S T R A C T

We have measured adiabatic calorimetry as well as dielectric relaxation spectroscopy in the linear and non-linear response regime of viscous cresolphthalein-dimethylether. On the basis of the Adam-Gibbs model, the experimental results facilitate the comparison of temperature versus field induced changes in entropy and of their impacts on the dielectric relaxation times. Across six decades of the structural relaxation times, the Adam-Gibbs model provides a good account of the temperature dependence of the dynamics, while a comparable amount of field induced total entropy change leads to a four-times smaller effect regarding the change of time constants. For this material, only a small fraction of the total entropy change that originates from strongly polarizing the sample appears to be relevant for the dynamics in the sense of Adam-Gibbs.

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1. Introduction

Numerous studies aim at understanding the dynamics of glass forming materials, but the origin of the super-Arrhenius temperature dependence of most supercooled liquids is yet to be determined [1]. Empirically, the primary structural relaxation time (τ_α) can be described by the Vogel-Fulcher-Tammann (VFT) relation [2–4],

$$\log\left(\tau_\alpha/s\right) = A + \frac{B}{T - T_0}.$$ (1)

This VFT behavior reflects an increasing activation energy as the temperature approaches the glass transition temperature (T_g) from above, because it extrapolates to a divergence of time constants at a finite temperature $T_0 > 0$. There are numerous indications of a link between relaxation time scales and thermodynamic quantities, with the correlation of dynamic to thermodynamic fragility being one example [5,6]. A prominent and extensively scrutinized approach to super-Arrhenius behavior is based on the considerable reduction of configurational entropy, $S_{cfg}(T)$, as the temperature is lowered towards T_g [7].

The relation connecting dynamics to entropy has been quantified by Adam and Gibbs (AG) [8],

$$\log_{10}\left(\tau_\alpha/s\right) = A + \frac{s_c^* \Delta\mu}{k_B T \times S_{cfg}(T)} \approx A + \frac{C}{T \times S_{exc}(T)}.$$ (2)

where s_c^* represents the critical entropy (usually assumed to be $k_B \ln 2$) and with Δm being the energy barrier associated with the cooperative rearrangement of a region (CRR). The values of s_c^*, $\Delta\mu$, and C, are assumed temperature invariant. Because configurational entropy can not be measured directly, testing the AG relation is based upon the excess entropy, S_{exc}, i.e., the entropy of the liquid that is in excess to that of the crystal. In that case, the constant $C = s_c^* \Delta\mu/(k_B f_S)$ is treated as temperature invariant adjustable parameter, with the ratio $f_S = S_{cfg}/S_{exc}$ representing the configurational fraction of the total excess entropy [9]. Measurements of $S_{exc}(T)$ can often be fit by $S_{exc}(T) = S_\infty\left(1 - T_K/T\right)$, which recovers the VFT relation if inserted into Eq. (2). In many cases, the Kauzmann temperature T_K, where $S_{exc}(T_K) = 0$, coincides with the Vogel temperature T_0, suggesting a connection between the disappearance of excess entropy and the divergence of structural relaxation times [10]. Although the assumptions of the AG approach are far from trivial [11], the relation between $\tau\alpha(T)$ and $S(T)$ implied in Eq. (2) has been verified by experimental data [12–17] and by simulation results [18–21]. Of particular interest is obtaining the sizes of CRR's via an AG analysis for both molecular [22,23] and polymeric [24] systems.

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Common to the above assessment of the role of entropy for the structural relaxation time is that entropy is modified by varying the temperature (or pressure). Here, we address the effect of tuning entropy by an electric field under isothermal conditions and ask whether the Adam-Gibbs model is equally applicable to this situation. The idea has been proposed by Johari [25], recognizing that the change of entropy of a liquid induced by an external electric field E should modify its transport properties by virtue of the AG relation. For the compound studied in this work, cresolphthalein-dimethylether, we find that temperature and field induced entropy change affect dynamics only in a qualitatively similar way. The AG approach provides a quantitatively satisfactory description only if the ratio f_S is allowed to differ considerably between the cases of changing entropy by temperature or by field. This may reflect that the fact that the high field leads to an anisotropic sample, structurally somewhat different from the usual liquid state that remains isotropic during temperature or pressure changes.

2. Experiment

The compound used for this study is cresolphthalein-dimethylether (CPDE, sometimes referred to as KDE). The material has been synthesized and purified by distillation and recrystallization in the group of H. Sillescu, Mainz, Germany.

2.1. Adiabatic calorimetry and DSC

The crystalline CPDE powder was dried under vacuum at 300 K for ca. 1 h. Then the sample of 0.5622 g (0.001502 mol) was loaded into the copper cell with helium gas which facilitates thermal equilibration inside the cell. The heat capacity measurements were performed with an in-house built adiabatic calorimeter [26] in the temperature range from 5 K to 375 K. The measurement was carried out using a standard intermittent heating method, i.e., repetition of equilibration and energizing intervals. The temperature increment for each measurement was 0.3 K around 5 K and increased with increasing temperature to reach 2.5 K at 200 K. The temperature increment was reduced to smaller than 1 K at around a thermal anomaly (e.g., glass transition). The resolution of the temperature measurement (with a Rh-Fe resistance thermometer) is ca. 100 μK and the heat leakage at adiabatic conditions is smaller than 3 μJ s^{-1}. The accuracy of the heat capacity measurement was better than 1% at $T < 10$ K, 0.5% at 10 K $< T < 30$ K, and 0.1% at $T > 30$ K.

The fusion ($T_{fus} = 383$ K) of CPDE could not be measured by the present calorimeter since its highest reachable temperature is 380 K. Hence, the liquid state was prepared outside of the calorimeter after the measurement of the crystalline state; the sample was heated up to 420 K ($>T_{fus}$) and cooled rapidly (ca. 100 K min^{-1}) down to 300 K ($<T_g$). The glassy sample was set back to the calorimeter and the heat capacities of glassy and liquid CPDE were measured from 5 K to 375 K. The fusion of CPDE was measured by a differential scanning calorimeter, Perkin Elmer DSC7, which was calibrated with indium ($T_{fus} = 429.8$ K) just before the measurement. Three sample pans (sample masses: 5.87 mg, 6.55 mg, 6.29 mg) were prepared and each pan was measured two or three times to reduce the statistical error. The heating rate of the DSC measurement was 10 K min^{-1}.

2.2. Dielectric relaxation

Standard low field impedance experiments are performed for frequencies $\nu = \omega/2\pi$ from 30 mHz to 1 MHz using a system based upon a Solartron SI-1260 gain/phase analyzer and a Mestec DM-1360 transimpedance amplifier. An Invar steel/sapphire cell described earlier [27] is used to measure the static dielectric constant, ε_s, versus temperature. For all measurements, i.e., both low

and high field cases, the instrumentation is calibrated using low loss (tan$\delta < 10^{-4}$) capacitors whose capacitances are determined with an Andeen-Hagerling AH-2700 ultra-precision capacitance bridge. Temperature control of the cell is achieved with a nitrogen gas cryostat and Novocontrol Quatro controller for all dielectric experiments.

For the high field impedance experiments, the capacitor cell consists of two polished stainless steel disks (17 and 20 mm $\oslash$), separated by a very small amount of glass beads (10–30 μm, Polysciences Inc.) added to the liquid sample. The voltage output of the SI-1260 analyzer is enhanced using a Trek PZD-700 voltage amplifier. The current is determined from the voltage drop across a shunt RC-network, which is connected to the analyzer via a voltage follower which protects the instruments against sample failures (dielectric breakdown). Details of this setup that measures steady state dielectric relaxation data under a high dc-bias field for frequencies between 1 Hz and 50 kHz are described elsewhere [28].

For measuring the high field effects in a time-resolved fashion, the applied voltage is derived from the arbitrary waveform function generator (Stanford Research Systems DS-345). The generator output is amplified by a factor of 200 using a Trek PZD-700 high-voltage amplifier. The waveform consists of an integer number of periods of a voltage signal, $V(t) = V_0 \sin(\omega t)$, with a bias voltage of magnitude V_B superposed for some intermediate periods. The signal sequence consists of a total of 320 periods: 80 periods without bias, 160 periods with positive or negative high bias field, followed by another 80 periods without bias field. A voltage ratio of $V_B/V_0 = 4$ is used. The waveform is repeated once every second, ensuring that the voltage is zero for times much longer than the duration of the waveform signal. With the phase of the harmonic signal unchanged, the experiment is repeated for positive and negative bias, and the average of the two is determined in order to eliminate the effect of the direct polarization response to the high field step. The signal frequencies used in this method span the range of 500 Hz $\leq \nu \leq$ 4 kHz. Voltage and current (using a 3000 Ω shunt) are recorded with a digitizing oscilloscope (Nicolet Sigma 100) with 10^6 points along the time axis and $\geq$12 bit vertical resolution. All results are averages over 5000 waveform repetitions. The resulting two signals, voltage $V(t)$ and current $I(t)$, are subject to period-by-period Fourier analysis, which allows us to determine the 'permittivity' for each of the 320 periods. Further details of this technique are described elsewhere [28,29].

3. Results

The heat capacities of liquid/glassy and crystalline CPDE measured in the range from 5 to 375 K are depicted in Fig. 1. The calorimetric results associated with the melting transition are $T_{fus} = 383.2 \pm 0.1$ K, $\Delta H_{fus} = 27.9 \pm 0.1$ kJ mol^{-1}, and $\Delta S_{fus} = 72.7 \pm 0.3$ J K^{-1} mol^{-1}. From these values, the excess entropy has been determined as a function of temperature using

$$S_{exc}(T) = \Delta_{fus}S + \int_{T_{fus}}^{T} \frac{C_p^{liquid}(T') - C_p^{crystal}(T')}{T'} dT', \qquad (3)$$

and the results in the vicinity of the glass transition temperature ($T_g = 314.3$ K, where $\tau_{max}(T_g) = 100$ s) are shown in Fig. 2. For the equilibrium liquid, i.e., for $T > T_g$, the observed $S_{exc}(T)$ values are represented with high fidelity by $S_{exc}(T) = S_\infty \left(1 - T_K/T\right)$ with $S_\infty = 181.0$ J K^{-1} mol^{-1} and $T_K = 255.9$ K.

We follow common practice and assess the relation between entropy and dynamics using an Adam-Gibbs plot, $\log(\tau_{max})$ vs $1/(TS_{exc})$, based upon the broadband dielectric relaxation data reported by Stickel [30]. These values of $\tau_{max} = 1/(2\pi\nu_{max})$ are derived from the peak frequencies, ν_{max}, of the dielectric loss spectra and for $T < 370$ K the temperature dependence of τ_{max} is