Intra- and Intermolecular Inhomogeneities in the Course of Glassy Densification of Polyalcohols

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To test basic assumptions inherent to most theories of molecular liquids and glasses, Infrared spectroscopy is carried out on short polyalcohols at temperatures ranging from far above to far below their glass transition. By analyzing specific vibrations, the thermal expansion of covalent bonds and hydrogen bridges is determined revealing striking differences. A comparison with density verifies the negligibility of intramolecular expansion but exposes severe inhomogeneities on intermolecular scale. This signals distinct roles in glassy densification and promotes an atomistic understanding.

The vitrification of a (super-cooled) liquid into a disordered solid is a central subject of experimental and theoretical soft condensed matter research. A distinctive feature of super-cooled liquids and glasses is the reduction of intermolecular volume, in other words an increase in density, reflected in the term glass densification. While the free volume model uses the inhomogeneity of the density only conceptually, early microscopic theories of liquids identify it as an additional key quantity. This has also been established for glasses and it became clear that heterogeneity in time and space, in other words a varying temporal and spatial scale on which molecules fluctuate is a fundamental attribute of both liquids and glasses. Consequently, modern theoretical approaches like the random first order transition (RFOT) theory incorporate an inhomogeneous density in their description.

Interestingly, even RFOT theory, one of the most sophisticated concepts of molecular glasses, is based on abstract beads and their packing density, i.e. particular intermolecular interactions are not specifically considered. Hence, this approach assumes that the impact of intermolecular interactions on structural relaxation is described by (packing) density. This means that certain presumptions are inherent to this model (similar to most other theoretical descriptions): i) intramolecular expansion is neglected, i.e. density changes are fully or almost fully ascribed to intermolecular expansion, and ii) no directionality or inhomogeneity of the intermolecular interactions is accounted for, i.e. the thermal expansion even on molecular scale is considered isotropic. While the first conjecture appears rather plausible, the second one is questionable for a vast range of systems involving directional interactions e.g. hydrogen (H-) bridges as in glycerol, one of the most studied model glass formers. Despite their essential nature, to the best of our knowledge these two conjectures, negligibility of intramolecular expansion and intermolecular bond directionality, have not yet been tested experimentally.

Here, we reexamine our previously published Infrared (IR) spectroscopy data of short polyalcohols from a wide temperature range above and below the calorimetric glass transition temperature \( T_g \). These molecules (glycerol, threitol, xylitol, and sorbitol) have a regular structure but the orientation of the hydroxy groups, which associate and form a H-bridge network, gives rise to a significant anisotropy. This intramolecular inhomogeneity leads to weak and strong intermolecular H-bridges, and with a novel extensive analysis we reveal their individual thermal expansions. Despite the supramolecular network formed by the mildly expanding strong H-bridges, the profoundly expanding weak H-bridges surprisingly allow for considerable changes in density. A consequence of this inhomogeneity of the intermolecular interactions is a decoupling of the structural relaxation (governed by strong bridges) from the thermal expansivity and density (dominated by weak bridges).

IR spectra were recorded using a Fourier transform infrared (FTIR) spectrometer (Bio–Rad FTS 6000) combined with an IR microscope (UMA 500) and a liquid nitrogen-cooled mercury-cadmiumtelluride (MCT) detector (Kolmar Technologies, Inc, USA) while a THMS 350V stage (Linkam Scientific Instruments, UK) flushed with dry nitrogen controlled the sample temperature; further information can be found elsewhere. Comparing the spectra of the polyalcohols under study reveals their molecular characteristics (Fig. 1a). In the low frequency range (\( \nu = 800 - 1200 \text{ cm}^{-1} \)) the CO stretching vibration \( \nu(\text{CO}) \) at \( \nu \approx 1125 \text{ cm}^{-1} \) and a combined CCO stretching vibration \( \nu(\text{CCO}) \) at \( \nu \approx 860 - 890 \text{ cm}^{-1} \) exhibit bands distinctive for each substance (Fig. 1b). The \( \nu(\text{CO}) \) vibration shows only minor changes, i.e. a shift to higher frequencies with increasing molecular weight by \( \sim 20 \text{ cm}^{-1} \) from glycerol to sorbitol. In contrast, the \( \nu(\text{CCO}) \) band not only shifts by \( \sim 40 \text{ cm}^{-1} \) but also undergoes pronounced changes in shape for each material due to superimposing complex structural oscillations. Density functional theory (DFT) calculations of glycerol reveal distinct spectra for the various conformers in this frequency range. Since a change in molecular weight alters not only the number of conformers but also
and identical in shape in all four polyalcohols (Fig. 1d).

The absorbance of CH stretching vibrations (ν(CH)) at the ν(CO) band (blue dashed line), c) the νas(CH2) band (pink dashed line), and d) the ν(OH) band (orange dashed line). The colored arrows in the molecular model of glycerol in a) exemplify the respective vibrations. The experimental uncertainty is smaller than the line width.

At higher frequencies, the vibrations become more localized and hence less complex, but also less distinct in the homologous series. Thus, the spectral region indicative of CH stretching vibrations (ν(CH) = 2800 – 3000 cm⁻¹) exhibits only minor differences (Fig. 1b). The asymmetric CH2 stretching vibration νas(CH2) at ν ≈ 2880 cm⁻¹ shifts by less than 5 cm⁻¹ from glycerol to sorbitol; its absorbance reduces with increasing molecular weight since CH2 stretching happens only at terminal carbons. Conversely, the absorbance of CH stretching ν(CH) (from non-terminal carbons) at ν ≈ 2950 cm⁻¹ increases; however, since it is superimposed by the symmetric CH2 stretching vibration νsym(CH2) at ν ≈ 2940 cm⁻¹ and the tail of the OH stretching vibration band ν(OH), only νas(CH2) is analyzed quantitatively. At even higher frequencies (ν ≈ 3000 – 3600 cm⁻¹), the broad ν(OH) peak, typical for alcohols [12], at ν ≈ 3350 cm⁻¹ is prominent and identical in shape in all four polyalcohols (Fig. 1d).

From the spectra, peak frequencies of the ν(OH), νas(CH2), and ν(CO) band were determined in a wide temperature range (Fig. 2a). The ν(OH) band exhibits a large red-shift with decreasing temperature (Fig. 2b) amounting to ~ 60 cm⁻¹/100 K above Tg in all substances. Further, the temperature dependence of the peak frequency has a distinct change of slope at Tg (similar to density). In contrast, the red-shift upon temperature reduction observed in the νas(CH2) band is as small as 3 cm⁻¹ in the entire range (150 – 250 K), and shows no distinct feature at Tg (Fig. 2b). The ν(CO) bands exhibit a small (~ 5 cm⁻¹ in the whole range) blue-shift as temperature decreases (Fig. 2b) with a gradually changing slope above Tg (though not as distinct as in ν(OH)).

A shift in IR absorption frequency of a stretching vibration typically reflects a change in bond length [42, 44]. Consequently, the large shift in ν(OH) means that the overall intramolecular thermal expansion is dominated by changes in OH length while variations in CH and CO lengths have only minor impact. Since a red-shift indicates an expansion (weakening of the bond), both OH and CH bond lengths increase upon cooling (Fig. 2h & b). This is caused by the respective intermolecular interactions, i.e. strong (OH···O) and weak (CH···O) H-bridges. A densification with decreasing temperature reduces intermolecular distances and brings the oxy-
gen atoms of surrounding molecules (H-bridge acceptors) closer. Hence, the (intermolecular) H-bridges become stronger while the (intramolecular) covalent bonds are stretched. In contrast, the blue-shift upon cooling in $\nu(CO)$ (Fig.2) implies a contraction of the covalent bonds in the backbone (i.e. normal thermal expansion).

In a simple quantitative approach, the change in bond length is approximated by employing the Morse potential to describe molecular vibrations (Fig.2 inset):

$$V(r) = E_d (1 - \exp[-a(r-r_0)])^2$$

Here, $E_d$ represents the dissociation energy and $a$ the inverse width of the potential. The latter can be related analytically to the difference of the energy eigenvalues in the ground state and the first excited state $\Delta E(\hat{\nu})$:

$$a(E(\hat{\nu}), E_d) = \sqrt{\frac{\mu}{2\hbar^2}} \left( \sqrt{E_d} - \sqrt{E_d - 2\Delta E(\hat{\nu})} \right)$$

Therein, $\mu$ is the reduced mass and $\hbar$ the reduced Planck constant. Using typical dissociation energies (e.g. from dimethylether $E_d(CO) = 225 kJ/mol$ and methane $E_d(CH) = 435 kJ/mol$) and inserting the measured IR absorption frequencies $\hat{\nu}(T)$ via $\Delta E(\hat{\nu}(T)) = 2\pi \hbar \hat{\nu}(T)$ yields $1/a(T)$, an estimate for the change in interatomic (i.e. intramolecular) distance with temperature. In order to approximate the absolute length of a bond $D(T)$ (Fig.2, & c), the respective interatomic distance obtained from DFT calculations of glycerol $D^{gly}$ were used for a calibration $D^{gly} = D(T_{ref})/1/a(T_{ref}) + D_0$ at the reference temperature $T_{ref} = 300 K$ with the correction $D_0$ ($D_{CH}$ = 109.47 pm, and $D_{CO}^{gly}$ = 142.4 pm with $D_{0,CH} = 54.8$ pm, and $D_{0,CO}^{gly} = 96.4$ pm respectively). Extended DFT calculations to reproduce a temperature dependence fail since intermolecular interactions are missing. (The latter are required to model an equilibrated, i.e. energetically minimized bond at different lengths). Therefore, eq. (2) is used to quantify the bond lengths $D_{CH}$ and $D_{CO}$.

For the OH bond as well as the respective OH-O bridge however, there exists a vast record of experimental work on lengths, among them also correlations to IR absorption frequencies. Studies of crystalline H-bonding materials combined X-ray and neutron diffraction with IR spectroscopy to deduce the relation between the intramolecular OH-O distance $D_{OH-O}$ and the peak position $\hat{\nu}(OH)$ (i.e. the respective intramolecular OH vibration) $\nu_{OH}$ ($\hat{\nu}(OH)$) is given by:

$$D_{OH-O}(\hat{\nu}) = 13.21 \log \left( \frac{304 \cdot 10^9}{3592 - \nu \cdot c m} \right) pm$$

Furthermore, these structural investigations established a relation between $D_{OH-O}$ and $D_{OH}$ which is used to obtain also the temperature dependence of the latter.

The thermal expansion of both $D_{OH-O}$ and $D_{OH}$ exhibits a characteristic kink at $T_g$ (Fig.3a & b), like the underlying peak frequency of $\nu(OH)$. Changes in density (indicating $T_g$) originate from inter- and intramolecular expansion; however, their respective contribution is yet unknown. For quantitative evaluation, we use the cubic root of the specific volume obtained from the mass density of glycerol $\rho(T)$ and its molar mass $M$ as reference. The resulting length $D_{mol} = \sqrt[3]{M/\rho N_A}$ (where $N_A$ is Avogadro’s number) resembles the average distance between the centers of adjacent molecules (i.e. a 1-dimensional equivalent to specific volume).

While vibrational spectroscopy provides no direct access to bond lengths (i.e. structural methods are required to establish a correlation), its extremely high resolution is excellent to trace changes in $D_{OH-O}$. Consequently, in the following we focus on these (absolute) changes using the respective value at $T_g$ as reference ($\Delta D(T) = D(T) - D(T_g)$). A comparison of $\Delta D_{mol}$ with $\Delta D_{OH}$, $\Delta D_{CH}$, and $\Delta D_{CO}$ reveals that all these intramolecular lengths exhibit a much weaker thermal expansion (about a factor of 20 for $\Delta D_{OH}$ and more than a factor of 100 for $\Delta D_{CH}$ and $\Delta D_{CO}$), and thus are negligible in the densification of the material (Fig.3b). Consequently, the expansion of intermolecular bridges must dominate densification. However, the change in $\Delta D_{OH-O}$ is by about a factor of 3 smaller than in $\Delta D_{mol}$. Considering the chemical structure of glycerol, the only other intermolecular interactions are of van der Waals type and weak CH-O H-bridges. The red-shift of $\nu_{as}(CH_2)$ with decreasing temperature indicates the latter. It is known that this type of bridge has a length of ~ 350 pm, considerably longer than $D_{OH-O}$ (~ 280 pm). Attempts to establish a relation between $\nu_{as}(CH_2)$ and $\Delta D_{CH-O}$, based on studies of crystalline materials, in order to extract a reliable temperature dependence fail because of too much scattering of the data. Additionally, due to the low polarity of the CH bond, its length is rather insensitive to the presence of H-bridge acceptors (in weak H-bridges longer than 300 pm, the distance between hydrogen and the H-bridge acceptor varies strongly, i.e. several tens of pm, while the change in donor bond length is < 1 pm, for CH-O even < 0.1 pm).

The overall thermal expansion $\Delta D_{mol}(T)$ is an average of all intra- and intermolecular expansivities. Since the former are negligible compared to the latter, we approximate $\Delta D_{mol}(T)$ as composition of intermolecular expansions only:

$$\Delta D_{mol}(T) = \phi_{OH} \Delta D_{OH-O}(T) + \phi_{CH} \Delta D_{CH-O}(T)$$

Here, $\phi_{OH}$ and $\phi_{CH}$ are weighing factors representing the fraction of OH and CH donors per molecule, respectively (e.g. for glycerol $\phi_{OH} = 3/8$ and $\phi_{CH} = 5/8$). Insertion of $\Delta D_{mol}$ obtained from density and $\Delta D_{OH-O}$ calculated from eq. (3) yields an approximation for the ther-
The only deviation is a slightly different chemical structure), of by about a factor of 6 larger than \( \Delta D_{OH-O}(T) \). Despite the lack of direct experimental data it is conceivable: due to their increased length and low polarity the CH· · · O bridges are more susceptible to temperature change than the OH· · · H bridges. Also, studies of semi-crystalline poly(3-hydroxybutyrate) reported thermally induced changes of inter-chain distance in the crystallites, which is governed by CH· · · O contacts (of methyl groups and ketones, i.e. different chemical structure), of \( \sim 0 \text{ pm} \) accompanied by shifts in \( \nu(CH_2) \) of \( \sim 3 \text{ cm}^{-1} \) \( [62] \) (the expansion of \( \Delta D_{CH-O}(T) \) estimated from eq. (4) is \( \sim 3 \text{ pm/cm}^{-1} \)).

In sorbitol, the thermal expansion of the different intra- and intermolecular lengths is almost identical to those in glycerol (Fig. 4). The only deviation is a slightly larger rate of \( \Delta D_{OH-O} \) in sorbitol, probably due to the elevated temperature. This striking similarity indicates that, despite increased molecular weight and number of conformations, density is controlled by the same mechanism. Although we have no extended density data for xylitol and threitol available, the similarity of their IR band evolution suggest an analogous picture. Hence, the view \( [63] \) is corroborated that glassy densification in these polyalcohols follows the same physical mechanisms \( [64–66] \).

Despite the fact that the biggest thermal expansion of these polyalcohols is found in the CH· · · O bridges, \( \bar{\nu}_{CH}(T) \) does not exhibit a characteristic feature at \( T_g \) - in contrast to the pronounced kink at \( T_g \) in \( \bar{\nu}_{OH}(T) \). Consequently, the picture is nurtured that the OH· · · O bridges govern dynamics since these pose the largest energetic barriers to structural relaxation while their impact on overall thermal expansion is small (evidenced by the reduced temperature dependence of density with increasing number of H-bridging groups \( [67] \)). That is because (weak) CH· · · O bridges enable considerable changes in average intermolecular distance and thus density (Fig. 4) while the network topology is stabilized by mildly expanding (strong) OH· · · O bridges.

That may illuminate a yet unresolved observation reported in the frame of the density scaling concept \( [68, 69] \). In this empirical approach, the structural relaxation time is considered to scale with the term \( \rho^\gamma/T \) with the exponent \( \gamma \) \( [68, 70] \). While many van der Waals liquids obey this scaling \( [65, 71] \), particularly associating liquids (and some polymers) defy it \( [65, 68, 71, 72] \). This defiance is caused by the difference in thermal expansion of strong and weak intermolecular bridges; their selective impact on density and structural relaxation loosens the relation between the latter two properties which in turn disrupts the scaling. From the interpretation that \( \gamma \) is connected to the (uni-form) intermolecular potential \( [68, 72] \), one can infer that the reason is the negligence of different (or inhomogeneous) intermolecular interactions. This corroborates previous views, that glycerol in particular and possibly associating liquids in general do not comply with common theories of glassy densification \( [74] \). Reports of separated rotational and translational

![FIG. 3. Absolute expansion of a) intra- and b) intermolecular distances, bond and hydrogen bridge lengths in glycerol, and c) and d) in sorbitol, respectively. \( \Delta D_{mol} \) is calculated from the mass densities \( [66] \) taken from \( [55, 61] \). \( T_g \) is indicated by a dashed vertical line. The arrows in the sketched molecules indicate the respective stretching vibrations of the bonds and lengths of the hydrogen bridges (same color code as the symbols). The uncertainty originating from the experimental error of the IR measurements is smaller than the symbol size.](image3.png)

![FIG. 4. Sketch of glycerol molecules to exemplify the transition from a) higher to b) lower density (dotted boxes visualize the specific volume of the same six molecules) at minimal expansion of strong CH· · · O bridges (orange solid lines). This is realized by expansion of weak CH· · · O H-bridges (magenta dashed lines) and possibly conformational changes.](image4.png)
dynamics in glycerol attributed to the H-bridge network fortify this [24, 27]. Since density scaling also fails in some polymers [27], our results likely reach beyond associating liquids.

In summary, the presented study evidences inhomogeneities of the thermal expansion on both intra- (Fig. 3a & c) and intermolecular (Fig. 3b & d) scale in the course of glassy densification. In turn, two fundamental presumptions which are inherent to most theoretical models of molecular liquids and their glass transition are checked experimentally (for short polyalcohols): firstly, it is confirmed that intramolecular expansion is negligibly small compared to intermolecular expansion. Secondly, the assumption of isotropic intermolecular interactions is an oversimplification in these systems. In contrast to the extreme cases of glass formation where the inhomogeneity of thermal expansion is negligible, i.e. inorganic glasses (like silica) characterized by extremely strong covalent bonds on the one hand and van der Waals glasses dominated by rather uniform weak interactions on the other hand, many molecular glasses contain both strong and weak interactions simultaneously. Particularly, the different impact of strong and weak bridges on structural relaxation and on density loosens the relation between the latter two properties which likely causes the open questions in the description of associating liquids [69]. All this should motivate the consideration of distinct atomistic interactions in order to gain a molecular understanding of the dynamic glass transition in organic matter. To what extent these findings apply beyond associating liquids to complex glass forming systems in general, remains a challenge for future experimental and theoretical work.

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