Inference of the Evolution from Caged Dynamics to Cooperative Relaxation in Glass-Formers from Dielectric Relaxation Data

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Isothermal dielectric relaxation measurements were carried out on xylitol and threitol. These, together with existing data on sorbitol and glycerol, enabled us to identify the general features in the frequency dispersion and the changes when increasing the number of carbon atoms in the molecule in these polyalcohols. These features are interpreted in the framework of the coupling model. In sorbitol, xylitol, and threitol, the Johari−Goldstein β-relaxation peaks at a frequency, ν_β, near the independent relaxation frequency, ν_0, obtained from calculations using the coupling model. This coincidence indicates that the Johari−Goldstein β-relaxation is the precursor to the cooperative structural α-relaxation. For glycerol and for some nonassociating glass-formers, which have no resolved Johari−Goldstein β-relaxation peak because ν_0 is too close to the α-relaxation peak frequency, a near-constant loss (NCL) contribution can be seen at frequencies much higher than ν_0. Evoking the physical meaning of ν_0, this ubiquitous feature in the dielectric spectra leads to a description of the evolution of the molecular dynamics from the short time regime, when essentially all molecules are caged (i.e., the NCL regime), to the intermediate time regime defined by $1/2\pi\nu_0$ (or by $1/2\pi\nu_\beta$ if the glass-former has a resolved Johari−Goldstein β-relaxation), and to the long time regime when all molecules participate in the fully cooperative structural α-relaxation described by the Kohlrausch function.

Introduction

The dynamics of molecules in glass-forming supercooled liquids continues to be an active research topic.[1−21] A challenging task is to find a viable description of the evolution of the molecular dynamics over all times, from short times when the molecules are caged to long times when the cooperative α-relaxation occurs and viscous flow ensues. The description would be physically appealing if it can identify at least a certain factor or factors that control the dynamic properties especially the development of intermolecular cooperativity with time, and explain their variation with change in chemical structure of the glass-former. In this work, we present broadband dielectric data of polyalcohols series, glycerol, threitol, xylitol, and sorbitol, and use the coupling model[8,9,15−17,22−24] to identify a key quantity that controls the evolution of the dynamics with time and determines its variation with the chemical structure of the glass-former. The quantity is the coupling parameter of the coupling model, n, appearing in the fractional exponent of the Kohlrausch−Williams−Watts (KWW) relaxation functions,[25,2]

$$\phi(t) = \exp -(t/\tau_\alpha)^{1-n} \tag{1}$$

The one-sided Fourier transforms of the KWW functions,

$$\epsilon^*(\omega) = \Delta\epsilon \int_0^\infty e^{-i\omega t}\left[-\frac{\mathrm{d}}{\mathrm{d}t} \exp -(t/\tau_\alpha)^{1-n}\right] \mathrm{d}t \tag{2}$$

are often used to represent the contribution of the α-relaxation to the complex dielectric susceptibility, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, of glass-formers.

The coupling model connects the cooperative α-relaxation to the basic independent relaxation of a molecule, which turns out to be closely related to the β-relaxation of Johari and Goldstein (J−G).[27−29] Accordingly we have found a plausible origin of the J−G β-relaxation, which is considered by many workers to be a universal feature of glass-formers. The independent relaxation frequency is nearly the same as the J−G β-relaxation frequency. Thus this approach is able to predict the relative separation of the α- and J−G β-relaxation frequencies, in good agreement with experiments. In reinterpreting the spectra of glass-forming liquids, with or without a resolved J−G β-relaxation, the location of the independent relaxation frequency leads naturally to a description of the evolution of the dynamic processes from short times when most of the molecules are still caged to the cooperative α-relaxation at long times when all molecules take part and the correlation function given by eq 1. The short time caged dynamics show up in glass-forming molten salt,[30,31] $0.4\text{Ca}(\text{NO}_3)_2 - 0.6\text{KNO}_3$ (CKN), as a very slow monotonic increase of dielectric loss, $\epsilon''(\nu)$, with decreasing frequency over more and more decades on lowering the temperature. Because of such slow increase of $\epsilon''(\nu)$ over decades in frequency at lower temperatures in CKN and ionic conductors in general,[30,31] the observed short time (high frequency) response has been referred to in the literature as the near constant loss (NCL). Alternatively it may be called the "background loss". The observation of the NCL in glass-formers is not restricted to dielectric relaxation measurement. Dynamic light scattering measurements on polyisobutylene,[19] poly(methyl methacrylate), and glycerol[20] have found the near constant loss in the imaginary part of the depolarized and polarized susceptibility, $\chi''(\nu)$, at high frequencies. The optical Kerr effect studies of several organic glass-forming liquids[21] have found the presence of the near constant from the measured time derivative

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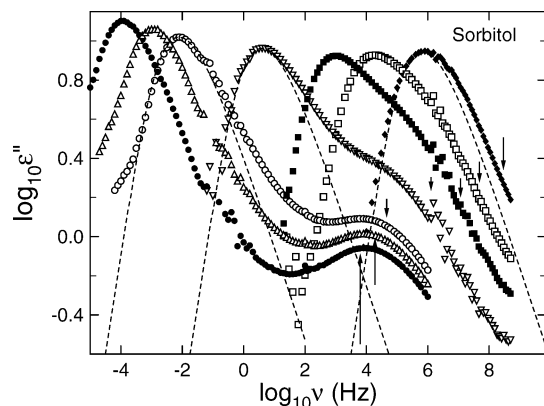† Naval Research Laboratory.
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Figure 1. The dielectric loss of sorbitol at atmospheric pressure. From left to right: 264, 266, 268, 276, 287, 296, and 312 K. The dashed lines are fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.52$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature. The data are taken from Nozaki et al.[6]

Figure 3. The dielectric loss of threitol at atmospheric pressure. From left to right: 218, 220, 224, 226, 228, 230 and 232 K. The dashed lines are fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.36$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature. The straight line with slope -0.14 is drawn to indicate the slow variation of ϵ'' at high frequencies.
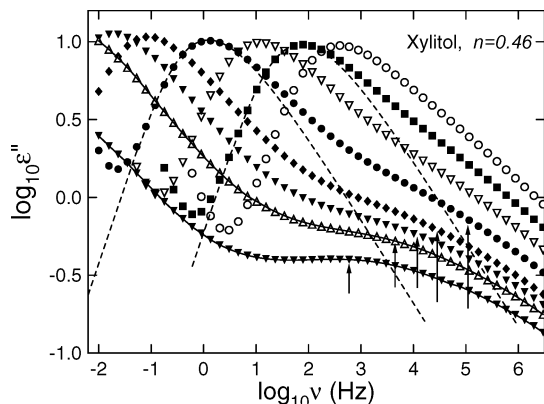

Figure 2. The dielectric loss of xylitol at atmospheric pressure. From left to right: 243, 248, 250, 252, 254, 258, 262, and 266 K. The dashed lines are fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.46$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature.

of the correlation function. In this work, we use broadband dielectric data of glycerol and threitol, as well as several non-associating van der Waals liquids, to show the presence of the NCL in their short time dynamics. At the end, we use all these data in conjunction with the coupling model to infer a description of the evolution of the molecular dynamics from short time caged dynamics to cooperative Kohlrausch dynamics. The description of the dynamics has general applicability to supercooled liquids and is not restricted to the polyalcohols.

Experimental Section

Threitol was obtained from Aldrich. Xylitol was obtained from Fluka and used as received. The complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ was measured in the frequency range from 10^{-2} Hz up to 10^7 Hz for each polyalcohol over a wide temperature range from below to above the glass transition temperature, T_g, using a Novocontrol Alpha analyzer.

Results

Some representative isothermal dielectric loss, $\epsilon''(\nu)$, for sorbitol, xylitol, threitol, and glycerol at some chosen temperatures are shown in Figures 1−3 and the inset of Figure 4, where
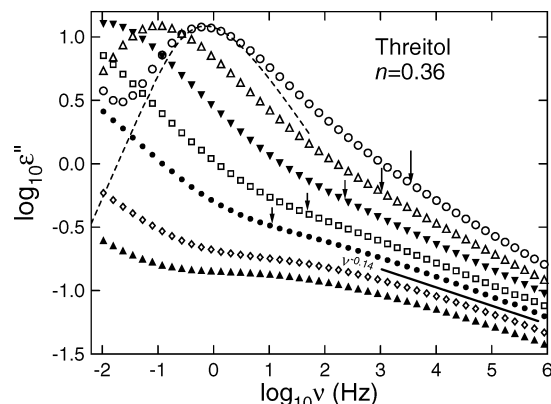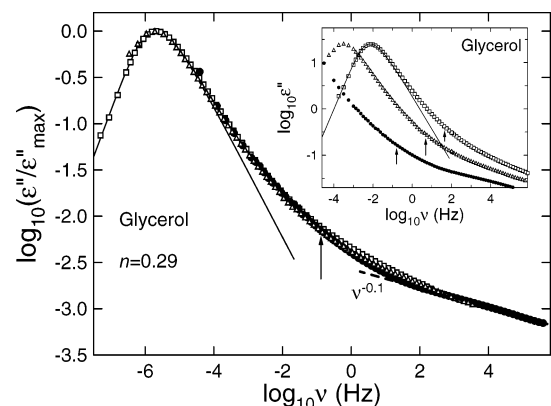

Figure 4. The inset shows the dielectric loss data of glycerol from reference 7 at three temperatures: (179 K, ●), (185 K, △), and (190 K, □). The data at 179 K was obtained after aging to achieve thermodynamic equilibrium. The line is fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.29$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature. The main figure shows the master curve obtained by shifting the normalized data, $\epsilon''/\epsilon''_{max}$, at the two higher temperatures to superpose on the normalized data at the lowest temperature 179 K (●). Again the vertical arrow indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5. The dashed line with frequency dependence, $\nu^{-0.1}$, indicates the slow variation of ϵ'' at high frequencies or the NCL regime.

$\nu = \omega/2\pi$. The dielectric data of sorbitol and glycerol are taken from previously published works by Nozaki et al.[6] and by Schneider et al.,[7] respectively. All four polyalcohols exhibit the slower structural α-relaxation as a peak, but only sorbitol, xylitol, and threitol show the faster secondary relaxation either as a shoulder or a peak, depending on the temperature. At higher temperatures the α-relaxation encroaches on the secondary relaxation peak or shoulder, and eventually they merge to form a single peak. Glycerol, with α-relaxation peak frequencies, ν_α, comparable to those of the other polyalcohols in Figures 1−3, shows no peak or shoulder that indicates a secondary relaxation, but instead an excess wing.[7] However, at much lower ν_α, the equilibrium liquid glycerol obtained after aging for many days shows a shoulder instead of the excess wing.[7] This is shown in the inset of Figure 4 by the data at 179 K. Thus, glycerol also

Cooperative Relaxation in Glass-Formers

J. Phys. Chem. B, Vol. 107, No. 28, 2003 **6867**

has a secondary relaxation but unresolved because it lies too close to the dominant α-relaxation peak.[7,8]

Discussion

(a) Sorbitol, Xylitol, and Threitol with Larger n and Resolved J−G β-Relaxation. Since there are no obvious internal degrees of freedom for secondary relaxation in the polyalcohols, the observed secondary relaxation has an intermolecular origin and is appropriately identified with the β-relaxation of Johari−Goldstein (J−G). Long ago, J−G showed the common occurrence of secondary relaxation of intermolecular origin in supercooled liquids and glasses even for rigid molecules and proposed that it is a universal feature of the dynamics of supercooled glass-forming liquids.[27−29] In a recent development,[16,17] by examining a large number of glass-formers, a close relation between the independent (primitive) relaxation time of the coupling model, τ_0, and the most probable J−G relaxation time, τ_β, has been established. The relevance of the coupling model (CM) to the dynamics of supercooled liquids is supported by (1) the results of a specific example of the former to mimic several key experimentally observed properties of the latter,[23] and (2) the ability of its predictions of explaining[24] the salient dynamic properties.[17] These examples and, in fact, all previous applications of the CM to the α-relaxation, consider only the case when all molecules are no longer caged and ready to execute the independent relaxation. However their intermolecular interactions and constraints make their independent relaxations simultaneously impossible, resulting in a dynamically heterogeneous and slowed α-relaxation with correlation function given by eq 1. The onset time of slowing down the independent relaxation, t_c, is of the order of 1 to 2 ps[32] for supercooled liquids and temperature independent, all reflecting that the slowing down is caused by the many-body effects from interaction between molecules. Operationally, a continuity between the independent relaxation, $\exp(-t/\tau_0)$, and the cooperative KWW relaxation function, justified by the small neighborhood of time in which the former crosses over to the latter from results of a model calculation,[22,23] leads to the relation

$$\tau_0 = t_c{}^n \tau_\alpha{}^{1-n} \tag{3}$$

Motivated by the fact that both the J−G relaxations and the independent relaxation of the CM are noncooperative processes, it was proposed[16] for the β-relaxation involving essentially an entire molecule that its relaxation time τ_β is comparable to τ_0, i.e., $\tau_0 \approx \tau_\beta$. Or the corresponding frequencies, $\nu_0 = 1/(2\pi\tau_0)$ and $\nu_\beta = 1/(2\pi\tau_\beta)$, are about the same, i.e.,

$$\nu_0 \approx \nu_\beta \tag{4}$$

This relation has been verified for many glass-formers at one characteristic temperature,[16] namely T_g. Furthermore, with $\nu_c = 1/(2\pi t_c)$, eq 4 implies that the distance between the α- and β-peaks, $(\log \nu_\beta - \log \nu_\alpha)$, approximately given by

$$(\log \nu_0 - \log \nu_\alpha) = n[\log \nu_c - \log \nu_\alpha] \tag{5}$$

is a decreasing function of the coupling parameter, n. This quantity, n, appearing in the exponent of the KWW function characterizes the deviation of the dielectric α-loss peak from that of a linear exponential decay.

Since the β-relaxation contributes to the dielectric loss on the high-frequency side of the α-relaxation peak and the viscosity weighs more heavily by the response at lower frequencies, the criterion we use in fitting the KWW function
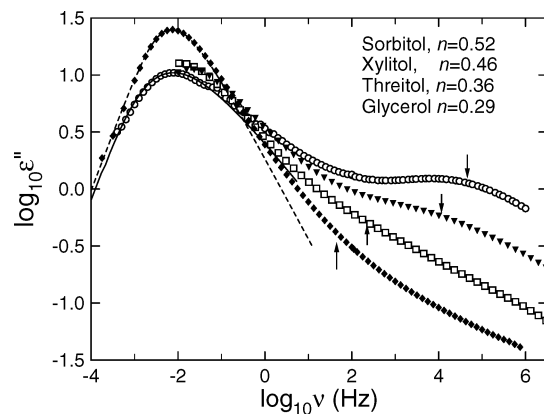

Figure 5. Dielectric loss data of the four polyalcohols with approximately the same ν_α. The vertical arrows indicate the locations of ν_0. The separation between ν_α and ν_0 increases with the coupling parameter, n.

to the latter is to emphasize good agreement with the data at lower frequencies. Some examples of the fits are shown in Figures 1−4 by dashed curves (note these KWW fits are carried out after removal of the small contribution to the loss at low frequencies from the dc-conductivity, $\epsilon''_{dc} \propto \nu^{-1}$, not shown in figures for clarity). From the fits, we obtain τ_α and the coupling parameter n. The values of n are 0.52 ± 0.02, 0.46 ± 0.02, 0.36 ± 0.02, and 0.29 ± 0.02 for sorbitol, xylitol, threitol, and glycerol, respectively, and they do not seem to depend on temperature when the α-relaxation peak frequencies fall below 10^2 Hz. These results indicate that there is an increase in the α-relaxation coupling parameter in increasing the number of carbon atoms in the molecules from 3 in glycerol to 6 in sorbitol and concomitantly decreasing the concentration of hydrogen bonds. A reduction in hydrogen bonding can be achieved by increasing molecular weight of propylene glycols from a small molecule to poly(propyleneglycol),[15,33] and again it was found that n increases with reduction in hydrogen bonding.

With n known, by eq 5 we can now calculate ν_0, the expected β-relaxation peak frequency, at all temperatures for each polyalcohol and compare with the experimental spectra. The location of any of the vertical arrows pointing to the isothermal data in Figures 1−4 is at the calculated ν_0 for that temperature. For sorbitol, xylitol, and threitol, which all show either a β-relaxation peak or shoulder, the calculated ν_0 corresponds reasonably well with ν_β, the location of the β-relaxation peak. For glycerol, which has an excess wing in the spectra and only a slight shoulder after aging at the lowest temperature,[7] there is also reasonable agreement between the calculated ν_0 and the assumed submerged β-relaxation frequency as discussed in detail in ref 8. In Figure 5 we select isothermal data from the four polyalcohols that have approximately the same $\nu_\alpha \approx 10^{-2}$ Hz to show the increase of separation between ν_α and ν_0 (or ν_β) with the coupling parameter n, as suggested by eq 5.

The good correspondence between the experimental ν_β of resolved J−G β-relaxation and ν_0 in the three higher members of the polyalcohols extends to other glass-formers, but these results are beyond the scope of the present work and will not be discussed.

(b) Glycerol and Other Glass-Formers with Smaller n and Unresolved J−G β-Relaxation. The β-relaxation of sorbitol is most prominent and is not very broad even at the lowest temperature of measurements shown in Figure 1. For the other polyalcohols, this relaxation becomes progressively weaker in intensity and more disperse with decreasing number of carbon atoms. In Figure 3 for threitol, the straight line with slope −0.14

is drawn to indicate the slow decrease of the β-relaxation at high frequencies. The ultimate of this trend is shown by glycerol in the main part of Figure 4. The isothermal data in the inset of Figure 4 were all obtained for glycerol in the equilibrium liquid state.[7] The KWW exponent of the α-relaxation does not change with temperature near T_g. However, the α-relaxation strength increases slightly with temperature as $1/T$. This change is compensated in constructing a master curve by normalizing each isothermal ϵ'' data by the peak height. Then by shifting the normalized curves, $\epsilon''/\epsilon''_{max}$, in the inset taken at $T = 185$ and 190 K horizontally to overlap the normalized data at $T = 179$ K, an approximate master curve over nearly 14 decades is obtained for equilibrium liquid glycerol and is shown in the main figure. From $\nu_\alpha = 10^{-5.7}$ Hz and $n = 0.29$ of the master curve, the expected β-relaxation peak frequency, ν_0, is calculated by eq 5 and its position is indicated by the vertical arrow. The decrease of $\epsilon''(\nu)$ with frequency at high frequencies is very slow, approximately as $\nu^{-0.1}$ as illustrated by the dashed line in the figure. Such a slow decrease of $\epsilon''(\nu)$ with frequency resembles the universal near constant loss found at high frequencies in glassy and molten[30,31,34] ionic conductors such as $0.4Ca(NO_3)_2$–$0.6KNO_3$ (CKN) and other glass-formers by other techniques.[19–21] Therefore we follow this nomenclature and the approximately $\nu^{-0.1}$-dependence of glycerol is henceforth referred to as the near constant loss (NCL). When temperature falls substantially below T_g, ν_α becomes so low that the entire α-relaxation peak of glycerol moves out of the experimental frequency window, and the NCL becomes the only observed feature in the dispersion.[1,35] The entire $\epsilon''(\nu)$ dispersion of glycerol shown in Figure 4 bears some analogy to the ionic conductors.[30] It broadly crosses over to a power law ν^{-n} (i.e., when the KWW function starts to fit the data) at lower frequencies where the near constant loss no longer holds. The only difference is that for ionic conductors, the frequency dependence of $\epsilon''(\nu)$ becomes ν^{-1} at low frequencies corresponding to d.c. conductivity of the mobile ions, instead of a dielectric loss peak. The ν^{-n} and the subsequent ν^{-1} at low frequencies correspond to a KWW correlation function of the cooperative motion of the mobile ions.[30,34] There is also an independent ion hopping frequency again denoted by ν_0 that can be calculated by an equation identical to eq 4. Generally it is found that ν_0 lies in the transition zone separating the near constant loss from the ν^{-n}-dependence of the KWW regime. These general properties found in ionic conductors have led to an interpretation of evolution of the dynamics of the ions from short time when they are caged to the long time when they are uncaged to engage in the slowed cooperative hopping motion. In the following paragraphs we shall give a similar interpretation to the molecular dynamics of glass-forming liquids. But before this we show that similar master curves can be constructed for other glass-formers from isothermal measurements reported in references 7, 9, and 36 for propylene carbonate (PC), cresol-phthalein-dimethyl ether (KDE) and *N*-methyl-ϵ-caplolactam (NMEC), respectively. The results in Figures 6–8 all show similar frequency dispersion as glycerol, even though they have widely different molecular structures and are van der Waals liquids without hydrogen bonding. They all have the NCL at high frequencies not much different from the approximate $\nu^{-0.1}$-dependence of glycerol. All these other glass-formers share the common characteristics of having smaller values of n, just like glycerol. Actually among these, glycerol has the largest n. The ratio of the NCL to the maximum loss of the α-peak seems to be about the same for two glass-formers having the same α-peak frequency, such as the pair glycerol and PC, and the other pair
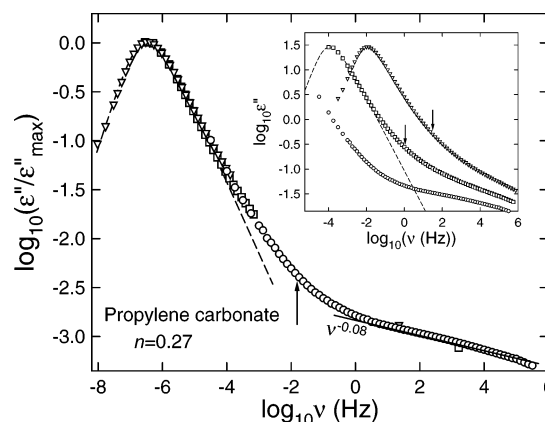

Figure 6. The inset shows the dielectric loss data of propylene carbonate from reference 7 at three temperatures: (152 K, ○), (155 K, □), and (158 K, ▽). The data at 152 K was obtained after aging to achieve thermodynamic equilibrium. The line is fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.27$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature. The main figure shows the master curve obtained by shifting the normalized data, $\epsilon''/\epsilon''_{max}$, at the two higher temperatures to superpose on the normalized data at the lowest temperature 152 K (○). Again the vertical arrow indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5. The dashed line with frequency dependence, $\nu^{-0.08}$, indicates the slow variation of ϵ'' at high frequencies or the NCL regime.

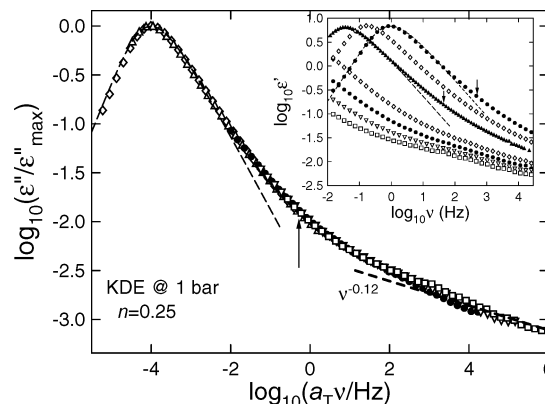**Figure 7.** The inset shows the dielectric loss data of cresolphthalein-dimethyl ether (KDE) from Reference 9 at several temperatures: (325 K, ●), (321 K, ◇), (318 K, ▲), (309 K, ◇), (305 K, ●), (301 K, ▽), and (297 K, □). The line is fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.25$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature. The main figure shows the master curve obtained by shifting the normalized data, $\epsilon''/\epsilon''_{max}$, at the two higher temperatures to superpose on the normalized data at 305 K (●). Again the vertical arrow indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5. The dashed line with frequency dependence, $\nu^{-0.12}$, indicates the slow variation of ϵ'' at high frequencies or the NCL regime.

KDE and NMEC. In Figure 8 the intensity of the NCL is given for several temperatures and it shows that the intensity increase with temperature.

The NCL is not the sole property of the glass-formers with no resolved J–G β-relaxation. First, by definition, glass-formers with well-resolved β-relaxation in the equilibrium liquid state necessarily have the β-peak frequency well separated from the α-peak frequency. Second, from the previous found correlation that the glass-formers having resolved J–G β-relaxation invariably have larger n values, it follows from eqs 4 and 5 that
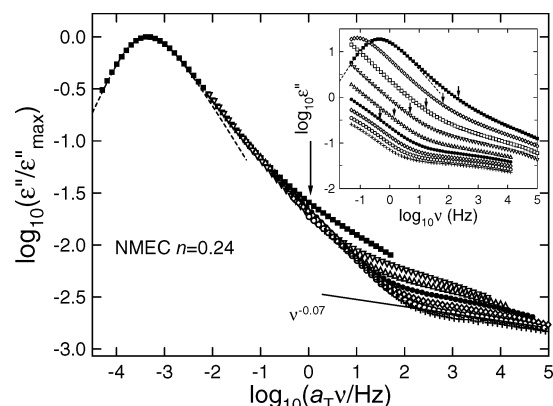
Cooperative Relaxation in Glass-Formers

J. Phys. Chem. B, Vol. 107, No. 28, 2003 **6869**

Figure 8. The inset shows the dielectric loss data of *N*-methyl-ϵ-caprolactam (NMEC) from reference 36 at several temperatures: (178 K, ■), (176 K, ◇), (174 K, □), (170 K, △), and (168 K ●). The line is fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.25$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5 for that temperature. The main figure shows the master curve obtained by shifting the normalized data, $\epsilon''/\epsilon''_{max}$, at the other temperatures to superpose on the normalized at 170 K (△). Again the vertical arrow indicates the location of the independent relaxation frequency, ν_0, calculated by eq 5. The dashed line with frequency dependence, $\nu^{-0.07}$, indicates the slow variation of ϵ'' at high frequencies or the NCL regime.

(log ν_β − log ν_α) tends to be larger. Thus the α- and β-peaks occupy a considerable number of decades in the experimental frequency window, consequently making the observation of the NCL located at the high frequency end impossible in most experimental setups and even in extraordinary setups that can measure frequencies continuously as high as the vibration frequencies.[37] The only possibility to observe the NCL is to go to the glassy state at temperatures considerably below T_g to move both the α- and β-peaks out of the experimental window. For these reasons, it is clear that a master plot, showing the evolution from the NCL to the cooperative α-relaxation as in Figures 4, 6−8, cannot be constructed unambiguously for glass-formers with larger n and showing a resolved J−G β-relaxation.

(c) Interpretation of the Evolution of the Molecular Dynamics. A common practice of analyzing the data is to best fit the $\epsilon''(\nu)$ data to a superposition of either the Fourier transform of the KWW function, eq 2, or a Cole−Davidson function for the α-relaxation and a symmetric Cole−Cole function for the β-relaxation. The dispersion of the β-relaxation obtained from the fit is very broad at temperature near or below T_g. Example from glycerol at 185 and 179 K can be found in Figure 1 of ref 8 and from PC at 152 and 155 K in Figure 2 of the same reference, where such fits yield extremely broad distributions of β-relaxation frequencies. Although the existence of the β-relaxation in glycerol and PC is not in doubt because of the evidence provided by aging[7,8] and other methods,[10,38,39] it is not easy to understand why such extremely broad distributions of β-relaxation frequencies can exist in an equilibrium liquid. In the following we shall give an alternative analysis and interpretation to the data in the equilibrium liquid state.

We start with the "master" spectra of glass-formers shown in the main parts of Figures 4, 6−8. The crux of the interpretation is the independent relaxation frequency, ν_0, we have calculated by eq 5 from the parameters ν_α and n of the α-peak obtained by fitting it to eq 2. In all cases, ν_0 is located between the α-peak and the NCL regime at high frequencies. Specifically, ν_0 is about two decades higher than the frequency,

ν_{x2}, below which the Fourier transform of the KWW function, eq 2, accurately describes the α-peak. Also about two decades separate ν_0 from the frequency ν_{x1}, above which the NCL regime takes hold. The interval $\nu_{x2} < \nu < \nu_{x1}$ is thus appropriately called the transition zone separating the NCL regime ($\nu_{x1} < \nu$) from the KWW regime ($\nu < \nu_{x2}$). Since ν_0 is the independent relaxation or reorientation time of a molecule, the fact that $\nu_0 \ll \nu_{x1}$ implies the probability of such independent reorientations, given by [1 − exp($-t/\tau_0$)] or [1 − exp($-\nu_0/\nu$)], is small. Hence negligible independent reorientations have occurred when the time t is less than t_{x1} or the frequency ν is larger than ν_{x1}. Certainly this is a prerequisite for low dielectric loss and very slow increase of ϵ'' with log ν, which are the signatures of the NCL regime (see Figures 4, 6−8). The exact dependence of ϵ'' on frequency in the NCL regime cannot be specified exactly from the data at this time. The data suggests that it can be approximately described by the $\nu^{-\lambda}$-dependence with a small exponent λ, a logarithmic function of ν, or some other slowly varying function of frequency that increases with decreasing ν. Whatever the relaxation process in this short time regime, it takes place when essentially all molecules remain caged. One would like to use the well-known caged dynamics theory (the mode coupling theory[40]) to describe the experimental data. Unfortunately, the standard mode coupling theory[40] does not predict the NCL except under very special potential and condition.[21,41] Thus, other mechanisms of caged dynamics such as that suggested in reference 42 are worth considering. The NCL as a background loss, which in concert with the high-frequency flank of the α-relaxation and the low-frequency flank of the vibrational contribution can generate a susceptibility minimum, which is observed by neutron and light scattering experiments at higher temperatures where the α-relaxation time becomes short. On the other hand, it is obvious that a susceptibility minimum predicted by the standard mode coupling theory conversely cannot account for the NCL.

As frequency is decreased (or time is increased), the probability of such independent reorientations monotonically increases and there will be a time t_{x1} (frequency ν_{x1}) beyond which the weak dependence of NCL on frequency, such as the approximate description by the $\nu^{-\lambda}$-dependence of ϵ'' with a small λ, no longer holds. The deviation of ϵ'' from the $\nu^{-\lambda}$-dependence of the NCL increases on further decrease of frequency below ν_{x1}, due to monotonically increasing probability of independent reorientations. When frequency is approaching ν_0, the probability of independent reorientations becomes significant. Many more molecules now attempt to make independent orientations, but not all of them are successful because of the omnipresent interaction/correlation between the molecules. Some degree of cooperativity has to be involved, where cooperativity is used here in the sense that attempts of some molecules to reorientations are unsuccessful so that the attempts of other molecules become possible. The degree of cooperativity increases with decreasing frequency (increasing time) because of increasing number of attempting molecules. When ν falls sufficiently below ν_0, all molecules have practically a hundred percent probability of attempting independent reorientations, and the regime of fully cooperative dynamics is reached and prevails thereafter. The degree of cooperativity reaches the maximum value in this long-time regime and is characterized by the value of n appearing in the KWW function, which describes its correlation function. This scenario, that all molecules (or basic units in the more general context of the coupling model) are attempting their independent relaxations, is assumed to be the case in all previous theoretical consider-

ations[22,23] and applications of the coupling model (CM)[24] to the α-relaxation (or the ultimate relaxation process of the basic units). In other words, no consideration had been given to the earlier stages of the dynamics when essentially most of the molecules are still caged (i.e., the NCL regime) and the gradual development of cooperativity when increasing number of molecules are attempting to rotate and translate independently (i.e., the transition zone). Here, for the first time, we include the dynamics at earlier time regimes and give a more complete description of the CM results. From the original CM,[22,23] the fully cooperative dynamics is described by the KWW function, and ϵ'' is the one-sided Fourier transform of the derivative of the KWW function. Thus ν_{x2}, as defined earlier, is the frequency for onset of fully cooperative dynamics. The slowing down of the independent reorientations in the fully cooperative dynamics is caused by the interactions between molecules, starting out from a temperature-independent time, t_c. Equation 3 (or the equivalent eq 5) is a consequence, which has been instrumental in locating the independent reorientation frequency, ν_0, from the parameters n and τ_α of the KWW function. The above description of the evolution of the molecular dynamics of glass-formers by division into the three time zones cannot be applied meaningfully to experimental data without locating τ_0 or ν_0. The interpretation would not be credible unless the independent reorientation frequency is known quantitatively and its location in the dielectric spectrum is consistent with the interpretation. The CM enables ν_0 to be calculated for all the glass-formers in Figures 1−8, and its location at any temperature is indicated by the vertical arrow pointing at the isothermal dielectric loss data for which ν_0 is calculated. For glycerol (Figure 4), PC (Figure 6), KDE (Figure 7), and NMEC (Figure 8), where the spectra all show the NCL at short times, the transition zone at intermediate times, and the ultimate fully cooperative KWW relaxation, invariably the location of ν_0 falls between ν_{x1} and ν_{x2} (not explicitly indicated but can be inferred from these figures). Therefore, the location of ν_0 justifies the interpretation of the origin of the NCL, the continuous buildup of cooperativity in the transition zone, and the fully cooperative KWW relaxation at the final stage.

Let us consider the NCL at some temperature. On cooling to a lower temperature, the NCL decreases in intensity, as demonstrated by comparing the data of NMEC shown as open triangles for $T = 170$ K and by filled circles for $T = 168$ K in the inset of Figure 8. This observed decrease of the NCL intensity with decreasing temperature continues to hold at temperatures below T_g,[1,35] where the mild temperature dependence of the NCL has been described by $\exp(bT)$ with a positive parameter b. We can rationalize the decrease of the NCL with decreasing temperature from the caged dynamics, whatever its origin. From its interpretation and definition, the NCL regime terminates at ν_{x1} when the probability of independent reorientation/translation of molecules becomes nonnegligible. From this it follows that ν_{x1} tracks along with the independent reorientation frequency, ν_0, when temperature changes. In particular, ν_{x1} decreases with temperature in approximately the same manner as ν_0, which has actually been found to be the case from analysis of the dielectric relaxation data of CKN.[30] At ν_{x1}, $\epsilon''(\nu_{x1})$ is the same for different temperatures because the same relaxation processes have transpired up to the time $t_{x1} \equiv (1/2\pi\nu_{x1})$. Thus, the same $\epsilon''(\nu_{x1})$ is spread over more decades of frequency when temperature is lowered, and the magnitude of the NCL has to decrease with a decrease in temperature. In this argument we have not taken into consideration the possible effect on the caged dynamics due to the Debye−Waller factor. If the latter has an

effect on the NCL, it will enhance the decrease of the NCL with decreasing temperature.

The coupling model description of the dynamics was built by first, in the absence of intermolecular coupling, taking appropriately into account of the dependences of the intrinsic molecular mobility on the thermodynamics variables including the configurational entropy, S_c, free volume, V_f, temperature, T, and pressure, P. In the second step, intermolecular coupling is incorporated to capture the effects due to complex molecular motions at longer times. The independent relaxation rate, ν_0, of the CM determines the intrinsic mobility and hence it is dependent on S_c, V_f, T, and P. Like entropy and volume, ν_0 senses the glass transition through its different dependence on temperature in the equilibrium liquid state and the nonequilibrium glassy state, i.e., the appearance of a change in slope or elbow-like shape of the quantity near the glass transition temperature. From the parallel temperature dependence of ν_{x1} and ν_0 and the dependence of the NCL intensity on ν_0, it follows that the NCL intensity exhibits also an elbow-like shape at T_g, as seen from analyses of experimental data.[31]

(d) Origin of the J−G β-Relaxations. For the glass-formers in Figures 4, 6−8 the description and interpretation of the molecular dynamics given in the previous paragraph could have been presented without ever mentioning the J−G β-relaxation and its correspondence with the independent reorientation. This is because these glass-formers have no resolved J−G β-relaxations, although we certainly believe they are there but submerged under the more intense α-peak.[7−9,38,39] On the other hand, for glass-formers having resolved J−G β-relaxations such as sorbitol, xylitol, and threitol, the CM confers a bonus in identifying the J−G β-relaxation observed *in the equilibrium liquid* with the independent reorientation of molecules, which is supported by the good agreement between ν_0 and ν_β (Figures 1−3). The previously given description of the dynamics also applies to glass-formers with resolved J−G β-relaxation. In particular, since ν_0 is nearly the same as ν_β, at frequencies in the neighborhood of ν_β the dynamics consist of localized or restricted independent reorientations/translations. The independent reorientations can occur anywhere. Hence the J−G β-relaxation is not restricted to certain regions, and stochastically it can occur anywhere and can involve any molecule. However, not all molecules can independently relax at the same time because of the interactions between them and thus not all molecules contribute to the β-relaxation. At the present time the identification of the nature of the J−G β-relaxation is controversial. Williams-Watts[43] and Williams[44] suggested that all molecules in a liquid contribute to the β-relaxation as small angle (thermally activated) reorientational motion and the β-process relaxes only a part of the total polarization. Two other suggestions of the origin of the J−G β-relaxation are for the glass-formers in the *glassy* state. Johari[13,28,29] had attributed the J−G β-relaxation in a frozen glass to reorientational/translational motions of only a *small number* of molecules confined to sites of frozen-in density fluctuations, where the structure is relatively loose ("islands of mobility"). On the other hand, from ^{2}H NMR measurements Vogel and Rössler[11,12] have recently attributed the J−G β-relaxation in the glassy state to reorientational motions of *all* molecules with a temperature-independent small angle for the majority and possibly larger angles for a minority, consistent with the conclusion drawn from an analysis of solvation dynamics measurement[5] on D-sorbitol. Relative merits of these apparently incompatible mechanisms by considering their consequences are documented by Johari in a recent work.[13] The consequences he considered include the change of the

Cooperative Relaxation in Glass-Formers

J. Phys. Chem. B, Vol. 107, No. 28, 2003 **6871**

orientation polarization or dielectric strength due to the β-process, $\Delta\epsilon_\beta$, with temperature and physical aging. Experiments on glasses, including toluene studied by Vogel and Rössler,[11,12] have shown that $\Delta\epsilon_\beta$ always decreases on cooling a glass. Densification of the glass by physical aging also diminishes $\Delta\epsilon_\beta$. Johari[13] pointed out that these results are inconsistent with reorientational motions of *all* molecules with a temperature-independent small angle as the mechanism for the β-process, which instead would predict an increase of $\Delta\epsilon_\beta$ on cooling or physical aging. Our proposed identification of the J–G β-process with the independent relaxation of the coupling model may help to resolve this controversy. This is because on one hand not all molecules can succeed to relax independently, but on the other hand all molecules have an equal chance to be the ones that succeed. From the attribute of our mechanism of the J–G β-process that not all molecules contribute to its dielectric strength, it seems that our mechanism of the β-process is consistent with those properties of $\Delta\epsilon_\beta$ emphasized by Johari.[13] While its other attribute, that all molecules have equal chance to be the ones that independently relax in the β-process, may make it consistent with the data from solvation dynamics[5] and ²H NMR.[11,12]

We note that it is customary[2,3,5,6,18] to obtain the dielectric strength $\Delta\epsilon_\beta$ of the J–G relaxation by fitting the very broad β-peak to either a Cole–Cole or a Havriliak–Negami function. Part of the high-frequency part of the broad peak is considered to be from the NCL contribution in the interpretation of the dielectric spectrum of this work. Since the NCL decreases in intensity with decreasing temperature and exhibits an elbow-like shape at T_g as we have shown earlier, consequently the same is true for $\Delta\epsilon_\beta$ of the J–G relaxation. Such characteristic temperature dependence of $\Delta\epsilon_\beta$ on crossing T_g has been emphasized by Johari and co-workers.[18] Without invoking the connection to the NCL, the temperature dependence of $\Delta\epsilon_\beta$ also can be directly deduced from the independent relaxation. As temperature is decreased, the specific volume decreases. Consequently the spatial extent of the local independent relaxation and its relaxation strength, $\Delta\epsilon_\beta$, are decreased. Since the specific volume as a function of temperature has different slopes in the equilibrium liquid and in the glassy states, the elbow-like dependence on T is transferred to spatial extent of the independent relaxation and $\Delta\epsilon_\beta$.

Small molecular glass-forming liquids show that the coupling parameter, n, decreases with increasing temperature.[17] Hence the distance between the α- and β-peaks, given approximately by eq 5, decreases with increasing temperature through both factors in the term appearing on the right-hand-side of eq 5. Moreover, when n becomes small, there is hardly any degree of cooperativity left in the α-relaxation, meaning that there is little difference between it and the independent relaxation or the J–G relaxation. Thus, it is natural that the two relaxations tend to merge into one at high temperatures, as observed experimentally.

Conclusion

The polyalcohols as a class offer a study of the changes of the molecular dynamics with a systematic and progressive change in molecular structure. The increase of the number of carbon atoms in a molecule causes a decrease in the number of hydrogen bonds and enhances the intermolecular coupling between the relaxing molecules. The latter is reflected in the increase of the stretching of the α-relaxation correlation function or the width of the α-relaxation dispersion. From the dielectric spectra of the polyalcohols in the equilibrium liquid-state we

find that the most probable Johari–Goldstein β-relaxation frequency, ν_β, invariably is nearly the same as the independent relaxation frequency, ν_0, of the coupling model. Hence the Johari–Goldstein β-relaxation in the polyalcohols can be identified with the independent relaxation of the coupling model, which is the precursor of the cooperative structural α-relaxation. For glycerol and other nonassociating glass-formers, which have no resolved Johari–Goldstein β-relaxation peak because ν_0 is too close to α-relaxation peak frequency, a near-constant loss (NCL) contribution can be seen at frequencies much higher than ν_0. Evoking the physical meaning of ν_0, this ubiquitous feature in the dielectric spectra leads to a description of the evolution of the molecular dynamics from the short time regime, when essentially all molecules are caged (i.e., the NCL regime), to the intermediate time regime defined by $1/2\pi\nu_0$ (or by $1/2\pi\nu_\beta$ if the glass-former has a resolved Johari–Goldstein β-relaxation) where cooperativity develops continuously, and to the long time regime when all molecules participate in the fully cooperative α-relaxation described by the Kohlrausch function. The properties of the proposed mechanism for the observed Johari–Goldstein relaxation are shown to be consistent with experimental data.

References and Notes

(1) Weidersich, J.; Blochowicz, T.; Benkhof, S.; Kudlik, A.; Surovtsev, N. V.; Tschirwitz, C.; Novikov, V. N.; Rössler, *J. Phys. Condens. Matter* **1999**, *11*, A147.

(2) Johari, G. P.; Kalinovskaya, O. E.; Vij, J. K. *J. Chem. Phys.* **2001**, *114*, 4634.

(3) Kalinovskaya, O. E.; Vij, J. K. *J. Chem. Phys.* **2001**, *114*, 2718.

(4) Faivre, A.; Niquet, G.; Maglione, M.; Fornazero, J.; Jal, J. F.; David, L. *Eur. Phys. J. B* **1999**, *10*, 277.

(5) Wagner, H.; Richert, R. *J. Non-Cryst. Solids* **1998**, *242*, 19.

(6) Nozaki, R.; Suzuki, D.; Ozawa, S.; Shiozaki, Y. *J. Non-Cryst. Solids* **1998**, *235–237*, 393.

(7) Schneider, U.; Brand, R.; Lunkenheimer, P.; Loidl, A. *Phys. Rev. Lett.* **2000**, *84*, 5560.

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

(9) Paluch, M.; Ngai, K. L.; Hensel-Bielowka, S. *J. Chem. Phys.* **2001**, *114*, 10872.

(10) Döss, A.; Paluch, M.; Sillescu, H.; Hinze, G. *Phys. Rev. Lett.* **2002**, *88*, 95701.

(11) Vogel, M.; Rössler, E. *J. Phys. Chem. B* **2000**, *104*, 4285.

(12) Vogel, M.; Rössler, E. *J. Chem. Phys.* **2001**, *114*, 5802.

(13) Johari, G. P. *J. Non-Cryst. Solids* **2002**, *307–310*, 317.

(14) Köplinger, J.; Kasper, G.; Hunklinger, S. *J. Chem. Phys.* **2000**, *113*, 4710.

(15) León, C, Ngai, K. L.; Roland, C. M. *J. Chem. Phys.* **1999**, *110*, 11585.

(16) Ngai, K. L. *J. Chem. Phys.* **1998**, *109*, 6982.

(17) Ngai, K. L. *J. Non-Cryst. Solids* **2000**, *275*, 7.

(18) Johari, G. P.; Powers, G.; Vij, J. K. *J. Chem. Phys.* **2002**, *116*, 5908.

(19) Sokolov, A. P.; Kisluik, A.; Novikov, V. N.; Ngai, K. L. *Phys. Rev. B* **2001**, *63*, 172204.

(20) Caliskan, G.; Kisluik, A.; Sokolov, A. P.; Novikov, V. N. *J. Chem. Phys.* **2001**, *114*, 10189.

(21) Cang, H.; Novikov, V. N.; Fayer, M. D. *J. Chem. Phys.* **2003**, *118*, 2800.

(22) Tsang, K. Y.; Ngai, K. L. *Phys. Rev. E* **1997**, *54*, 3067.

(23) Ngai, K. L.; Tsang, K. Y. *Phys. Rev. E* **1999**, *60*, 4511.

(24) Ngai, K. L. *IEEE Trans. Dielectr. Elec. Insul.* **2001**, *8*, 329.

(25) Kohlrausch, R. *Pogg. Ann. Phys.* **1847**, *12*, 393.

(26) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.

(27) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.

(28) Johari, G. P. *J. Chem. Phys.* **1973**, *58*, 1766.

(29) Johari, G. P. In *Plastic Deformation of Amorphous and Semicrystalline Materials*, Les Edition de Physique; G'Sell, C., Perez, J., Eds.; Les Ullis, France, 1983; p 109.

(30) Ngai, K. L.; León, C. *Phys. Rev. B* **2002**, *66*, 064308.

(31) Casalini, R.; Ngai, K. L. *J. Non-Cryst. Solids* **2001**, *293−295*, 318.

(32) Ngai, K. L.; Rendell, R. W. *Supercooled Liquids, Advances and Novel Applications*; Fourkas, J. T.; Kivelson, D.; Mohanty, U.; Nelson, K., Eds.; ACS Symposium Series, American Chemical Society: Washington, DC, 1997; Vol. 676, Chapter 4, p 45.

(33) Bergmann, R.; Svanberg, C.; Andersson, D.; Brodin, A.; Torell, L. M. *J. Non-Cryst. Solids* **1998**, *235−237*, 801.

(34) Ngai, K. L. *J. Chem. Phys.* **1999**, *110*, 10576.

(35) Hoffmann, A.; Kremer, F.; Fischer, E. W.; Schönhals, A. In *Disorder Effects on Relaxational Processes*; Richert, R., Blumen, A., Eds.; Springer-Verlag: Berlin, 1994.

(36) Schüller, J.; Richert, R.; Fischer, E. W. *Phys. Rev. B* **1995**, *52*, 15232.

(37) Lunkenheimer, P.; Schneider, U.; Brand, R.; Loidl, A. *Contemp. Phys.* **2000**, *41*, 5.

(38) Svanberg, C.; Bergman, R.; Jacobsson, P.; Börjesson, L. *Phys. Rev. B* **2002**, *66*, 054304.

(39) Paluch, M.; Casalini, R.; Hensel-Bielowka, S.; Roland, C. M. *J. Chem. Phys.* **2002**, *116*, 9839.

(40) Götze, W. *Liquids, Freezing and the Glass Transition*; North-Holland: Amsterdam, 1991.

(41) Fabbian, L.; Götze, W.; Sciortino, F.; Tartaglia, P.; Thiery, F. *Phys. Rev. E* **2002**, *60*, 2430.

(42) Ngai, K. L. *J. Phys.: Condens. Matter* **2000**, *12*, 6437.

(43) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *67*, 1971.

(44) Williams, G. *Adv. Polym. Sci.* **1979**, *33*, 60. In the view of Williams (private communication), "it is essential to recognize that a given dipolar group moves by partial relaxation (β-process) and total relaxation (α-process) and that one needs to sum up over the ensemble, taking into account temporary local environments to obtain the experimental behavior, and that procedure naturally gives heterogeneity in the overall β-process."