Coupling of Caged Molecule Dynamics to JG β-Relaxation: I

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Abstract

The paper [Juraj Sibik, Stephen R. Elliott, and J. Axel Zeitler, 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, $\varepsilon''(\nu)$ at ν=1 THz, increase monotonically with temperature and change dependence at two temperatures, first deep in the glassy state at T_{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_{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 is 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 $\varepsilon''(\nu)$ 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_β=0.67T_g for flufenamic acid and T_β=0.58T_g or T_β=0.62T_g for indomethacin, which can be compared with experimental values of T_{THz} from THz-TDS measurements when 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.

Keywords: THz absorption, dielectric spectroscopy, Johari-Goldstein , fast dynamics, nearly constant loss, polyalcohols

1. Introduction

The high frequency measurements of 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 including 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[30-33]. 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), $<u^2(T)>$, measured by quasielastic neutron scattering (QENS) 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 $<u^2(T)>$ at T_g. The remarkably weak T-dependence of $<u^2(T)>$ at temperatures below T_g changes to a stronger T-dependence above T_g.[2,3,6-11,34,35,36] Moreover[34], measured by spectrometer with the same resolution, $<u^2(T)>$ is larger and the change at T_g is sharper if the structural α-relaxation of the glass-former has broader frequency dispersion or smaller value of the exponent, (1-n), of its Kohlrausch correlation function,

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

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 coworkers[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 function of the 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 particles systems with different interaction potentials[30].

These two examples, i.e. the T-dependences of $<u^2(T)>$ 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 $\lambda<<1$ 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 leaves 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 paper[51] 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 $\tau_{\rm JG}$ 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 of 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, $\varepsilon''(\nu)$ at ν=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 $\varepsilon''(\nu)$ at ν=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 $\varepsilon''(\nu)$ at ν=1 THz in 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 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 few degrees above the melting point under nitrogen atmosphere and then cooling. Novocontrol Alpha-Analyzer was used for dielectric measurements from 1 mHz to

10 MHz, whereas for higher frequencies (1 MHz – 6 GHz) measurements have been carried out by means of a reflectometric technique using the Agilent 8753ES Network Analyser.

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 $\varepsilon''(\nu)$ 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 Nozaki[63] from 40 Hz to 10 GHz by dielectric spectroscopy of these polyalcohols. Direct observations of the NCL in the time domain from ps to ns range (note that 1 ps corresponds to 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 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, $\varepsilon''(\nu)$ at ν=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 Fig.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 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 K, 160 K, 165 K, 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,

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

with n from Eq.(1) and t_c=1-2 ps for molecular glass-formers and for all four polyalcohols.

The values of T_β/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 $\varepsilon''(\nu)$ 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, but the location of the change is also consistent with T_{β}/T_g=0.74. In the case of glycerol, Sibik et al. apparently was looking for the change near 0.65T_g because they considered the thermal changes in the losses originates 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_{β}/T_g=0.85 for glycerol determined in Fig.1 seems to correspond to a change of ε'' approximately at this value, as shown by Fig.2 where the $\varepsilon''(\nu$=1 THz) and $\varepsilon''(\nu$=0.6 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 change in $\varepsilon''(\nu)$ 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 $\varepsilon''(\nu)$ observed in THz region. But 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}. Fig.3 shows our own isothermal loss spectra of sorbitol at selected temperatures, 160, 164, 168, 176 K, 183 K in the neighborhood centered at T_{β}=169 K. In addition, data at higher frequencies and higher temperatures from this study and from the literature[23,59,60,63,72] are shown. Over many decade of frequencies up to 10^5 Hz and beyond, $\varepsilon''(\nu)$ has the power law temperature dependence of $\nu^{-0.13}$ and weak temperature, which are the characteristics of the nearly constant loss (NCL) of the caged molecules found in many glassformers[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 cut-off frequency $\nu_{\mathrm{NCL}}(T)$ by onset of the primitive relaxation. Thus the power law seen in Fig.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 $\varepsilon''(\nu)$ at 1 THz and change of temperatures 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 Fig.2 for glycerol, where $\varepsilon''(\nu=0.6\ \mathrm{THz})$ exhibits a stronger temperature change than $\varepsilon''(\nu=1\ \mathrm{THz})$.

The lower bound of the NCL regime, $\nu_{\mathrm{NCL}}(T)$, is higher than the primitive relaxation frequency, $\nu_0(T)\approx\nu_{\mathrm{JG}}(T)$, 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[37,39,44,45,46] and also from some spectra in Fig.3. This relation between $\nu_{\mathrm{NCL}}(T)$ and $\nu_0(T)\approx\nu_{\mathrm{JG}}(T)$ holds in the spectra of xylitol (see Fig.4), threitol, and glycerol (see Figs.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 $\varepsilon''(\nu)$ 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 Fig.S3 (see Supporting Information) the weak temperature dependence of the NCL proportional to $\exp(T/T_o)$ in a range of temperatures around T_β=157 K of glycerol is shown. Therefore, by these figures, the NCL is identified as the dynamic process contributing to the $\varepsilon''(\nu)$ at 1 THz and giving rise to the change of temperatures 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 present in the next section are dielectric measurements of two pharmaceutical glass-former, flufenamic acid and indomethacin to determine the α- and the 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 Fig.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 $\nu_{\mathrm{JG}}(T)$ 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 logarithm of $\tau_\alpha(T)$ and $\tau_{\mathrm{JG}}(T)$ in Fig.6 enable determination of the dielectric T_g=261 K when $\tau_\alpha(T)$=100 s and extrapolation of the Arrhenius dependence of $\tau_{\mathrm{JG}}(T)$ down to T_β=189 K at which $\tau_{\mathrm{JG}}(T)$=100 s. Thus T_β/T_g=0.67 in the case of flufenamic acid, and this value is predicted at or near which the $\varepsilon''(\nu)$ 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 the β-relaxation out of the instrument frequency window, the NCL appears at higher frequencies and lower temperatures in the loss spectra (Fig.5). The $\varepsilon''(\nu)$ data at T_β=189 K and below show clear power law dependence $\nu^{-\lambda}$ with λ of the order of 0.1 and weak temperature dependence typical of the NCL. The $\nu^{-\lambda}$-dependence seen by conventional dielectric measurements at frequencies lower than 10^5 Hz should persists up to the terahertz region, and the dynamics probed by THz-TDS is the NCL of caged molecules at temperatures below and above T_β=189.

In contrast to flufenamic acid, the JG β-relaxation of indomethacin has 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 by 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 determines[73] T_β=184.5 K at which $\tau_{JG}(T)$=100 s. This together with T_g=316.25 K gives T_β/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 $\tau_0(T_g)=2.42\times10^{-4}$ 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 Dranca[76] 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 $\tau_0(T_g)=2.42\times10^{-4}$ s, the Arrhenius dependence of $\tau_{JG}(T)\approx\tau_0(T)$ is given by $1.35\times10^{-13}\exp(6736/T)$. 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_β/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_γ=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 $\lambda<<1$, 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] but 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 involving 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 glassformers[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 finding also provides additional evidence that ν_0 is an lower bound of the NCL frequency regime.

The NCL is terminated when it reaches the critical value, ε''_{max}, at the cut-off 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 increase 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,

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

On heating, the value of $\nu_c(T)$ increases following $\nu_0(T)\approx\nu_{JG}(T)$, and the denominator in relation (3) decreases and hence $NCL(\nu)$ increases. This monotonic increase of $NCL(\nu)$ 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 consequence of the vitrification of the β-relaxation (i.e. the secondary glass transition[83]) on crossing T_β, the change of $\nu_0(T)\approx\nu_{JG}(T)$ with temperature above T_β is stronger than below T_β. This change of T-dependence of $\nu_0(T)\approx\nu_{JG}(T)$ and as well the cut-off frequency $\nu_c(T)$ at T_β gives 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,

$\nu_0(T,P) \equiv 2\pi/\tau_0(T,P)$, 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 $\nu_0(T) \approx \nu_{JG}(T)$ at T_g from the Arrhenius dependence below to a stronger dependence above. The same relation (3) explains the corresponding change in temperature dependence of $NCL(\nu)$ 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 glassformers[84-86] and from experiment[87] 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 Coupling Model 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 increasing number of molecules. These spatially and dynamically heterogeneous relaxation processes, collectively considered as the JG β-relaxation, is 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 shown[93] to contribute to glass entropy and enthalpy. These findings imply that glasses have a non-equilibrium 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 $T_{f,JG}$ (close to T_β) that corresponds to kinetic freezing of local fluctuations. Based on 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 time correlation function given by the Kohlrausch function in eq.(1), and its relaxation time τ_α is connected to $\tau_0 \approx \tau_{JG}$ by eq.(2) which also has been amply verified in many glassformers and mixtures by experiments.

The termination of caged molecules 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 molecules dynamics with relaxation processes. The cage molecules dynamics manifested in susceptibility as the nearly constant loss (NCL) is thus related in its magnitude to the relaxation frequencies $\nu_0(T)\approx\nu_{\mathrm{JG}}(T)$. The well understood changes of temperature dependence of $\nu_0(T)\approx\nu_{\mathrm{JG}}(T)$ 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} can be checked against THz-TDS data of these glass-formers[61] when published in the future.

Although we focus our attention on data from 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 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 the 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 molecules dynamics and the primitive relaxation, the precursor of the JG β-relaxation, showing up before in many other experimental investigations.

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Supporting Information Available

More details on the dielectric loss spectra of polyalcohols are provided in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org

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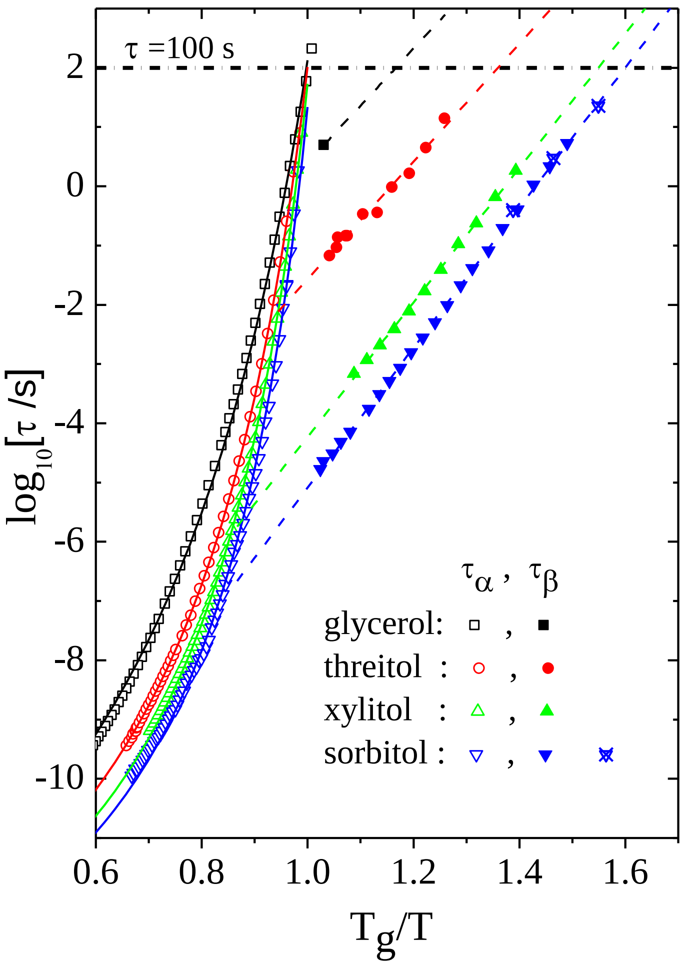

Figure.1: Relaxation map of logarithm of the α- (open symbols) and JG β-relaxation (filled symbols) times, τ_α and τ_β, against T_g/T of the four polyalcohols adapted from the data of Doβ et al.[69,70] and additional data from this study (crossed symbols). Squares, circles, up and down triangles are 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 τ=100 s.

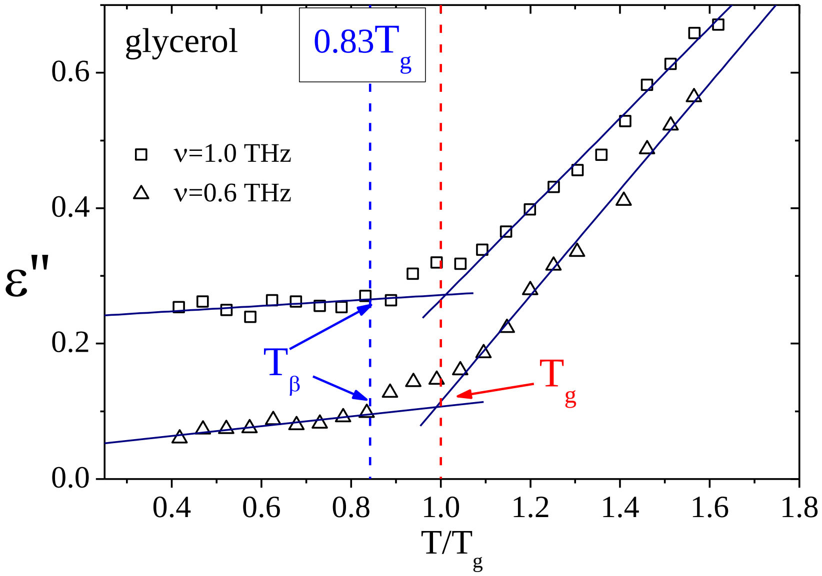

Figure 2: Dielectric losses of glycerol at 0.6 THz (open triangles) and at 1 THz (open squares) versus reduced temperature T/T_g. Data are from Ref.[60]. Straight lines are linear regressions to the low and high temperature data. Blue and red dashed vertical lines mark the occurrence of T_β and T_g as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

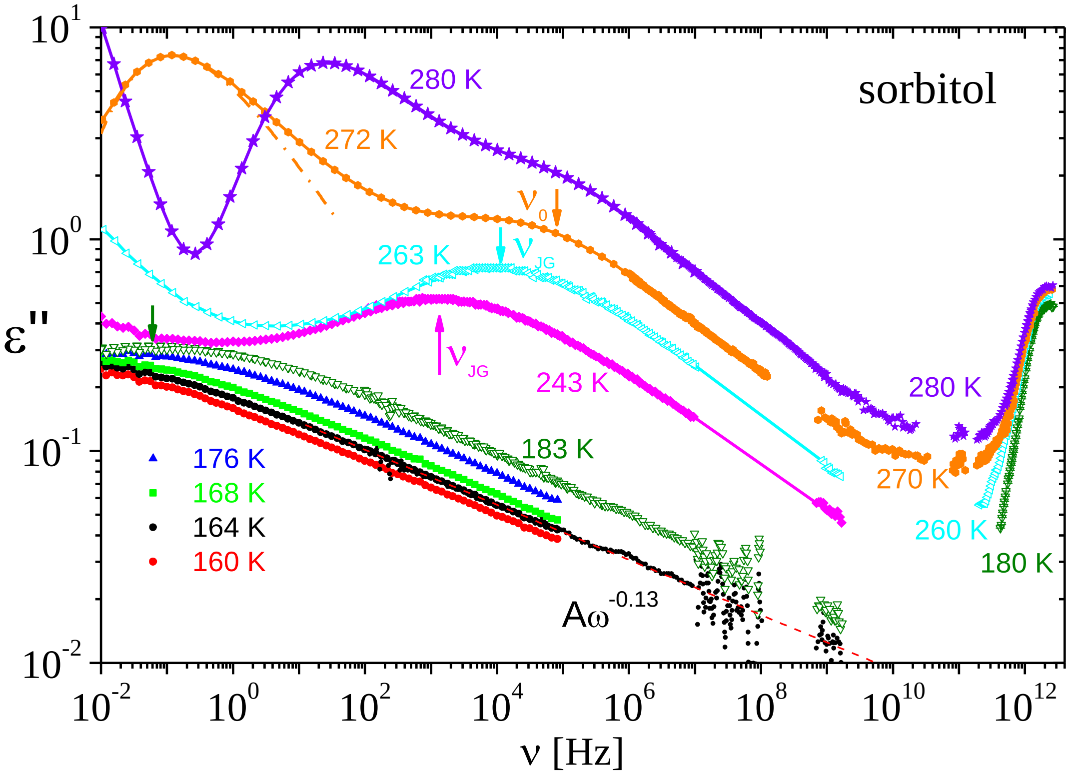

Figure 3: Dielectric loss spectra of sorbitol at selected temperatures ranging from below T_β to above T_g. Dashed line is a power law fit of the high frequency flank of data at 164 K. Dash-dotted line is a fit with a Fourier-transformed derivative of the Kohlrausch correlation function (n=0.52). Vertical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

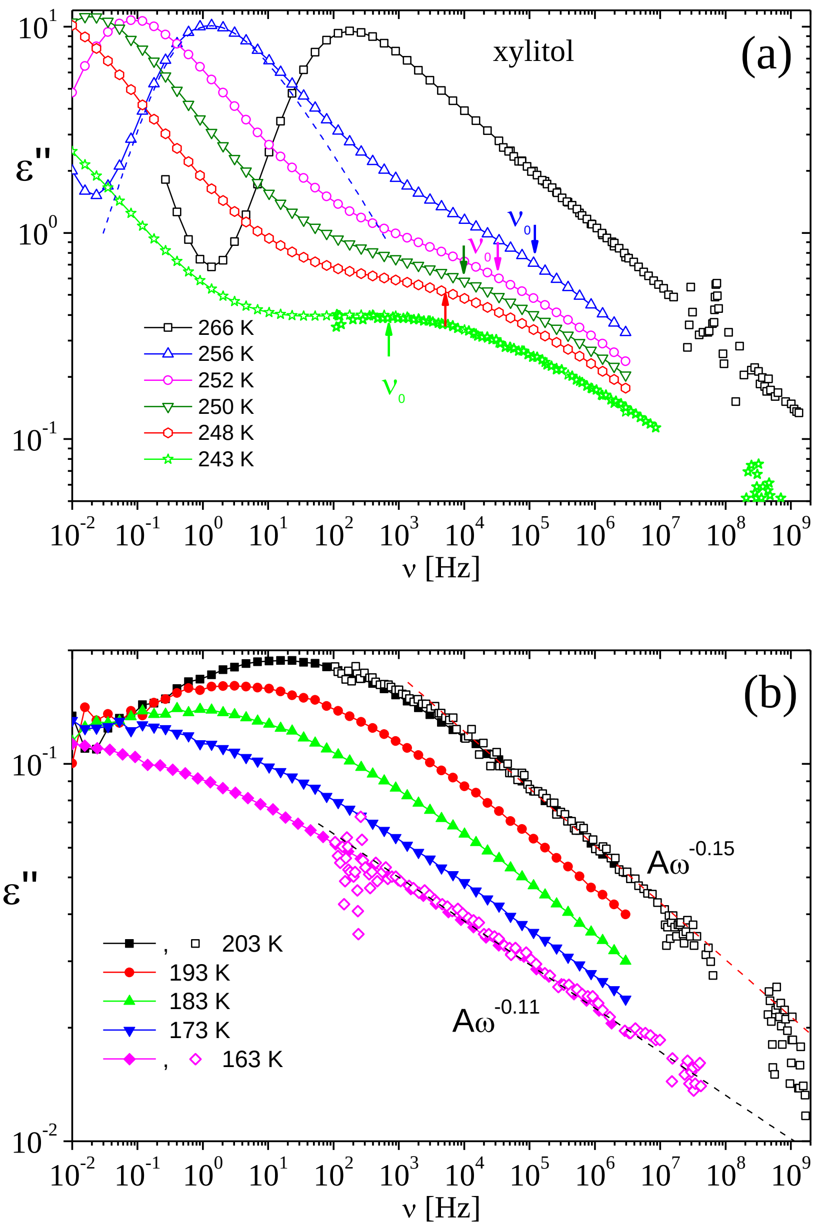

Figure 4: Dielectric loss spectra of xylitol at selected temperatures. Panel (a): from right to left: 266 K, 256 K, 252 K, 250 K, 248 K, 243 K. The dashed line is a fit to the α-relaxation peak by the one-sided Fourier transform of the Kohlrausch function with *n*=0.46. Each vertical arrow pointing toward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

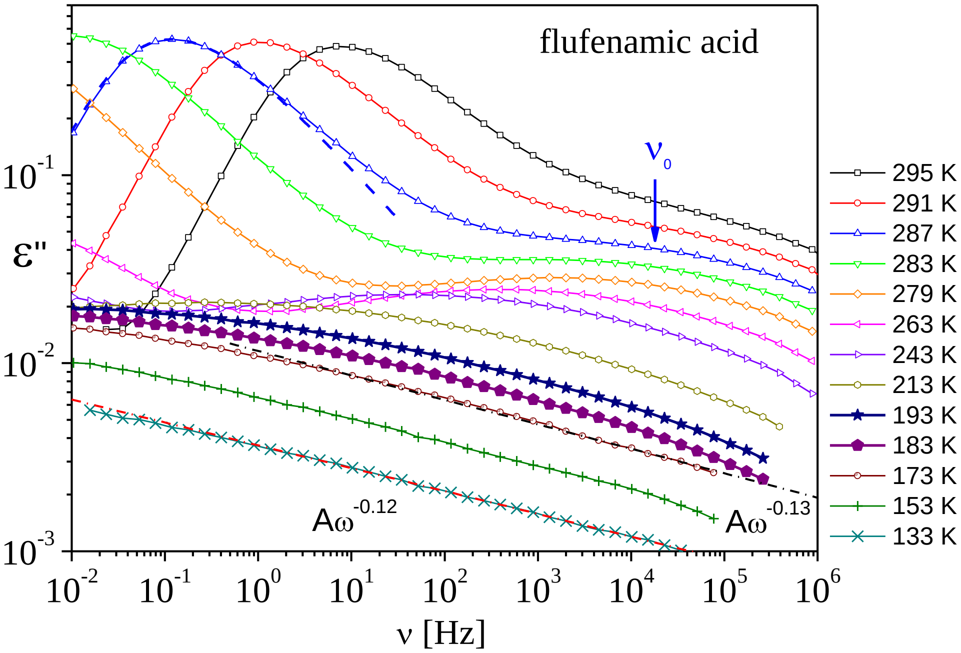

Figure 5: Dielectric loss spectra of flufenamic acid at selected temperatures. The dashed line is a fit to the α-relaxation peak at 287 K by the one-sided Fourier transform of the Kohlrausch function with *n*=0.46. The vertical arrow mark the location of the primitive relaxation frequency, ν_0. The dash-dotted lines are power law fits of the high frequency flank of data at 153 K and 173 K. The two thick lines and bigger symbols are for 193 K and 183 K bracketing the T_β=189 K.

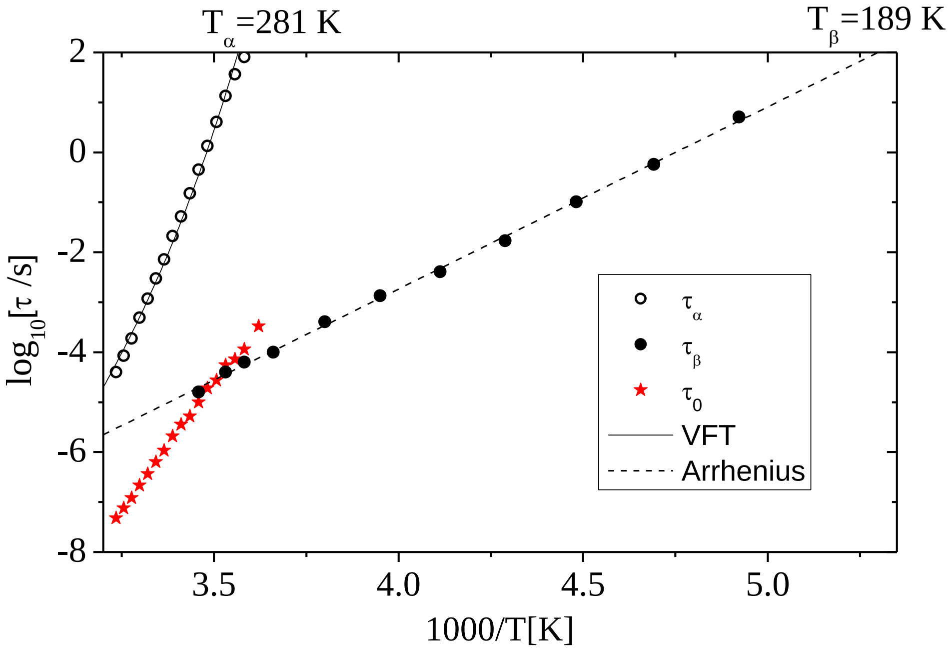

Figure 6:Relaxation map for flufenamic acid: α- (open circles) and JG β-relaxation (filled circles) times, τ_α and τ_β, plotted against reciprocal temperature. Red star symbols are for primitive relaxation times, calculated according to eq.(2). Continuous line is a Vogel-Tammann-Fulcher fit to τ_α, dashed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