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On the non-exponential versus non-Arrhenius behaviour of the structural relaxation in glass-forming liquids

L M Torell, L Börjesson and M Elmroth

Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

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Abstract. The various routes by which a liquid may form a glass have recently been related to the structural properties of the glass, at one extreme represented by network glasses of strong covalent bondings and at the other by typical non-network systems of weak van der Waals or Coulomb bonding types. We examine the success of such an approach by comparing data on structural relaxations in glass-forming liquids chosen to cover a wide range of behaviour from non-network ionic and molecular systems to a network forming oxide glass. We also include data of a glass-forming polymeric system. While there seems to be a strong correlation between increasing fragility (i.e. decreasing temperature and resistance in the medium-range order) and increasing departure from Arrhenius behaviour of the relaxation time, there is no simple relation between the degree of fragility and non-exponentiality as has been suggested.

1. Introduction

Most liquids can be supercooled below their equilibrium melting points and solidified to glass provided that the cooling rate is fast enough to avoid crystallization. The most significant features on approaching the glass transition are the rapid increase in the viscosity and the slowing down of the structural relaxation process. The relaxation of different glass-forming liquids shows several common features which seem to be independent of the microscopic interactions in the liquid. These are for example a cooling-rate-dependent glass transition temperature T_g , a non-Arrhenius temperature dependence of the relaxation time τ and a non-exponential time decay. The latter is often expressed with the KWW relaxation function

$$\varphi(t) = \varphi \exp[-(t/\tau)^\beta] \quad (1)$$

where $0 < \beta \leq 1$.

Although there are similarities in the relaxation properties of different glass-forming materials, there are significant differences. The different structural relaxation characteristics have recently been used for a classification scheme in which the dynamics of the supercooled liquid state are related to structural properties of the glassy state [1]. The classification is based on the observation that systems of similar abilities to form intermediate-range order present similar patterns for the temperature dependence of

the structural relaxation time, at one extreme represented by the structurally 'strong' network forming glasses, and at the other by typical non-network systems classified as 'fragile'. Strong glass formers, i.e. various network formers such as silicates, are characterized by low coordination numbers and only a small change in heat capacity at the glass transition. They show an almost Arrhenius temperature dependence of the average structural relaxation time $\langle\tau\rangle$ and a narrow time distribution. At the other extreme the so-called fragile liquids demonstrate the opposite behaviour. These materials have generally larger coordination numbers, which fluctuate from ion to ion (or from molecule to molecule), and there is no network structure. Examples are simple molecular and ionic liquids. Large heat capacity changes at the glass transition reflect the 'disorder' of the fragile systems, which can be attributed to the multiplicity of configurations of the ground states. Non-network glass formers show a non-Arrhenius temperature dependence of $\langle\tau\rangle$, which can roughly be characterized by two different activation energies E_A representing the high- and low-temperature behaviours, respectively. The crossover between the two regimes seems to occur at smaller $\langle\tau\rangle$ -values (lower viscosity) for increasing fragility. It may, however, not only be the temperature dependence of $\langle\tau\rangle$ which changes at the crossover. We have previously reported from light-scattering studies of various ionic melts that the broad distribution of relaxation times (non-exponential decay), which characterizes the low-temperature high- E_A region, sharpens to become a single-exponential decay in the high-temperature low- E_A region [2–6].

In the present work we investigate a molecular glass and an ionic glass of similar fragilities to see whether fragile liquids in general show similar relaxation behaviours or whether materials of different microscopic interactions exhibit different relaxation properties. We present new results on the structural and reorientational relaxation characteristics of the fragile molecular glass former propylene carbonate (PC) obtained with Brillouin and depolarized Rayleigh scattering. We make use of a wide-frequency-window Brillouin spectrometer and a new analysing technique which allows investigation of the relaxation properties over wide frequency and temperature ranges. The results are compared with those previously reported for an ionic glass former of similar fragility, namely $2\text{Ca}(\text{NO}_3)_2\text{-3KNO}_3$ [2]. Comparisons will also be made with other systems investigated in this laboratory, namely another fragile ionic glass former $\text{Ca}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$ [4], a weak network-forming system ZnCl_2 [5], a strong oxide glass B_2O_3 [6, 7] and a polymeric system poly(propylene glycol) (PPG) [8].

2. Brillouin scattering technique

We briefly summarize the novel technique that we have employed for the Brillouin scattering experiment of PC. The experimental approach used in the studies of the other materials has been described previously [2–4, 8].

The present technique makes it possible to study the relaxation characteristics over relatively large temperature and frequency ranges. For the frequency resolution we have taken advantage of a Sandercock tandem Fabry–Pérot interferometer [9] which provides a unique combination of a wide frequency window and a high resolution and is thus ideal for Brillouin studies of the liquid–glass transition. The obtained spectra are well resolved, undistorted by neighbouring interference orders and of such high quality that they can be used for a detailed comparison with theories. Therefore, a new analysing procedure has been developed in which the dynamic structure factor $S(Q, \omega)$ of a general

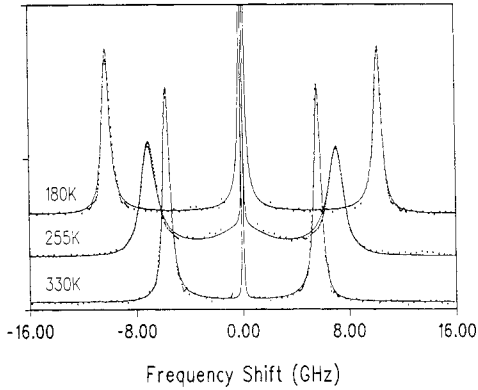


Figure 1. Brillouin spectra of PC taken at temperatures corresponding to $\omega\tau \gg 1$ (180 K), $\omega\tau \approx 1$ (255 K) and $\omega\tau \ll 1$ (330 K): ●, experimental data; —, fits to linearized hydrodynamic theory.

linearized hydrodynamic theory [10] including non-exponential relaxation is fitted to the complete spectrum. This is different from fitting only the width and peak positions of the Brillouin component to a simplified theoretical model which is the rough procedure commonly used in Brillouin scattering.

We allow for non-exponential relaxation through the introduction of a Cole–Davidson relaxation function via

$$M_x - M^*(i\omega) = M_r / (1 + i\omega\tau)^{\beta_{CD}} \quad (2)$$

where $0 < \beta_{CD} \leq 1$, M^* is the complex longitudinal modulus, $M_r = M_x - M_0$, and M_x and M_0 are the limiting high- and low-frequency values, respectively. It should be noted that the common decomposition of $S(Q, \omega)$ into four components, representing the longitudinal Brillouin modes, a Mountain mode and a Rayleigh mode, is not performed in this treatment. Such a simple decomposition is not possible in case of a non-exponential relaxation and, furthermore, it involves a series of approximations whose validity are questionable for supercooled liquids. In the present fitting procedure the limiting low- and high-frequency sound velocities v_0 and v_x , the relaxation time τ , the non-exponentiality parameter β_{CD} and an arbitrary intensity scaling variable were free parameters. However, the only completely unknown parameter is β_{CD} since the others can in fact be directly measured in parts of the investigated temperature range. In order to compare the results for the non-exponentiality with reported results from other investigations the β_{CD} -values were converted to β -values of the KWW function according to the procedure suggested in [11]. The fits of $S(Q, \omega)$ were at every temperature in excellent agreement with the experimental spectra (figure 1). The analysis gave realistic values of all the fitting parameters only when the relaxation was allowed to be non-exponential, which then motivates the extra parameter β introduced via the Cole–Davidson function. Details of the experiment and the analysis can be found elsewhere [12].

3. Results

3.1. Relaxation data of a molecular glass former, propylene carbonate

Strong relaxation effects were observed for PC in the Brillouin spectra in the temperature range 200–300 K ($T_g = 160$ K). They show up as a dispersion of the hypersound velocity v_L (approximately equal to the Brillouin frequency shift), and a large hypersound

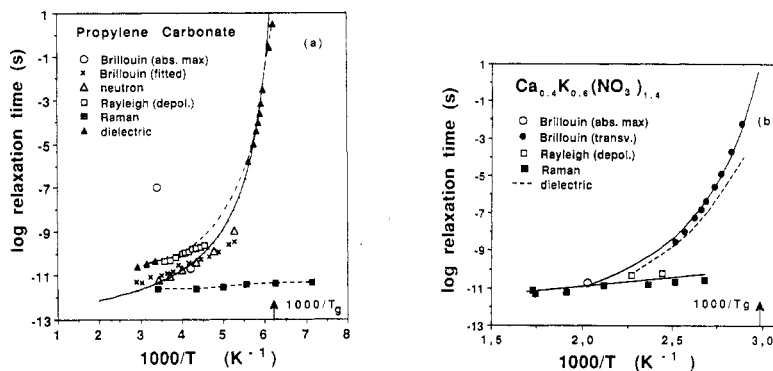


Figure 2. Arrhenius plots of the temperature dependences of structural and reorientational relaxation times for (a) PC and (b) $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$; \circ , data determined from the Brillouin linewidth maximum; \blacktriangle , dielectric relaxation [13]; \square , depolarized Rayleigh scattering; \blacksquare , represents Raman results [14]; \times , from fits of Brillouin spectra to the full $S(q, \omega)$; \triangle , quasielastic neutron scattering [15]; —, a fit of equation (3) with parameters given in the text; ---, guides for the eye to follow in (a) and (b) the dielectric relaxation results [16] and in (a) the Raman reorientational relaxation results. The other results are from [2, 6, 7, 17].

attenuation α (approximately equal to the Brillouin linewidth), with a maximum at a temperature of about 245 K (see figure 1). Maximum absorption occurs when the frequency ν_B of the Brillouin component is comparable with the inverse of the average relaxation time, i.e. at $\omega(\tau) \approx 1$ where $\omega = 2\pi\nu_B$. The so-determined average longitudinal relaxation time at 245 K is 2.24×10^{-11} s. The structural relaxation time for every investigated temperature was obtained by use of the detailed analysis of the full Brillouin spectral shape [12] and the results are shown in figure 2(a). As seen in figure 2(a), the relaxation time calculated from the maximum of the sound attenuation is in accordance with those obtained from the analysis of the full Brillouin spectrum.

The reorientational relaxation was investigated by use of the depolarized spectra (depolarized Rayleigh scattering). The central line is observed to be significantly broadened in the temperature range 190–300 K. The width narrows rapidly with decreasing temperature. A Lorentz function gave excellent fits, thus indicating a single relaxation time behaviour. The reorientational relaxation time τ_{ray} is obtained from the half-width $\Delta\nu_{\text{reor}}$ at half-maximum using $\tau_{\text{ray}} = 1/(2\pi \Delta\nu_{\text{reor}})$ and the results are presented in figure 2(a). In the figure, data for dielectric relaxation times [13] τ_{diel} , single-particle (incoherent) reorientational times τ_{Ram} obtained with Raman scattering [14] and structural relaxation times reported from quasielastic neutron-scattering experiments [15] are included. As seen in figure 2(a), the time scales of the cooperative reorientations measured by depolarized Rayleigh scattering and dielectric relaxation almost coincide. However, the data are substantially different from the single-particle reorientation time τ_{Ram} and with a different temperature dependence, which indicates strong cooperative effects for the reorientations in the glass transition range.

Figure 2(a) shows that at high temperatures there seem to be at least three different dynamics for the relaxation processes: single-particle reorientations measured by Raman scattering, cooperative reorientations measured by dielectric and depolarized Rayleigh scattering, and structural relaxations measured by neutron and Brillouin scattering. At temperatures close to the glass transition temperature the cooperative

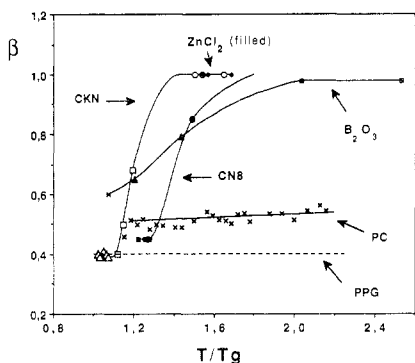


Figure 3. Temperature dependence of the stretching parameter β of the kww relaxation function (equation (1)) for $2\text{Ca}(\text{NO}_3)_2\text{-3KNO}_3$ (CKN), $\text{Ca}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$ (CN8), ZnCl_2 , B_2O_3 , PC and PPG obtained from photon correlation (Δ) [20–22], ultrasonic (\square) [18, 19, 23, 24] and Brillouin scattering techniques (\circ) [2–6, 8]. The temperature axis has been normalized by the respective values of T_g . The full lines are guides for the eye.

reorientations and the structural relaxations seem to merge while the single-particle reorientational motion persists well into the glassy state without any dramatic slowing down.

Now we turn to the form of the relaxation time decay. The advanced Brillouin technique and analysing procedure of the present study allow for the determination of the stretching parameter for each Brillouin spectrum, i.e. for each temperature [12]. A temperature-independent β -value of about 0.5 was obtained over the wide temperature range 180–345 K (figure 3). Thus, time–temperature scaling is obeyed for the whole temperature range.

Interestingly, the dielectric relaxation show a broad distribution of relaxation times close to T_g which rapidly narrows and becomes a single relaxation time at frequencies corresponding to the Brillouin absorption maximum (about 250 K, 6 GHz). Consistently, the depolarized Rayleigh results also indicate exponential relaxation for the reorientation relaxation in the gigahertz range.

3.2. Relaxation data of ionic glass-forming systems

Strong relaxation effects were observed for $2\text{Ca}(\text{NO}_3)_2\text{-3KNO}_3$ as discussed previously [2, 6, 7]. The temperature evolution of the spectra reflects transverse, longitudinal and molecular reorientational relaxations, respectively. The obtained relaxation times (τ_s , τ_L and τ_{Ray}) are plotted in figure 2(b). The values of τ_s extrapolate to the τ_L -value at short times and high temperatures and we conclude that the shear and longitudinal relaxations are closely related.

Also shown in figure 2(b) is the single-particle reorientational time τ_{Ram} obtained at shorter times and higher temperatures using Raman scattering [17]. Note that the depolarized Rayleigh results almost coincide with the Raman values despite the fact that, in depolarized Rayleigh scattering, collective behaviour is observed while the Raman technique measures the individual molecular reorientations. It is even more interesting to note that the characteristic times τ_{reor} for reorientational motions, become decoupled from the relaxation times for longitudinal and shear stresses at lower temperatures. The phenomenon may be the first in a series of decoupling processes which subsequently occur as the temperature is lowered towards the glass transition temperature. At still lower temperatures the dielectric relaxation time [16] decouples from the τ_L versus τ_s curve. The decoupling may in this case be explained by diffusive motions of the cations similar to that observed for fast ion-conducting glasses.

In figure 3 we plot the temperature dependence of the stretching parameter β for $2\text{Ca}(\text{NO}_3)_2\text{-}3\text{KNO}_3$ [2] and compare with data from some other ionic glass-forming systems, namely $\text{Ca}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$ [4], and ZnCl_2 [5], by combining the Brillouin scattering results with those of ultrasonic attenuation [18, 19] and photon correlation [20]. It is found that the relaxation function tends to a single exponential at high temperatures for all the ionic glass-forming systems. Similar behaviour has also been observed for the strong network glass former B_2O_3 with covalent microscopic interaction which is also shown in figure 3.

4. Discussion

The strong-fragile classification scheme [1] has been shown to be useful in comparing the relaxation behaviour of glass-forming liquids of different structures. Then, describing the temperature dependence of the structural relaxation time by the Vogel-Tamman-Fulcher (VTF) expression

$$\tau = 10^{-13.5} \exp[DT_0/(T - T_0)] \quad (3)$$

the parameter D may take a value in the wide range 3–100 depending on the fragility of the system. The full curves in figure 2 correspond to D -values of 3.0 and 4.3 for PC and $2\text{Ca}(\text{NO}_3)_2\text{-}3\text{KNO}_3$, respectively. Thus, these two liquids are of similar fragilities and represent the fragile extreme of the classification scheme. $\text{Ca}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$ is also extremely fragile [4] while ZnCl is intermediate [4] and B_2O_3 is near the strong extreme ($D \approx 35$).

It is interesting to compare the relaxation characteristics of molecular PC and ionic $2\text{Ca}(\text{NO}_3)_2\text{-}3\text{KNO}_3$ since they are of similar fragilities but represent different microscopic interactions: van der Waals and Coulomb interactions, respectively. The relaxation maps of the molecular (figure 2(a)) and the ionic (figure 2(b)) glass exhibit significant differences. For the molecular glass, three distinctly different relaxation mechanisms can be distinguished in the high-temperature (about $1.6T_g$) region: a fast single-particle reorientation relaxation with a weak temperature dependence, a slow (longitudinal) structural relaxation and an even slower cooperative reorientation relaxation. The relaxation times of the two slow relaxations increase rapidly as the temperature approaches the glass transition temperature. The cooperative reorientation time is about an order of magnitude slower than the corresponding single-particle relaxation time. This together with the similar temperature dependence of the cooperative reorientation and the structural relaxation indicate considerable coupling of the collective reorientational motions to the dynamics determining the glass transition.

In contrast, for $2\text{Ca}(\text{NO}_3)_2\text{-}3\text{KNO}_3$ (figure 2(b)) the different relaxation times merge in the high-temperature (about $1.6T_g$) range. At lower temperatures, the reorientational motion starts to decouple from the slower structural relaxation and at still lower temperatures the dielectric relaxation decouples. Note that the single-particle and the cooperative reorientation times closely follow each other in the investigated temperature range, which suggests weak cooperative effects in the reorientation motions of the nitrate ions in $2\text{Ca}(\text{NO}_3)_2\text{-}3\text{KNO}_3$. Also from the decoupling it seems that the nitrate ion reorientations are only weakly coupled to the dynamics of the glass transition.

It is not only the maps of the average relaxation times of the ionic glass and the molecular glass which are different. The temperature dependences of the stretching parameter β show different behaviours as well (see figure 3). For $2\text{Ca}(\text{NO}_3)_2\text{-}3\text{KNO}_3$,

β changes from about 0.45 at low temperatures near the glass transition to approach 1 (exponential relaxation) at high temperatures where the Brillouin absorption maximum is observed. A similar behaviour of the stretching parameter is observed for $\text{Ca}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$ (see figure 3). For the weak network glass ZnCl_2 and the strong glass former B_2O_3 the relaxation function crosses over towards a single exponential already at the longer average relaxation times (lower temperatures) probed in ultrasonics (see figure 3). These observations from the ionic and covalent glasses have led us previously to suggest that the crossover was directly connected to the fragility of the system [4, 6]. However, such a generalization of the relaxation behaviour is invalidated when the molecular glass PC is included in the comparison since in this case a temperature-independent value of β (about 0.5) is found in sharp contrast to the previous results. Moreover, the β -value is constant over a remarkably large temperature interval from near T_g to above $2T_g$. We are aware of only one previous study which shows non-exponential relaxation at the high frequencies and temperatures of Brillouin scattering, namely for PPG [8]. Also in this case the β -value was observed to be temperature independent over a large temperature range (see figure 3). Interestingly, also for PPG the cooperative reorientation times are significantly longer than the longitudinal structural relaxation time. It is then notable that the inter-chain interactions in PPG are, like the intermolecular bondings in PC, of van der Waals type.

Moreover, comparing the stretching of the relaxation for the molecular and the ionic glasses of similar fragilities we find that just above the transition the β -value is higher for PC ($\beta \approx 0.5$) than for the somewhat less fragile ionic system $2\text{Ca}(\text{NO}_3)_2-3\text{KNO}_3$ ($\beta \approx 0.4$) (see figure 3). This is in contrast to the often-proposed relation between the degree of non-exponentiality of the relaxation function and the departure from Arrhenius behaviour, i.e. decreasing β for increasing fragility [1]. By including in the comparison the results for PPG, which is intermediate between strong and fragile, the even lower β -value of 0.4 (see figure 3) further emphasizes the inadequacy of such a simple relation.

5. Conclusion

We conclude that systems of similar fragilities but with different microscopic interactions between the constituting particles may show completely different relaxation characteristics. This is demonstrated by the molecular 'van der Waals glass' PC and the ionic 'Coulomb glass' $2\text{Ca}(\text{NO}_3)_2-3\text{KNO}_3$ which exhibit significantly different behaviours of the cooperative reorientation relaxations, the decoupling of various relaxation mechanisms when approaching T_g and the temperature dependences of the stretching parameter. The results emphasize the need to take the microscopic interactions into account for drawing general conclusions about the relaxation behaviour of glass-forming liquids. In particular it has been suggested that there is a relationship between non-Arrhenius behaviour and the non-exponentiality of the relaxation function. The present study shows that there is no such simple relation.

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