PHYSICAL REVIEW B **76**, 064201 (2007)

Primary and secondary relaxation time dispersions in fragile supercooled liquids

Li-Min Wang and Ranko Richert
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA

(Received 3 April 2007; revised manuscript received 6 June 2007; published 13 August 2007)

The relaxation time dispersions of the primary (α) and secondary (β) dielectric relaxations are studied for molecular glass-forming liquids regarding their dependence on structural relaxation time [or lack thereof observed as time-temperature superposition (TTS)], their changes with fragility, and a possible correlation of the values for the α and β processes. Toward more fragile liquids, the width w_α of the α peak at the glass transition temperature T_g is known to increase significantly. Additionally, we observe that TTS extends over a broader range of peak relaxation times in the case of higher fragility, with the approach to exponential (Debye) relaxation being delayed to faster dynamics. The width w_β of the β relaxation at T_g is somewhat lower for more fragile liquids and appears correlated with that of the primary relaxation. The extrapolated coincidence of the dispersions of the α and β processes occurs at the fragility "limit" of $m=170$, implying that $w_\alpha \leqslant w_\beta$ for all molecular supercooled liquids. Materials of high fragility are also those with no clear low-frequency cutoff in the relaxation time distribution—i.e., their susceptibilities require Havriliak-Negami instead of Cole-Davidson fits. For sorbitol, the value of w_β is seen to change steadily through the α-β-merging region, whereas w_α displays a kink at the crossover temperature.

DOI: 10.1103/PhysRevB.76.064201 PACS number(s): 64.70.Pf, 77.22.Gm

I. INTRODUCTION

The structural relaxation of glass-forming liquids involves a wide range of time scales, particularly for materials near their glass transition temperature T_g. Apart from smaller contributions at higher frequencies, the dominant processes seen in viscous liquids by dielectric relaxation spectroscopy are the primary (α) and secondary (β) processes, both displaying significant deviations from simple exponential correlation functions.[1–3] The former is associated with the structural relaxation and the calorimetric glass transition, as well as viscous flow, while the latter is often identified as Johari-Goldstein[4] (JG) relaxation if no intramolecular mode is responsible. The microscopic picture behind the JG process is still not clear, but its significance for the slower α process is being recognized.[5–7] The two statistically interdependent processes are elementary degrees of freedom which govern the dynamics in supercooled liquid and glasses.[8–12] The kinetics of β relaxations and their merging scenario of the α and β processes near a crossover temperature T_c have been studied extensively in terms of the average relaxation times.[5,13–17] This is particularly true for glass-forming liquids with high fragility index m, which uses the slope of the logarithmic relaxation time scale versus T_g/T to gauge the deviation from an Arrhenius-like temperature dependence, $m = d\log_{10}\tau/d(T_g/T)$. Compared with the amount of studies focused on the secondary relaxation time τ_β, little systematic work is found regarding the degree of dispersion (or deviation from exponentiality) of the β relaxation and how it is related to that of the α process.

There are various approaches to quantifying the dispersion of relaxation processes, and a single parameter which gauges the deviation from exponential kinetics is usually preferred over more than one. The empirical Kohlrausch-Williams-Watts (KWW) decay pattern

$$\varphi(t) = \varphi_0 \exp[-(t/\tau)^{\beta_{\mathrm{KWW}}}] \tag{1}$$

casts the nonexponential character into a single exponent β_{KWW} with $0 < \beta_{\mathrm{KWW}} \leqslant 1$, where $\beta_{\mathrm{KWW}} = 1$ restores the exponential case. In a dielectric experiment, $\varphi(t) = (\varepsilon(t) - \varepsilon_s)/(\varepsilon_\infty - \varepsilon_s)$ would correspond to the normalized polarization response. This KWW law accounts for a large number of observed relaxation patterns and is more often used for time domain data, but frequency domain KWW fits are also common.[18] In the case of frequency domain experiments—e.g., dielectric measurements of $\varepsilon^*(\omega)$ by impedance techniques—the dispersion is more easily characterized by the shape parameters of the Havriliak-Negami (HN) function,

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau)^{\alpha_{\mathrm{HN}}}]^{\gamma_{\mathrm{HN}}}}, \tag{2}$$

where ε_s is the steady state and ε_∞ the high-frequency limit of the dielectric constant ($\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the relaxation strength). The exponents α_{HN} and γ_{HN} control the symmetric and asymmetric broadening of the relaxation time distribution, respectively, and their product $\alpha_{\mathrm{HN}}\gamma_{\mathrm{HN}}$ can be used as a single-parameter gauge for the dispersion and is related to the high-frequency logarithmic slope by $d\ln\varepsilon''/d\ln\omega = -\alpha_{\mathrm{HN}}\gamma_{\mathrm{HN}}$. The primary dielectric peak of many supercooled materials is well represented by this empirical HN approach.[19]

If sufficiently separated from the primary relaxation peak, the JG β relaxations appear as broad but symmetric loss profiles $\varepsilon''(\omega)$, which are therefore better described by the Cole-Cole (CC) function. The CC profile is a special case of Eq. (2) where $\gamma_{\mathrm{HN}} = 1$, and the remaining shape parameter is denoted α_{CC} instead of α_{HN} for clarity. Situations where the symmetric broadening is not required are referred to as Cole-Davidson (CD) cases, where $\alpha_{\mathrm{HN}} = 1$ and γ_{HN} is renamed to γ_{CD}. Although KWW and HN fits are not equivalent, the dispersions implied in the parameters can be compared on the basis of the approximation $\beta_{\mathrm{KWW}} = (\alpha\gamma)^{1/1.23}$,[20] where we use $\alpha\gamma = \alpha_{\mathrm{CC}}$ for β relaxations. While the value of 1.23 has been obtained by Alvarez *et al.* via numerical fits to synthetic data, matching the moments of the KWW and HN distributions leads to a slightly lower value of 1.12 based on the work of Burger.[21]

Apart from the broad and symmetric loss profiles seen in β-relaxation studies on glass-forming systems, common features of secondary relaxations are its occurrence in the glassy state for $T<T_g$, an Arrhenius temperature dependence of the average relaxation time τ_β, relaxation strengths $\Delta\varepsilon_\beta$ that gain amplitude with increasing temperature, the merging behavior with the α process at T_β, and a systematic variation of the spectral separation of primary and secondary peaks with fragility m (Ref. 22) (or β_{KWW}).[5,7] Because secondary processes other than JG type do exist, criteria have been devised to discriminate genuine JG processes from others.[23] The aim of this work is to provide additional insight into the secondary relaxations and their correlation with properties of the primary structural processes. The focus of the study is comparing the relaxation time dispersions for the α and β relaxations on the basis of dielectric relaxation data on a number of molecular liquids. The fragility m is seen to affect not only the β_{KWW} parameter at T_g, as is well known,[24] but its entire temperature dependence $\beta_{\mathrm{KWW}}(T)$, since the Debye case is always recovered above peak frequencies of above 1 GHz. The width of the secondary peak (at T_g) displays only little dependence on the particular glass former or its fragility. While the secondary process is always broader than the primary one, we find that the widths approach each other with increasing fragility m and coincide by extrapolation at a "limiting" fragility index of approximately 170. In parallel, primary loss profiles are more symmetrically broadened for very fragile materials relative to the stronger ones. As observed for sorbitol, the dispersion of the secondary peak gradually approaches that of the total process as the temperature is increased.

II. EXPERIMENTS

In order to supplement literature data, four additional glass-forming liquids have been studied by dielectric spectroscopy. The compounds together with the abbreviations and nominal purities are methyl-*m*-toluate (MMT, 98%, Avocado Research Chemicals Ltd.), 3-methoxy-1-butanol (3M1B, 99%), 3-dimethylamino-1-propanol (3DA1P, 99%), and 2-*iso*-propoxyethanol (2iPE, 99%). Unless specified otherwise, the chemicals are obtained from Aldrich and all materials are used as received. These liquids display good glass-forming ability, and their main dielectric processes reflect the structural relaxations, which are associated with the calorimetric glass transitions. The dielectric measurements are performed with impedance methods for frequencies in the range $10\ \mathrm{mHz} \leqslant \nu \leqslant 1\ \mathrm{MHz}$ using a Solartron 1260 gain-phase analyzer equipped with a Mestec DM-1360 transimpedance amplifier. Two metal disks with diameters 30 mm and 20 mm serve as electrodes, whose spacing is maintained at 50 μm with Teflon strips. The empty capacitor is used as reference for the geometric capacitance. The temperature control is based on a Novocontrol Quatro liquid-nitrogen-cooling system.

III. RESULTS AND DISCUSSION

According to the classification along the strong-fragile pattern proposed by Angell, glass-forming liquids are sorted in terms of their steepness index m, defined as the slope $d\log_{10}\tau/d(T_g/T)$ evaluated at the glass transition temperature T_g.[25] Equivalent to the steepness index m, this scale determines how rapidly the structural relaxation time (or viscosity $\eta=\tau G_\infty$) changes at T_g. Many other properties of supercooled liquids are correlated with this fragility concept. Examples are the stretching exponent β_{KWW},[24] the impact of the crossover temperature T_B on the dynamics,[26,27] and the spectral separation of τ_α and τ_β,[22] as well as thermodynamic quantities such as $\Delta C_p(T_g)/\Delta S_m$ (Refs. 28 and 29)—i.e., the heat capacity step at T_g divided by the melting entropy. The average change of the relaxation time dispersion with fragility is well accounted for by the relation $m=250(\pm 30)-320\beta_{\mathrm{KWW}}$.[30] This observation refers to the KWW exponent β_{KWW} taken at T_g only. A more complete picture of how fragility affects the degree of dispersion is provided in Fig. 1, which shows β_{KWW} versus the peak frequency $\nu_{\max}$ of the structural (α) relaxation process for a variety of glass-forming systems. Using $\nu_{\max}$ as the abscissa scale instead of temperature rests on the observation that the structural relaxation time τ_α is the key quantity which determines the dispersion (i.e., independent of temperature and pressure), as reported by Ngai *et al.*[31]

Time-temperature superposition (TTS) refers to the situation in which temperature shifts only the time scale of the response, without modifying the shape of the susceptibility or correlation function. Here, we approximate the validity of TTS by requiring only a temperature-invariant dispersion parameter β_{KWW}. Clearly, the ambiguity inherent in the fitting with KWW allows two different relaxation spectra to yield the same exponent β_{KWW} and the current approach is bound to be approximate only. The values for β_{KWW} are derived from the HN fits, and other techniques could yield deviating values for the stretching exponent. For the results of Fig. 1, the important aspect regarding fitting is the consistency across the temperatures for a given material.

The curves in Fig. 1 clearly show that the question of TTS or temperature-invariant β_{KWW} should not be answered by "yes" or "no" only. Instead, there is a gradual change of the range over which TTS appears to be applicable, extending from T_g or $\log_{10}(\nu_{\max}/\mathrm{Hz})=-2.8$ to T_c or $\log_{10}(\nu_{\max}/\mathrm{Hz}) \approx 6.5$ for very fragile cases to practically no range in which TTS applies for the stronger liquids. For systems of intermediate fragility, TTS holds across several decades of $\nu_{\max}$ just above T_g, but not within the entire T_g–T_c range. According to Fig. 1, an appreciable TTS range sets in for $\beta_{\mathrm{KWW}}(T_g) \leqslant 0.57$, entirely consistent with the link to the $\omega^{-1/2}$ slope reported by Olsen *et al.*[32] However, a difference between the present method and the more exact approach of Olsen *et al.* regarding analyzing TTS behavior is that β_{KWW} is governed solely by the α peak, while the high-frequency slope is affected by both the α and β processes, particularly for fragility systems. Because the transition to the high-temperature Debye-like behavior does not occur until $T \approx T_c$ for fragile glass formers, the change of $\beta_{\mathrm{KWW}}(T)$ is accordingly more rapid above T_c than for less fragile cases. This is consistent with earlier observations of different rapidities of change of $n=1-\beta_{\mathrm{KWW}}$ at the dynamic crossover temperature T_B ($\approx T_c$) by León and Ngai.[33] According to the results compiled

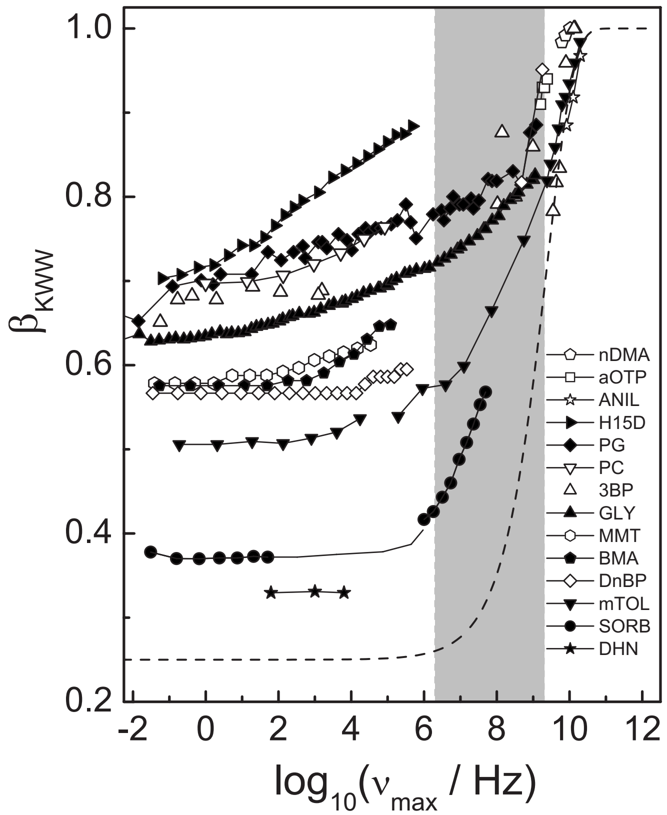

FIG. 1. Relaxation time dispersion parameter β_{KWW} versus peak frequency ν_{max} of the α process for 14 glass-forming liquids that differ in their fragility. In the order from high to low β_{KWW}, the systems are n,n-dimethylaniline (nDMA, Ref. 69), 4-acetyl-o-terphenyl (aOTP, Ref. 70), aniline (ANIL, Ref. 69), hexane-1,5-diol (H15D), propylene glycol (PG, Ref. 71), propylene carbonate (PC), 3-bromopentane (3BP, Ref. 72), glycerol (GLY, Ref. 73), methyl-m-toluate (MMT), butylmethacrylate (BMA), di-n-butylphthalate (DnBP), m-toluidine (mTOL, Refs. 57 and 74–76), D-sorbiltol (SORB, Ref. 10), and decalin (DHN, Ref. 77). The structure of the diol H15D might not be as simple as that of the other liquids with generic behavior. The gray area shows that the steepest rates of change for β_{KWW} often occur in the $T_c - T_A$ range. The dashed line indicates a possible case of extreme fragility with $\beta_{KWW}(T_g) = 0.25$.

in Fig. 1, $\beta_{KWW}(T_c)$ appears to be more sensitive to the steepness index m than is $\beta_{KWW}(T_g)$. Common to all liquids is the lack of dispersive structural dynamics for peak frequencies in excess of $\nu_{max} \approx 10$ GHz—i.e., at temperatures beyond T_A at which a transition to true Arrhenius behavior sets in.[34,35] That the top curve (hexane-1,5-diol) approaches Debye dynamics more rapidly than the others could be a result of hydrogen bonding. Monohydroxy alcohols have been omitted from this graph, as their prominent dielectric peak is a Debye process at all frequencies and not related to structural relaxation.[36–39] The gray area in Fig. 1 marks the temperature range of the steepest β_{KWW} transitions, which occurs between T_B ($\approx T_c$) and T_A based on typical values (not implying that all systems display the same relaxation time at their respective T_c and T_A). The dashed line provides an idea of how $\beta_{KWW}(\nu_{max})$ could change in the limit of a very fragile molecular liquid, characterized by $m = 170$ and $\beta_{KWW}(T_g) = 0.25$.[28]

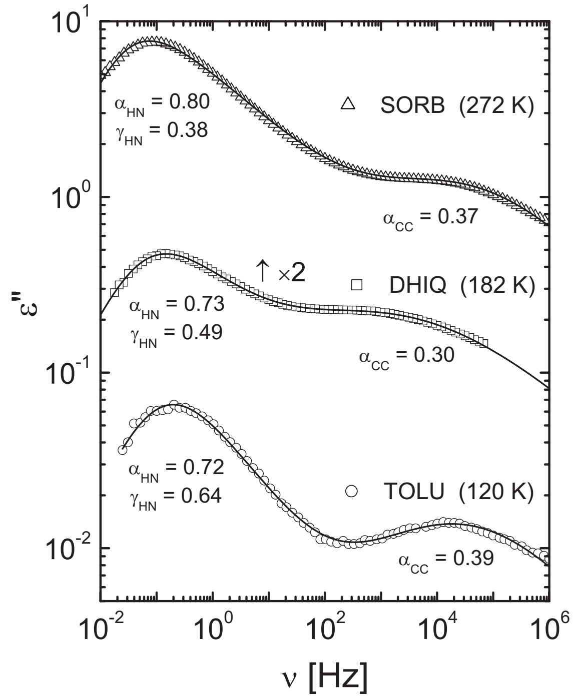

FIG. 2. Frequency-resolved dielectric loss $\varepsilon''(\omega)$ of three glass-forming liquids with high fragility indices m: sorbitol (SORB, Ref. 9), decahydroisoquinoline (DHIQ, Ref. 42), and toluene (TOLU, Ref. 11). Two pronounced features in these liquids are the deviations of these profiles from the Cole-Davidson pattern and the development of secondary relaxation maxima. Lines are HN+CC fits to the experimental data. Sample temperatures (selected for $\nu_{max} \approx 0.1$ Hz regarding the α process), as well as the exponents (α_{HN}, γ_{HN}, α_{CC}), are provided in the graph. The DHIQ curves are shifted up 2× for clarity.

The above discussion on $\beta_{KWW}(\nu_{max})$ has disregarded how well the data match KWW-type correlation decays. A survey of the dynamics of molecular glass formers shows that most systems with strong or intermediate fragility are well accounted for by the CD function—i.e., the HN type susceptibility of Eq. (2) with α_{HN} set to unity.[40] For such systems, the probability density $g(\tau)$ of relaxation time constants possesses a well-defined longest time scale—i.e., a cutoff in $g(\tau)$. The loss profile of such liquids will show a slope of $d \ln \varepsilon''(\omega)/d \ln \omega = +1$ for frequencies sufficiently below the peak value ω_{max}. Occurrences of significant deviations from these CD-type loss curves correlate with the liquid being very fragile in terms of the steepness index m. Figure 2 shows the dielectric loss spectra $\varepsilon''(\omega)$ of three fragile liquids: sorbitol (SORB, $m = 100$),[9] toluene (TOLU, $m = 103$),[8,41] and decahydroisoquinoline (DHIQ, $m = 139$),[42] at a common α-relaxation time of $\tau_\alpha \approx 1$ s. All examples display pronounced secondary processes in terms of an additional higher-frequency peak (where that of DHIQ is not a JG-type β process),[43] very high values of m, and low-frequency slopes $\alpha_{HN} < 1$ of the primary peaks that are inconsistent with CD behavior. The observation of $\alpha_{HN} < 1$ is seen more clearly and across a wider range of frequencies at higher

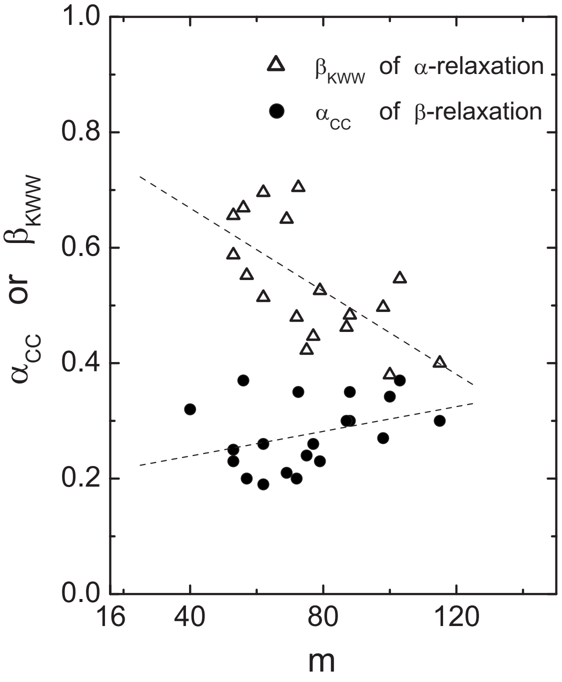

FIG. 3. The dispersion parameters β_{KWW} of the α relaxation and α_{CC} of the β relaxation as a function of fragility m for various glass formers as compiled in Table I. The value of α_{CC} is less sensitive to the fragility than is β_{KWW}, the inequality $\beta_{KWW} > \alpha_{CC}$ holds, and the two parameters tend to converge in the limit of high fragility. Lines are linear fits to the respective data sets.

temperatures; the values are not derived solely from the spectra displayed in Fig. 2. This observation is equivalent to relaxation functions of more or less fragile liquids all following the KWW pattern, because HN fits to Eq. (1) yield near-CD behavior ($0.9 < \alpha_{HN} \leqslant 1$) for all $\beta_{KWW} \geqslant 0.6$ and a significant departure from CD fits for $\beta_{KWW} < 0.6$.[20,21]

Similar to earlier work by Böhmer *et al.*[24] but with the axes swapped, we plot in Fig. 3 the dependence of the stretching exponent $\beta_{KWW}(T=T_g)$ on the value of m. Albeit with considerable scatter involved, a correlation ($R=-0.65$) of the two quantities is visible. The molecular liquids of Fig. 3 are those compiled in Table I and include only cases where a CC-type secondary relaxation has been detected and characterized in terms of $\alpha_{CC}(T=T_g)$. The resulting symmetric dispersion parameters α_{CC} are shown as open symbols in Fig. 3 versus the steepness index m. An approaching trend of the two dispersion parameters for the α and β relaxations is seen with increasing fragility, despite the large uncertainty in the correlation of β_{KWW} and α_{CC} with m (see also Ref. 31). That the dispersions of the primary and secondary processes are correlated quantities is shown in Fig. 4 by graphing the ratio of α_{CC} to β_{KWW} as a function of fragility, which includes both JG- and non-JG-type secondary processes. We observe that α_{CC}/β_{KWW} displays an improved correlation with m relative to α_{CC} or β_{KWW} individually, as in Fig. 3. This notion is particularly true if the non-JG-type β relaxations (open symbols in Fig. 4) are removed from consideration.[23,44] We conclude that the widths of the primary and secondary contributions to structural relaxation are not independent quantities. It should be noted that the scatter in Fig. 4 is partially due to errors in the determination of $\alpha_{CC}(T=T_g)$, which shows a strong temperature dependence (see below). The trend seen in Fig. 4 is consistent with $\alpha_{CC}/\beta_{KWW} \rightarrow 0$ if extrapolated to the minimum fragility, $m=16$. This suggests that for the stronger liquids, the β relaxation is not only near the spectral position of the α peak but also subject to an extremely broad loss profile with an accordingly low amplitude, which adds to the problem of discriminating a JG peak from an excess wing behavior.[45–47]

The inset of Fig. 4 shows the ratio of the relaxation widths, w_α/w_β, for the α and β relaxations, restricted to the subset of systems for which the β process is a true JG-type relaxation. The widths w are determined as full-width-half-maximum (FWHM) values from the dielectric loss profiles. The advantage of this quantity over α_{CC}/β_{KWW} is that the two parameters w_α and w_β are based on the same metric and the ratio is more meaningful. The dashed line in the w_α/w_β versus m plot represents the linear change from $w_\alpha/w_\beta=0$ at the minimum fragility $m_{\min}=16$ to matching widths, $w_\alpha/w_\beta=1$, in the case of fragilities reaching $m \approx 170$. This value is near our recent prediction of an upper limit of fragility of organic small molecular liquids, $m_{\max}$ being around 170.[28] The important implication in Fig. 4 is that the width of the relaxation time distribution of the α relaxation at T_g will not exceed that of the β relaxation at T_g for molecular systems.

The equality $w_\alpha=w_\beta$ (at T_g) will occur only in cases near the limiting fragility, $m_{\max}=170$, where the spectral separation of the primary and secondary relaxations would be as large as 10 orders of magnitude at the glass transition according to the coupling model.[7] For fragile real systems with $m \approx 100$, the primary relaxation time dispersion remains significantly below that of the secondary process at T_g. Because of the α-β-merging scenario at T_c—i.e., the existence of only a single relaxation process above T_c—the α and β peaks cannot both follow TTS across the T_g-T_c range. Therefore, it is interesting to investigate the temperature or (better) peak frequency dependence of the primary and secondary dispersions for a glass former that obeys TTS near T_g, such as sorbitol (see Fig. 1). Sorbitol is a high-fragility liquid which has been investigated extensively regarding its dynamics.[9,10,15,48–50] Figure 5 shows the two dielectric relaxation dispersions in a wide frequency range using the inverse width (FWHM) as the dispersion parameter, w_D/w, normalized to the width of Debye relaxation, $w_D=1.14$. The results are based on two independent broadband dielectric data sets,[9,15] which agree favorably. Both data sets are analyzed by the sum of two statistically independent processes. While this approach is questionable in the merging region,[51] the values just below T_c are not relevant to the scope of Fig. 5. A notable feature of the dispersion widths is the different behavior of the α and β relaxations below the frequency $\nu_{\max}=10^6$ Hz—i.e., below the dynamic crossover temperature $T_B \approx T_c$.[52] Below T_c, the width of the α peak is not sensitive to temperature (or peak frequency), indicative of TTS. By contrast, the dispersion width of the β relaxation rapidly decreases toward that of the α relaxation in the temperature range between T_g and T_c.[53] Above T_c, only a single peak remains and its value of w_D/w changes with approximately the same slope seen for the secondary relaxation below T_c.

TABLE I. Characteristic parameters for the dynamics of materials compiled in Figs. 3 and 4: Glass transition temperature T_g, fragility m, and the dispersion exponents α_{HN}, γ_{HN}, and β_{KWW} for the α process, as well as the value of α_{CC} for the β process. The lower eight rows refer to liquids with non-JG secondary relaxation.

	α process					β process	
Materials	T_g (K)	m	α_{HN}	γ_{HN}	β_{KWW}	α_{CC}	Ref.
m-toluidine	186	98	0.94	0.45	0.5	0.27	57
toluene	117	103	0.72	0.66	0.55	0.37	13
o-terphenyl	246	88	0.87	0.47	0.48	0.3	58
methyl-*m*-toluate	165	53	1	0.52	0.59	0.25	This work
butyronitrile	95	56	1	0.61	0.67	0.37	59
sorbitol	268	100	0.8	0.38	0.38	0.34	9
squalane	167	75	0.77	0.45	0.42	0.24	42
2-ethyl-1-hexanol	146	72	0.9	0.45	0.48	0.2	37 and 38
3-methoxy-1-butanol	145	62	1	0.64	0.7	0.19	This work
3-dimethylamino-1-propanol	146	57	0.86	0.56	0.55	0.2	This work
2-isopropoxyethanol	141	69	0.98	0.6	0.65	0.21	This work
xylitol	248	87	0.85	0.475	0.48	0.3	22 and 60
threitol	224	79	0.84	0.54	0.53	0.23	22 and 60
1,1′-di(4-methoxy-5-methylphenyl)cyclohexane	261	66	0.9	0.49	0.51	0.26	61
cresolphthalein-dimethylether	312	72.5	0.97	0.67	0.7	0.35	62
2-ethylhexylamine	141	77	0.7	0.53	0.45	0.26	37
dimethyl phthalate	193	80	0.92	0.5	0.53	0.32	63
diethyl phthalate	187	73	1	0.45	0.52	0.38	64
di-*n*-butyl phthalate	177.4	82	0.96	0.518	0.57	0.43	65
di-*iso*-butyl phthalate	191.1	78	0.965	0.521	0.57	0.46	65
bis-5-hydroxypentylphthalate	205	71	0.85	0.36	0.38	0.38	66
decahydroisoquinoline	180	139	0.9	0.25	0.3	0.32	42 and 43
3-fluoro aniline	172	70	0.91	0.58	0.6	0.32	67
tri-propylene glycol	193	80	0.96	0.6	0.64	0.288	68

Near the merging temperature, the two peaks have attained very similar dispersions and the secondary peak might be changing to a more asymmetric (HN instead of CC) profile.[54] The change in the slope, w_D/w, of the β relaxation at T_g is somewhat related to the behavior of the dielectric relaxation strength $\Delta\varepsilon(T)$ at T_g.[46,55,56] Whether this behavior of w_D/w_α and w_D/w_β is generic or sorbitol specific remains to be seen.

IV. SUMMARY AND CONCLUSIONS

Based upon a series of representative molecular glass-forming liquids, we have studied the dependence of the dielectric dispersions of the α and β relaxations (mainly of the Johari-Goldstein type) on fragility m and on the peak frequency ν_{max} of the primary structural relaxation. Additionally, we are interested in assessing possible correlations of the primary and secondary processes regarding their degree of deviation from an exponential or Debye type correlation function. Gauged in terms of β_{KWW} at $T=T_g$, the α process displays the well-documented decrease with m,[24] observed here as $\beta_{KWW}=0.81-m/278$ for the present selection of those liquids that show discernible β peaks. The analogous parameter for the secondary process, α_{CC}, is much less dependent on fragility than β_{KWW} and has an opposite slope $\alpha_{CC}=0.20+m/935$. For a more quantitative assessment of the primary and secondary loss profiles, their dispersions are compared in terms of their widths w_α and w_β, respectively. While w_α increases and w_β decreases with the fragility index m, their values would coincide only in the case of a fragility as high as $m_{max}\approx 170$, consistent with earlier estimates of this limiting value.[28] Therefore, the inequality $w_\alpha < w_\beta$ holds for all molecular systems. Note that as w_α approaches w_β with increasing m, the respective relaxation times τ_α and τ_β separate increasingly. Additionally, w_α and w_β appear to be correlated quantities; i.e., a liquid with above average w_α (for its particular value of m) will display an accordingly wide secondary process.

As the temperature of a supercooled liquids is increased, the dispersion of the α process becomes smaller; i.e., β_{KWW} tends to its limiting value of unity—without exception. We observe that this gradual increase from $\beta_{KWW}(T_g)$ to 1 changes systematically with the fragility index m if β_{KWW} is plotted versus the peak frequency ν_{max} of the primary struc-

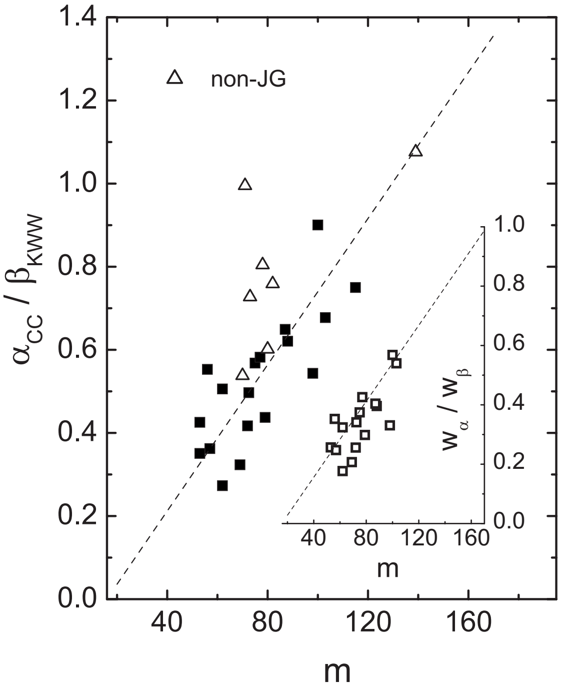

FIG. 4. The ratio α_{CC}/β_{KWW} versus fragility m for the glass formers as compiled in Table I, derived from the dispersion parameters α_{CC} of the β relaxation and β_{KWW} of the α relaxation. The data demonstrate a significant correlation of the α- and β-relaxation dispersions. In the inset, the widths w (FWHM) of the α-process (w_α) and JG-type β-process (w_β) loss profiles are used to extrapolate to a high-fragility limit that could occur at $w_\alpha/w_\beta \rightarrow 1$. Lines are guides to the eye only.

tural relaxation. Strong systems with concomitantly large $\beta_{KWW}(T_g)$ are subject to a mild increase of $\beta_{KWW}(\lg \nu_{max})$ which begins at T_g. Accordingly, no TTS is observed for these cases. Toward more fragile systems with lower $\beta_{KWW}(T_g)$, the increase of $\beta_{KWW}(\lg \nu_{max})$ is delayed to peak frequencies ν_{max} approaching the crossover temperature T_B or T_c, beyond which the change to the Debye case occurs more rapidly. As a result, the regime of TTS above T_g expands systematically with m, starting from zero for strong liquids to a range which reaches T_c for very fragile glass formers such as sorbitol. Common to all liquids is the Debye behavior with $\beta_{KWW}=1$ once the structural process has reached a peak frequency of $\nu_{max} \approx 10$ GHz.

The dispersion parameter α_{CC} of the secondary process or its width w_β shows only little variation with fragility index m, but a surprisingly strong dependence on the primary relaxation frequency, as seen for sorbitol. While the α peak follows TTS across eight decades, with a temperature invariant β_{KWW} between T_g and T_c, the secondary dispersion changes a factor of 2 between T_g and the merging temperature near T_c. Interestingly, the secondary width quantified as w_D/w_β changes continuously through the merging regime, whereas the primary counterpart w_D/w_α is subject to a kink which indicates the end of the TTS range and the onset of approaching exponential dynamics at high temperatures.

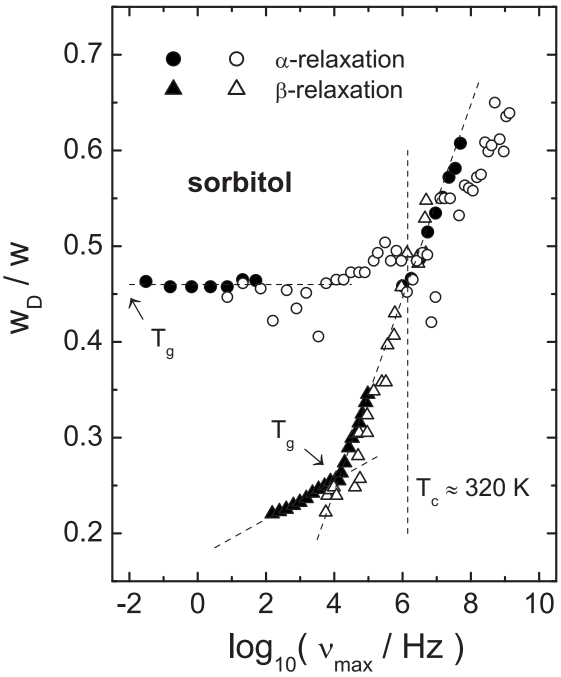

FIG. 5. The width w (FWHM) of the α and β relaxations derived from the dielectric loss of sorbitol as a function of peak frequency ν_{max}. The ordinate scale w_D/w represents the reciprocal width w normalized to the Debye value $w_D=1.14$. The open symbols are based on the data of Ref. 15; solid symbols are from Ref. 9. For this fragile liquid, w_β is more sensitive to temperature (or peak frequency) than w_α. The primary and secondary relaxation peaks merge near the crossover temperature $T_c \approx 320$ K. Lines are guides to the eye only.

In conclusion, the fragility correlates not only with the stretching exponent β_{KWW} of the α process at T_g, which implies deviations from Cole-Davidson behavior for cases of large m that lead to $\beta_{KWW} < 0.6$. Instead, also the range over which β_{KWW} remains constant (and only eventually reaches unity at $\nu_{max} \approx 10$ GHz) changes systematically with m, as does the secondary dispersion in terms of $\alpha_{CC}(T_g)$. The impact of $\beta_{KWW}(T_g)$ or m on the TTS behavior is summarized by the TTS range increasing with fragility from no TTS at all to a small range near T_g and eventually toward covering the entire $T_g - T_c$ interval. It is hoped that the present observations regarding the dispersion features of the primary and secondary relaxations will help to establish a better understanding of the complex dynamics of supercooled liquids. In particular, a single correlation function description of the two processes instead of a superposition of seemingly independent peaks is highly desirable.

ACKNOWLEDGMENTS

The authors thank Daniele Prevosto and Albena Nielsen for informative discussions. Acknowledgement is made to the donors of the American Chemical Society Petroleum Research Fund (ACS-PRF) for support of this research under Grant No. 42364-AC7.

[1] J. Jäckle, Rep. Prog. Phys. **49**, 171 (1986).

[2] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).

[3] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

[4] G. P. Johari and M. Goldstein, J. Phys. Chem. **74**, 2034 (1970); J. Chem. Phys. **53**, 2372 (1970); **55**, 4245 (1971).

[5] K. L. Ngai, J. Phys.: Condens. Matter **15**, S1107 (2003); K. L. Ngai and S. Capaccioli, Phys. Rev. E **69**, 031501 (2004).

[6] R. Richert and K. Samwer, New J. Phys. **9**, 36 (2007).

[7] K. L. Ngai, J. Chem. Phys. **109**, 6982 (1998).

[8] W. Schnauss, F. Fujara, and H. Sillescu, J. Chem. Phys. **97**, 1378 (1992).

[9] H. Wagner and R. Richert, J. Non-Cryst. Solids **242**, 19 (1998).

[10] H. Wagner and R. Richert, J. Phys. Chem. B **103**, 4071 (1999).

[11] M. Vogel and E. Rössler, J. Chem. Phys. **114**, 5802 (2001); J. Phys. Chem. B **115**, 10883 (2001).

[12] R. Böhmer, G. Diezemann, B. Geil, G. Hinze, A. Nowaczyk, and M. Winterlich, Phys. Rev. Lett. **97**, 135701 (2006).

[13] A. Kudlik, S. Benkhof, T. Blochowitz, C. Tschirwitz, and E. Rössler, J. Mol. Struct. **479**, 201 (1999).

[14] M. Beiner, H. Huth, and K. Schröter, J. Non-Cryst. Solids **279**, 126 (2001).

[15] T. Fujima, H. Frusawa, and K. Ito, Phys. Rev. E **66**, 031503 (2002).

[16] M. Paluch, C. M. Roland, S. Pawlus, J. Ziolo, and K. L. Ngai, Phys. Rev. Lett. **91**, 115701 (2003).

[17] C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).

[18] G. Williams, D. C. Watts, S. B. Dev, and A. M. North, Trans. Faraday Soc. **67**, 1323 (1971).

[19] S. Havriliak, Jr. and S. J. Havriliak, J. Non-Cryst. Solids **172-174**, 297 (1994).

[20] F. Alvarez, A. Alegria, and J. Colmenero, Phys. Rev. B **44**, 7306 (1991).

[21] C. Burger, Ph.D. thesis, Marburg University, Marburg, Germany, 1994.

[22] A. Döß, M. Paluch, H. Sillescu, and G. Hinze, Phys. Rev. Lett. **88**, 095701 (2002); J. Chem. Phys. **117**, 6582 (2002).

[23] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).

[24] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).

[25] C. A. Angell, J. Non-Cryst. Solids **131-133**, 13 (1991).

[26] F. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **104**, 2043 (1996).

[27] R. Richert and C. A. Angell, J. Chem. Phys. **108**, 9016 (1998).

[28] L.-M. Wang and C. A. Angell, J. Chem. Phys. **118**, 10353 (2003); L.-M. Wang, R. Richert, and C. A. Angell, *ibid.* **125**, 074505 (2006).

[29] V. Lubchenko and P. G. Wolynes, J. Chem. Phys. **119**, 9088 (2003).

[30] R. Böhmer and C. A. Angell, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994).

[31] K. L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, and C. M. Roland, J. Phys. Chem. B **109**, 17356 (2005).

[32] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. Lett. **86**, 1271 (2001).

[33] C. León and K. L. Ngai, J. Phys. Chem. B **103**, 4045 (1999).

[34] C. Hansen, F. Stickel, R. Richert, and E. W. Fischer, J. Chem. Phys. **108**, 6408 (1998).

[35] K. L. Ngai, J. H. Magill, and D. J. Plazek, J. Chem. Phys. **112**, 1887 (2000).

[36] C. Hansen, F. Stickel, T. Berger, R. Richert, and E. W. Fischer, J. Chem. Phys. **107**, 1086 (1997).

[37] L.-M. Wang and R. Richert, J. Phys. Chem. B **109**, 11091 (2005).

[38] L.-M. Wang and R. Richert, J. Chem. Phys. **121**, 11170 (2004).

[39] H. Huth, L.-M. Wang, C. Schick, and R. Richert, J. Chem. Phys. **126**, 104503 (2007).

[40] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990).

[41] J. Wiedersich, T. Blochowicz, S. Benkhof, A. Kudlik, N. V. Surovtsev, C. Tschirwitz, V. N. Novikov, and E. Rössler, J. Phys.: Condens. Matter **11**, A147 (1999).

[42] R. Richert, K. Duvvuri, and L.-T. Duong, J. Chem. Phys. **118**, 1828 (2003).

[43] M. Paluch, S. Pawlus, S. Hensel-Bielowka, E. Kaminska, D. Prevosto, S. Capaccioli, P. A. Rolla, and K. L. Ngai, J. Chem. Phys. **122**, 234506 (2005).

[44] S. Capaccioli, D. Prevosto, M. Lucchesi, P. A. Rolla, R. Casalini, and K. L. Ngai, J. Non-Cryst. Solids **351**, 2643 (2005).

[45] K. L. Ngai, P. Lunkenheimer, C. León, U. Schneider, R. Brand, and A. Loidl, J. Chem. Phys. **115**, 1405 (2001).

[46] T. Blochowicz, C. Tschirwitz, S. Benkhof, and E. A. Rössler, J. Chem. Phys. **118**, 7544 (2003).

[47] J. Mattsson, R. Bergman, P. Jacobsson, and L. Börjesson, Phys. Rev. Lett. **90**, 075702 (2003).

[48] H. Yardimci and R. L. Leheny, J. Chem. Phys. **124**, 214503 (2006).

[49] C. A. Angell, R. C. Stell, and W. Sichina, J. Phys. Chem. **86**, 1540 (1982).

[50] N. B. Olsen, J. Non-Cryst. Solids **235-237**, 399 (1998).

[51] G. Williams, Adv. Polym. Sci. **33**, 59 (1979).

[52] T_c=320 K is an average from two different data sources: 309 K from V. N. Novikov and A. P. Sokolov, Phys. Rev. E **67**, 031507 (2003); 330 K from J. Rault, J. Non-Cryst. Solids **271**, 177 (2001).

[53] T. Blochowicz and E. A. Rossler, Phys. Rev. Lett. **92**, 225701 (2004).

[54] R. Bergman and C. Svanberg, Phys. Rev. E **72**, 043501 (2005). It has been speculated that the shape of α relaxations could transform continuously from a symmetric to an asymmetric shape when the temperature approaches the α-β-merging regime.

[55] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. E **62**, 4435 (2000); J. C. Dyre and N. B. Olsen, Phys. Rev. Lett. **91**, 155703 (2003).

[56] S. Corezzi, M. Beiner, H. Huth, K. Schröter, S. Capaccioli, R. Casalini, D. Fioretto, and E. Donth, J. Chem. Phys. **117**, 2435 (2002).

[57] A. Mandanici, M. Cutroni, and R. Richert, J. Chem. Phys. **122**, 084508 (2005).

[58] R. Richert, J. Chem. Phys. **123**, 154502 (2005).

[59] N. Ito, K. Duvvuri, D. V. Matyushov, and R. Richert, J. Chem. Phys. **125**, 024504 (2006).

[60] K. L. Ngai and M. Paluch, J. Phys. Chem. B **107**, 6865 (2003).

[61] R. Casalini, M. Paluch, and C. M. Roland, Phys. Rev. E **67**, 031505 (2003).

[62] M. Paluch, K. L. Ngai, and S. Hensel-Bielowka, J. Chem. Phys. **114**, 10872 (2001).

[63] A. Brodin, R. Bergman, J. Mattsson, and E. A. Rössler, Eur. Phys.

J. B **36**, 349 (2003).

[64] S. Pawlus, M. Paluch, M. Sekula, K. L. Ngai, S. J. Rzoska, and J. Ziolo, Phys. Rev. E **68**, 021503 (2003); G. Power, J. K. Vij, and G. P. Johari, J. Chem. Phys. **124**, 044513 (2006).

[65] L.-M. Wang and R. Richert, J. Phys. Chem. B **111**, 3201 (2007); M. Sekula, S. Pawlus, S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, *ibid.* **108**, 4997 (2004).

[66] S. Maślanka, M. Paluch, W. W. Sułkowski, and C. M. Roland, J. Chem. Phys. **122**, 084511 (2005).

[67] S. Hensel-Bielówka, M. Paluch, and K. L. Ngai, J. Chem. Phys. **123**, 014502 (2005).

[68] R. Casalini and C. M. Roland, Phys. Rev. Lett. **91**, 015702 (2003).

[69] E. L. Grubb and C. P. Smyth, J. Am. Chem. Soc. **83**, 4879 (1961).

[70] F. K. Fong and C. P. Smyth, J. Am. Chem. Soc. **85**, 548 (1963).

[71] A. Schönhals, F. Kremer, and E. Schlosser, Phys. Rev. Lett. **67**, 999 (1991).

[72] J. G. Berberian and R. H. Cole, J. Chem. Phys. **84**, 6921 (1986).

[73] N. Menon, K. P. O'Brien, P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, J. Non-Cryst. Solids **141**, 61 (1992).

[74] M. Cutroni, A. Mandanici, A. Spanoudaki, and R. Pelster, J. Chem. Phys. **114**, 7118 (2001).

[75] L. Carpentier, R. Decressain, and M. Descamps, J. Chem. Phys. **121**, 6470 (2004).

[76] A. E. Lutskii and M. F. Shalimov, Russ. J. Phys. Chem. **44**, 908 (1970).

[77] K. Duvvuri and R. Richert, J. Chem. Phys. **117**, 4414 (2002).