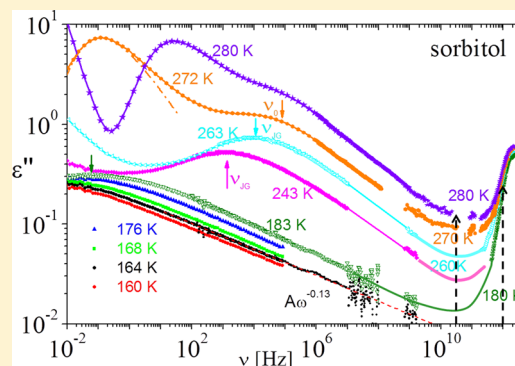


Coupling of Caged Molecule Dynamics to JG β -Relaxation: IS. Capaccioli,^{*,†,‡} K. L. Ngai,^{*,‡,§} M. Shahin Thayyil,^{||} and D. Prevosto[‡][†]Dipartimento di Fisica, Università di Pisa, Largo Bruno Pontecorvo 3, I-56127, Pisa, Italy[‡]CNR-IPCF, Largo Bruno Pontecorvo 3, I-56127, Pisa, Italy[§]State Key Lab of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, Hebei, 066004 China^{||}Department of Physics, University of Calicut, Kerala, India

S Supporting Information

ABSTRACT: The paper (Sibik, J.; Elliott, S. R.; Zeitler, J. A. *J. Phys. Chem. Lett.* **2014**, *5*, 1968–1972) used terahertz time-domain spectroscopy (THz-TDS) to study the dynamics of the polyalcohols, glycerol, threitol, xylitol, and sorbitol, at temperatures from below to above the glass transition temperature T_g . On heating the glasses, they observed the dielectric losses, $\epsilon''(\nu)$ at $\nu = 1$ THz, increase monotonically with temperature and change dependence at two temperatures, first deep in the glassy state at $T_{\text{THz}} = 0.65T_g$ and second at T_g . The effects at both temperatures are most prominent in sorbitol but become progressively weaker in the order of xylitol and threitol, and the sub- T_g change was not observed in glycerol. They suggested this feature originates from the high-frequency tail of the Johari–Goldstein (JG) β -relaxation, and the temperature region near $0.65T_g$ is the universal region for the secondary glass transition due to the JG β -relaxation. In this paper, we first use isothermal dielectric relaxation

data at frequencies below 10^6 Hz to locate the “second glass transition” temperature T_β at which the JG β -relaxation time τ_{JG} reaches 100 s. The value of T_β is close to $T_{\text{THz}} = 0.65T_g$ for sorbitol ($0.63T_g$) and xylitol ($0.65T_g$), but T_β is $0.74T_g$ for threitol and $0.83T_g$ for glycerol. Notwithstanding, the larger values of T_β of glycerol are consistent with the THz-TDS data. Next, we identify the dynamic process probed by THz-TDS as the caged molecule dynamics, showing up in susceptibility spectra as nearly constant loss (NCL). The caged molecule dynamics regime is terminated by the onset of the primitive relaxation of the coupling model, which is the precursor of the JG β -relaxation. From this relation, established is the connection of the magnitude and temperature dependence of the NCL and those of τ_{JG} . This connection explains the monotonic increase of NCL with temperature and change to a stronger dependence after crossing T_β giving rise to the sub- T_g behavior of $\epsilon''(\nu)$ observed in experiment. Beyond the polyalcohols, we present new dielectric relaxation measurements of flufenamic acid and recall dielectric, NMR, and calorimetric data of indomethacin. The data of these two pharmaceuticals enables us to determine the value of $T_\beta = 0.67T_g$ for flufenamic acid and $T_\beta = 0.58T_g$ or $T_\beta = 0.62T_g$ for indomethacin, which can be compared with experimental values of T_{THz} from THz-TDS measurements when they become available. We point out that the sub- T_g change of NCL at T_β found by THz-TDS can be observed by other high frequency spectroscopy including neutron scattering, light scattering, Brillouin scattering, and inelastic X-ray scattering. An example from neutron scattering is cited. All the findings demonstrate the connection of all processes in the evolution of dynamics ending at the structural α -relaxation.



1. INTRODUCTION

The high frequency measurements in the gigahertz to terahertz range have been a major area of activity in research on the dynamics in glass-forming systems to join in the effort to solve the glass transition problem. Techniques used included quasielastic neutron scattering,^{1–11} Brillouin light scattering,¹² dynamic light scattering,^{13–17} inelastic X-ray scattering,^{18–20} extraordinary high frequency dielectric spectroscopy up to a few hundred gigahertz,^{21–23} and terahertz time-domain spectroscopy.^{24–27} The counterparts of the high frequency measurements are the time domain optical heterodyne detected optical Kerr effect experiments from 1 ps to tens of ns,²⁸ and molecular dynamics simulations.^{29–33} There are some studies attempting to link dynamic quantities measured at higher frequencies/

short times to variables either determining the glass transition or quantifying some salient properties at the glass transition temperature T_g . One example is the mean-square-displacement (MSD), $\langle u^2(T) \rangle$, measured by elastic incoherent neutron scattering (EINS) at temperatures below and above T_g . Found generally in glass-formers of different kinds, smaller molecular, polymeric, and inorganic alike, is the change of the temperature dependence of $\langle u^2(T) \rangle$ at T_g . The remarkably weak T dependence of $\langle u^2(T) \rangle$ at temperatures below T_g changes to a stronger T dependence above T_g .^{2,3,6–11,34–36} Moreover,³⁴

Received: May 7, 2015

Revised: June 7, 2015

measured by a spectrometer with the same resolution, $\langle u^2(T) \rangle$ is larger and the change at T_g is sharper if the structural α -relaxation of the glass-former has a broader frequency dispersion or a smaller value of the exponent, $(1 - n)$, of its Kohlrausch correlation function

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

where τ_α is the α -relaxation time. Another notable example is the inelastic X-ray scattering (IXS) measurements of the dynamic structure factor and the determination of the nonergodicity factor $f(Q, T)$ by Scopigno and co-workers.¹⁹ They found in glass-formers a correlation between the temperature dependence of $f(Q, T)$ in the glassy state and fragility.^{35,36} The latter is the rate of increase of $\log_{10} \tau_\alpha$ as a function of T_g/T on cooling at $T_g/T = 1$. This correlation from experiment was confirmed by molecular dynamics simulations of the binary Lennard-Jones particle systems with different interaction potentials.³⁰

These two examples, i.e., the T dependences of $\langle u^2(T) \rangle$ and $f(Q, T)$, together with others not mentioned are empirical facts suggesting that the fast processes somehow are related to the slow dynamics. This connection was made explicit in the coupling model (CM)^{37–39} specifically in considering the dynamics evolving with time in the order of the caged molecules, the primitive relaxation which is a part of the Johari–Goldstein (JG) β -relaxation, and the structural α -relaxation.^{37–44} Initially, at short times, molecules are caged. In this caged dynamics regime, the susceptibility, $\chi''(T, \nu) = B(T)(\nu)^{-\lambda}$, originates from the dissipation of movements confined by the anharmonic potential. Its weak temperature dependence $B(T)$ is well described by $A \exp(T/T_0)$. Its power law frequency dependence with $\lambda \ll 1$ leads to the term of the nearly constant loss (NCL). The NCL is not a relaxation process with a characteristic time. It persists to lower frequencies/longer times until the atoms, or molecules, leave the cage. It is the first or primitive relaxation with relaxation time, τ_0 , that effectively terminates the caged dynamics regime, and the NCL dependence of the susceptibility no longer holds at frequencies of the order of $\nu_0 = 1/(2\pi\tau_0)$.^{37,39,45,46} Of particular interest is ref 46 where the experimental results presented therein are for the polyalcohols. Ions in molten and glassy ionic conductors caged at short times exhibit the NCL, which is also terminated by the primitive ion hop frequency ν_0 .^{47–50} The paper⁵¹ shows the remarkable similarities, and also a correlation of the magnitude of the NCL with the primitive relaxation time τ_0 or approximately the JG β -relaxation time τ_{JG} to be defined later.

This relation between the NCL and the primitive relaxation has the consequence of any change of the primitive relaxation is reflected by the corresponding change of the NCL, and vice versa. The sequential relation of the primitive relaxation or the JG β -relaxation with the α -relaxation is the core result of the CM, which has been confirmed in various ways and in many glass-forming systems,^{52–57} and in the analogue ionic systems.^{58,59}

A recent paper by Sibik et al.⁶⁰ used terahertz time-domain spectroscopy (THz-TDS) in the frequency range 0.2–3 THz to study the dynamics of the family of polyalcohols, glycerol, threitol, xylitol, and sorbitol, at temperatures between 80 and 310 K. On heating the glasses, they observed the dielectric losses, $\epsilon''(\nu)$ at $\nu = 1$ THz, increase monotonically with temperature but the temperature dependence changes at two temperatures, first deep in the glassy state at a sub- T_g

temperature of $0.65T_g$ and second at T_g . The effects at both temperatures are most prominent in sorbitol but become progressively weaker in the order of xylitol and threitol, and the sub- T_g change was not observed in glycerol. They suggested this feature originates from the high-frequency tail of the JG β -relaxation and the temperature region near $0.65T_g$ is the universal region for the secondary glass transition due to the JG β -relaxation. Also, they proposed that the thermal changes in the losses near $0.65T_g$ seem to be underpinned by a universal change in the hydrogen bonding structure of the samples. The study by THz-TDS has been extended to several pharmaceutical glass-formers including flufenamic acid and indomethacin.⁶¹

In this paper, we critically reexamine the experimental data of the polyalcohols by Sibik et al. and relate the observed $\epsilon''(\nu)$ at $\nu = 1$ THz to the proper dynamic process responsible for its changes of temperature dependences at sub- T_g temperature and at T_g . By analyses of the dielectric relaxation spectra of the polyalcohols, we identify the proper dynamic process is the NCL of caged molecules. We provide dielectric measurements of flufenamic acid and indomethacin to characterize the α -relaxation and the JG β -relaxation, and determine their relaxation time as well as that of primitive relaxation time. The results are used to obtain the value of T_β to predict the temperature of the sub- T_g change of temperature dependence of $\epsilon''(\nu)$ at $\nu = 1$ THz in the THz-TDS experiment. Previously published data of indomethacin are employed to make the same prediction for this pharmaceutical. In the final part of the paper, theoretical arguments supported by experimental facts are given to demonstrate the inseparable link of the NCL of caged molecules to the primitive relaxation and the JG β -relaxation. There is a change of the temperature dependence of the JG β -relaxation at T_β below which it falls out of equilibrium. Due to the linkage, the change is transferred to the corresponding change of the temperature dependence of the NCL. Justification of this explanation by theory with support from other experimental facts is given.

2. EXPERIMENTAL DETAILS

Sorbitol and flufenamic acid were purchased in anhydrous form at high purity grade from Sigma-Aldrich and used as received, with the precaution of storing and handling them under a dry atmosphere. A parallel plate capacitor separated by a quartz spacer and filled by the sample was placed in the nitrogen flow Quatro cryostat. Glassy and supercooled systems were obtained by heating a few degrees above the melting point under a nitrogen atmosphere and then cooling. A Novocontrol Alpha-Analyzer was used for dielectric measurements from 1 mHz to 10 MHz, whereas for higher frequencies (1 MHz to 6 GHz) measurements have been carried out by means of a reflectometric technique using the Agilent 8753ES Network Analyzer.

3. WHICH DYNAMIC PROCESS BELOW T_g IS RESPONDING TO TERAHERTZ TIME DOMAIN SPECTROSCOPY?

For a fundamental understanding of the THz-TDS data of the polyalcohols, it is vital to identify the dynamic process or processes probed at the terahertz level to exhibit the changes of $\epsilon''(\nu)$ at T_g and below T_g . The answer can be found by examining the dielectric spectra obtained at these temperatures. Usually the measurement frequencies are orders of magnitude lower than terahertz. Notwithstanding, by extrapolating the

observation to terahertz, the dynamic process probed at 1 THz and showing the change can be deduced. At these low temperatures as shown by dielectric loss data at frequencies below 10^6 Hz in various molecular glassformers,^{45–47} including the polyalcohols, the process probed is the NCL of caged dynamics. This can be verified from the figures presented later on in this paper as well as the data published by Nakanishi and Nozaki⁶³ from 40 Hz to 10 GHz by dielectric spectroscopy of these polyalcohols. There have been direct observations of the NCL in the time domain from the ps to ns range (note that $\tau = 1$ ps corresponds to a characteristic frequency of 0.16 THz) by optically heterodyne detected optical Kerr effect (OHD-OKE) experiments of a variety of small molecular glass-formers including ortho-terphenyl, salol, benzophenone, and others at temperatures above T_g ,^{64–67} and certainly will continue to be observed in the glassy state. The light scattering spectra of polyisobutylene, poly(methyl methacrylate), and glycerol measured in the gigahertz frequency range all show the NCL up to 3 GHz at temperatures below the glass transition.¹⁷ All of these observations higher than 1 GHz indicate the presence of the NCL at higher frequencies up to 1 THz where it is superposed on top of the microscopic peak, which is almost independent of temperature.⁶⁸ Thus, the observed increase of the dielectric losses, $\epsilon''(\nu)$ at $\nu = 0.6$ and 1 THz, with temperature and the break at T_β below T_g is contributed by the NCL.

To proceed further, we consider the plots of the α - and JG β -relaxation times, τ_α and τ_{JG} , against T_g/T of the four polyalcohols adapted from the data of Doβ et al.^{69,70} and additional data obtained by us in this study in Figure 1. Defined as the temperature at which $\tau_\alpha(T_g) = 100$ s, T_g is equal to 185 K for glycerol, 224 K for threitol, 248 K for xylitol, and 268 K for sorbitol. The Arrhenius temperature dependences of τ_{JG} have been extrapolated to lower scaled reciprocal temperatures to reach 100 s at T_g/T_β . In the case of glycerol, only one point was identified for τ_{JG} and the activation energy was obtained by

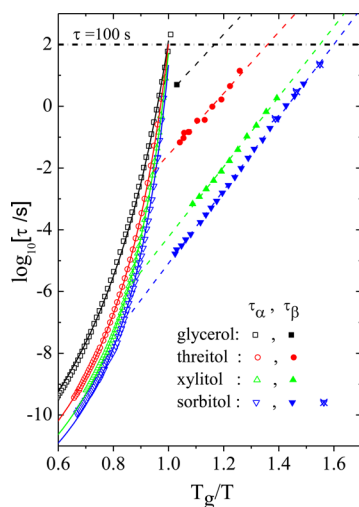


Figure 1. Relaxation map of the logarithm of the α - (open symbols) and JG β -relaxation (filled symbols) times, τ_α and τ_β , against T_g/T of the four polyalcohols adapted from the data of Doβ et al.^{69,70} and additional data from this study (crossed symbols). Squares, circles, and up and down triangles are the symbols for glycerol, threitol, xylitol, and sorbitol, respectively. Continuous lines are from Vogel–Tammann–Fulcher fits to τ_α ; dashed lines for the Arrhenius fit to τ_β . The horizontal dotted–dashed line marks the glass transition as $\tau = 100$ s.

Doβ et al. from extrapolation of the values of the series of polyalcohols. Nevertheless, these values are in good agreement with τ_{JG} of glycerol, as estimated near T_g from an aging experiment.⁷¹ The value of T_g/T_β for sorbitol, xylitol, threitol, and glycerol are 1.60, 1.55, 1.36, and 1.17, respectively, with the corresponding values of 0.63, 0.65, 0.74, and 0.85 for T_β/T_g and 169, 160, 165, and 157 K for T_β . As shown before,³⁹ there is approximate agreement between τ_{JG} and the primitive relaxation time τ_0 calculated by the CM equation

$$\tau_0 = (\tau_\alpha)^{1-n} (t_c)^n \approx \tau_{JG} \quad (2)$$

with n from eq 1 and $t_c = 1$ –2 ps for molecular glass-formers and for all four polyalcohols.

The values of $T_\beta/T_g = 0.63$ and 0.65 for sorbitol and xylitol, respectively, are effectively coincident with the value of 0.65 determined by Sibik et al. by fitting the sub- T_g change of T dependence of $\epsilon''(\nu)$ at 1 THz by two lines. The sub- T_g change of threitol is much weaker. Although Sibik et al. suggested the same value of 0.65 , the location of the change is also consistent with $T_\beta/T_g = 0.74$. In the case of glycerol, Sibik et al. apparently were looking for the change near $0.65T_g$ because they considered the thermal changes in the losses originate from a universal change in the hydrogen bonding structure of the samples. Not found in glycerol was rationalized by it remaining unobservable in that case. However, the value of $T_\beta/T_g = 0.85$ for glycerol determined in Figure 1 seems to correspond to a change of ϵ'' approximately at this value, as shown by Figure 2

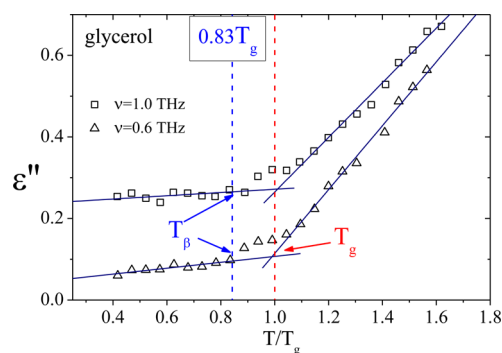


Figure 2. Dielectric losses of glycerol at 0.6 THz (open triangles) and at 1 THz (open squares) versus reduced temperature T/T_g . Data are from ref 60. Straight lines are linear regressions to the low and high temperature data. Blue and red dashed vertical lines mark the occurrence of T_β and T_g , as shown in Figure 1.

where the $\epsilon''(\nu = 1 \text{ THz})$ and $\epsilon''(\nu = 0.6 \text{ THz})$ data of glycerol are reproduced. The major result so far in this section is coincidence of the vitrification temperature T_β of the JG β -relaxation with the temperature at which the sub- T_g changes in $\epsilon''(\nu)$ of all four polyalcohols were found.

The results given above indicate that the kinetic glass-like transition of the JG β -relaxation is reflected in the dynamic process responsible for the $\epsilon''(\nu)$ observed in the THz region. However, definitely the dynamic process is not the JG β -relaxation itself because its frequency ν_{JG} at T_β is nearly 15 decades lower than 1 THz. To identify the dynamic process involved, we can get some hint of it from the dielectric relaxation spectra of the polyalcohols at temperatures below and above their respective T_β . Figure 3 shows our own isothermal loss spectra of sorbitol at selected temperatures, 160, 164, 168, 176 K, and 183 K, in the neighborhood centered at T_β

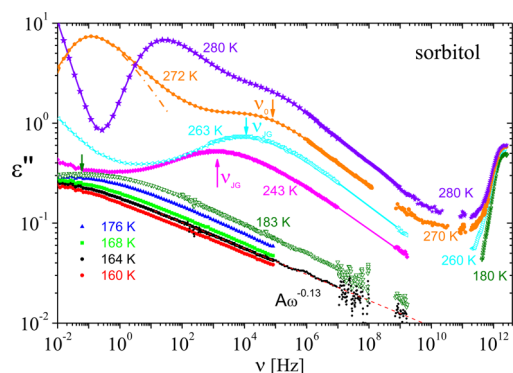


Figure 3. Dielectric loss spectra of sorbitol at selected temperatures ranging from below T_β to above T_g . The dashed line is a power law fit of the high frequency flank of data at 164 K. The dash-dotted line is a fit with a Fourier-transformed derivative of the Kohlrausch correlation function ($n = 0.52$). Vertical arrows mark the primitive relaxation frequency ν_0 or the JG relaxation frequency ν_{JG} . Data are collected from this study ($\nu = 10$ mHz to 1 GHz, $T = 272$ and 280 K and $\nu = 10$ mHz to 100 kHz, $T = 160, 164, 168, 176, 183, 243$, and 263 K) and from ref 63 ($\nu = 100$ Hz to 3 GHz, $T = 164, 183, 243$, and 263 K), ref 23 ($\nu = 0.8$ GHz to 1 THz, $T = 270$ and 280 K) and ref 60 ($\nu = 0.2$ –4 THz, $T = 180, 260, 270$, and 280 K).

= 169 K. In addition, data at higher frequencies and higher temperatures from this study and from the literature^{23,60,63} are shown. Over many decades of frequencies up to 10^5 Hz and beyond, $\epsilon''(\nu)$ has the power law frequency dependence of $\nu^{-0.13}$ and weak temperature dependence, which are the characteristics of the nearly constant loss (NCL) of the caged molecules found in many glass-formers.^{37,39,45,46,62,63} The dynamics of caged molecules is neither relaxation nor diffusion, and has no characteristic time constant. The NCL with power law frequency dependence extends from the onset frequency of the order of the microscopic excitations frequency in the infrared region,^{68,72} and persists indefinitely to lower frequencies until it is terminated at the cutoff frequency $\nu_{NCL}(T)$ by onset of the primitive relaxation. Thus, the power law seen in Figure 3 will continue to hold when extended to higher frequencies, and at the THz regime, it is superposed on top of the microscopic peak, which is almost independent of temperature.⁶⁸ The NCL is thus the dynamic process responsible for the $\epsilon''(\nu)$ at 1 THz and change of temperature dependence near T_β for sorbitol. The same discussion can be applied also to the data of the other polyalcohols. In particular, it can rationalize the results of Figure 2 for glycerol, where $\epsilon''(\nu = 0.6$ THz) exhibits a stronger temperature change than $\epsilon''(\nu = 1$ THz).

The lower bound of the NCL regime, $\nu_{NCL}(T)$, is higher than the primitive relaxation frequency, $\nu_0(T) \approx \nu_{JG}(T)$, but normally the former is higher than the latter by one or two decades at temperatures above T_g , as can be seen from examples shown in refs 37, 39, and 44–46 and also from some spectra in Figure 3. This relation between $\nu_{NCL}(T)$ and $\nu_0(T) \approx \nu_{JG}(T)$ holds in the spectra of xylitol (see Figure 4), threitol, and glycerol (see Figures S1 and S2 in the Supporting Information), justifying that the primitive/JG β -relaxation is the terminator of the caged dynamics regime.⁴¹ Again, the dielectric $\epsilon''(\nu)$ data of these three polyalcohols exhibit the NCL starting at frequencies about 10 decades below 1 THz at temperatures above their respective T_β , and is expected to remain as NCL for all temperatures below. In Figure S3 (see the Supporting Information), the weak temperature dependence of the NCL

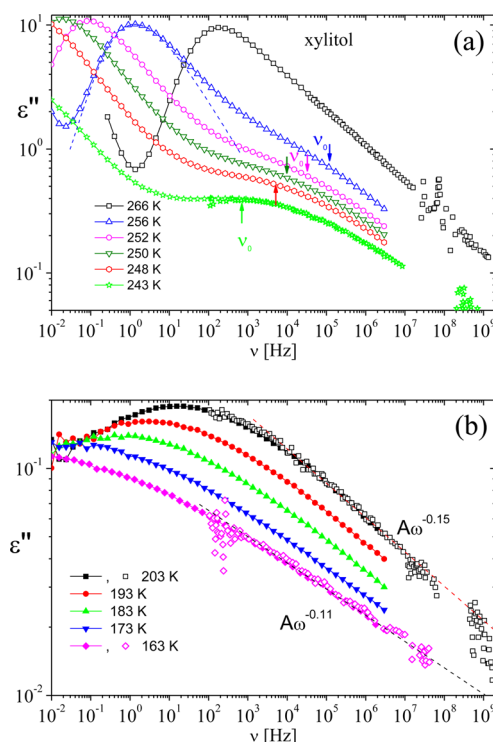


Figure 4. Dielectric loss spectra of xylitol at selected temperatures. Panel a, from right to left: 266, 256, 252, 250, 248, and 243 K. The dashed line is a fit to the α -relaxation peak by the one-sided Fourier transform of the Kohlrausch function with $n = 0.46$. Each vertical arrow pointing toward certain data taken at some temperature indicates the location of the primitive relaxation frequency, ν_0 . Panel b, from right to left: 203, 193, 183, 173, and 163 K. The dashed lines are power law fits of the high frequency flank of data at 203 and 163 K. Data are collected from this study and from ref 63 ($\nu = 100$ Hz to 3 GHz, $T = 163$ and 203 K).

proportional to $\exp(T/T_0)$ in a range of temperatures around $T_\beta = 157$ K of glycerol is shown. Therefore, by these figures, the NCL is identified as the dynamic process contributing to the $\epsilon''(\nu)$ at 1 THz and giving rise to the change of temperature dependence near T_β for these other polyalcohols. Naturally, the question following this identification is why the NCL is sensitive to the vitrification of the JG β -relaxation. The answer to this question will be given later, and before that, presented in the next section are dielectric measurements of two pharmaceutical glass-formers, flufenamic acid and indomethacin, to determine the α - and JG β -relaxation times, T_β and the ratio T_β/T_g for comparison with THz-TDS data when it becomes available in the open literature.

4. DIELECTRIC RELAXATION DATA OF FLUFENAMIC ACID AND INDOMETHACIN

The isothermal dielectric loss spectra of flufenamic acid are shown in Figure 5. The prominent α -loss peak is fitted by the Fourier transform of the Kohlrausch function with $n = 0.44$ shown by example at one temperature. At higher frequencies is a well resolved secondary relaxation loss peak. There is approximate agreement between the secondary relaxation frequency $\nu_{JG}(T)$ and the primitive relaxation frequency $\nu_0(T)$ calculated by eq 2. This satisfies one criterion to indicate that the observed secondary relaxation is the JG β -relaxation. Against reciprocal temperature, the plots of the logarithm of $\tau_\alpha(T)$ and $\tau_{JG}(T)$ in Figure 6 enable determination of the

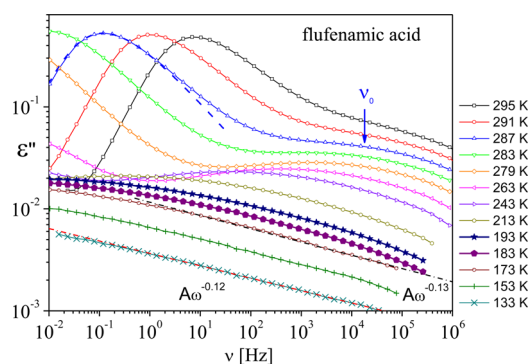


Figure 5. Dielectric loss spectra of flufenamic acid at selected temperatures. The dashed line is a fit to the α -relaxation peak at 287 K by the one-sided Fourier transform of the Kohlrausch function with $n = 0.44$. The vertical arrow marks the location of the primitive relaxation frequency, ν_0 . The dash-dotted lines are power law fits of the high frequency flank of data at 153 and 173 K. The two thick lines and bigger symbols are for 193 and 183 K bracketing the $T_\beta = 189$ K.

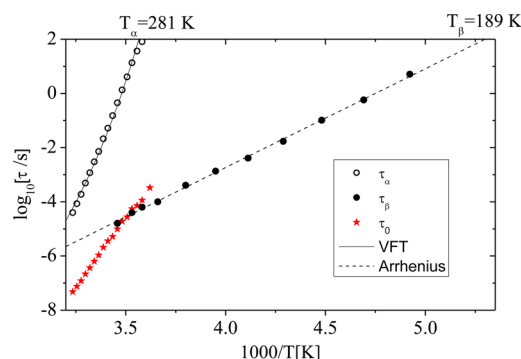


Figure 6. Relaxation map for flufenamic acid: α - (open circles) and JG β -relaxation (filled circles) times, τ_α and τ_β plotted against reciprocal temperature. Red star symbols are for primitive relaxation times, calculated according to eq 2. The continuous line is a Vogel–Tammann–Fulcher fit to τ_α and the dashed line is the Arrhenius fit to $\tau_\beta = 5 \times 10^{-18} \exp(8400/T)$ s.

dielectric $T_g = 261$ K when $\tau_\alpha(T) = 100$ s and extrapolation of the Arrhenius dependence of $\tau_{JG}(T)$ down to $T_\beta = 189$ K at which $\tau_{JG}(T) = 100$ s. Thus, $T_\beta/T_g = 0.67$ in the case of flufenamic acid, and this value is predicted at or near which the $\epsilon''(\nu)$ observed by THz-TDS at 1 THz will change temperature dependence.⁶¹

On cooling the sample much further below T_g to move the α - and β -relaxation out of the instrument frequency window, the NCL appears at higher frequencies and lower temperatures in the loss spectra (Figure 5). The $\epsilon''(\nu)$ data at $T_\beta = 189$ K and below show a clear power law dependence $\nu^{-\lambda}$ with λ of the order of 0.1 and a weak temperature dependence typical of the NCL. The $\nu^{-\lambda}$ dependence seen by conventional dielectric measurements at frequencies lower than 10^5 Hz should persist up to the terahertz region, and the dynamics probed by THz-TDS is the NCL of caged molecules at temperatures below and above $T_\beta = 189$ K.

In contrast to flufenamic acid, the JG β -relaxation of indomethacin has a very small dielectric strength and is not easily resolved in isothermal dielectric spectra.^{73–76} However, its presence has been detected by either applying elevated pressure or first compressing a sample in the liquid state followed by cooling the sample below T_g and releasing the

pressure.⁷⁴ An extrapolation of the suggested Arrhenius temperature dependence of $\tau_{JG}(T)$ down to 100 s determines⁷³ $T_\beta = 184.5$ K at which $\tau_{JG}(T) = 100$ s. This together with $T_g = 316.25$ K gives $T_\beta/T_g = 0.58$. There is a large uncertainty in this value because of the long extrapolation from values of $\tau_{JG}(T)$ at two temperatures each with large uncertainty. Another way to determine T_β is to use the calculated value of $\tau_0(T_g) = 2.42 \times 10^{-4}$ s by eq 2 with $n = 0.41$ and $\tau_\alpha(T_g) = 100$ s and $T_g = 316.25$ K, and the fact that $\tau_0(T_g) \approx \tau_\beta(T_g)$. The same value of $n = 0.41$ was obtained by both Carpentier et al.⁷³ and Wojnarowska et al.⁷⁴ By manipulating the differential scanning calorimetry (DSC) technique, Vyazovkin and Dranca⁷⁶ were able to detect the β -relaxation in the glassy state of indomethacin and found that its activation energy E_β is 56 kJ/mol. Combining this value of E_β with $\tau_0(T_g) = 2.42 \times 10^{-4}$ s, the Arrhenius dependence of $\tau_{JG}(T) \approx \tau_0(T)$ is given by $1.35 \times 10^{-13} \exp(6736/T)$ s. Hence, another estimate of T_β is equal to 196.5 K by the definition of $\tau_{JG}(T_\beta) \approx \tau_0(T_\beta) = 100$ s, and $T_\beta/T_g = 0.62$. The two predicted values of T_β/T_g can be compared with the THz data when published. It is worth pointing out that present in the glassy state of indomethacin is the well resolved and intense γ -relaxation. Faster than the JG β -relaxation with Arrhenius activation energy $E_\gamma = 38$ kJ/mol, the γ -relaxation is pressure-insensitive and intramolecular in origin because it is pressure-insensitive.⁷⁴ The NCL is eclipsed by the γ -relaxation and cannot be observed directly in the low frequency dielectric spectra.

5. RELATION OF THE NCL WITH THE PRIMITIVE/JG β -RELAXATION

In the CM, the dynamics evolve and change with time.^{37,39,41–44} Starting at short times is the motion of molecules confined within cages via the intermolecular potential, and the loss is determined by anharmonicity of the potential. The caged dynamics is not a normal relaxation process. It has no characteristic time, and hence, the loss is a power law, $\chi''(\nu) = B(T)\nu^{-\lambda}$, with $\lambda \ll 1$, or appropriately referred to as the nearly constant loss (NCL) in the susceptibility spectrum. Neither cooperativity nor heterogeneity applies to the NCL of caged dynamics because molecules remain caged throughout the regime, and the loss originates from the anharmonicity of the potential. Although caged dynamics form the core issue of the idealized mode coupling theory,^{66,67,78} the NCL is not a prediction of it.^{16,17,28} This NCL regime persists until the cages are dissolved by the onset of the primitive relaxation of the CM,^{37,39,41–44} the motion of which involves the entire molecule (i.e., a generalization and analogue of the totally rigid molecules studied by Johari and Goldstein).⁷⁹ Thus, the primitive relaxation time, $\tau_0(T, P)$, is an order-of-magnitude upper bound of the NCL time regime, a prediction verified by experimental data and molecular dynamics simulations in many molecular glass-formers,^{37–46} and ionic conductors.^{47–51,57–59} Application of high electric fields in dielectric spectroscopy has the effect of increased loss from all genuine relaxation processes including the JG β -relaxation starting from the primitive relaxation in glycerol and sorbitol.^{80–82} The cause of the increased loss originates from the heterogeneous dynamics of the relaxation processes. However, no effect of the high field was found in the NCL in these high field experiments, as pointed out in a more recent paper.⁴⁴ The analyses of these experimental findings also provide additional evidence that ν_0 is a lower bound of the NCL frequency regime.

The NCL is terminated when it reaches the critical value, ε''_{\max} , at the cutoff frequency $\nu_c(T)$ equal to ν_0 in order of magnitude, by the onset of the primitive relaxation. The magnitude of ε''_{\max} is independent of the value of $\nu_c(T)$ or $\nu_0(T)$ because the same criterion for the termination of the NCL applies. Since from its onset frequency, ν_{on} , to $\nu_c(T)$, the $\varepsilon''(\nu)$ of the NCL increases by the same amount, it follows from the power law dependence of $\varepsilon''(\nu) = B(T)\nu^{-\lambda}$ that at any intermediate frequency ν we have the proportionality relation for the magnitude of the NCL

$$\text{NCL}(\nu) \propto \varepsilon''_{\max} / [\log \nu_{\text{on}} - \log \nu_c(T)] \quad (3)$$

On heating, the value of $\nu_c(T)$ increases following $\nu_0(T) \approx \nu_{\text{JG}}(T)$, and the denominator in relation 3 decreases and hence $\text{NCL}(\nu)$ increases. This monotonic increase of $\text{NCL}(\nu)$ with temperature is commonly observed in dielectric^{23,37,39,45,46} and light scattering^{16,17} studies, and also in THz-TDS.^{60,61} Moreover, as a consequence of the vitrification of the β -relaxation (i.e., the secondary glass transition⁸³) on crossing T_β , the change of $\nu_0(T) \approx \nu_{\text{JG}}(T)$ with temperature above T_β is stronger than that below T_β . This change of T dependence of $\nu_0(T) \approx \nu_{\text{JG}}(T)$ and also the cutoff frequency $\nu_c(T)$ at T_β give rise to a corresponding change of T dependence, as can be inferred from relation 3. The weak temperature dependence of the intensity factor, $A(T) \propto \exp(T/T_0)$, where $T < T_0$, is also derivable from the primitive relaxation frequency, $\nu_0(T, P) \equiv 1/(2\pi\tau_0(T, P))$, acting as the lower bound of the NCL frequency regime.⁴⁹ Although the derivation in ref 49 is for caged ions of ionically conducting systems, it is applicable also to cage molecules in glass-formers.

Even better known from experiments^{43,52–54} and theoretically from eq 2 is the change of the temperature dependence of $\nu_0(T) \approx \nu_{\text{JG}}(T)$ at T_g from the Arrhenius dependence below to a stronger dependence above. The same relation 3 explains the corresponding change in the temperature dependence of $\text{NCL}(\nu)$ on crossing T_g , which was observed in neutron scattering,^{2–11,34} and by dynamic light scattering.^{16,42} In closing this section, we mention other studies by simulations of the fast dynamics in model glass-formers^{84–86} and from experiment⁸⁷ offering different interpretations than ours. Mainly focused on the relation between cooperative motions, elasticity, and free volume, the authors of these studies did not take into account the contribution of the JG relaxation, and thus, no prediction or explanation was provided for the change of fast dynamics at T_β .

6. SUMMARY AND CONCLUSION

The isothermal and isochronal dielectric relaxation data of the polyalcohols we presented have identified the nearly constant losses in susceptibility spectra of caged molecules are the process probed by THz-TDS in the study by Sibik et al.^{60,61} Therefore, the NCL is the process responsible for the observed change in the temperature dependence of $\varepsilon''(\nu)$ at 1 THz in the experiment. From the relaxation spectra of the polyalcohols, we determine the structural α -relaxation time τ_α and the JG β -relaxation time τ_{JG} . The nominal glass transition temperature T_g and the “secondary glass transition” temperature T_β are determined as the temperatures at which τ_α and τ_{JG} reach 100 s, respectively.

The crux of the paper is a CM description of the evolution of dynamics with time. The dynamics start from the caged molecules regime, which is terminated by the primitive relaxation involving rotation and/or translation of individual molecules. In turn, the primitive relaxation is the start or

precursor of the evolution of the relaxation dynamics with time that involves the participation of an increasing number of molecules. These spatially and dynamically heterogeneous relaxation processes, collectively considered as the JG β -relaxation, are spatially and dynamically heterogeneous as well as to some extent cooperative. These properties of the JG β -relaxation explain why it shows up at some temperature T_β below T_g in heat capacity measurements by various techniques of calorimetry,^{77,88–91} and positronium annihilation spectroscopy,^{83,92} and justify calling it the secondary glass transition consistent with the $T\rho^{-\gamma}$ dependence of τ_{JG} .⁵⁷ Furthermore, the freezing of the motions related to JG β -relaxation has been recently shown⁹³ to contribute to glass entropy and enthalpy. These findings imply that glasses have a nonequilibrium structure characterized by two fictive temperatures:⁹³ the highest T_f (close to T_g) that corresponds to the kinetic freezing of α -cooperative motions and the lower T_{fJG} (close to T_β) that corresponds to kinetic freezing of local fluctuations. On the basis of these experimental facts and theoretical considerations, the occurrence of secondary glass transition of the JG β -relaxation at T_β is natural. The temperature dependence of τ_{JG} changes from the stronger Arrhenius dependence above T_β to a weaker one below T_β . The final stage of the evolution of dynamics is the heterogeneous and cooperative α -relaxation having a time correlation function given by the Kohlrausch function in eq 1, and its relaxation time τ_α is connected to $\tau_0 \approx \tau_{\text{JG}}$ by eq 2 which also has been amply verified in many glass-formers and mixtures by experiments.

The termination of the caged molecule dynamics regime by the onset of the primitive relaxation acting as the precursor of the JG β -relaxation is the origin of the connection of the caged molecule dynamics with relaxation processes. The cage molecule dynamics manifested in susceptibility as the nearly constant loss (NCL) is thus related in its magnitude to the relaxation frequencies $\nu_0(T) \approx \nu_{\text{JG}}(T)$. The well understood changes of the temperature dependence of $\nu_0(T) \approx \nu_{\text{JG}}(T)$ at T_g and T_β are transferred to the corresponding changes of the NCL. Density changes on crossing T_g and T_β also can independently rationalize the changes of the T dependence of NCL. Through the steps summarized in the above, we have a microscopic explanation of the sub- T_g change of $\varepsilon''(\nu)$ data at T_{THz} observed in the polyalcohols by THz-TDS. In this explanation, the sub- T_g change of $\varepsilon''(\nu)$ data should occur at T_β obtained from the analysis of conventional dielectric spectroscopy. The good agreements of T_β with T_{THz} in the polyalcohols are strong support of the explanation. Analysis of the dielectric spectra of flufenamic acid and indomethacin gives the values of T_β for these two pharmaceutical glass-formers. The prediction that T_β should be approximately equal to T_{THz}^{61} can be checked against THz-TDS data of these glass-formers⁶¹ when published in the future.

Although we focus our attention on THz-TDS data, other high frequency/short time techniques such as dynamic light scattering and neutron scattering will serve the same purpose of showing the presence of the sub- T_g change originating from the NCL of caged dynamics. As an example, we cite the neutron scattering data of a cis/trans mixture of decalin by Plazanet and Schober.⁸ The mean square displacements from elastic intensity measurements show a change of temperature dependence at $T_n \approx 90$ K and at $T_g = 137$ K. The ratio is $T_n/T_g = 0.66$. If the low frequency susceptibility spectra of decalin are available to deduce the vitrification temperature of the primitive or JG β -relaxation, T_β , it can be compared with T_n . In the case of

decalin, the dielectric strength is too weak, and the β -relaxation has not been detected.⁹⁴ Notwithstanding, there are other glass-formers for which the sub- T_g change was observed at T_n by other high frequency techniques other than THz-TDS, and to be compared with T_β which also can be determined by low frequency dielectric spectroscopy and calorimetry. These will be the subject of a follow-up paper.

As a final remark, this paper should not be considered as just an explanation of the data from THz-TDS. Rather, it serves as another demonstration of the link between the caged molecule dynamics and the primitive relaxation, the precursor of the JG β -relaxation, showing up before in many other experimental investigations.

■ ASSOCIATED CONTENT

● Supporting Information

More details on the dielectric loss spectra of polyalcohols. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b04408.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: simone.capaccioli@df.unipi.it.

*E-mail: Kia.Ngai@pi.ipcf.cnr.it.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Juraj Sibik for stimulating discussions of his experimental data by THz-TDS. This study has been supported by Italian Foreign Affairs Ministry—DGPSP within the Executive Programme for Scientific and Technological Cooperation between the Italian Republic and the People's Republic of China 2013–2015 (Significant Research Project PGR00137).

■ REFERENCES

- (1) Knaak, W.; Mezei, F.; Farago, B. Observation of Scaling Behaviour of Dynamic Correlations near Liquid-Glass Transition. *Europhys. Lett.* **1988**, *7*, 529.
- (2) Petry, W.; Bartsch, E.; Fujara, F.; Kiebel, M.; Sillescu, H.; Farago, B. Dynamic Anomaly in the Glass Transition Region of Orthoterphenyl. *Z. Phys. B* **1991**, *83*, 175.
- (3) Frick, B.; Farago, B.; Richter, D. Temperature Dependence of the Nonergodicity Parameter in Polybutadiene in the Neighborhood of the Glass Transition. *Phys. Rev. Lett.* **1990**, *64*, 2921.
- (4) Mezei, F.; Russina, M. Intermediate Range Order Dynamics Near the Glass Transition. *J. Phys.: Condens. Matter* **1999**, *11*, A341.
- (5) Arbe, A.; Buchenau, U.; Willner, L.; Richter, D.; Colmenero, J. Study of the Dynamic Structure Factor in the β Relaxation Regime of Polybutadiene. *Phys. Rev. Lett.* **1996**, *76*, 1872.
- (6) Frick, B.; Richter, D.; Petry, W.; Buchenau, U. Study of the Glass Transition Order Parameter in Amorphous Polybutadiene by Incoherent Neutron Scattering. *Z. Phys. B: Condens. Matter* **1989**, *70*, 73–79.
- (7) Mermet, A.; Duval, E.; Surovtsev, N. V.; Jal, J. F.; Dianoux, A. J.; Yee, A. F. Localized Fast Relaxation in Poly(methyl methacrylate) Glass. *Europhys. Lett.* **1997**, *38*, 515–520.
- (8) Plazanet, M.; Schöber, H. Anharmonicity in a Fragile Glass-Former Probed by Inelastic Neutron Scattering. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5723–5729.
- (9) Inoue, R.; Kanaya, T. Heterogeneous Dynamics of Polymer Thin Films as Studied by Neutron Scattering. *Adv. Polym. Sci.* **2013**, *252*, 107–140.
- (10) Buchenau, U.; Zorn, R.; Ramos, M. A. Probing Cooperative Liquid Dynamics with the Mean Square Displacement. *Phys. Rev. E* **2014**, *90*, 042312.
- (11) Ngai, K. L.; Habasaki, J. An Alternative Explanation of the Change in T-Dependence of the Effective Debye-Waller Factor at T_c or T_b . *J. Chem. Phys.* **2014**, *141*, 114502.
- (12) Monaco, G.; Fioretto, D.; Masciovecchio, C.; Ruocco, G.; Sette, F. Fast Relaxational Dynamics in the *o*-Terphenyl Glass. *Phys. Rev. Lett.* **1999**, *82*, 1776.
- (13) Li, G.; Du, W. M.; Hernandez, J.; Cummins, H. Z. Locating the Nonergodicity-Parameter Anomaly near the Liquid-to-Glass Crossover Temperature in CaKNO₃ by Brillouin Scattering. *Phys. Rev. E* **1993**, *48*, 1192.
- (14) Steffen, W.; Patkowski, A.; Glaser, H.; Meier, G.; Fischer, E. W. Depolarized-Light-Scattering Study of Orthoterphenyl and Comparison with the Mode-Coupling Model. *Phys. Rev. B* **1994**, *49*, 2992.
- (15) Gapinski, J.; Steffen, W.; Patkowski, A.; Sokolov, A. P.; Kisiuk, A.; Buchenau, U.; Russina, M.; Mezei, F.; Schöber, H. Spectrum of Fast Dynamics in Glass Forming Liquids: Does the “Knee” Exist? *J. Chem. Phys.* **1999**, *110*, 2312–2315.
- (16) Sokolov, A. P.; Kisiuk, A.; Novikov, V. N.; Ngai, K. L. Observation of Constant Loss in Fast Relaxation Spectra of Polymers. *Phys. Rev. B* **2001**, *63*, 172204.
- (17) Kisiuk, A.; Novikov, V. N.; Sokolov, A. P. Constant Loss in Brillouin Spectra of Polymers. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 201.
- (18) Sette, F.; Krisch, M. H.; Masciovecchio, C.; Ruocco, G.; Monaco, G. Dynamics of Glasses and Glass-Forming Liquids Studied by Inelastic X-ray Scattering. *Science* **1998**, *280*, 1550–1555.
- (19) Scopigno, T.; Ruocco, G.; Sette, F.; Monaco, G. Is the Fragility of a Liquid Embedded in the Properties of Its Glass? *Science* **2003**, *302*, 849–852.
- (20) Comez, L.; Corezzi, S.; Monaco, G.; Verbeni, R.; Fioretto, D. Ergodic to Nonergodic Transition in Liquids with a Local Order: The Case of *m*-Toluidine. *Phys. Rev. Lett.* **2005**, *94*, 155702.
- (21) Lunkenheimer, P.; Pimenov, A.; Loidl, A. Fast Dynamics in CKN and CRN Investigated by Dielectric Spectroscopy. *Phys. Rev. Lett.* **1997**, *78*, 2995.
- (22) Lunkenheimer, P.; Pimenov, A.; Dressel, M.; Goncharov, Y.; Böhrer, R.; Loidl, A. Fast Dynamics of Glass-Forming Glycerol Studied by Dielectric Spectroscopy. *Phys. Rev. Lett.* **1996**, *77*, 318–321.
- (23) Kastner, S.; Köhler, M.; Goncharov, Y.; Lunkenheimer, P.; Loidl, A. High-Frequency Dynamics of Type B Glass Formers Investigated by Broadband Dielectric Spectroscopy. *J. Non-Cryst. Solids* **2011**, *357*, 510–514.
- (24) Yomogida, Y.; Sato, Y.; Nozaki, R.; Mishina, T. Comparative Dielectric Study of Monohydric Alcohols with Terahertz Time-Domain Spectroscopy. *J. Mol. Struct.* **2010**, *981*, 173–178.
- (25) Miao, Q.; Tian, L.; Zhao, K.; Zhou, Q.; Shi, Y.; Zhao, D.; Zhao, S.; Zhang, C. Detection and Identification of Selected Alcohols Using Terahertz Time-domain Spectroscopy. *J. Phys. (Paris)* **2011**, 012220.
- (26) Sibik, J.; Shalaev, E. Y.; Zeitler, J. A. Glassy Dynamics of Sorbitol Solutions at Terahertz Frequencies. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11931–11942.
- (27) Wietzke, S.; Jansen, C.; Reuter, M.; Jung, T.; Kraft, D.; Chatterjee, S.; Fischer, B. M.; Koch, M. Terahertz Spectroscopy on Polymers: A Review of Morphological Studies. *J. Mol. Struct.* **2011**, *1006*, 41–51.
- (28) Cang, H.; Novikov, V. N.; Fayer, M. D. Logarithmic Decay of the Orientational Correlation Function in Supercooled Liquids on the ps to ns Time Scale. *J. Chem. Phys.* **2003**, *118*, 2800–2807.
- (29) Donati, C.; Glotzer, S. C.; Poole, P. H.; Kob, W.; Plimpton, S. J. Spatial Correlations of Mobility and Immobility in a Glass-Forming Lennard-Jones Liquid. *Phys. Rev. E* **1999**, *60*, 3107.
- (30) Bordat, P.; Affouard, F.; Descamps, M.; Ngai, K. L. Does the Interaction Potential Determine Both the Fragility of a Liquid and the Vibrational Properties of its Glassy State? *Phys. Rev. Lett.* **2004**, *93* (10), 105502.

- (31) Habasaki, J.; Ngai, K. L. Molecular Dynamics Simulation of Ion Dynamics in Glassy Ionic Conductors: Evidence of the Primitive Ion Hopping Process. *J. Non-Cryst. Solids* **2006**, *352*, 5170–5177.
- (32) Coslovich, D.; Roland, C. M. Density Scaling in Viscous Liquids: From Relaxation Times to Four-Point Susceptibilities. *J. Chem. Phys.* **2009**, *131*, 151103.
- (33) Roland, C. M.; Fragiadakis, D.; Coslovich, D.; Capaccioli, S.; Ngai, K. L. Correlation of Nonexponentiality with Dynamic Heterogeneity From Four-Point Dynamic Susceptibility $\chi_4(t)$ and its Approximation $\chi_1 T$. *J. Chem. Phys.* **2010**, *131*, 124507.
- (34) Ngai, K. L. Dynamic and Thermodynamic Properties of Glass-Forming Substances. *J. Non-Cryst. Solids* **2000**, *275*, 7–51.
- (35) Angell, C. A. Ten Questions on Glassformers, and a Real Space 'Excitations' Model with Some Answers on Fragility and Phase Transitions. *J. Phys.: Condens. Matter* **2000**, *12*, 6463.
- (36) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. Relaxation in Glassforming Liquids and Amorphous Solids. *J. Appl. Phys.* **2000**, *88*, 3113.
- (37) Ngai, K. L. *Relaxation and Diffusion in Complex Systems*; Springer: New York, 2011.
- (38) Ngai, K. L. Relation between Some Secondary Relaxations and the Alpha Relaxations in Glass-Forming Materials According to the Coupling Model. *J. Chem. Phys.* **1998**, *109*, 6982.
- (39) Ngai, K. L. An Extended Coupling Model Description of the Evolution of Dynamics with Time in Supercooled Liquids and Ionic Conductors. *J. Phys.: Condens. Matter* **2003**, *15*, S1107–S1125.
- (40) Ngai, K. L.; Paluch, M. Classification of Secondary Relaxation in Glass-Formers Based on Dynamic Properties. *J. Chem. Phys.* **2004**, *120*, 857.
- (41) Ngai, K. L. In *Slow Dynamics in Complex Systems: 3rd International Symposium*; Tokuyama, M., Oppenheim, I.; *AIP Conf. Proc.* **2004**, *708*, 515.
- (42) Ngai, K. L. Why the Fast Relaxation in the Picosecond to Nanosecond Time Range Can Sense the Glass Transition. *Philos. Mag.* **2004**, *84*, 1341.
- (43) Capaccioli, S.; Paluch, M.; Prevosto, D.; Wang, L.-M.; Ngai, K. L. Many-Body Nature of Relaxation Processes in Glass-Forming Systems. *J. Phys. Chem. Lett.* **2012**, *3*, 735.
- (44) Ngai, K. L. Interpreting the Nonlinear Dielectric Response of Glass-formers in Terms of the Coupling Model. *J. Chem. Phys.* **2015**, *142*, 114502.
- (45) Capaccioli, S.; Thayyil, M. S.; Ngai, K. L. Critical Issues of Current Research on the Dynamics Leading to Glass Transition. *J. Phys. Chem. B* **2008**, *112*, 16035.
- (46) Ngai, K. L.; Paluch, M. Inference of the Evolution from Caged Dynamics to Cooperative Relaxation in Glass-Formers from Dielectric Relaxation Data. *J. Phys. Chem. B* **2003**, *107*, 6865–6872.
- (47) León, C.; Rivera, A.; Várez, A.; Sanz, J.; Santamaria, J.; Ngai, K. L. Origin of Constant Loss in Ionic Conductors. *Phys. Rev. Lett.* **2001**, *86*, 1279.
- (48) Ngai, K. L.; León, C. Cage Decay, Near Constant Loss, and Crossover to Cooperative Ion Motion in Ionic Conductors: Insight from Experimental Data. *Phys. Rev. B* **2002**, *66*, 064308.
- (49) Ngai, K. L.; Habasaki, J.; Hiwatari, Y.; León, C. A Combined Molecular Dynamics Simulation, Experimental and Coupling Model Study of the Ion Dynamics in Glassy Ionic Conductors. *J. Phys.: Condens. Matter* **2003**, *15*, S1607.
- (50) Rivera, A.; León, C.; Sanz, J.; Santamaria, J.; Moynihan, C. T.; Ngai, K. L. Crossover from Ionic Hopping to Nearly Constant Loss in the Fast Ionic Conductor $\text{Li}_0.18\text{La}_{0.61}\text{TiO}_3$. *Phys. Rev. B* **2002**, *65*, 224302.
- (51) Ngai, K. L.; Habasaki, J.; Leon, C.; Rivera, A. Comparison of Dynamics of Ions in Ionically Conducting Materials and Dynamics of Glass-Forming Substances: Remarkable Similarities. *Z. Phys. Chem.* **2005**, *219*, 47–70.
- (52) Paluch, M.; Roland, C. M.; Pawlus, S.; Ziolo, J.; Ngai, K. L. Does the Arrhenius Temperature Dependence of the Johari-Goldstein Relaxation Persist above T_g ? *Phys. Rev. Lett.* **2003**, *91*, 115701.
- (53) Mierzwa, M.; Pawlus, S.; Paluch, M.; Kaminska, E.; Ngai, K. L. Correlation between Primary and Secondary Johari-Goldstein Relaxations in Supercooled Liquids: Invariance to Changes in Thermodynamic Conditions. *J. Chem. Phys.* **2008**, *128*, 044512.
- (54) Kessairi, K.; Capaccioli, S.; Prevosto, D.; Lucchesi, M.; Sharifi, S.; Rolla, P. A. Interdependence of Primary and Johari-Goldstein Secondary Relaxations in Glass-Forming Systems. *J. Phys. Chem. B* **2008**, *112*, 4470.
- (55) Böhmer, R.; Diezemann, G.; Geil, B.; Hinze, G.; Nowaczyk, A.; Winterlich, M. Correlation of Primary and Secondary Relaxations in a Supercooled Liquid. *Phys. Rev. Lett.* **2006**, *97*, 135701.
- (56) Bedrov, D.; Smith, G. D. Secondary Johari-Goldstein Relaxation in Linear Polymer Melts Represented by a Simple Bead-Necklace Model. *J. Non-Cryst. Solids* **2011**, *357*, 258.
- (57) Ngai, K. L.; Habasaki, J.; Prevosto, D.; Capaccioli, S.; Paluch, M. Thermodynamic Scaling of α -Relaxation Time and Viscosity Stems from the Johari-Goldstein β -Relaxation or the Primitive Relaxation of the Coupling Model. *J. Chem. Phys.* **2012**, *137*, 034511.
- (58) Jarosz, G.; Mierzwa, M.; Ziolo, J.; Paluch, M.; Shirota, H.; Ngai, K. L. Glass Transition Dynamics of Room-Temperature Ionic Liquid 1-Methyl-3-trimethylsilylmethylimidazolium Tetrafluoroborate. *J. Phys. Chem. B* **2011**, *115*, 12709–12716.
- (59) Hensel-Bielowka, S.; Ngai, K. L.; Swietly-Pospiech, A.; Hawelek, L.; Knapik, J.; Sawicki, W.; Paluch, M. On the Molecular Origin of Secondary Relaxations in Amorphous Protic Ionic Conductor Chlorpromazine Hydrochloride—High Pressure Dielectric Studies. *J. Non-Cryst. Solids* **2015**, *407*, 81–87.
- (60) Sibik, J.; Elliott, S. R.; Zeitler, J. A. Thermal Decoupling of Molecular-Relaxation Processes from the Vibrational Density of States at Terahertz Frequencies in Supercooled Hydrogen-Bonded Liquids. *J. Phys. Chem. Lett.* **2014**, *5*, 1968–1972.
- (61) Sibik, J.; Zeitler, J. A. XIV International Workshop on Complex Systems, Fai della Paganella, Italy, March 22–25, 2015; in press.
- (62) Kudlik, A.; Benkhof, S.; Blochowicz, T.; Tschirwitz, C.; Rössler, E. The Dielectric Response of Simple Organic Glass Formers. *J. Mol. Struct.* **1999**, *479*, 201–218.
- (63) Nakanishi, M.; Nozaki, R. High-Frequency Broadband Dielectric Spectroscopy on Sugar Alcohols Below T_g . *J. Non-Cryst. Solids* **2010**, *356*, 733–737.
- (64) Gottke, S. D.; Brace, D. D.; Hinze, G.; Fayer, M. D. Time Domain Optical Studies of Dynamics in Supercooled O-terphenyl: Comparison to Mode Coupling Theory on Fast and Slow Time Scales. *J. Phys. Chem. B* **2001**, *105*, 238.
- (65) Brace, D. D.; Gottke, S. D.; Cang, H.; Fayer, M. D. Orientational Dynamics of the Glass Forming Liquid, Dibutylphthalate: Time Domain Experiments and Comparison to Mode Coupling Theory. *J. Chem. Phys.* **2002**, *116*, 1598.
- (66) Hinze, G.; Brace, D. D.; Gottke, S. D.; Fayer, M. D. A Detailed Test of Mode-Coupling Theory on all Time Scales: Time Domain Studies of Structural Relaxation in a Supercooled Liquid. *J. Chem. Phys.* **2000**, *113*, 3723–3733.
- (67) Cang, H.; Novikov, V. N.; Fayer, M. D. Logarithmic Decay of the Orientational Correlation Function in Supercooled Liquids on the ps to ns Time Scale. *J. Chem. Phys.* **2003**, *118*, 2800.
- (68) Strom, U.; Hendrickson, J. R.; Wagner, R. J.; Taylor, P. C. Disorder-Induced Far Infrared Absorption in Amorphous Materials. *Solid State Commun.* **1974**, *15*, 1871–1875.
- (69) Döb, A.; Paluch, M.; Sillescu, H.; Hinze, G. From Strong to Fragile Glass Formers: Secondary Relaxation in Polyalcohols. *Phys. Rev. Lett.* **2002**, *88*, 095701.
- (70) Döb, A.; Paluch, M.; Sillescu, H.; Hinze, G. Dynamics in Supercooled Polyalcohols: Primary and Secondary Relaxation. *J. Chem. Phys.* **2002**, *117*, 6582.
- (71) Ngai, K. L.; Lunkenheimer, P.; Leon, C.; Schneider, U.; Brand, R.; Loidl, A. Nature and Properties of the Johari-Goldstein Beta-Relaxation in the Equilibrium Liquid State of a Class of Glass-Formers. *J. Chem. Phys.* **2001**, *115*, 1405–1413.

- (72) Schneider, U.; Lunkenheimer, P.; Brand, R.; Loidl, A. Dielectric and Far-Infrared Spectroscopy of Glycerol. *J. Non-Cryst. Solids* **1998**, 235–237, 173–179.
- (73) Carpentier, L.; Decressain, R.; Desprez, S.; Descamps, M. Dynamics of the Amorphous and Crystalline Alpha-, Gamma-Phases of Indomethacin. *J. Phys. Chem. B* **2006**, 110, 457.
- (74) Wojnarowska, Z.; Adrjanowicz, K.; Włodarczyk, P.; Kaminska, E.; Kaminski, K.; Grzybowska, K.; Wrzalik, R.; Paluch, M.; Ngai, K. L. Broadband Dielectric Relaxation Study at Ambient and Elevated Pressure of Molecular Dynamics of Pharmaceutical: Indomethacin. *J. Phys. Chem. B* **2009**, 113, 12536.
- (75) Correia, N. T.; Moura Ramos, J. J.; Descamps, M.; Collins, G. Molecular Mobility and Fragility in Indomethacin: A Thermally Stimulated Depolarization Current Study. *Pharm. Res.* **2001**, 18, 1767.
- (76) Bhugra, C.; Shmeis, R.; Krill, S. L.; Pikal, M. J. Different Measures of Molecular Mobility: Comparison between Calorimetric and Thermally Stimulated Current Relaxation Times Below T_g and Correlation with Dielectric Relaxation Times Above T_g . *Pharm. Res.* **2006**, 23, 2277.
- (77) Vyazovkin, S.; Dranca, I. Probing Beta Relaxation in Pharmaceutically Relevant Glasses by Using DSC. *Pharm. Res.* **2006**, 23, 422–428.
- (78) Götze, W. Recent Tests of the Mode-Coupling Theory for Glassy Dynamics. *J. Phys.: Condens. Matter* **1999**, 11 (A1), 118.
- (79) Johari, G. P.; Goldstein, M. Viscous Liquids and the Glass Transition. II. Secondary Relaxations in Glasses of Rigid Molecules. *J. Chem. Phys.* **1970**, 53, 2372.
- (80) Bauer, Th.; Lunkenheimer, P.; Kastner, S.; Loidl, A. Nonlinear Dielectric Response at the Excess Wing of Glass-Forming Liquids. *Phys. Rev. Lett.* **2013**, 110, 107603.
- (81) Samanta, S.; Richert, R. Limitations of Heterogeneous Models of Liquid Dynamics: Very Slow Rate Exchange in the Excess Wing. *J. Chem. Phys.* **2014**, 140, 054503.
- (82) Samanta, S.; Richert, R. Nonlinear Dielectric Behavior of a Secondary Relaxation: Glassy D-Sorbitol. *J. Phys. Chem. B* **2014**, DOI: 10.1021/jp506854k.
- (83) Wang, C. L.; Hirade, T.; Maurer, F. H. J.; Eldrup, M.; Pedersen, N. J. Free-Volume Distribution and Positronium Formation in Amorphous Polymers: Temperature and Positron-Irradiation-Time Dependence. *J. Chem. Phys.* **1998**, 108, 4654.
- (84) Pazmino Betancourt, B. A.; Hanakata, P. Z.; Starr, F. W.; Douglas, J. F. Quantitative Relations between Cooperative Motion, Emergent Elasticity, and Free Volume in Model Glass-Forming Polymer Materials. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, 112, 2966.
- (85) Larini, L.; Ottocchian, A.; De Michele, C.; Leporini, D. Universal Scaling between Structural Relaxation and Vibrational Dynamics in Glass-Forming Liquids and Polymers. *Nat. Phys.* **2008**, 4, 42.
- (86) Puosi, F.; Michele, C. D.; Leporini, D. Scaling between Relaxation, Transport and Caged Dynamics in a Binary Mixture on a Per-Component Basis. *J. Chem. Phys.* **2013**, 138, 12A532.
- (87) Buchenau, U.; Zorn, R. A Relation Between Fast and Slow Motions in Glassy and Liquid Selenium. *Europhys. Lett.* **1992**, 18, 523–528.
- (88) Fujimori, H.; Oguni, M. Correlation Index $(T_{ga} - T_{gb})/T_{ga}$ and Activation Energy Ratio as Parameters Characterizing the Structure of Liquid and Glass. *Solid State Commun.* **1995**, 94, 157–162.
- (89) Bershtein, V. A.; Egorov, V. M. *Differential Scanning Calorimetry of Polymers*; Ellis Horwood: New York, 1994.
- (90) Bershtein, V. A.; Egorov, V. M.; Emelyanov, Y. A.; Stepanov, V. A. The Nature of β -Relaxation in Polymers. *Polym. Bull.* **1983**, 9, 98–105.
- (91) Bershtein, V. A.; Egorova, L. M.; Prud'homme, R. E. Peculiarities of the segmental dynamics in amorphous miscible polymer blends as a consequence of the common nature of α and β relaxations. *J. Macromol. Sci., Part B: Phys.* **1997**, B36, 513.
- (92) Hristov, H. A.; Bolan, B.; Yee, A. F.; Xie, L.; Gidley, D. W. Measurement of Hole Volume in Amorphous Polymers Using Positron Spectroscopy. *Macromolecules* **1996**, 29, 8507–8516.
- (93) Aji, D. P. B.; Johari, G. P. Kinetic-freezing and unfreezing of local-region fluctuations in a glass structure observed by heat capacity hysteresis. *J. Chem. Phys.* **2015**, 142, 214501.
- (94) Duvvuri, K.; Richert, R. Dynamics of glass-forming liquids. VI. Dielectric relaxation study of neat decahydro-naphthalene. *J. Chem. Phys.* **2002**, 117, 4414.