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Abstract
We discuss the dynamics of the glass-forming liquids glycerol, propylene carbonate, and benzophenone, as revealed in their dielectric behaviour and in depolarized light scattering (DLS) data. Above the melting point, the liquids exhibit two-step stretched relaxation behaviour typical of 'glassy dynamics' at all attainable temperatures $\gtrsim 2T_g$. There is no sign of a transition to exponential relaxation; rather, the stretching depends only weakly on the temperature. The spectral change, in first approximation, amounts to shifting the α-relaxation peak with the temperature. This behaviour is in contrast with the temperature-dependent spectral shapes observed in the low-temperature state close to T_g. Analysing corresponding dielectric spectroscopic (DS) data for comparisons, similar tendencies are observed, except that the stretching parameters are different. Below a certain temperature in glycerol, the tail of the excess wing, which is clearly pronounced in the DS data, appears also in the DLS spectra, with the same ratio of the wing exponents in DLS versus DS as of the stretching exponents at higher T. In propylene carbonate, the presence of a wing in the DLS data is not immediately obvious. However, its low-temperature DLS spectra are fully compatible with an empirical model for the temperature-dependent spectral shape that adequately describes the DS data of both materials and includes the wing. We were however unable to reconcile the DLS results of glycerol with this model. This, together with the pronounced difference in DLS and DS spectral widths of glycerol, cast doubts over the general validity of universal scaling procedures for different techniques.

1. Introduction

The most basic features of glassy dynamics are commonly believed to be the two-step stretched relaxation and the slowing down by many orders of magnitude of the structural relaxation as a liquid is supercooled towards its glass transition temperature T_g. Experimental physics over the last two decades has brought forth a sizeable body of data, including broadband spectroscopic

results over large temperature intervals, which has helped in identifying and analysing more subtle features of the glassy dynamics. For instance, the characteristic stretching was suggested to correlate with the fragility close to T_g [1], while reducing to non-stretched behaviour at high temperatures [2, 3]. At low temperatures $\geqslant T_g$ and in the subclass of glass formers that do not exhibit a secondary relaxation peak but rather an excess wing, a universal shape of the relaxation spectrum beyond a simple stretched function was anticipated, so that dielectric loss spectra of different systems at different temperatures can be rescaled to overlap [2]. This scaling, often referred to as 'Nagel scaling', implies that the complex temperature-dependent shape of the relaxation spectrum can be described by two parameters only—the relaxation time and a single shape parameter. It also implies that the excess wing, being an excess contribution over the stretched high-frequency flank of the α-relaxation peak that is sometimes regarded as a kind of a secondary relaxation process [4, 5], is an inseparable part of α-relaxation.

The search for such universal characteristics proved, however, a somewhat elusive subject. This is in part due to the enormous time/frequency range spanned by the glass transition dynamics, so that analysing data of rather limited dynamic range can easily lead to false conclusions. As an example, the validity and accuracy of the mentioned scaling was challenged [6, 7] and modified scaling approaches were suggested [6, 8]. In particular, the analysis of [8] suggested that the characteristic spectral shape with an excess wing persists only up to a certain temperature, transforming thereafter into a simple peak without the wing. As to further transition to exponential relaxation at still higher temperatures, it has never been, as far as we are aware, observed experimentally. Instead, experimental evidence appears to suggest that, while at low temperatures the stretching parameter may increase, and thus the stretching itself decrease with increasing the temperature, it then saturates, so that in the high-temperature regime the relaxation spectrum is still stretched and its shape approximately temperature independent [9, 10]. Such a situation is in fact reminiscent of the mode coupling theory (MCT) [11] scenario above the critical temperature. Moreover, in benzene, which cannot even be supercooled by usual procedures, a stretched two-step relaxation spectrum was observed up to the boiling point [12]. As for the stretching–fragility relation, the stretching appears to be different for relaxation spectra obtained by different techniques [10, 13], so that the relation deduced by analysing *en masse* data obtained by different methods appears to be internally inconsistent. Conversely, most of the other analyses aimed at finding generic features are usually based on experimental results obtained by one single technique, the dielectric spectroscopy. While this is completely understandable given the enormous dynamic range of the technique, generality claims based on a single technique cannot be considered satisfactory.

In the following, we will look more carefully at these and related issues, taking primarily as examples glycerol and propylene carbonate, and secondly benzophenone. Plenty of various experimental data exist of these two classical glass-forming systems. In particular, they are among the few systems for which extremely broadband dielectric spectra over the whole glass transition temperature range are available [13]. Both have also been studied by light scattering spectroscopy [10, 14, 15]. The scaling of Dixon *et al* [2] works extraordinarily well for these systems [16]. This is rather remarkable given that glycerol and propylene carbonate are quite different materials. Specifically, propylene carbonate is a 'fragile' glass former with primarily van der Waals intermolecular interactions, while glycerol is markedly non-fragile and forms a hydrogen-bonded network. Their dielectric spectral shapes do not seem, however, to be affected by these differences. A natural question then arises, namely whether such universal features can likewise be identified in relaxation spectra of other properties than the dielectric polarization. Of particular interest appear comparisons with results of depolarized light scattering (DLS) spectroscopy, which, similarly to the dielectric spectroscopy, probes molecular reorientations as revealed in fluctuations of the electronic polarizability tensor, rather

than the electric polarization that is detected by dielectric techniques. A recent DLS work on glycerol [10] shows that, despite the frequency window of the technique being limited to $\geqslant 300$ MHz, the DLS spectra at low temperatures show indications of an excess wing with a similar temperature dependence as in the DS data. The stretching of the DLS spectra, concerning both the α-peak at high temperatures and the wing at low temperatures, appears however to be significantly larger than that of the DS spectra. Still, these results would fit into the scaling procedures discussed above, if a system- and method-dependent correction to the spectral width parameter were allowed for.

At high temperatures, rather than reducing to a non-stretched exponential relaxation as originally suggested in [2], both the DLS and DS results discussed in [10] suggest a nearly temperature-independent *stretched* behaviour, the existence of such a high-temperature regime actually appearing to be a universal feature of molecular glass formers [8, 9]. In a recent light scattering work on propylene carbonate [15] the authors were able to successfully fit their DLS spectra assuming a Cole–Davidson shape for the α-peak with a temperature-independent stretching at *all* temperatures from 350 K down to $T_g = 160$ K, without the need to introduce additional spectral features, such as the excess wing. The latter result indicates that the excess wing may not be a universal feature of structural relaxation, even though it is a ubiquitous feature of dielectric relaxation spectra. Such results should however be taken with caution, since conventional frequency-domain light scattering spectroscopy does not provide access to frequencies lower than about 300 MHz, and thus does not allow one to unambiguously conclude on the relaxation spectral shape at low temperatures. Photon correlation spectroscopy (PCS), however, covers the necessary time/frequency range. Recent PCS results of several molecular liquids [17] indicate the presence of an excess wing in 2-picoline close to T_g, albeit with a different magnitude than in the corresponding DS spectra. By contrast, no sign of such feature was identified in salol [17].

The situation outlined above is rather contradictory and far from satisfactory. In particular, it seems impossible to reconcile the widely accepted notion, deduced from dielectric data, of the transition to exponential relaxation at high temperatures [3], with experimental results that indicate a rather different high-temperature scenario. Conversely, the well-established result of a universal shape of the dielectric loss spectra appears to be impossible to unambiguously verify for other types of relaxation spectra, in particular those obtained by light scattering spectroscopy. In this paper, we attempt to shed more light on these and related phenomena, in particular to clarify the following points. Is there a distinguishable high-temperature regime of dynamics, possibly characterized by a nearly exponential relaxation? How large is the difference between relaxation spectra of different properties that are probed in different experiments, such as light scattering and dielectric spectroscopy? Is the excess wing, which is usually not discussed in the light scattering literature, indeed a common feature similarly pronounced at low temperatures? In order to achieve these goals, we re-analysed our existing DLS data of glycerol, concentrating in particular on high temperatures. In addition and for comparisons, we obtained DLS spectra of benzophenone and a new set of DLS data of propylene carbonate, extending in the latter case the temperature range up to about twice the melting point, as well as attempting to obtain accurate data at the lowest frequencies down to about 200 MHz close to T_g. Whenever possible, we compared these results with those obtained by dielectric spectroscopy and computer experiments.

2. Experimental details

Propylene carbonate (Fluka, >99%, $T_b = 513$ K, $T_m = 218$ K, $T_g = 160$ K) was vacuum-distilled and transferred under nitrogen into 15 mm diameter screw-capped glass vials used as
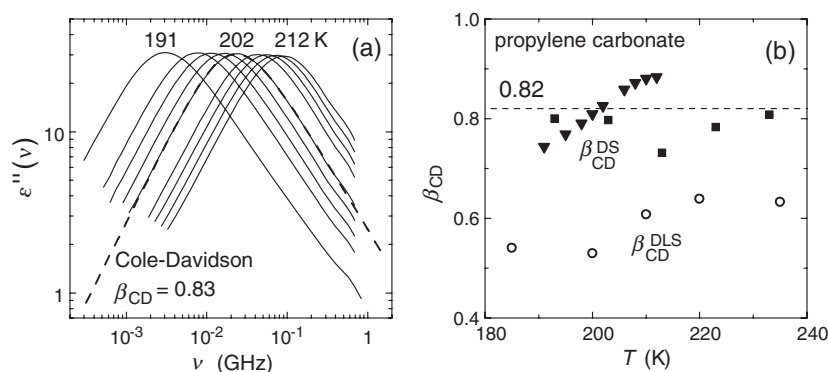
Figure 1. (a) Dielectric loss spectra of propylene carbonate at temperatures 191–212 K from [8] and a sample fit to the Cole–Davidson function. (b) Stretching exponents of propylene carbonate from fits of (a) (triangles), from hybrid fits to the spectra of [13] (squares), and from DLS results in figure 6 (open circles).

sample cells. Benzophenone (Sigma-Aldrich, >99%, $T_b = 578$ K, $T_m = 322$ K, $T_g = 213$ K) was re-sublimed under vacuum and transferred under nitrogen into 10 mm diameter glass sample cells that were flame sealed under vacuum. A sample cell was mounted either in an optical continuous-flow liquid helium cryostat (CryoVac) for measurements below room temperature, or in a home-built mini-furnace. The spectroscopic set-up consisted of a 532 nm single mode solid-state laser (Coherent Verdi V2), a double-grating monochromator (Jobin-Yvon U1000), and a three-pass scanning tandem interferometer (JRS Scientific Instruments). Further details of the experimental set-up and procedures, as well as of the normalization and Fourier-transform procedures, can be found elsewhere [10].

3. Results

Recalling that the supposed transition to exponential relaxation at high temperatures was originally based on extrapolations of dielectric data from lower temperatures [2, 3], we first examine DS results from more recent literature [8, 13]. Figure 1(a) presents dielectric loss spectra of propylene carbonate from [8] at the highest temperatures studied there, 191–212 K. At these temperatures, the relaxation peaks are indeed rather symmetric, i.e. close to the Lorentzian spectral shape of exponential relaxation. The spectra have no extra contributions, such as excess wings, and can be perfectly fitted to the Cole–Davidson function, as shown in the figure for $T = 202$ K. The resulting stretching parameters versus temperature are shown in figure 1(b) by triangles. The values are indeed not far from unity, the latter corresponding to exponential relaxation. At first sight, these data alone might be easily interpreted to suggest (linear) extrapolation to $\beta = 1$ already at $T \sim 220$ K, which would imply some kind of a dynamic transition at this temperature, since relaxation cannot be faster than exponential. This is however not the case—a closer inspection of these data in figure 1(b) reveals a tendency to level off above about 208 K. Moreover, the dielectric spectra of [13], which cover a wider temperature range up to 293 K, do not support the existence of an exponential relaxation regime. The analysis of [13] does suggest some levelling-off of $\beta_{CD}(T)$ at high T, but at a value 0.85 that is clearly less than unity. Squares in figure 1(b) represent results for the Cole–Davidson exponent β_{CD} of our own analysis of the spectra of [13]. We considered only those temperatures where the data were of sufficient quality, and fitted them to the same hybrid model with $a = 0.3$
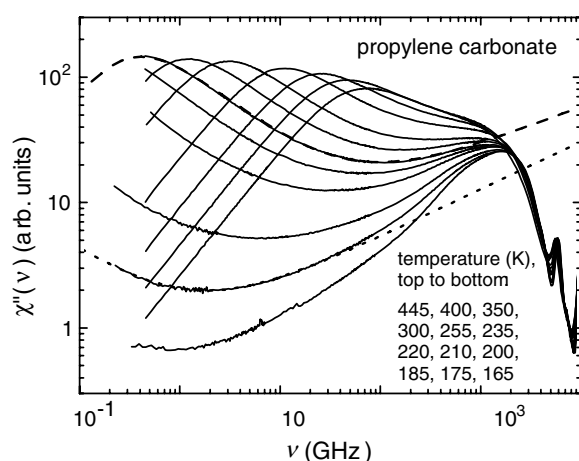
Figure 2. Depolarized light scattering data of propylene carbonate, presented as susceptibilities, at $T = 165$–445 K. Broken lines are examples of fits to the hybrid model of equation (1) at high T (dashed), and to the simplified model of equation (2) at low T (dotted).

as we used for our DLS spectra, to be explained below. Our conclusion from this analysis is that the spectra of [13] suggest levelling-off of $\beta_{CD}(T)$ at a value close to 0.8 already at $T \sim 190$ K. We therefore assume that the stretching of the dielectric data of propylene carbonate above about 190 K is given by the average value $\beta_{CD}^{DS} = 0.82$ (dashed line in figure 1(b)). Otherwise, the difference between the two dielectric datasets gives a feeling of the errors involved. In the same figure (1(b)) we also include (open circles) some results of our DLS data analysis (figure 6 below), intending to show that (i) there is no tendency of $\beta_{CD} \to 1$ in these data either, and (ii) the stretching, detected by the two techniques, is clearly different, $\beta_{CD}^{DLS} \approx 0.6$ (see figure 1(b)).

Now we turn to our new DLS results of propylene carbonate that are available for temperatures significantly higher than those discussed above. Figure 2 presents DLS spectra of propylene carbonate at $T = 165$–445 K, converted to susceptibilities. It is evident from figure 2 that even at the highest temperature of $T = 445$ K, which is almost twice the melting temperature of 218 K and not so far from the boiling point at 523 K, the α-peak remains stretched (asymmetric) and does not merge with the quasi-harmonic band at about 1 THz (we identify the latter, for the purposes of this discussion, with the boson beak). Thus, the relaxation still proceeds in two steps. Another observation from the spectra of figure 2, which are normalized to the same integral intensity of the (harmonic) Raman spectrum of intramolecular vibrations above 10 GHz, is that the α-peak intensity decreases with increasing the temperature, which is reminiscent of Curie's law (cf [10] for related results of glycerol).

The DLS data of propylene carbonate can likewise be analysed in the time domain, where the notion of a two-step relaxation acquires literal sense. In figure 3(a) we present the high-temperature data of propylene carbonate in the time-domain representation, as normalized relaxation or, equivalently, correlation functions. Procedures for obtaining the time-domain data of figure 3(a) from the corresponding spectra were similar to those used in [10]. Specifically, we excluded from the transform the Raman spectrum of intramolecular vibrations above about 10 THz. At $T < 300$ K, when the measured spectra do not extend to sufficiently low frequencies below the α-peak, we extrapolated into this region using fits that are described below.

It is again evident that at high temperatures the relaxation retains two-step character and remains stretched. Moreover, the stretching in this high-temperature regime seems to be rather
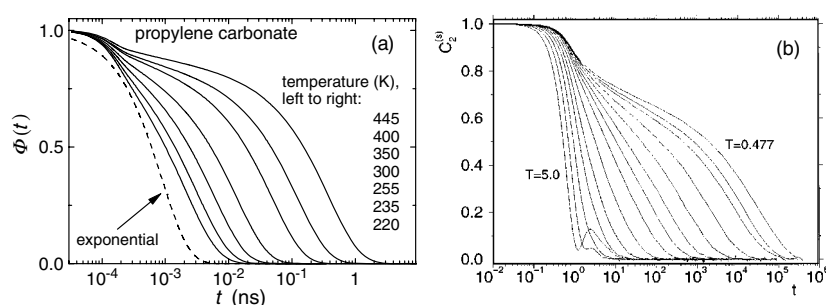
Figure 3. (a) Normalized relaxation (correlation) functions of propylene carbonate at $T = 220$–445 K, obtained from spectra in figure 2; the dashed line is an exponential function. (b) Second rank orientational self-correlation functions of a model liquid of diatomic molecules at reduced temperatures from 0.477 to 5.0 (approx. log-spaced) versus reduced time, molecular dynamics simulation results [18].
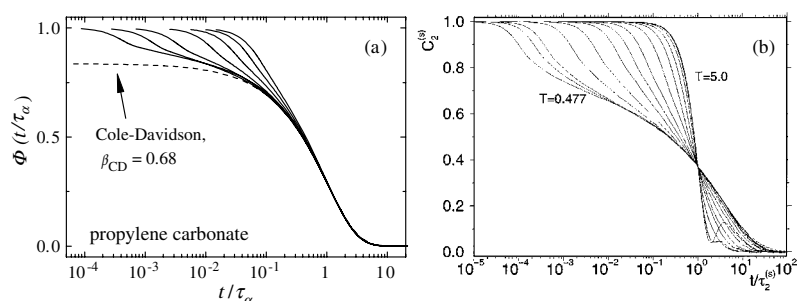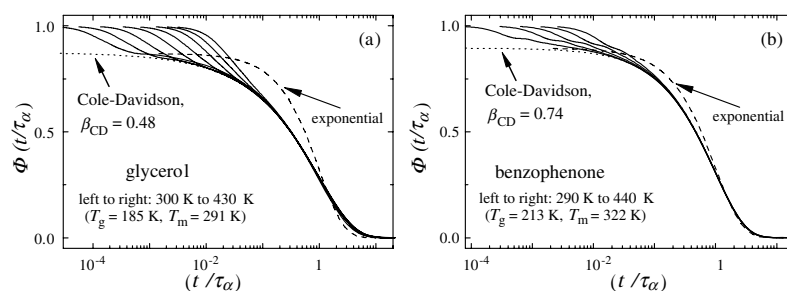

Figure 4. Relaxation (correlation) functions, rescaled by their α-relaxation times. (a) Experimental data of propylene carbonate from figure 3(a); the broken line corresponds to the Cole–Davidson function with $\beta_{CD} = 0.68$. (b) MD results from [18].

insensitive to the temperature. At first glance, this appears to be in stark contrast with computer simulation results of [18] shown in figure 3(b), where a transition from a two-step stretched behaviour to a single exponential relaxation is clearly seen. The correlation functions $C_2^{(s)}(t)$ in figure 3(b) are those relevant for depolarized light scattering from anisotropic molecules, so that figures 3(a) and (b) can be directly compared. Concerning their marked difference, it should be immediately realized that the simulation temperature and density can be varied at will, the temperature in this particular case changing by a factor of more than 10; see figure 3(b). Such high temperatures are evidently beyond physical bounds for a laboratory, rather than a computer, liquid, while it is precisely at the highest simulation temperatures that the transition to non-stretched relaxation is observed in figure 3(b). We believe that the inability of molecular dynamics simulations to detect phase transitions and thereby establish physical boundaries of the simulation parameters constitutes an inherent drawback of the computer experiments.

The near temperature independence of the stretching is best seen when the relaxation functions are plotted versus rescaled time, as in figure 4(a). It is evident that the long-time parts of the curves essentially overlap, and thus are similarly stretched. For comparisons, figure 4(b) shows rescaled plots of the correlation functions obtained in the MD simulations of [18]. At low simulation temperatures, the long-time parts of the correlation functions overlap similarly to our high-temperature experimental data. It is once more evident that the transition to

Figure 5. DLS relaxation (correlation) functions of (a) glycerol (data from [10]) and (b) benzophenone at indicated temperatures, versus rescaled time. Dotted lines correspond to Cole–Davidson functions with indicated stretching exponents. Dashed lines are exponential functions with the same amplitudes as the corresponding Cole–Davidson functions.
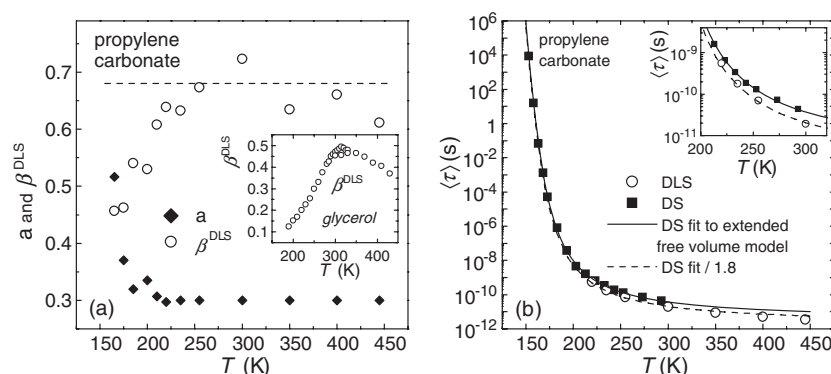
Figure 6. Hybrid fit results of the spectra of propylene carbonate in figure 2(a). (a) Exponents a and β^{DLS}; inset: exponent β of glycerol [10]. (b) Relaxation times from the fits compared to dielectric results of [13]; the inset shows the overlapping region of DLS and DS data in more detail; error bars are less than the symbol size.

non-stretched behaviour, observed in figure 4(b) at high simulation temperatures, is far beyond the reach of a laboratory experiment.

In figure 5(a) we present our previous DLS data of glycerol [10] in the time-domain representation versus rescaled time, as in figure 4(a) of propylene carbonate. As in the case of propylene carbonate, the curves overlap at long times, the region of overlap being even wider than in figure 4(a), and are markedly different (stretching exponent $\beta_{\mathrm{CD}} = 0.48$) from the exponential function (dashed line, $\beta = 1$). Thus, the stretching is rather independent of temperature, which is also true for the corresponding dielectric data [9]. As a contrasting example of a 'close to exponential' relaxation, figure 5(b) presents in the same fashion our newly obtained high-temperature ($T \gtrsim T_{\mathrm{m}}$) DLS data of benzophenone, which has a rather high $\beta_{\mathrm{CD}} = 0.74$. Still, the data are unmistakably different from the exponential function, and again overlap at long times, with the stretching thus being temperature independent.

Now we turn to a quantitative analysis of the DLS relaxation spectra of propylene carbonate (figure 2) below about 100 GHz, i.e. well below the boson beak. In this spectral range and at temperatures below about 250 K, the susceptibility spectra of figure 2 exhibit a clear minimum, and therefore cannot be described by a stretched α-relaxation peak alone, since they in addition include a 'fast' relaxation part above the minimum. In order to interpolate

both the α-relaxation and fast relaxation, we used in analogy with glycerol a generic 'hybrid' model that encompasses a Cole–Davidson function for the α-peak and a power law for the fast relaxation [10]:

$$\chi''(\omega) = \text{Im } A\left[(1 - \text{i}\omega\tau_{\text{CD}})^{-\beta} + \text{i}\omega B(\tau_{\text{CD}}^{-1} - \text{i}\omega)^{a-1}\right] \qquad (1)$$

or, close to the minimum, a simplified version

$$\chi''(\omega) = A\omega^{-\beta} + C\omega^{a}. \qquad (2)$$

At high temperature the minimum disappears, and thus determining a as a free fit parameter is impossible. We therefore followed the approach of [15] and at $T > 230$ K fixed $a = 0.3$, the value that followed from the analysis at lower temperatures. But being specifically interested in a possible temperature dependence of β, we let it vary as a free parameter at all temperatures. Two sample fits are shown in figure 2. The fit results are presented in figure 6(a). The exponent a (diamonds) is rather insensitive to the temperature, except close to T_{g}, where it sharply increases, which is in accordance with the results of [15]. At high temperatures, as mentioned, it is an ill-defined parameter. We therefore do not dwell any longer on its temperature behaviour. We also note that the dielectric data leave even less room for a reliable estimation of a, and thus a comparison between DLS and DS results in this respect is not possible. As for the stretching exponent β^{DLS} (circles in figure 6(a)), one unmistakably identifies, despite the scatter, two different temperature regimes. At low temperatures, β^{DLS} increases with increasing the temperature. At high T, it stays rather constant, showing even a slight tendency to decrease. The transition between the two temperature regimes occurs somewhere between 200 and 250 K. The dashed line corresponds to $\beta^{\text{DLS}} = 0.68$, the value used in [15] for *all* temperatures down to T_{g}, which is thus only compatible with our data above about 200 K. Comparing with the similar results of glycerol [10], we note that there, too, exists a similar high-temperature regime with nearly temperature-independent β; see the inset in figure 6(a). Departure from this 'plateau' of β versus T at lower temperatures in glycerol was identified with the appearance in the DLS spectra of the excess wing [10] that is clearly seen in the dielectric spectra of [13]. In the present case of propylene carbonate, the situation is less clear, as the β values that we observe at low temperatures in figure 6(a) appear to be too large for a wing exponent. We will return to this point later.

In figure 6(b) circles represent the mean relaxation times τ_{α} of propylene carbonate at different temperatures, which is another result of the fitting described above ($\tau_{\alpha} = \tau_{\text{CD}} \beta$ for the Cole–Davidson function). The relaxation times could only be deduced at $T > 210$ K, when the relaxation peak was within the accessible frequency window. Squares in figure 6(b) represent dielectric relaxation data of Schneider *et al* [13] along with their extended-free-volume fit (solid line). As is usually the case, in particular in glycerol (see reference [10] and discussion therein), the light scattering relaxation times are somewhat faster than the dielectric ones, the two temperature dependences being however parallel. The dashed line, which is the dielectric fit divided by 1.8, follows the light scattering relaxation times well. We expect that it gives an accurate estimate of $\tau_{\alpha}^{\text{DLS}}$ at all temperatures, which we will need later.

Comparing our β^{DLS} with the dielectric results, as was already done in figure 1(b), we reiterate that the dielectric values are certainly larger, i.e. the dielectric relaxation is less stretched. Specifically, and as discussed in relation to figure 1, at T above about 210 K, where the dielectric spectra do not yet show any sign of the excess wing, β^{DS} is about 0.82. We find instead that β^{DLS} is less than 0.7; see figure 6(a). Using the average $\beta^{\text{DLS}} \sim 0.68$, we conclude that the stretching parameter is $\beta^{\text{DS}}/\beta^{\text{DLS}} \sim 0.82/0.68 = 1.2$ times larger in the DS than in the DLS data. This is not as spectacular a ratio as about 1.4 in glycerol [10], but plotting DS and DLS spectra together at temperatures where their relaxation times coincide, see figure 7(a),
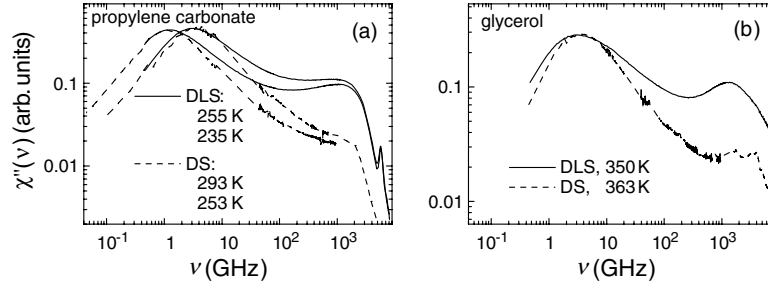
Figure 7. Comparing dielectric [13] and light scattering spectra of (a) propylene carbonate and (b) glycerol, the latter data being from [10].

the difference in stretching is unmistakable: the light scattering relaxation peaks are obviously wider. Figure 7(b) gives a similar comparison for glycerol [10].

4. Discussion

We shall now attempt to address the question: Are the depolarized light scattering results presented above compatible with the presumably universal scaling properties of the *dielectric* relaxation discussed in the introduction? We have already seen that the stretching is clearly different, but if the same ratio applied to the excess wing exponents as to the stretching exponents, it might still be possible to put the (inaccessible at low T) DLS relaxation spectra on the dielectric master curve. Results for glycerol [10] suggest that, indeed, the same factor describes the difference in 'stretching' of the excess wing and of the main peak in DS and DLS data of this system. We do not find such clear indications in the case of propylene carbonate, and in any case, this sort of argument can only lead so far: the kHz–MHz light scattering spectra, needed to examine their scaling properties, are still not accessible in practice. We therefore take a somewhat different route.

The scaling of Dixon *et al* can be taken to imply that the shape of the relaxation spectrum is determined by only two parameters: the relaxation time and a spectral width, or stretching parameter that may be, and usually is, itself temperature dependent. In a quite recent work, Blochowicz *et al* [8] suggest a different but related approach, based on their analyses of dielectric data of various systems. Instead of *rescaling* experimental spectra, they *fit* them to a suitable phenomenological model that adequately describes both the α-peak and the excess wing, and then analyse the system- and temperature-dependent behaviour of the parameters of the model. More specifically, the model is defined in the relaxation time domain through the following distribution [8]:

$$G_{\text{GGE}}(\tau) = N_{\text{GGE}} e^{\frac{\beta}{\alpha}\left(\frac{\tau}{\tau_0}\right)^{\alpha}} \left(\frac{\tau}{\tau_0}\right)^{\beta} \left[1 + \left(\frac{\tau\sigma}{\tau_0}\right)^{\gamma-\beta}\right], \tag{3}$$

where $N_{\text{GGE}} = N_{\text{GGE}}(\alpha, \beta, \gamma)$ is a normalization factor. Susceptibility spectra are then determined by a convolution of $G_{\text{GGE}}(\tau)$ with the Lorentz function $(1 + i\omega\tau)^{-1}$. Exponents β and γ of equation (3) are related but not necessarily identical to the corresponding stretching and excess wing exponents observed in the spectra. To avoid confusion, in particular with the stretching exponent β_{CD} discussed above, we will add subscript GGE, which stands for 'generalized gamma extended' (distribution), to the parameters that appear in the distribution function. Blochowicz *et al* found in analogy with Dixon *et al* that, for a given system and
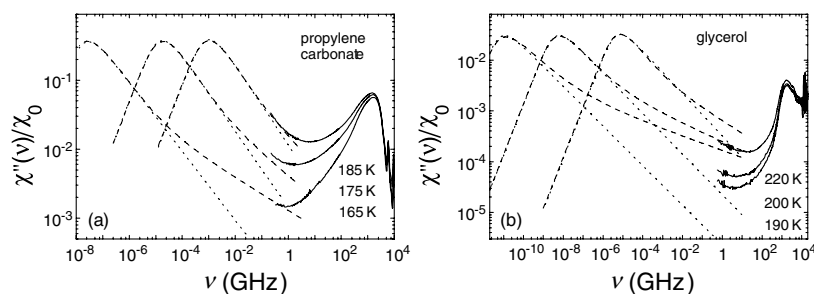
Figure 8. Normalized low-temperature DLS susceptibility spectra (full lines) of (a) propylene carbonate and (b) glycerol [10], compared with generated ones (broken lines): Cole–Davidson (dotted) and calculated from equation (3) (dashed); see text for details.

at temperatures below the high-temperature regime discussed in the previous section, the spectral shape parameters at different temperatures were interrelated. Moreover, they found that the spectral width parameters uniquely correlate with the relaxation time, the latter actually remaining the main parameter controlling the shape. Then, a set of empirical relations can be established to relate all except one shape parameter, appearing in the distribution function, to the mean relaxation time τ_α [19]:

$$\gamma_{\mathrm{GGE}}^{\mathrm{DS}} = 5.0/(\log \tau_\alpha + 15.0) - 0.1, \tag{4a}$$

$$\beta_{\mathrm{GGE}}^{\mathrm{DS}} = (3.0 \pm 0.5)\, \gamma_{\mathrm{GGE}}^{\mathrm{DS}}, \tag{4b}$$

$$\log \sigma_{\mathrm{GGE}}^{\mathrm{DS}} = 2.4 + 0.24\, \log \tau_\alpha, \tag{4c}$$

where we added superscript 'DS' to the parameters to make it clear that they refer to dielectric data. That still leaves $\alpha_{\mathrm{GGE}}^{\mathrm{DS}}$ undefined, but this parameter was found to influence the spectral shape only insignificantly, and to be temperature independent. In particular, $\alpha_{\mathrm{GGE}}^{\mathrm{DS}} = 10$ and 20 for glycerol and propylene carbonate, respectively. According to [19], somewhat different sets of factors, appearing in equation (4), can be deduced depending on the fitting procedures and constraints. The resulting spectral shapes are, however, rather similar. We note in addition that an alternative phenomenological analysis was recently reported [20] that is at least as successful in fitting the experimental spectra as the approach of Blochowicz *et al*, but that is based on a very different model ansatz and leads to different conclusions. We do not attempt to judge which approach is more adequate in general, and shall use equations (3) and (4) as a convenient and rather accurate parameterization of the experimental spectra.

Thus, using the relations (3) and (4) above, a model spectrum that closely resembles the experimental dielectric spectra can be generated, requiring only the knowledge of the α-relaxation time and, less importantly, α_{GGE}. Likewise, our DLS spectra can be tested against generated ones for compatibility with the scaling properties that are inherent in the model spectra.

Normalized (see the appendix for details) spectra of propylene carbonate at 165, 175, and 185 K are plotted in figure 8(a) together with model spectra for the same temperatures. We computed the model spectra as discussed above, assuming $\alpha_{\mathrm{GGE}} = \alpha_{\mathrm{GGE}}^{\mathrm{DS}} = 20$ and using as input for equations (4) relaxation times estimated from the fit (dashed line) in figure 6(b). In order to account for the different stretching of DLS and DS data, we assume that both the width parameters β^{DLS} and γ^{DLS} are proportional to the corresponding β^{DS} and γ^{DS} with the same factor 1.2, as found at high temperatures (see at the end of the previous section). The results, obtained *without any further adjustment* of the parameters, are presented in figure 8(a) with dashed lines. It is immediately obvious that the generated spectra join up almost perfectly

with the experimental ones. In contrast, simple Cole–Davidson spectral shapes, computed with $\beta_{CD}^{DLS} = \beta_{CD}^{DS}/1.2$ and also shown in the figure, are clearly not compatible with the experimental data. Thus, an excess wing must be present in the experimental DLS spectra of figure 8(a).

These results imply that DLS relaxation spectra may indeed be compatible with the universal dielectric spectral shapes, allowing for a correction to the width parameter to account for the difference in stretching, detected by different techniques. Still, such conclusions should be taken with great caution, as we will show shortly. Recalling the reasons given in the beginning of this section that glycerol is likely compatible with the scaling, we would expect a further confirmation of this, making a comparison such as in figure 8(a). This is however not the case. We followed the same prescription as above, using normalized spectra and relaxation times of glycerol from [10] and $\alpha_{GGE} = \alpha_{GGE}^{DS} = 10$ together with β, $\gamma_{GGE}^{DLS} = \beta$, $\gamma_{GGE}^{DS}/1.4$, to make similar comparisons as in figure 8(a) of propylene carbonate. The results are shown in figure 8(b). In this case, the generated spectra (dashed) do not join up with the experimental ones at all. In fact, simple Cole–Davidson shapes appear more appropriate at 200 and 220 K. Thus, the model for the dielectric spectral shapes and the corresponding universal scaling may indeed be incompatible with other, in this case light scattering, data. Else, the relation between DS and DLS spectral widths at low temperatures may be different from what we assumed based on the high-temperature results, and/or differently affect β and γ. Such effects would likely be more pronounced in the case of glycerol, given its exceptionally high ratio of the stretching exponents $\beta^{DS} = 1.4\,\beta^{DLS}$.

5. Conclusions

We analysed depolarized light scattering spectra of two classical glass forming materials glycerol and propylene carbonate at high temperatures well above the melting point and did not find any sign of a transition to exponential relaxation. We believe that such a transition does not exist in reality for molecular glass-forming liquids and can only be achieved in computer experiments at temperatures/densities that are not attainable in practice for most molecular liquids.

Instead of turning exponential at high temperatures, we find that relaxation remains stretched and that the stretching above certain temperature is nearly temperature independent. We note that such a high-temperature regime of molecular dynamics, where changes of the spectra with temperature amount chiefly to shifting the α-peak of otherwise constant shape, is seen in light scattering and dielectric data alike, is identified in molecular dynamics simulation, and is reminiscent of the mode coupling theory scenario above the critical temperature. We conclude that the existence of this regime is a universal feature of molecular glass formers. It may even be characteristic of strong, network forming glasses, e.g. boron trioxide [21]. Thus, 'glassy dynamics' are a general property of molecular liquids even well above T_m.

The relaxation stretching is clearly different as detected by dielectric spectroscopy versus light scattering spectroscopy. This result partly undermines attempts to find general correlations between the stretching and other material parameters, e.g. the fragility [1], since the stretching, being method dependent, cannot be uniquely defined.

At low temperatures, where the dielectric spectra exhibit a universal complex shape with the excess wing and characteristic changes with temperature, we find that light scattering data exhibit similar features, too. Depolarized light scattering spectra of propylene carbonate are in fact quantitatively compatible with the dielectric ones, when the latter are corrected for a different stretching as detected by these techniques. In the case of glycerol this correspondence is much less convincing, even though the excess wing was shown [10] to be present in both kinds of spectra. In yet other cases of 2-picoline and salol, the light scattering and dielectric

spectral shapes are clearly different at low temperatures, beyond a difference in stretching of the α-peak [17]. It therefore appears that general scaling properties of relaxation spectra, established solely on the basis of dielectric data, may be of limited validity as universal characteristics of structural relaxation as such.

Appendix

Model susceptibility spectra $\chi''(\omega)$, obtained by convoluting the normalized distribution $G_{GGE}(\tau)$ (equation (3)) with the Lorentzian, are normalized, $\int_{-\infty}^{\infty} \chi''(\omega)\,d\ln\omega = \pi/2$. In order to compare them with experimental spectra, the latter should be likewise normalized. For propylene carbonate (figure 2(a)) such normalization by numerical integration can only be applied to those spectra in figure 2(a), where the α-peak is in the spectral window, i.e. at high temperatures. At low temperatures, we assumed that the spectral integrals that are proportional to the corresponding static susceptibilities follow the Curie law, i.e. are inversely proportional to the temperature, $\chi_0 \propto T^{-1}$. This assumption is fully supported by the observed behaviour of propylene carbonate at high temperatures, where we computed the spectral integrals numerically. Thus, to achieve amplitude normalization, we first multiplied the spectra of figure 2(a) by their temperatures, to compensate for the Curie temperature dependence of the static susceptibility χ_0. We then computed $\chi_0 = 2/\pi \int_{-\infty}^{\ln 10\,\mathrm{THz}} \chi''(\nu)\,d\ln\nu$ of the 255 K spectrum that was extrapolated to zero frequency using fits, described in the main text. The limit of integration of 10 THz leaves out the Raman spectrum of intramolecular vibrations. We then divided all the spectra by χ_0.

Normalized spectra of glycerol in figure 8(b) were obtained in a similar manner, as described in [10].

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