Glass Transition Dynamics and Boiling Temperatures of Molecular Liquids and Their Isomers

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Glass Transition Dynamics and Boiling Temperatures of Molecular Liquids and Their Isomers

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The relation between a dynamic and a thermodynamic temperature, glass transition T_g and boiling point T_b, is investigated for various glass-forming liquids, with emphasis on monohydroxy alcohols. As is well known, T_b and T_g are positively correlated across a large variety of liquids. However, we found that the same quantities show a negative correlation within an isomeric series, i.e., T_b decreases with increasing T_g for different isomers of the same chemical formula. For the alcohol series, $C_nH_{2n+1}OH$ with $3 \leq n \leq 10$, a master curve of the negative $T_g - T_b$ correlation is obtained if the temperatures are normalized to the respective values of the *n*-alkanols. This $T_g - T_b$ dependence of isomeric liquids is linked to entropic effects and responsible for much of the scatter of the correlation observed for a large number of molecular organic glass-formers with $45 < T_g < 250$ K. Dielectric relaxation is measured for three groups of isomers: (a) 3-methoxyl-1-butanol and 2-*iso*-propoxyethanol, (b) 1,4-, 1,2-, and 2,4-pentanediol, and (c) di-*n*- and di-*iso*-butyl phthalate. Two key parameters of the dynamics, fragility *m* and stretching exponent β, are found to be indistinguishable within isomers of moderately different T_gs. Larger fragility differences are readily expected with pronounced structural change, but no systematic trend is observed within an isomer series. The results provide a useful tool for assessing T_g, *m*, and β for marginal glass formers on the basis of their isomers.

1. Introduction

The glass transition temperature T_g is a characteristic property of supercooled liquids, indicating the kinetic process of solidification, provided that crystallization can be avoided. Because no phase transition occurs at T_g, its value is dependent on the cooling or heating rate or on the time scale used to discriminate the liquid and solid states. In practice, threshold criteria for a kinetic T_g such as a relaxation time constant of $\tau = 100$ s or a viscosity of $\eta = 10^{13}$ P are common,[1–4] and the values obtained in different laboratories are usually consistent.[4,5] Another typical approach to T_g is to determine the calorimetric glass transition, which is taken as the onset temperature of the heat capacity jump with a certain heating rate. For typical rates around 20 K/min, the calorimetric result for T_g agrees with the kinetic counterpart. Regarding the glass transition of monohydroxy alcohols, it needs to be emphasized that the criterion of $\tau = 100$ s should be applied to the smaller higher frequency peak instead of to the dominant Debye type dielectric peak.[6] Only then are the kinetic and calorimetric T_g values of many monohydroxy alcohols in agreement.[7]

In the equilibrium liquid state above T_g, the temperature dependence of viscosity η and relaxation time constants τ usually follows the empirical Vogel–Fulcher–Tammann (VFT) law

$$\log_{10} (\tau/s) = A + B/(T - T_0) \tag{1}$$

where *A*, *B*, and T_0 are material-specific but temperature-invariant parameters. The extent to which $\eta(T)$ or $\tau(T)$ deviates from the Arrhenius case ($T_0 = 0$) is used to characterize supercooled liquids in terms of their fragility.[8] The most common metric for fragility is the steepness index *m* defined by

$$m = \frac{d \log_{10} \langle \tau \rangle}{d(T_g/T)}\bigg|_{T=T_g} \tag{2}$$

equivalent to the slope in an Angell plot, $\log_{10}\langle\tau\rangle$ vs T_g/T, evaluated at $T = T_g$.[9] Strong deviations from simple activation behavior (large *m*) correlate with significantly non-exponential relaxation patterns (small β).[9] Correlation functions in glass-forming systems often follow the Kohlrausch–Williams–Watts (KWW) decay, $\varphi(t) = \exp[-(t/\tau)^\beta]$, where the stretching parameter β gauges the degree of relaxation time dispersion.

The glass transition phenomenon and liquid dynamics in general are complex problems and far from being understood completely.[10–13] Experimental results for T_g have been correlated with molecular structure parameters (such as molecular weight,[14] molecular size,[15] polarity[16]) and other physical properties of bulk liquids such as melting points,[17] boiling points,[18] heat of vaporization,[19] sublimation enthalpy,[20] and fragility.[21] However, all these correlations are only approximate and little detailed information is available. Predictions of T_g values based on calculations involve many parameters, and it is difficult to discern which property is dominant in determining the glass transition of liquids.[22,23] Theories on the glass transition usually do not provide a straightforward expression to predict T_g without experimental input.[24–26] While the value of T_g is governed by kinetics, an intimate link to thermodynamic variables is well established.[27,28]

The aim of this work is to assess a novel correlation between the glass transition temperature T_g and the boiling temperature T_b. Within a series of isomeric liquids, T_g and T_b are negatively correlated, in contrast to the overall trend where T_g increases with T_b. The relation can be used quantitatively to predict the T_g value for a liquid on the basis of its isomers, for instance in cases where the liquid in question tends to crystallize. The systematic variation of the $T_b - T_g$ relation with molecular structure also provides insight into the different roles of energy and entropy. Moreover, fragilities (*m*) and stretching exponents (β) have been determined by dielectric relaxation spectroscopy as a function of structure within different isomer series. Both

m and β display no significant and systematic structure dependence if the chemical formula is kept constant.

2. Experimental

Several groups of isomers of monohydroxy alcohols, such as hexanols, heptanols, and octanols, have been measured. These series possess a number of steric variants, many of which show good glass-forming ability. Unless stated otherwise, samples are purchased from Aldrich. Hexanols: 2-methyl-1-pentanol (99%), 3-methyl-1-pentanol (99%), 4-methyl-1-pentanol (99+%, from TCI America), 2-ethyl-1-butanol (98%), 2-hexanol (99%), 3-methyl-2-pentanol (99%, mixture of isomers), 4-methyl-2-pentanol (98%), 2-methyl-3-pentanol (99+ %); heptanols 5-methyl-2-hexanol (98%); Octanols: 2-ethyl-1-hexanol (99+ %), 4-methyl-3-heptanol (99+ %); others 2-methyl-1-butanol (99+ %) and 3,7-dimethyl-1-octanol (99%). All the T_g values were determined using a Perkin-Elmer DSC-7 with a cooling/heating rate of $-/+$ 20 K/min, as described in our previous work.[5] This method yields reliable and comparable values among isomers. Some data for monohydroxy alcohols are taken from the literature: methanol,[29] ethanol,[29] propanols,[29,30] butanols,[29,31] pentanols,[29,31,32] hexanols,[29,32,33] heptanols,[29,32] octanols,[29,32,34,35,36] nonanols,[32] and decanols.[32]

Additionally, we compiled T_g data of a number of organic small-molecule glass formers. The majority of these T_g data are based on heat capacity measurements, some are from differential thermal analyses, and some from dynamic measurements using a relaxation time of 100 s or a viscosity of 10^{13} Poise. All the entries used here are selected carefully from numerous studies. Throughout this work, the boiling point T_b is based on the standard condition with 1 atm pressure.

For the more detailed dynamics studies, we chose three groups of isomers: (a) di-*n*-butylphthalate (DnBP, 99%) and di-*iso*-butylphthalate (DiBP, 99%), (b) 1,2-pentanediol (12PD, 96%), 1,4-pentanediol (14PD, 99%), and 2,4-pentanediol (24PD, 98%), and (c) 3-methoxy-1-butanol (3M1B, 99%) and 2-*iso*-propoxy-ethanol (2iPE, 99%). All chemicals are obtained from Aldrich and used as received. These isomers are of good glass forming ability and stable in wide temperature ranges down to their glass transition temperatures. None of the above isomers display the prominent Debye dielectric loss peak typical of monohydroxy alcohols, which implies that their main dielectric processes reflect the structural relaxations that are associated with the calorimetric glass transitions and viscous flow. The dielectric measurements are performed with frequency domain impedance methods ($10^{-2} \leq \nu \leq 10^6$ Hz) using a Solartron 1260 gain-phase analyzer equipped with a Mestec DM-1360 transimpedance amplifier. The temperature control is based on a Novocontrol Quatro liquid nitrogen cooling system.

3. Results

The overall trend of T_b vs T_g is shown in Figure 1, which includes liquids of various chemical classes as indicated in the legend. This positive correlation is well established and can be explained qualitatively by the notion that higher cohesive forces increase both T_b and T_g. The situation changes when we compare T_b and T_g data within series of isomers. Again, a clear systematic dependence appears, but now the two quantities are correlated with a negative slope. In Figure 2, we present much of the available T_b–T_g data of glass forming isomers of various liquids, which involve alkanes, alcohols, aliphatic halides, and aromatics. The rich data in the family of monohydroxy alcohols is shown separately in Figure 2a. The correlation is evident that, for most isomeric liquid series, T_b decreases with increasing T_g within
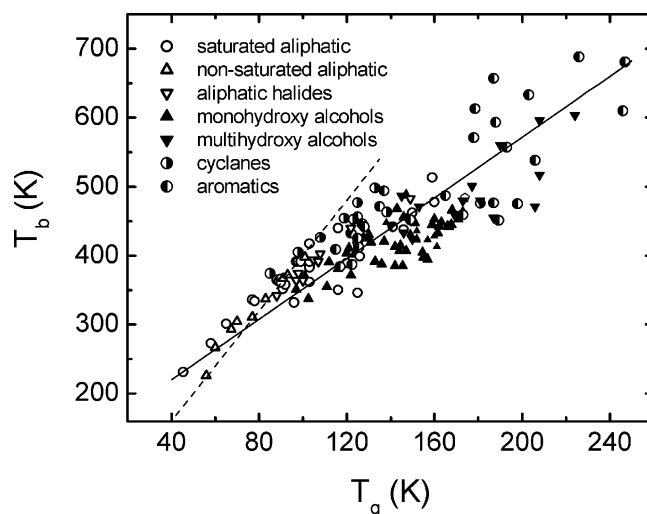

Figure 1. Correlation of T_g and T_b of various small molecule organic glass-forming liquids. Different symbols are for different chemical classes as identified in the legend. As a general trend, T_b increases systematically with T_g. The solid line represents the linear relation $T_b = 132 + 2.2T_g$, while the dashed line indicates the proportionality $T_b = 4T_g$.
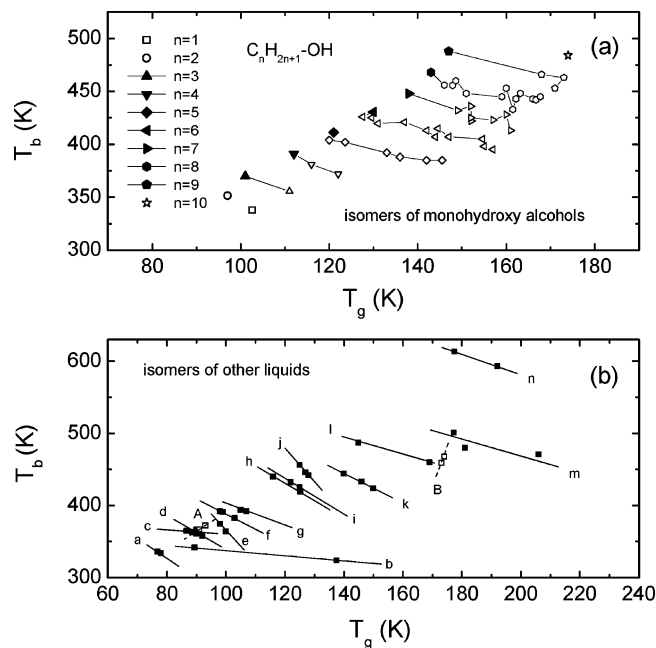

Figure 2. Correlation of T_g and T_b within isomer series of monohydroxy alcohols (a) and other liquids (b), both suggesting an inverse trend of T_b with T_g. In panel a, the *n*-alkanol of an isomer series is identified by a solid symbol. The labels in panel b are as follows. a, hexanes; b, chloroheptanes; c, heptanes; d, butanethiols; e, butylbromides; f, octanes; g, pentylbromides; h, decanes; i, propylbenzenes; j, butylbenzenes; k, butoxyethanols; l, propanediols; m, pentanediols; n, dibutyl phthalates. Practically all data show a reduction of T_b with increasing T_g among isomers, with only the following two exceptions. A: 1(2)-heptene, and B: *o*(m)-fluoroaniline (open symbols and dashed lines).

the isomers, which is especially obvious in Figure 2a for the monohydroxy alcohols.

The comparison of molecular structure of isomers of monohydroxy alcohols shows that the chainlike normal alkanols have the highest T_b and the lowest T_g, and the same holds for alkanes. From primary, secondary, to tertiary alcohols, T_b decreases in that order. It also appears that the steric hindrance plays a significant role in determining T_b. Thus far, only two exceptions

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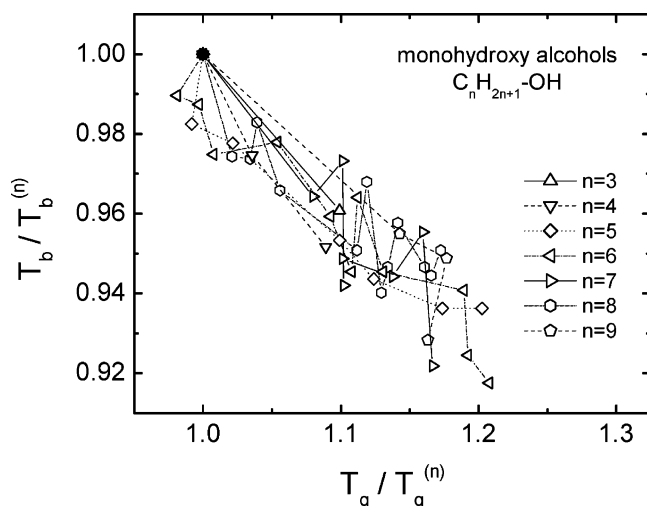
Figure 3. T_b vs T_g data of Figure 2a but with both temperatures normalized to the values of the respective *n*-alkanols, which show the highest T_b and lowest T_g within isomeric monohydroxy alcohols. All the isomers are seen to follow a master curve, $T_b/T_b^{(n)} \approx 1 - 0.38 T_g/T_g^{(n)}$, where the superscript *n* indicates the *n*-alkanol case.
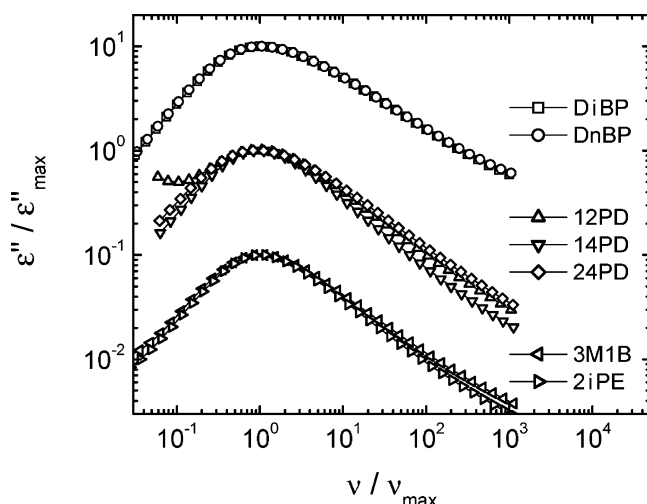
Figure 4. Comparison of the peak normalized dielectric loss profiles of three pairs of glass-forming isomers to reveal whether the broadening changes systematically with molecular structure. Each dielectric spectrum is chosen at a temperatures at which the peak frequency ν_{max} is around 1 Hz. The three series are: (a) di-*n*-butylphthalate (DnBP, 185 K) and di-*iso*-butylphthalate (DiBP, 199 K), shifted up one decade; (b) 1,4-pentanediol (14PD, 185 K), 1,2-pentanediol (12PD, 190 K), and 2,4-pentanediol (24PD, 213 K); (c) 3-methoxyl-1-butanol (3M1B, 154 K) and 2-*iso*-propoxyethanol (2iPE, 148 K), shifted down one decade.

from the general correlation in Figure 2 have been found, 1(2)-heptenes[4] and *m*,*o*-fluoroaniline,[18] with both cases bearing only little significance.

Figure 3 exhibits the data of the alcohol isomers of Figure 2a but with the T_b and T_g scales normalized to the respective values of each *n*-alcohol. Along each curve, the relative change in T_b is smaller than that in T_g. A more surprising feature is that all the alcohol isomers follow a master curve, which indicates an approximately linear dependence. This suggests that materials within the same class of intermolecular interaction are subject to the same isomeric effect if scaled properly.

In Figure 4, we show the profiles of the dielectric spectra of the three pairs of isomers. Most of these liquids have been the subject of experimental work on dynamics, e.g., di-*n*-

butylphthalate,[37-39] but not in view of the present interest of comparing isomers. In order to have comparable situations, all curves are chosen to have peak positions ν_{max} around 1 Hz. These typical cases demonstrate that the primary or α-relaxation functions are not very different, although the T_g values differ by as much as 29 K within the pentanediol series. In consideration of the two decades of frequency around the loss peak, no systematic change of the profile with molecular structure is observed.

In order to obtain time constants and dispersion parameters for the isomer series, dielectric relaxation spectra are analyzed using the Havriliak–Negami (HN) expression plus a direct current (dc) conductivity (σ_{dc}) term

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^\alpha)^\gamma} + \frac{\sigma_{dc}}{\epsilon_0 i\omega} \qquad (3)$$

where ϵ_∞ is the dielectric constant in the high-frequency limit and $\Delta\epsilon$ the relaxation strength. The exponents α and γ quantify the broadening and asymmetry of the relaxation time dispersion. The translation from the HN parameters α and γ to the time domain KWW exponent β is done using the simple approximation $\beta \approx (\alpha\gamma)^{0.81}$.[40]

The temperature dependence of the characteristic relaxation times, $\tau(T)$, is fit by the VFT law of eq 1 to facilitate a short extrapolation to determine T_g using the glass transition criterion $\tau_g = 100$ s. Fragility indices *m* are determined from the $\tau(T)$ data on the basis of eq 2. All present dynamic parameters are summarized in Table 1, together with some results compiled from the literature. Fragilities for 2-methylpentane and 3-methylpentane are from refs 41 and 42 (viscosity), *n*-, and *iso*-butyl bromide from ref 43 (dielectric), 3-bromopentane and *iso*-amylbromide from refs 44–46 (dielectric), *m*- and *o*-xylene from ref 47, *n*- and *iso*-propylbenzene from refs 48 (dielectric) and 42 (viscosity), and *n*-eugenol and *iso*-eugenol from ref 49 (dielectric). The table includes two isomeric monohydroxy alcohols, 2-ethyl-1-hexanol and 4-methyl-3-heptanol. The fragility of the former is based on the calorimetric fictive temperature method,[5] while the fragility of the latter is from dielectric measurements where the true α-relaxation is dominant.

4. Discussion

The overall relationship between T_g and T_b for various organic small-molecule glass-forming liquids is examined in Figure 1, with the lowest but reliable T_g value being 45.5 K for propane.[50] The trend that T_g increases with T_b is approximately a linear correlation within this 45 to 250 K temperature range

$$T_b = 132 + 2.2 T_g \ (T_g > 45 \text{ K}) \qquad (4)$$

The above relation is shown as solid line in Figure 1, with the deviations from this linear behavior being significant. This correlation is different from previous reports where a proportionality $T_b = \alpha T_g$ was considered, with factors α between 4 and 3.[17,19] The constant ratio of T_b/T_g could have been justified with the approximation $\Delta H_{vap}/k T_g \approx 44$[19] ($\Delta H_{vap}$ is heat of evaporation) combined with Trouton's rule of $\Delta S_{vap} \approx 88$ J mol^{-1} K^{-1}. However, proportionality holds only in a narrow range of low T_b and T_g, while eq 4 links the two temperatures in a wider range. The dependence of T_b and T_g on molecular weight has been studied previously.[51] Our data shows that for most of these liquids, the dependence of the two temperatures on molecular weight displays larger deviations than that among

TABLE 1: Characteristic Parameters of Various Glass-Forming Isomer Series: Glass Transition Temperature T_g, Fragility m, HN Shape Parameters α and γ, and KWW Stretching Exponent β at $T = T_g$

	isomers	T_g (K)	m	α	γ	β	ref
1	2-methylpentane	78[a]	58				41,42
	3-methylpentane	77[a]	56	0.92	0.42	0.462	
2	*n*-butyl bromide	96.5	50				40
	iso-butyl bromide	99.1	55				
3	3-bromopentane	108	53	1	0.57	0.633	44,45,46
	iso-amyl bromide	109	55	0.96[c]	0.54	0.586	
4	*m*-xylene	120[b]	56				47
	o-xylene	123[b]	55				
5	propylbenzene	122	69			0.48[d]	42,48
	iso-propylbenzene	125	70			0.5[d]	
6	3-methoxy-1-butanol	145.3	62	1	0.64	0.696	this work
	2-*iso*-propoxyethanol	141	67	0.98	0.6	0.649	
7	2-ethyl-1-hexanol	146	72	0.75	0.55	0.487	this work
	4-methyl-3-heptanol	162.2	57	0.71	0.65	0.533	
8	di-*n*-butylphthalate	177.4	82	0.96	0.518	0.567	this work
	di-*iso*-butylphthalate	191.1	78	0.965	0.521	0.572	
9	1,4-pentanediol	175.8	53	1	0.636	0.692	this work
	1,2-pentanediol	181	58	0.95	0.6	0.633	
	2,4-pentanediol	205	68	0.95	0.59	0.625	
10	1,5-hexanediol	179.4	60	0.975	0.665	0.703	this work
	2,5-hexanediol	203.5	61	0.98	0.67	0.71	
11	*n*-eugenol	192.7	90			0.68	49
	iso-eugenol	220.1	73			0.62	

[a] T_g values are based on the calorimetric measurements from ref 88 [b] T_g values are based on calorimetric measurements from ref 18. [c] This is an approximate average value near T_g from ref 45. [d] β are from the viscoelastic compliance of ref 89.

the two temperatures themselves, indicating a closer correlation of T_b and T_g.

When comparing the various categories of liquids in Figure 1, no clear segregation of the various behaviors is apparent. The cyclic compounds tend to exhibit higher T_b/T_g ratios than liquids with chainlike structures, and aromatic glass formers have high T_g values because of their generally higher molecular weight. In total, too many parameters are changed simultaneously in this compilation and no strong correlation with chemical class is seen. We note that all liquids of this study are small molecule liquids with molecular weight <200 for non-aromatic and <400 for aromatic compounds. A different behavior is found for polymers, where T_g (associated with the segmental dynamics) saturates at molecular weights around 2000 g/mol.[52]

It is observed in Figure 1 that the degree of scattering, ΔT_g, of the data around eq 4 increases with T_b or T_g, while the increase in relative deviation $\Delta T_g/T_g$ is moderate. In order to elucidate the cause of the large scattering in the higher temperature region, we divide all the liquids into 7 groups: saturated aliphatic, nonsaturated aliphatic, aliphatic halides, monohydroxy alcohols, multihydroxy alcohols, cyclanes, and aromatics. Within each of the various categories the extent of the scattering is somewhat reduced relative to the entire data set. The isomer effect within one category is particularly clear for the monohydroxy alcohols, shown separately in Figure 2a. Here, T_b and T_g for the *n*-alkanols (top left solid symbol for each *n*) are highly correlated, while the complete data set displays considerable scatter. We conclude that the isomer effect is responsible for much of the scatter of how T_b and T_g are related.

The decrease of T_g with increasing T_b for glass-forming isomers is a surprising result not reported previously. The glass

transition at T_g is not the immediate signature of a thermodynamic transition as is T_b and commonly considered a kinetic transition. Therefore, it might seem unexpected that T_b and T_g exhibit such a good correlation for isomers. Particularly noteworthy is the observation presented in Figure 3, that the negative $T_g - T_b$ correlation is not only a general feature within many isomer series but quantitatively similar if scaled properly for numerous monohydroxy alcohols.

Boiling occurs when the vapor pressure of the liquid reaches the pressure of the surrounding atmosphere, usually ambient conditions of 1 atm. T_b is thus related to the cohesive energy in liquids, which is the energy involved in vaporization.[53,54] In this respect, T_b is an indicator of the strength of intermolecular interactions, which in turn depend upon features of the molecular structure (such as geometric shape, volume, surface area) and electrostatic interactions (intramolecular charge distribution).[55] Numerous experimental data show that the compactness of molecules within an alkane isomer series decreases the boiling point.[56] This was often explained in two ways: electrons in an elongated molecule are much more easily polarized than are those in a more compact isomer,[57] and more compact molecules have less surface area and accordingly weaker interactions.

Without doubt, the intermolecular interaction energy (barrier) is also an important factor in determining the molecular dynamics in both the fluid and viscous regime of a liquid. The large difference in intermolecular interaction energy for various glass formers appears to be responsible for the roughly linear increase of T_g with T_b in Figure 1. Alternatively, studies have highlighted the configurational entropy as an important variable in determining the dynamics of structural relaxation and the glass transition.[13,24,58,59,60] This means that T_g would be governed by the interplay of energy and entropy of liquids. In what follows, we argue that intermolecular interaction energy causes

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the systematic increase of T_g with T_b, while the role of entropy dominates the negative $T_g - T_b$ correlation within an isomeric series via geometrical considerations.

More branched alkane isomers have been demonstrated to have reduced entropies, while the normal alkanes have the largest entropy values at room temperature.[61,62] Moreover, the normal alkanes have the largest entropy of fusion. Likewise, the entropy at 298 K and the entropy of fusion of primary alcohols are also higher than those of their secondary or tertiary counterparts. Additionally, the lower heat capacity of primary alcohols at room temperature might imply that the high entropy at high temperature (room temperature) will be preserved also at low temperatures. Studies of thermal expansion coefficients, α, have shown that the rigid isomers have higher α values than flexible ones,[63] i.e., more compact molecules lead to more dense structures and lower configurational entropy at T_g. Although the slightly stronger H-bonds in primary alcohols might produce a stronger association of molecules, and thus lower entropy,[64] it appears that the difference in the H-bond strength cannot compensate the entropy increase of the linear chain structure. A recent study of H-bonds in solutions also revealed that 1-propanol displays this larger entropy penalty for H-bond formation relative to 2-propanol, which leads to the former being enthalpically favored but entropically disfavored.[65] We conclude that the structural changes among isomers have a smaller influence on intermolecular interaction compared with the concomitant entropic effects. Although we also found that the linear *n*-alkenes do not necessarily have higher liquid entropy than those of their isomers (perhaps leading to the exceptional behavior in Figure 2b), other high entropy liquids always have lower T_g values.

The thermodynamic weight of the entropy term depends on absolute temperature. As a result, the entropy effect will be expected to lead to small T_g difference within isomers in the lower temperature regime, in accord with the smaller scattering in the total $T_g - T_b$ correlation of Figure 1 for the lower T_g values. Thus, it can be concluded that the intermolecular interaction energy determines the overall linear dependence, while entropy effects result in the scattering which is more pronounced in the regime of higher T_g values.

While the correlation of T_b and T_g of all the monohydroxy alcohol isomers follow the decreasing trends shown in Figure 2a, the steric hindrance effect on T_b and T_g is more complex than in the case of alkanes. For example, 2-methyl-1-pentanol has a lower T_b (422.15 K) than 3-methyl-1-pentanol (426.15 K) because of its increased steric hindrance of the hydroxyl group by the methyl group, but 4-methyl-1-pentanol (425.05 K) does not have a higher T_b than 3-methyl-1-pentanol. The same situation is also found for 3-methyl-2-pentanol (407.45 K) and 4-methyl-2-pentanol (404.75 K).

The Kauzmann temperature T_K $(<T_g)$ is defined as the extrapolated temperature at which the configurational entropy of the liquid vanishes.[17] Its value is below but usually not far away from T_g and thermodynamically better defined than is the kinetic glass transition. Therefore, a similar correlation between T_K and T_b is expected, but more T_K data than currently available is required to confirm this. The existing data for 2-methylpentane vs 3-methylpentane[41,66] and 2-butoxyethanol vs 2-tert-butoxyethanol[67] do support the anticipated similarity.

Glass-forming liquids exhibit five characteristic temperatures across their liquid region: the boiling point T_b, the melting point T_m, the crossover temperature T_x, the glass transition at T_g, and the Kauzmann temperature T_K. T_x is the crossover or bifurcation temperature, where structural relaxation times approach values around 10^{-7} s,[68,69] where the decoupling of translational from rotational degrees of freedom sets in,[70,71] and near the merging of the extrapolated Johari–Goldstein β-relaxation time into the α-relaxation time.[34,72] T_x is generally located near the critical temperature T_c of the (idealized) mode coupling theory,[73] and the Stickel temperature T_B,[74] i.e., $T_x \approx T_c \approx T_B$. Many studies suggest that the characteristic temperatures involved in the liquid-to-glass transition are interrelated.[75] For organic small molecule liquids, it has been suggested that T_K/T_g is around 0.70–0.86,[76] that $T_c/T_K \approx 1.6$,[10,77] or $T_c/T_g \approx 1.2$,[69,78] and $T_g/T_m \approx {}^{2}/_{3}$.[17,27,79,80] Since typical deviations from these ratios are not severe, similar correlations as shown here are to be expected between T_b and the other characteristic temperatures of these liquids. It should be mentioned that the ratio of T_b/T_g indicates how rapidly a given liquid is excited through its liquid range,[15] and thus, it is fragility dependent.[18] Accordingly, the ratios of T_g/T_K, T_c/T_g and even T_m/T_K have been demonstrated to change systematically with fragility.[21,81–83]

We now turn from inspecting the characteristic temperatures of liquids to the two main properties of supercooled liquid dynamics related to fragility: steepness index m and stretching exponent β. As can be observed in Table 1, the well-documented[9] correlation between m and β holds also within and among series of structurally different compounds with identical chemical formula (with the exception of eugenol). For a fixed chemical formula, however, pronounced changes in m or β are rare, although T_g can change by a few tens of degrees. Examples of how well preserved the relaxation time dispersion is within a series of isomers are shown in Figure 4, at constant τ_α,[84] where differences of the molecular structure amount only to small changes in the loss profile far away from the main loss peak. Although a correlation between relaxation time dispersion (or KWW exponent β) and structural features of the molecules may be expected,[85] no indications for such behavior is found for the present materials.

The signature of significant structural changes within the isomeric series investigated here is the glass-transition shift of up to 29 K. Such a ΔT_g is equivalent to a change of the relaxation time or viscosity by many orders of magnitude if compared at the same absolute temperature. The resulting changes in terms of fragility m are compiled graphically in Figure 5 as Δm vs ΔT_g. Larger deviations are observed only for more pronounced structural changes and concomitant ΔT_g, but a systematic trend remains absent. For example, the nonaromatic H-bond isomeric groups, 3M1B vs 2iPE and 2E1H vs 4M3H, show a negative correlation between T_g and m, while a positive one is seen for the diols (nos. 9 and 10 in Table 1). One more feature to be highlighted in Figure 5 is that for moderate values of ΔT_g the fragility changes are within $|\Delta m| \leq 5$ (dashed lines), i.e., hardly exceeding the level of uncertainty.

Therefore, the fragility correlates less strongly with the molecular geometry if compared with the characteristic temperatures T_g and T_b. This implies that, within an isomeric series, the stronger intermolecular interaction of a primary (more linear) molecular structure does not necessarily develop a stronger liquid character (lower m). The present results support previous explanations of the strong–fragile pattern in terms of the type of intermolecular interaction,[86,87] which remains unchanged within a series of isomers. Our recent study determined a quantitative correlation between fragility and thermodynamic variables in organic molecular glass-forming liquids, $m = 56\Delta C_p T_g/\Delta H_m$, where ΔC_p is the glass-to-liquid heat capacity jump and ΔH_m is the heat of fusion.[27] This correlation does emphasize that the kinetic fragility is determined by a combination of
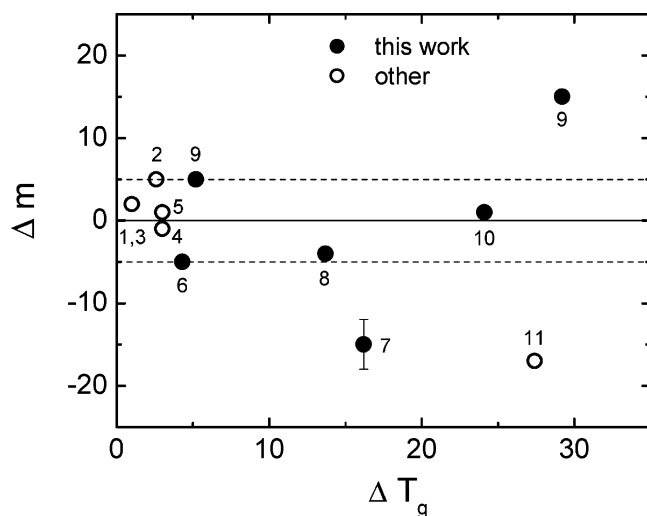
Figure 5. Deviations of fragility, Δm, within isomeric glass-forming liquids vs the difference of the corresponding glass transition temperature, ΔT_g. For each isomer series, the reference values for m and T_g are for the lowest T_g compound. Numbers identify the systems according to Table 1. Small T_g differences appear not to affect the fragility in a systematic way.

thermodynamic variables that will not easily map onto a single quantity such as molecular structure or interaction strength.

5. Conclusions

As an overall trend, glass transition temperatures T_g and boiling temperatures T_b of glass-forming molecular liquids both increase with increasing strength of the intermolecular interactions. As a result, T_b and T_g data are positively correlated, but also subject to considerable scatter. Isomers of the same chemical formula, however, display highly systematic T_b-T_g relations and, unlike the overall trend, with T_b decreasing as T_g increases. This isomer effect accounts for much of the scatter of the overall T_b-T_g dependence. The unexpected correlation within isomer series is explained with the entropy effects dominating over the differences in intermolecular interaction. The observed correlations can be used to assess the glass transition temperature of marginal glass formers on the basis of isomers with better glass-forming ability. The work supports the view that the characteristic temperatures of glass-forming liquids are systematically related among each other.

The dependence of fragility on the value of T_g within an isomer series is also investigated. It is found that no systematic trend of fragility is observed with the deviation of T_g within various isomeric organic molecular liquids. A further result concerning the dynamics is that even a significant change of T_g of almost 30 K produces very little influence on the steepness index m or KWW stretching exponent β, provided that the chemical formula remains the same. Therefore, a link between molecular structure and fragility is not obvious. The observed correlations can be used to assess the glass transition temperature and dynamics of marginal glass formers on the basis of isomers with better glass-forming ability.

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