Dielectric and shear mechanical alpha and beta relaxations in seven glass-forming liquids

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We present shear mechanical and dielectric measurements taken on seven liquids: triphenylethylene, tetramethyltetra-phenyltrisiloxane (Dow Corning 704® diffusion pump fluid), polyphenyl ether (Santovac® 5 vacuum pump fluid), perhydrosqualene, polybutadiene, decahydroisoquinoline (DHIQ), and tripropylene glycol. The shear mechanical and dielectric measurements are for each liquid performed under identical thermal conditions close to the glass transition temperature. The liquids span four orders of magnitude in dielectric relaxation strength and include liquids with and without Johari-Goldstein beta relaxation. The shear mechanical data are obtained by the piezoelectric shear modulus gauge method giving a large frequency span (10^{-3}–$10^{4.5}$ Hz). This allows us to resolve the shear mechanical Johari-Goldstein beta peak in the equilibrium DHIQ liquid. We moreover report a signature (a pronounced rise in the shear mechanical loss at frequencies above the alpha relaxation) of a Johari-Goldstein beta relaxation in the shear mechanical spectra for all the liquids which show a beta relaxation in the dielectric spectrum. It is found that both the alpha and beta loss peaks are shifted to higher frequencies in the shear mechanical spectrum compared to the dielectric spectrum. It is in both the shear and dielectric responses found that liquids obeying time-temperature superposition also have a high-frequency power law with exponent close to $-1/2$. It is moreover seen that the less temperature dependent the spectral shape is, the closer it is to the universal $-1/2$ power-law behavior. The deviation from this universal power-law behavior and the temperature dependencies of the spectral shape are rationalized as coming from interactions between the alpha and beta relaxations. © *2005 American Institute of Physics.*
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I. INTRODUCTION

The relaxation in glass-forming liquids is complex and a full understanding is far from reach. Even the characteristics of the phenomenology are controversial; the temperature dependence of the alpha relaxation time, the shape of alpha relaxation, the generality of time-temperature superposition, and the role of the Johari-Goldstein beta relaxation[1,2] are among the central issues addressed.[3,4]

Dielectric spectroscopy is a standard method in the field and a strong tool because an exceptionally large dynamical range can be reached.[5,6] However, in order to verify that the findings of dielectric spectroscopy are intrinsic, and not specifically related to the probe, it is necessary to probe the dynamics by different methods. The dynamic shear modulus is one of the fundamental macroscopic quantities of interest, but shear mechanical data are relatively scarce[7] and are rarely available above 100 Hz (e.g., Refs. 8–10).

The shear relaxation data are of special interest in combination with dielectric data because a common hypothesis is that the shear mechanical and the dielectric responses are connected. This relation has typically been investigated by comparing characteristic time scales (either directly based on loss peak position[8,9,11–15] or on, e.g., the Debye-Stokes-Einstein relation[8,9,11,12,16]). Moreover, several authors compare shear and dielectric responses via different models.[17–22]

Here we present shear and dielectric relaxation spectra taken on seven liquids in the temperature region just above the glass transition temperature. The shear data are taken in a large frequency span (10^{-3}–$10^{4.5}$ Hz) which is significantly larger on the high-frequency side than what is commonly reported. The large frequency range makes it possible to access the shear mechanical Johari-Goldstein beta relaxation and to make a better overall analysis of the temperature dependence of the shape of the shear relaxation spectrum.

Most of the liquids have previously been studied by dielectric spectroscopy. However, if details in the two responses are to be compared, it is necessary to be sure that the experimental conditions are the same for the two measurements, which is difficult since measurements are normally performed using different apparatus and different cryostats. We have therefore chosen to perform new dielectric measurements on all seven liquids. This ensures that the samples

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are exactly the same and minimizes the uncertainty in absolute temperatures. The data set is hence ideal for making direct comparisons between the dielectric and shear mechanical relaxations.

In this paper we compare the shear mechanical and dielectric responses from a phenomenological point of view, thereby addressing the question of how conclusions are altered by altering the response function used in probing the relaxation. The comparison is done between the dielectric susceptibility $\epsilon(\nu)$ and the shear modulus $G(\nu)$. Hence we do not introduce the dielectric modulus $M(\nu)=1/\epsilon(\nu)$ as it is sometimes suggested.[3,23,24] In a second paper, Ref. 25, we present a more elaborated model-based comparison of the two data sets. In Ref. 25 we furthermore introduce a modulus-type formulation and argue that it is not *a priori* relevant to compare the shear modulus and the traditional dielectric modulus.

The seven liquids span four orders of magnitude in dielectric relaxation strength. The dielectric relaxation strength is defined macroscopically as the difference between high- and low-frequency limits of the dielectric constant, and its size is controlled by the number density and the size of the permanent dipole moment of the molecule in question. The set of liquids includes four liquids which are known to exhibit a Johari-Goldstein beta relaxation in their dielectric spectrum and three liquids for which only the alpha process can be seen in the dielectric spectrum.

The liquids and experimental details are described in Sec. II. In Sec. III we present the experimental results. In Sec. III A we discuss dielectric and shear mechanical beta relaxations. The temperature dependence of, respectively, the dielectric and shear mechanical alpha loss peak frequency is discussed in Sec. III B. In Sec. III C we discuss the alpha loss peak shape and the deviations from time-temperature superposition in the framework of Olsen *et al.* (see Ref. 26). Finally we summarize our findings in Sec. IV.

II. EXPERIMENT

The dielectric cell used is a multilayered gold-covered capacitor, with an empty capacitance of 70 pF. The shear measurements are performed by using the piezoelectric shear modulus gauge (PSG) method. In the PSG method the shear modulus is obtained from measurements of the frequency-dependent capacitance of the empty and the loaded gauge, a transducer based on piezoelectric plates (see Ref. 27 for further details). Both methods are based on the measurement of a frequency-dependent capacitance and the measuring devices are of similar sizes. It has therefore been possible to obtain the two different types of data by using the same setup for measuring capacitances and the same cryostat for temperature control. We have moreover kept the same cooling rate and performed the shear mechanical measurements and the dielectric measurements on samples taken from the same bottle [except for decahydroisoquinoline (DHIQ) where shear mechanical and dielectric data were taken on samples from two bottles, which had their respective original seal broken just before the measurement]. Thus the shear and

dielectric spectra have, for each sample, been taken on identical samples under the same thermal conditions.

The cooling rate was chosen to ensure that the liquids were in thermodynamic equilibrium; this was further ensured by taking two measurements at each temperature, and only accepting data where no systematic difference could be seen.

Capacitances where measured with an HP 3458A multimeter in conjunction with a Keithley AWFG used at frequencies in the range of 10^{-3}–10^2 Hz, and an HP 4284A *LCR* meter used at 10^2–10^6 Hz. The PSG transducer has a resonance which gives an upper frequency limit at $10^{4.5}$ Hz for the shear data. The temperature was controlled by a home-built nitrogen-cooled cryostat which has an absolute accuracy on the temperature better than 0.2 K and a temperature stability better than 20 mK.

The seven liquids studied are triphenylethylene (TPE), tetramethyltetra-phenyltrisiloxane (DC704), polyphenyl ether (PPE), perhydrosqualene, polybutadiene (PB20), decahydroisoquinoline, and tripropylene glycol (TPG). Five of the liquids are molecular van der Waals bonded liquids, while tripropylene glycol has hydrogen bonds and polybutadiene is a polymer. More details on the samples are given in Table I. All liquids were used as acquired and no further purification was performed. The PPE used is the Santovac® 5 vacuum pump fluid, and DC704 is the Dow Corning 704® diffusion pump fluid. Everything else was acquired from Sigma-Aldrich.

The measurements on DHIQ were taken right after the seal of the bottle was broken, and the sample was kept in an atmosphere of a high (N_2) concentration during the entire procedure to avoid reaction with oxygen. TPE was obtained as a solid and it recrystallizes after melting when kept at room temperature. The sample was melted at 370 K and loaded in a preheated gauge, followed by fast cooling to obtain the supercooled liquid.

III. RESULTS

The data set consists of the complex frequency-dependent dielectric constants $\epsilon(\nu)$ and the complex frequency-dependent shear modulus $G(\nu)$.

In Figs. 1–4 we present the shear mechanical relaxation spectra for six of the seven liquids and one example of a dielectric spectra at selected temperatures. (Dielectric and shear mechanical spectra including Cole-Cole plots for all the liquids are shown in Ref. 28). We show the imaginary part of the shear modulus $[G''(\nu)]$ (the shear mechanical loss) and minus the imaginary part of the dielectric constant $[-\epsilon''(\nu)]$ (the dielectric loss) as a function of frequency. In Figs. 5 and 6 the temperature dependency of the loss peak frequency of, respectively, the shear mechanical and dielectric relaxations are shown.

The dielectric data on TPG, DC704, squalane, and TPE are in good agreement with what has previously been reported by our group[22,26] and others.[29,30] Our DC704 shear data reproduce and extend the data reported by one of us.[22] The dielectric loss peak frequency we find for DHIQ is systematically 0.2 decade above the values reported in Ref. 29. The frequency-dependent shear modulus of squalane has

TABLE I. Refraction index (n), molecular weight (M), dielectric relaxation strength ($\Delta\epsilon$), and position of the beta loss peak ($\nu_{\beta,lp}$). The refraction index (taken at 25 °C) and molecular weight of PPE are from Scientific Instrument Services, Inc. (information found on their webpage http://www.sisweb.com/). The refraction index of PB20 was measured on a PZO RL3 refractometer at approximately 28 °C. No refraction index is given for TPE because it is a solid at room temperature. The refraction index (taken at 20 °C) and molecular weight of other liquids are from Sigma-Aldrich (information found on their webpage http://www.sigmaaldrich.com). $\Delta\epsilon$ and the position of the beta loss peaks are rough numbers found from our dielectric data, the precise value is temperature dependent.

Sample	Abbreviation	n^2	M (g/mol)	$\Delta\epsilon$	$\nu_{\beta,lp}$ (Hz)
Triphenylethylene	TPE	⋯	256.3	0.05	⋯
Tetramethyltetraphenyltrisiloxane	DC704	2.430	484	0.2	⋯
Polyphenyl ether	PPE	2.659	454	1.5	⋯
Perhydrosqualene	Squalane	2.105	422.8	0.015	$10^{4.5}$
Polybutadiene[a]	PB20	2.310	5000	0.15	$10^{4.5}$
Decahydroisoquinoline	DHIQ	2.221	139.2	1.5	$10^{2.7}$
Tripropylene glycol	TPG	2.085	192.3	20	$10^{4.0}$

[a]The polybutadiene (PB20) is composed of chains with an average of 80% 1,4- and 20% 1,2-butadiene monomers. The monomer molecular weight is 54.09 g/mol and the average molecular weight of a chain is 5.000 g/mol.

been reported over a smaller frequency range by Deegan *et al.* (Ref. 9). The shear loss peak frequencies which we find for squalane are roughly 0.5 decade below the earlier reported values.

A. Johari-Goldstein beta relaxation

Secondary beta relaxations of the Johari-Goldstein type can be seen in our dielectric data for three of the liquids (TPG, DHIQ, and PB20). Moreover, it has previously been reported[29] that squalane shows a beta relaxation in the dielectric spectra, though it could not be seen in the data we report here due to the weakness of the dielectric relaxation strength of squalane and the limitations of our dielectric setup. In all these four cases the low-temperature shear data
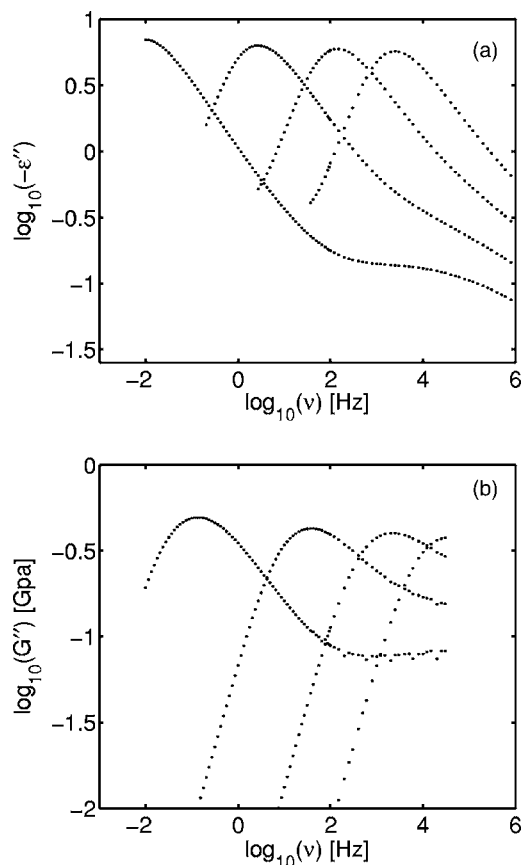

FIG. 1. Loss spectra of TPG. (a) Dielectric data. (b) Shear mechanical data. The spectra are taken at 192.0, 200.0, 208.0, and 216.0 K. It is easily seen that the shear mechanical loss peak is at a higher frequency than the dielectric loss peak when comparing at the same temperatures.
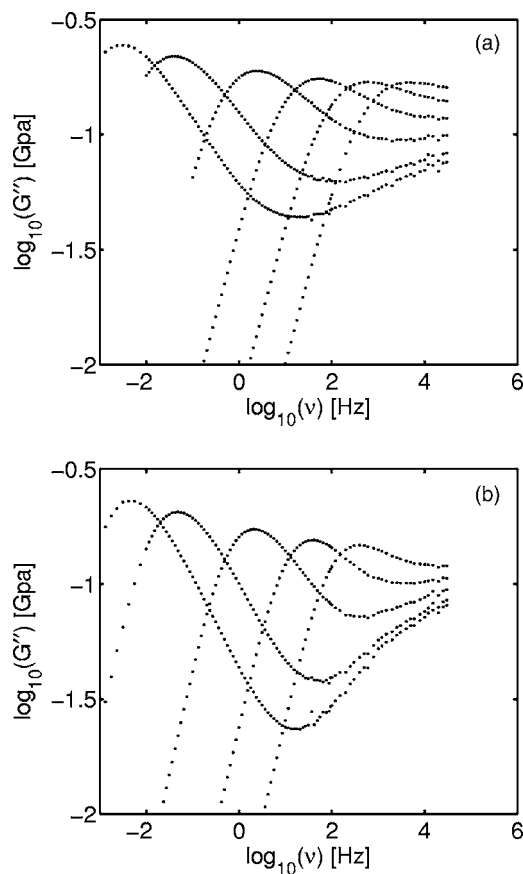

FIG. 2. Shear mechanical loss spectra. (a) PB20 at 176.0, 178.0, 182.0, 186.0, 190.0, and 194.0 K. (b) Squalane at 168.0, 170.0, 174.0, 178.0, and 182.0 K. The loss increases on the high-frequency side of the alpha peak for both liquids at low temperatures. This increase is interpreted as the shear signature of the Johari-Goldstein peak seen in the dielectric loss of both liquids.
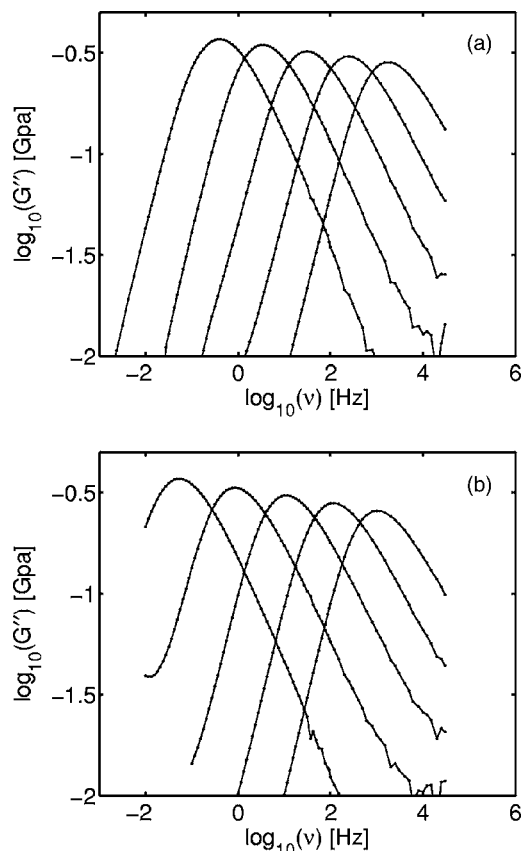
FIG. 3. Shear mechanical loss spectra. (a) TPE at 256.0, 260.0, 264.0, 268.0, and 272.0 K. (b) PPE at 248.0, 252.0, 256.0, 260.0, and 264.0 K. No sign of a beta relaxation is seen in the spectra of these liquids.

show a rise in the shear loss at frequencies above the alpha relaxation (see Figs. 1, 2, and 4). We interpret the rise seen in the shear loss as evidence of a shear mechanical Johari-Goldstein beta relaxation. In the case of DHIQ which exhibits the beta relaxation at a very low frequency, the actual shear mechanical beta *peak* is resolved in the spectra at the lowest temperature (See Fig. 4). Secondary shear mechanical relaxation has been known from the spectra of glassy polymers already several decades ago.[31] However, the data we report here are to our knowledge the first example of a shear
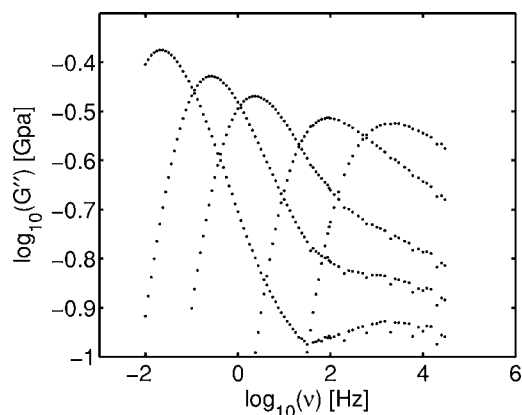

FIG. 4. Shear mechanical loss spectra of DHIQ at 180.0, 181.5, 183.0, 186.0, and 189.0 K. A clear Johari-Goldstein beta peak is seen at the lowest temperature. The notches seen in the spectra are artifacts from the used HP 4284A *LCR* meter.
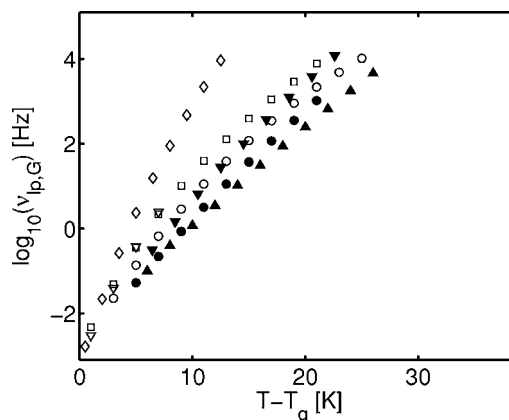

FIG. 5. Shear mechanical loss peak position as a function of $T-T_g$. The temperature is shifted by T_g in order to make it possible to show data of all liquids in one plot. The loss peak frequency is the maximum of $G''(\nu)$. T_g is in this figure taken as the temperature where the shear mechanical loss peak frequency is 10^{-3} Hz. TPE, T_g=248 K (▲), DC704, T_g=209 K (▼), PPE, T_g=243 K (●), squalane, T_g=167 K (□), PB20, T_g=175 K (▽), DHIQ, T_g=178 K (◇), and TPG, T_g=187 K (○).

mechanical beta peak seen in the data from a molecular liquid in thermodynamical equilibrium.

The remaining three liquids (TPE, DC704, and PPE) do not show a beta relaxation in the dielectric spectrum. For these three liquids no high-frequency rise in the shear mechanical loss is seen (see Fig. 3), that is, no signature of a shear mechanical Johari-Goldstein beta relaxation is observed. This demonstrates that the shear beta relaxation is present in the same liquids as those which exhibit a dielectric beta relaxation, while we find no shear mechanical beta relaxation in the cases without a dielectric beta relaxation. However, the dielectric spectra of PPE show a deviation from power-law behavior in the high-frequency tail, while no similar deviation is seen in the shear mechanical spectra.

The shear mechanical beta loss peak position cannot be directly accessed, in all but one case, because the peak position lies above the upper frequency limit of the PSG method
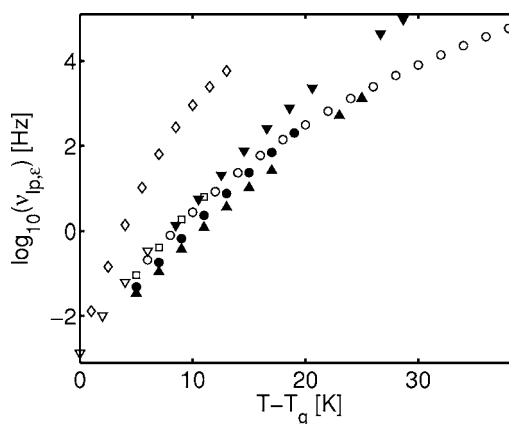

FIG. 6. Dielectric loss peak position as a function of temperature. The temperature is shifted by T_g in order to make it possible to show data of all liquids in one plot. The loss peak frequency is defined as the position of the maximum of $-\epsilon''(\nu)$. T_g is in this figure taken as the temperature where the dielectric loss peak frequency is 10^{-3} Hz. TPE, T_g=249 K (▲), DC704, T_g=211 K (▼), PPE, T_g=245 K (●), squalane, T_g=167 K (□), PB20, T_g=176 K (▽), DHIQ, T_g=179 K (◇), and TPG, T_g=190 K (○).
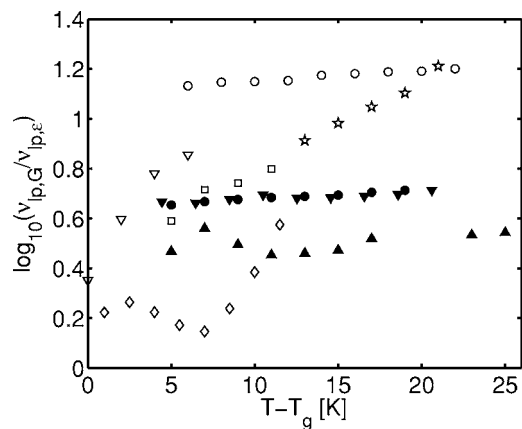
FIG. 7. Difference in shear mechanical and dielectric loss peak position, in terms of the decoupling index [$\log_{10}(\nu_{lp,G}/\nu_{lp,\epsilon})$] as a function of temperature. The decoupling index was suggested by Zorn *et al.* (see Ref. 14). We have compared the shear loss peak position of squalane to the dielectric loss peak positions determined from the VTF fit given by Richert *et al.* (Ref. 29) in the high-frequency region which is not covered by our dielectric measurements on squalane. This is the frequency region which is covered by the data from Ref. 29. The VTF fit is excellent and can therefore be regarded as an interpolation of the data. TPE (▲), DC704 (▼), PPE (●), squalane (□), squalane using dielectric data from Richert *et al.* (Ref. 29) (☆), PB20 (▽), DHIQ (◇), and TPG (○).

($10^{4.5}$ Hz). However, by comparing the spectra directly (e.g., Fig. 1) we find that the shear mechanical beta loss peak position is at higher frequencies than the dielectric beta loss peak position found at the same temperature.

It would be interesting to compare the relative beta relaxation strength (defined as the fraction of the total change in real part, due to the beta relaxation) of the shear mechanical beta relaxation and the dielectric beta relaxation. However, it is necessary to extrapolate and only qualitative conclusions can be drawn, because the high-frequency limit of the shear spectra is never reached in the spectra where we see a clear signature of the shear beta relaxation. From extrapolation we find that the shear mechanical beta relaxation strength is much larger than the dielectric beta relaxation for TPG, and for PB20. In the case of squalane the shear beta appears to be somewhat larger, while the shear mechanical and the dielectric beta relaxations have similar relative strength in the case of DHIQ. Hence the relative strength of the shear mechanical beta relaxation is generally larger than that of the respective dielectric beta relaxation.

B. Time scale of the alpha relaxation

The shear mechanical and dielectric spectra shown for TPG in Fig. 1 are taken at the same temperatures. It can immediately be seen that the alpha loss peak frequency of the shear spectra ($\nu_{lp,G}$) is higher than the corresponding dielectric loss peak frequency ($\nu_{lp,\epsilon}$). By comparing Fig. 5 to Fig. 6 it is seen that this behavior is general for the liquids which we have investigated; similar results exist in the literature,[8,9,11,19,22,32,33] indicating that it is indeed general that $\nu_{lp,G} > \nu_{lp,\epsilon}$.

Figure 7 illustrates the temperature dependence of the difference between the shear and the dielectric alpha loss peak positions. This is done in terms of the decoupling index.[14]

In the case of squalane and PB20 the difference between the dielectric and the shear alpha loss peak positions decreases as temperature decreases. In the case of DHIQ a complicated temperature dependence is seen; at high temperatures the difference decreases with decreasing temperature, but a slight peak is observed. For the remaining liquids (TPE, DC704, PPE, and TPG) the difference in loss peak position is only weakly temperature dependent. In contrast to our result Richert *et al.* (Ref. 29) see no decoupling between shear mechanical loss peak position and dielectric loss peak position in squalane. However, this earlier result is based on shear mechanical data[9] which only covers a small dynamic range and on an extrapolation of the dielectric data.

It is striking that the large temperature dependence of the decoupling index is seen for squalane, PB20, and DHIQ which all exhibit beta relaxations. However, in the case of TPG, where a huge beta relaxation is seen in the shear spectrum and a very small one in the dielectric spectrum, the decoupling index is virtually temperature independent. It is thus not possible to establish a clear connection between beta relaxation and decoupling.

The difference in the position of the alpha loss peak leads to a trivial difference in the glass temperature determined by the two methods when the definition $\nu_{lp}(T_g) = 10^{-3}$ Hz is used. As the shear loss peak position is higher, the shear glass transition temperature is lower. Generally we estimate a difference in T_g of a few degrees. A general analysis of what governs the alpha relaxation time is out of the scope of this paper. However, it is clear from above that very detailed models or theories need to consider a specific probe, as both the alpha relaxation time and its temperature dependence, in general, depend on how it is measured.

One of us has earlier proposed the shoving model as an explanation of the temperature dependence of the alpha relaxation time.[34] The shoving model relates the alpha relaxation time (or equivalently the loss peak position frequency) to the high-frequency value of the shear modulus, G_∞. It can therefore be tested from the frequency-dependent shear mechanical spectra without the need of other types of data. The shoving model relates G_∞ to the loss peak position, ν_{lp}, by $\ln(\nu_{lp}(T)) = \ln(\nu_0) - (G_\infty(T)V_c)/(k_BT)$, where the prefactor ($\nu_0$) is assumed to the phonon frequency and V_c is a temperature-independent characteristic volume. If time-temperature superposition (TTS) is obeyed, it follows that $G''_{max} \propto G_\infty$. When plotting $G''(\nu)/T$ as a function of $\ln(\nu)$ the shoving model therefore predicts that the maxima of $G''(\nu)/T$ lie on a straight line which intersects the point $(\ln(\nu_0), 0)$. In the following section we show that TTS in the shear spectra holds well for DC704, TPE, and PPE (see Figs. 9 and 11). The predictions of the shoving model have earlier been demonstrated to hold for DC704. In Fig. 8 we show that it also holds for TPE and PPE.

When there is no TTS the prediction of the shoving model can be tested directly by comparing G_∞ to $\ln(\nu_{lp})$. However, G_∞ is not reached within the frequency region we
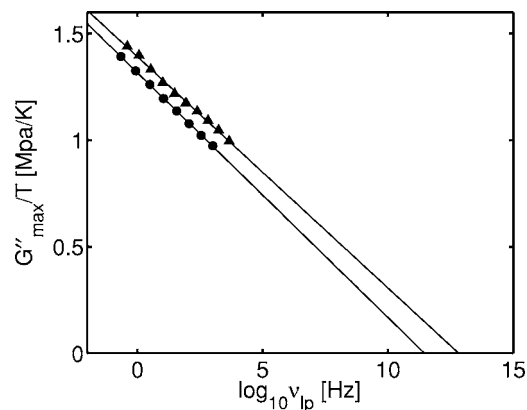
FIG. 8. The maximum of the imaginary part of the shear modulus divided by T, G''_{max}/T, as a function of the logarithm of the loss peak frequency $\log_{10}(\nu_{lp})$. TTS is fulfilled for TPE and PPE, which means that $\max(G''(\omega)) \propto G_\infty$. Hence the figure demonstrates $\ln(\nu_{lp}) = -K(G_\infty/T) + \ln(\nu_0)$ with $\ln(\nu_0) \approx 13$. This behavior is in agreement with the prediction of the shoving model. TPE (▲) and PPE (●).

access in the remaining four liquids (squalane, PB20, DHIQ, and TPG) due to the beta relaxation. A test of the shoving model would therefore require extrapolation of the data.

C. Spectral shape

The shape of the relaxation spectra and its temperature dependence are often characterized by different fitting parameters. The stretched exponential, which has two adjustable parameters, is the most commonly used function in the time domain. The Cole-Davidson is a commonly used two-parameter fitting function in the frequency domain. Functions with two parameters can give resonable fits as long as no secondary relaxation is seen in the spectra, but the result depends on how much of the relaxation curve is experimentally available, which again, in practice, depends on the temperature. The Havriliak-Negami function which has three adjustable parameters is often used in the frequency domain. The function gives good fits over a very extended frequency range, as long as there is no secondary relaxation, but the parameter values are correlated, meaning that different combinations of parameters give equally good fits. Fitting spectra with beta relaxations requires additionally at least one parameter and a choice of how the alpha and beta parts of the spectra should be merged (e.g., by addition or convolution). Hence using fitting functions to characterize the shape of the relaxation spectra involves a number of *ad hoc* choices which will influence the conclusions that can be drawn. We have therefore chosen to follow the simple and unbiased line suggested in Ref. 26. We study the temperature dependence of the minimal slope of the alpha relaxation α_{min} and the full width at half maximum of the loss W both found in a log-log plot of $-\epsilon''(\nu)$ or $G''(\nu)$ against frequency. The data on the slope are shown in Figs. 9 and 10 and the data on the width are presented in Figs. 11 and 12. Details about α_{min} and W are found in the figure captions.

If the shape of the imaginary part of the response function when plotted in a log-log plot is temperature independent then the liquid is said to obey TTS. Both α_{min} and W will be temperature independent if the liquid obeys TTS. In
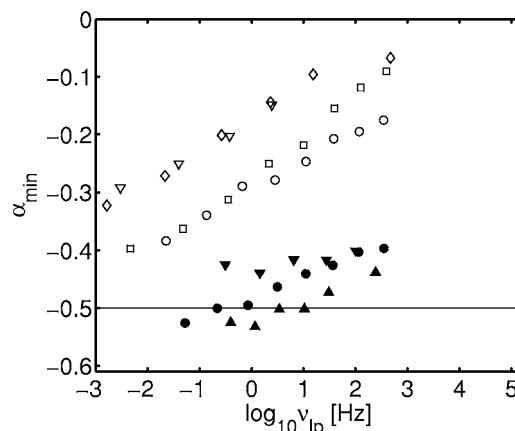

FIG. 9. Shear mechanical data. The minimal slope of the alpha relaxation (α_{min}) in a log-log plot of G'' as a function of frequency, plotted against the loss peak frequency. For the liquids without a visible beta relaxation, the minimal slope is taken as the slope of the high-frequency limiting power law, for liquids with a beta relaxation the minimal slope before the beta relaxation is used. The gauge used for measuring the shear modulus consists of three piezoceramic plates and the method becomes sensitive to relaxation in the piozoceramics when G'' is very small. The problem enters at high frequencies and low temperatures for liquids with no apparent beta relaxation. Therefore we only report slope parameters down to loss peak frequencies around 0.1–1 Hz for these liquids (TPE, DC704, and PPE). The line is a guide to the eye at $\alpha_{min} = -1/2$; it is speculated in Ref. 26 that a connection exists between time-temperature superposition and $\alpha_{min} = -1/2$. This assertion is supported from the data reported here insofar as the stronger temperature dependence is seen the more α_{min} differs from 1/2. TPE (▲), DC704 (▼), PPE (●), squalane (□), PB20 (▽), DHIQ (◇), and TPG (○).

Ref. 26 it is suggested on the basis of dielectric data that $\alpha_{min} = -1/2$ when TTS is obeyed and it is speculated that deviations from TTS could be attributed to the influence from the beta relaxation. The $\alpha_{min} = -1/2$ behavior has moreover been predicted for the dielectric relaxation from a model which has recently been proposed by Dyre (Ref. 35). Here we analyze these assertions on the basis of the dielectric as well as the shear mechanical behavior.

The analysis has not been possible on the dielectric spectra for squalane and PB20 due to the small dielectric strength
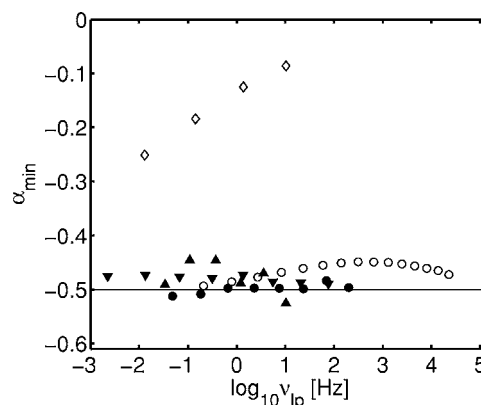

FIG. 10. Dielectric data. The minimal slope (α_{min}) in a log-log plot of $-\epsilon''$ as a function of frequency, plotted against the loss peak frequency. See Fig. 9 for details. No such data exists for squalane and PB20 as their data are too noisy due to their small dielectric relaxation strength. TPE has a small dielectric strength as well, but the data are easier to analyze due to the lack of beta relaxation. However, the α_{min} values are determined with a smaller accuracy than for the other liquids. TPE (▲), DC704 (▼), PPE (●), DHIQ (◇), and TPG (○).
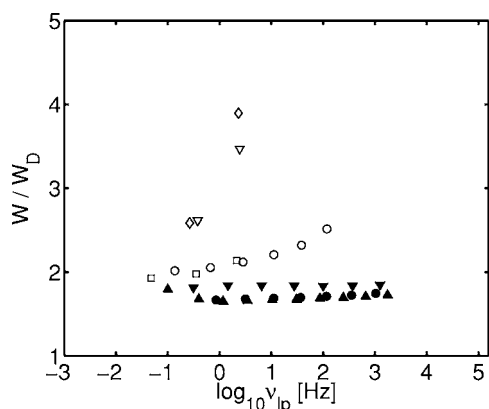
FIG. 11. Shear mechanical data. Loss peak width (W) of the shear mechanical relaxation curve, defined by the full width at half maximum in a log-log plot of G'' as a function of frequency normalized by the same quantity for a Debye process (W_D) (Ref. 38), plotted against the loss peak frequency. When TTS is obeyed W/W_D is temperature independent. In the case of liquids with a beta relaxation (marked by unfilled symbols) the width includes the beta relaxation until sufficient separation has occurred. The reason for not reporting data at lower temperatures (lower loss peak frequency) is the lack of data on the low-frequency side of the loss peak, making it impossible to calculate the full width. In the case of DHIQ and PB20 the amount of high-temperature data is likewise limited because the pronounced beta relaxation and the limited frequency ranges of the data make it impossible to reach the half maximum value on the high-frequency side of the loss peak. TPE (▲), DC704 (▼), PPE (●), squalane (□), PB20 (▽), DHIQ (◇), and TPG (○).

combined with the relative complicated spectral shape. The dielectric data of TPE, which also has a very small dielectric signal, are easier to analyze as there is no beta relaxation in the spectra. However, α_{min} and W are determined with larger uncertainty than for the other spectra which can also be seen in the scatter of the dielectric TPE values in Figs. 10 and 12.

Two different general behaviors can immediately be distinguished when looking at the overall temperature dependence of α_{min} as it is shown in Figs. 9 and 10. The spectra
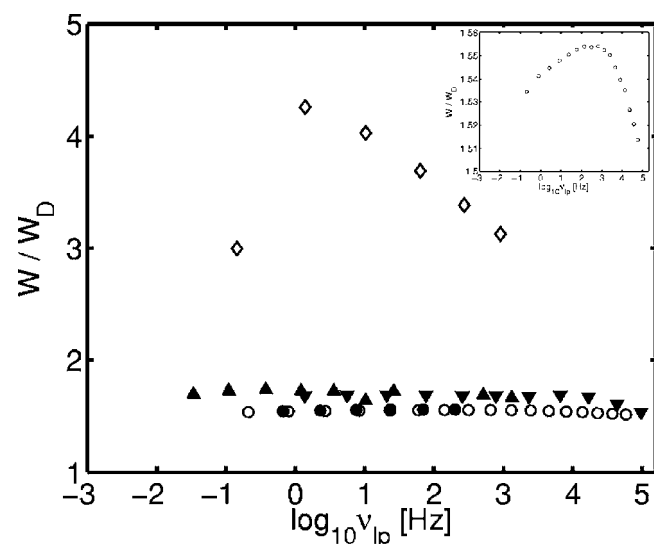

FIG. 12. Dielectric data. Loss peak width (W/W_D) of the dielectric relaxation curve based on $-\epsilon''$, (see Fig. 11 for details). No such data exist for squalane and PB20 as their data are too noisy due to their small dielectric relaxation strength. The inset shows the same data for TPG with a different scaling. TPE (▲), DC704 (▼), PPE (●), DHIQ (◇), and TPG (○).

with filled symbols (from liquids without a visible Johari-Goldstein beta relaxation) show little temperature variation in α_{min} and have values around $\alpha_{min}=-1/2$. The other group of the spectra, the ones with unfilled symbols (from the liquids with a visible beta relaxation), have α_{min} values which are strongly temperature dependent: the value of α_{min} decreases with decreasing temperature except in the case of the dielectric results on TPG where a more complicated behavior can be seen. This classification in two groups is followed by the data on the width W (see Figs. 11 and 12), with a somewhat larger variation in W for the temperature-independent spectra when comparing one liquid to another.

In comparing the shear and the dielectric data of the same liquids we find the general trend that the shear spectra have an equal or large α_{min} corresponding to a less steep high-frequency behavior. The shear spectra are also slightly broader than the dielectric spectra—except in the case of TPE. For the liquids without beta relaxation it is seen that the spread in the level of α_{min} is larger in the case of the shear mechanics than for the dielectric.

It has previously been reported[26] that DC704 and a number of other liquids with no visible beta peak have virtually temperature-independent α_{min} values of approximately $-1/2$. In Fig. 10 it is shown that this behavior is followed by PPE and TPE thus supporting the ideas from Refs. 26 and 35. That is, the dielectric alpha peaks which are not influenced by a beta relaxation obey TTS with a close to universal high-frequency power-law behavior ($\alpha_{min}=-1/2$).

The shear spectra for the liquids without a visible beta relaxation in the spectra show a significantly larger derivation from TTS than the corresponding dielectric data. DC704 shows a virtual temperature-independent behavior, while TPE and PPE have a small temperature dependency in the shape parameters (mostly visible in α_{min}). For both TPE and PPE α_{min} and W decrease with decreasing temperature. However, α_{min} and W seem to converge toward a constant value, with α_{min} close to $-1/2$; hence it can be speculated that the temperature dependence could be due to a hidden shear mechanical beta relaxation. Following the results in Sec. III A it is possible that a beta relaxation is much larger in the shear mechanics, which would explain why an influence is seen on the shear alpha peak, while none is seen on the dielectric alpha peak.

Though TTS is not found to the same degree in the shear data as in the dielectric data, the general pattern is reproduced: It is evident that the liquids without a visible beta relaxation are much closer to obeying TTS than what is the case for the liquids with a beta relaxation. Furthermore we find that the α_{min} is close to universal when comparing the different liquids without a visible beta relaxation and that it roughly fulfills $\alpha_{min}=-1/2$. This provides support for the hypotheses that there is a connection between TTS and $\alpha_{min}=-1/2$ and that such a relation can be extended to shear relaxation.

The temperature dependence of the shape parameters in the liquids with a beta relaxation differs between each liquid and in some cases also between the shear and the dielectric response. DHIQ has a strong temperature dependency of α_{min} and W in both the shear mechanical and the dielectric
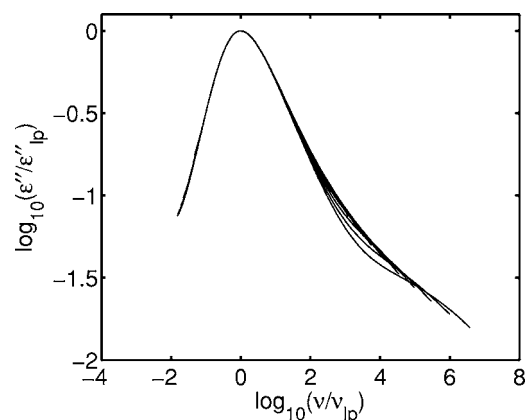
FIG. 13. Dielectric loss of TPG scaled by the max loss and the loss peak frequency. The temperatures shown are 196.0–212.0 K in steps of 2 K. There is a spreading of the curves at the high-frequency side where the Johari-Goldstein beta peak appears, while the alpha peaks appear to collapse on a single master curve.
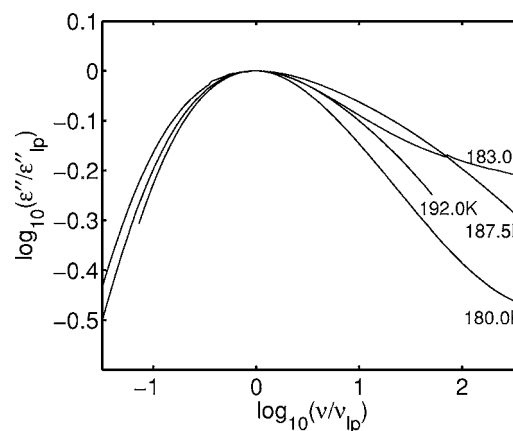

FIG. 14. Dielectric loss of DHIQ scaled by the maximum loss and the loss peak frequency (note the scale of the axis, the beta peak is outside the zoom). It is seen that the alpha peak broadens upon cooling as the beta peak emerges, while it gets narrower again as the beta peak separates from the alpha peak.

responses. The α_{min} and W of TPG show a behavior similar to DHIQ in the shear data while the temperature dependence is weak in the case of the dielectric spectra. Looking to the raw spectra it is seen that the relative strength of the beta relaxation in DHIQ is of the same size in the shear and dielectric relaxations, while the relative strength of the beta relaxation of TPG is much smaller in the dielectric relaxation than in the shear mechanical relaxation. Hence the temperature dependence found of α_{min} and W appears larger when the beta peak is stronger, consistent with the hypothesis that it is the influence of the beta peak which yields the temperature dependence. The open question is then why the shear and dielectric beta relaxations are of similar strength in some cases while they are very different in others.

1. Detailed analysis of TPG and DHIQ dielectric data

The dielectric TPG data are less noisy than any of the other data due to the large dielectric strength of TPG and more details can therefore be extracted from the temperature dependence of these spectra. First of all it is seen that the dielectric shape parameters (Figs. 10 and 12) lie very close to the corresponding parameters of liquids which exhibit no beta relaxation. This can be easily understood from looking at Fig. 13, in which it is clearly seen that the dielectric spectral shape is strongly dominated by the alpha relaxation. It is moreover tempting to suggest that the alpha relaxation, in fact, obeys TTS as the curves in Fig. 13 fall on a master curve in the low-frequency part up to about 1 decade above the peak position of the alpha relaxation. Looking closer to the temperature dependence of the shape parameters it is seen that the minimal slope of the spectra increases upon cooling while the beta peak emerges and that it falls again apparently approaching $\alpha_{min}=-1/2$ as the two relaxations separate. A similar behavior is seen for W (see Fig. 12, especially the inset), the width increases upon cooling and decreases upon further cooling.

As DHIQ has a beta relaxation at very low frequency it is interesting to take a closer look at the temperature evolution of the DHIQ dielectric alpha peak on the basis of the spectra themselves as they are shown in Fig. 14. As the tem-

perature is decreased, the peak gets broader and the beta peak appears as a shoulder. At even lower temperatures the two peaks separate and the alpha peak becomes narrower again. Thus the behavior is analogous to that of TPG.

These two examples show that the interaction of an alpha and a beta relaxation might lead to very complicated temperature dependencies of the shape of the spectra. This emphasizes that it is difficult to make assertions regarding the intrinsic temperature dependence of the alpha relaxation.

The broadening of the alpha peak is seen even when the beta peak is not visible as a distinct feature in the spectra. It is therefore difficult to establish when the alpha peak is unaffected by the beta relaxation. As an example we mention that the narrowing of the squalane shear alpha relaxation which is illustrated in Fig. 11 was reported earlier by Deegan et al.[9] However, the data of Deegan et al. have an upper frequency limit of 1 Hz, which means that the beta relaxation is out of the measured frequency range. The earlier data, therefore, did not reveal the possible connection between the beta peak and the apparent change of the alpha peak shape.

IV. SUMMARY

We have reported detailed measurements of the shear mechanical and dielectric relaxations on seven glass-forming liquids. This data set gives a unique possibility for comparing dielectric and shear mechanical relaxations.

We find that the Johari-Goldstein relaxation which is commonly reported on the basis of dielectric data has a signature in the shear mechanical data as well, and for one liquid we resolve the actual shear mechanical beta relaxation peak. Moreover it appears that when a beta relaxation is present in one of the relaxations for a liquid it is also present in the other, but that the strength of the beta relaxation might be very different. This suggests that the shear mechanical and dielectric beta relaxations are closely related, but in a nontrivial manner.

The loss peak frequency of both alpha and beta peaks is always found at a higher frequency for the shear spectrum

than for the corresponding dielectric spectrum taken at the same temperature. No significant decoupling between the shear and the dielectric loss peak positions is found in the liquids without visible beta relaxation. Decoupling between the shear and dielectric maximum losses is only seen when maximum loss carries information of both the beta and the alpha relaxation; it is, however, seen that for TPG no pronounced decoupling exists even though a beta relaxation with a very different strength is seen in the two signals; hence no general connection between decoupling and beta relaxation is found.

The dielectric spectra of the liquids without visible beta relaxation exhibit a close to temperature-independent shape, and a close to universal shape, with a high-frequency power-law behavior with an exponent of $-1/2$. The liquids which show a beta relaxation have a significant temperature dependency of the shape of the alpha relaxation. It is possible to attribute the temperature dependencies of the latter case to the influence of the beta relaxation, and hence speculate that the alpha relaxation in itself has a temperature-independent shape. The shape of the shear mechanical spectra exhibits some temperature dependence for all the liquids. However, the general picture is reproduced: The high-frequency behavior is close to a $-1/2$ power law when the spectral shape is weakly temperature dependent, and this type of behavior is found when no beta relaxation is visible in the spectra. This altogether provides support for the hypotheses of a connection between TTS and $\alpha_{min} = -1/2$, and that such a relation can be extended to shear relaxation.

The dielectric data presented span three orders of magnitude of dielectric relaxation strength. The dielectric relaxation strength is roughly proportional to the dipole moment of the molecule, and it is therefore a measure of the dipole interactions in the liquid. Moreover, the dielectric relaxation strength determines the difference between the applied macroscopic field and the average local field acting on the molecules.[25,36,37] Therefore it is of interest to note that we find no systematic dependence on the dielectric strength, neither in the characteristics of the dielectric relaxation itself nor in the way the dielectric relaxation relates to the shear mechanical relaxation.

ACKNOWLEDGMENTS

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