Glass transition and fragility in the simple molecular glassformer CS$_2$ from CS$_2$-S$_2$Cl$_2$ solution studies.

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Abstract.

With an interest in finding the fragility for a simple, single component, molecular glassformer, we have determined the dielectric relaxation and glass transition behavior for a series of glasses in the CS$_2$-S$_2$Cl$_2$ and CS$_2$-toluene systems. Crystallization of CS$_2$ can be completely avoided down to the composition 20 mol% second component, and the fragility proves almost independent of CS$_2$ content in each system. Since the glass temperature $T_g$ obtained from both thermal studies and from dielectric relaxation (using $T_{g,dielec}$=$T_\tau$=$100s$) is quite linear over the whole composition range in each system, and since relaxation time data for pure CS$_2$ fall on the same master plot when scaled by the linearly extrapolated $T_g$ value, we deduce that pure CS$_2$ has the same high fragility as the binary solutions. The value is $m=86$, as for ortho-terphenyl OTP. Based on observations of independent studies for the vibrational density of states VDoS (of inherent structures for OTP and instantaneous, at-temperature structures for CS$_2$), we attribute the high fragility to an excess vibrational heat capacity originating in the behavior of the low frequency modes of the VDoS (the boson peak modes). Both low frequency DoS and anharmonicity increase with increasing temperature, augmenting the configurational entropy drive to the top of the system energy landscape. The surprising implication is that fragility is determined in the vibrational, not configurational, manifold of microstates.

Introduction.

The quest for understanding of the anomalies of supercooled liquids and of the experimental glass transition, remains incomplete. One of the stumbling blocks has been the molecular complexity that has so far been a characteristic of molecular glassformers.

Application of the Turnbull-Cohen predictor of glassforming ability (the boiling point to melting point ratio >2.0) suggests that carbon disulfide, a short rod-like molecule illustrated below, should be a marginal glassformer ($T_b=319.3K$, $T_m=161.2K$, $T_b/T_m=1.97$). Indeed, the glass transition temperature $T_g$ for this simply constituted liquid has been determined using microemulsion samples, and short extrapolations of binary molecular solution data. Some aberrant behavior in vapor-deposited CS$_2$ glass will be considered in the concluding remarks section. CS$_2$ liquid has been the subject of many studies of a fundamental nature, but its behavior near the glass transition has so far not been amongst them except in computer simulation studies. Below we give reasons for taking a special interest in its liquid fragility. A simple method for estimating fragility from the “width” of the glass transition endotherm, has suggested that CS$_2$ solutions in sulfur monochloride, S$_2$Cl$_2$, (a 4-atom molecule that is easily glassforming itself) are quite fragile, but the $T_g$ width metric is controversial. It is certainly unreliable for solutions when they are non-ideal with positive deviations from ideality. The present
work seeks to provide unambiguous fragility measurements to shed light on the following observations.

Molecular dynamics simulations have shown that 3-atom molecules can have substantial contributions to their thermodynamic properties arising from an excess vibrational entropy that is not present in simple atomic mixtures like the Kob-Andersen binary Lennard-Jones (KABLJ) system that has been the object of so many studies. Unlike KABLJ\textsuperscript{15}, the vibrational density of states (VDoS) of the Wahnström-Lewis (W-L) model of \textit{ortho}-terphenyl\textsuperscript{16}, a 3-bead model, has been found\textsuperscript{17} to have a strong dependence on the level of the energy landscape at which the liquid structure becomes fixed (either by conjugate gradient cooling from an equilibrated state\textsuperscript{17} or by continuous cooling\textsuperscript{15}) i.e. the \textit{shape} of the typical "basin of attraction" occupied by the system depends strongly on the temperature at which the system is equilibrated.

The first results for this model were presented for constant volume studies. Mossa \textit{et al}\textsuperscript{17} reported that under these conditions the effect of heating OTP is to decrease the vibrational entropy below the value it would have for a glass heated over the same temperature interval without structure change. This is because changing the structure by heating at constant volume changes the VDoS to favor high frequency modes. An isosbestic point was reported\textsuperscript{17}. A subsequent examination of the same data set, but now chosen to examine behavior at constant pressure\textsuperscript{18} as in the normal experimental protocol, showed that the VDoS of the inherent structures for different temperatures change shape in the \textit{opposite} direction from that observed at constant volume, i.e., so as to favor lower frequency modes as the temperature rises. Again an isosbestic point was observed\textsuperscript{18}. The inevitable result is\textsuperscript{19} that, at constant pressure, the vibrational entropy of the liquid rises more rapidly with increasing temperature than does that of any given glassy state or crystalline state (in each of which the structure - hence also the VDoS - is fixed). Related effects had been seen in the earlier studies of Moore and Keyes\textsuperscript{12} on CS\textsubscript{2} but were obscured by the presence of the imaginary modes present when instantaneous rather than inherent structures are studied.

The above are highly significant findings in view of an observation made by Goldstein in 1976\textsuperscript{20} concerning the implications of a model of ZnCl\textsubscript{2} glassformer thermodynamics. Goldstein pointed out that increases in low frequency vibrational mode populations with increasing temperature, like those seen in the W-L model at constant pressure, would cause an increase in the rate of vibrational entropy production which would then drive the liquid to the top of its energy landscape more rapidly than if only the excitation of the configurational degrees of freedom were involved. Obviously, increased anharmonicity in the lower frequency modes will enhance such effects, and the relative importance of the two (VDoS vs anharmonicity) must be decided by experiment. Goldstein provided criteria for making the distinction\textsuperscript{20}, and there is a current discussion by Wyart\textsuperscript{21}. Rapidity of ascent of the energy landscape is another description for liquid fragility, the origin of which has been a continuing and unresolved problem in viscous liquid phenomenology. An excess vibrational heat capacity, with or without increased anharmonicity, thus can be a source of fragility in liquids. Indeed, it was a finding of a recent study of direct configurational excitation of glassformers near their T\textsubscript{g} by one of the present authors\textsuperscript{22}, that polar molecular liquids have an excess heat capacity that exceeds their configurational heat capacity – and, further, that the percentage excess indeed increases with increasing fragility.
The Wahnström-Lewis model of OTP molecule is a gross simplification of the real molecule which has three disc-like phenyl rings linked together non-rigidly. In W-L, OTP is approximated by a rigid, bent 3-bead form that is more like ozone than any other molecule. Interestingly enough, ozone \( (T_m = 80.5\,\text{K}) \) also is indicated as a 3-atom molecular glassformer by its \( T_g/T_m \) value of 2.02, and indeed its ability to supercool has been noted\(^23\). However, ozone is very unstable and is an explosion threat to sensitive apparatus. Since it is obviously important, from the above discussion of the W-L model, for us to know more about the laboratory behavior of W-L-like systems, we have carried out a study of the less hazardous 3-atom molecule \( \text{CS}_2 \). In the crystal, \( \text{CS}_2 \), which is not bent, packs in a herring-bone structure. Evidently the lattice energy is not very competitive with the liquid structure cohesive energy, because the melting point is low relative to the boiling point - as noted earlier. We have shown elsewhere that this is a characteristic property of rod-like molecules of dimensions similar to, and shorter than, those of \( \text{CS}_2 \)\(^24\), and a comparable packing problem has been demonstrated for hard ellipsoids\(^25\).

Dielectric relaxation measurements can be made with high precision on small samples that can be rapidly quenched in situ to minimize the chance of crystallization. While the quench is not rapid enough to permit the vitrification of pure \( \text{CS}_2 \), it has proved possible to quench a series of solutions containing up to 80 mol % of \( \text{CS}_2 \) in the binary systems \( \text{CS}_2-\text{S}_2\text{Cl}_2 \) and \( \text{CS}_2\)-toluene and then to determine the dielectric relaxation times during warming above \( T_g \) over several decades before crystallization occurs. The presence of a second component with a dipole moment is necessary to provide some polar character, since \( \text{CS}_2 \) itself is non-polar. \( \text{S}_2\text{Cl}_2 \) has just four heavy atoms in a compact non-symmetrical arrangement, which leaves a dipole moment that is adequate for precise equipment.

Previous work on these two binary systems\(^3\) has shown that they are simple eutectic in their phase relations, most compositions being readily glassforming. The \( T_g \) vs. composition relation is linear. In the present work we will report their dielectric relaxation behavior, and give evidence that all compositions with large \( \text{CS}_2 \) contents are highly fragile in character. Such data as exist for pure \( \text{CS}_2 \) at higher temperatures will be shown consistent with this assignment.

**Experimental section**

Carbon disulfide 99.9% from Alfa Aesar and \( \text{S}_2\text{Cl}_2 \) 98% from Aldrich were used without further purification. Toluene 99.5% from Aldrich was further purified by reflux condensation.

The dielectric measurement cell consists of a pair of stainless steel disks, designed for fast cooling at rates of order 10 K/s as determined elsewhere\(^26\). Solutions were located between the electrodes with 20 mm diameter and a separation determined by six spacer strips of 25 \( \mu \text{m} \) thickness Teflon. The resulting geometric capacity is \( C_0 = 111.3 \, \text{pF} \). Together with a support frame, the filled dielectric cell was immersed in liquid nitrogen to provide rapid cooling. The cell was then transferred to a precooled nitrogen-gas filled cryostat, the temperature of which was controlled and measured by a Novocontrol Quatro controller. The stability of the temperature reading is better than 0.05 K. Frequency-dependent impedance measurements were performed at fixed temperatures in a frequency range from \( 3\times 10^{-2} \, \text{Hz} \) to 1 MHz (scanned from high to low frequency) using a Solartron
SI-1260 gain-phase analyzer equipped with a Mestec DM-1360 transimpedance amplifier. This measuring method requires a reference measurement with the empty capacitor to calibrate the frequency-dependent transimpedance $Z(\omega)$. Relaxation times were determined from the peak frequencies $\nu_{\text{max}}$ of the dielectric loss, $\tau = (2\pi\nu_{\text{max}})^{-1}$.

**Results**

Real and imaginary parts of the complex dielectric constant $\varepsilon^\ast = \varepsilon' - i\varepsilon''$ for a solution containing 80 mol % CS$_2$ in the system CS$_2$-S$_2$Cl$_2$ are shown in Figure 1. The highly fragile behavior of the solution is indicated by the two orders of magnitude shift in peak frequency with each of the small (3K) temperature increments. Crystallization limited the measurements to temperatures at and below 109K. The comparable behavior of the CS$_2$ + toluene system at the same molar composition, 80 % CS$_2$, is seen in Figure 2. In this case the solution was more stable against crystallization and the data were limited by the frequency range of the equipment rather than by loss of the solution to crystallization.

Data of comparable quality were obtained for other solutions with lower CS$_2$ contents, in each system, the limiting factor in all cases being the frequency range of the equipment.

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Figure 1. Real and imaginary part of the dielectric susceptibility for four temperatures above $T_g$.

Figure 2. Real and imaginary parts of the dielectric constant for a CS$_2$ + toluene solution with 80 mol% CS$_2$.

Figure 3. Arrhenius plots of the relaxation times for several solutions in the two binary systems of this study.
For each solution, the most probable relaxation times at each temperature, obtained from the peak frequencies by the relation \( \tau_{\text{max}} = \left( \frac{2\pi \nu_{\text{max}}}{\lambda} \right)^{-1} \), are plotted in Fig. 3 in Arrhenius form. The solid lines passing through the points are in each case obtained by fitting to the Vogel-Fulcher-Tammann (VFT) equation after fixing the pre-exponent at a physical \( 10^{-14} \) s. The temperatures where the relaxation times reach 100s in each case are marked by the horizontal line and used to define the values of \( T_g \) for comparison with data obtained from earlier thermal studies.

**Discussion.**

To begin the discussion of these results we plot the temperatures at which the dielectric relaxation time reaches 100s (called \( T_{g,\text{diel}} \)) for each solution against the molar percent of the second component in Figure 4 and compare them with the calorimetrically determined\(^3\) onset heating glass temperatures \( T_g \) measured at 20 Kmin\(^{-1}\) (called \( T_{g,\text{cal}} \)). These two quantities correlate well, as has been demonstrated on numerous occasions\(^{27,28}\), most recently and definitively in ref. 29. We then use these \( T_g \) values as the basis for a scaled Arrhenius plot of the kind commonly used for comparing the temperature dependences of transport for different glassformers.

The impressive result is shown in Figure 5. To a good approximation, all CS\(_2\)-containing solutions studied have the same fragility (based on slope of the plot at \( T_g \)). It is not easy to distinguish the data from those for the fragile toluene\(^3\) \( m = 105 \), though at low temperature they appear closer to the less fragile ortho-terphenyl. By direct VFT best fitting we obtain \( m = 86 \). Some distinction is apparent in the temperature range near mid-relaxation time, \( \log(t/s) = -6 \). We needed to make an adjustment to the relaxation times reported by Rössler and Sillescu\(^3\) to have them reflect the same “most probable” values as we report for the CS\(_2\) solutions (the values in ref. 31 are from Cole-Davidson fits). The \( F_{1/2} \) fragility\(^{27}\), which is assessed at the relaxation time of \( 10^{-6} \) s, for CS\(_2\) solutions seems to be the same as for toluene.

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**Figure 4.** Comparison of \( T_{(\tau = 100s)} \) for binary solutions of this study with the calorimetric glass temperatures reported in ref. 3.

**Figure 5.** \( T_g \)-scaled Arrhenius plot of relaxation times for pure CS\(_2\) and CS\(_2\)-S\(_2\)Cl\(_2\) solutions.
Using the value of $T_g$ for pure CS$_2$ that is extrapolated convincingly in Figure 4, it is possible to place relaxation data for pure CS$_2$ on the Figure 5 plot. Data are available from NMR spin-lattice relaxation times, from which single particle rotational correlation times for CS$_2$ have been extracted$^8$, and from optical Kerr effect (OKE) data$^9$ (collective reorientation times). These seem to overlap closely with the NMR-based data of Rössler and Sillescu$^{31}$ on toluene which are included in Figure 5, thus implying the same fragility.

It is natural to conclude that CS$_2$ itself is a very fragile liquid with values of $m$ and $F_{1/2}$ close to those of OTP and toluene. It is then also natural to suspect that the source of the fragility is the same as found for OTP in the W-L model. It would be desirable to obtain neutron scattering data on these solutions to permit commentary on the VDoS. For pure CS$_2$, however, the possibility of obtaining such data is, unfortunately, eliminated by the poor glassforming ability of the neat liquid.

In the absence of such data we turn to the molecular dynamics studies of CS$_2$ which have been performed. These have been primarily the efforts of Keyes and coworkers, though some data from a more detailed model matched to gas phase properties are also available$^5,11$ (and there are some preliminary results from an ab initio MD study of crystalline CS$_2$ (VDoS data) in the authors’ laboratory). Moore and Keyes$^{12}$ reported densities of vibrational states from a instantaneous normal mode INM analysis of their model which they considered to have a $T_g$, (based on vanishing of diffusivity and imaginary eigenfrequencies), of about 100K. Li and Keyes$^{13}$, in particular, presented the VDoS for different components of the vibrational spectrum, of which the lowest frequency components (the translational modes) are the most relevant to us. As with all normal mode analyses of vibrational dynamics above $T_g$, there are modes of negative eigenfrequency, corresponding to shoulder or saddlepoint modes, the number of which decreases with decreasing temperature and vanishes at the $T_g$. Figure 6, from Li and Keyes, shows the low frequency part of the translational mode VDoS for different temperatures, and it is seen that no imaginary modes remain in evidence at 100K. In the Keyes group simulations, the density for each simulation$^{12}$ was chosen from the experimental data so the simulations were effectively conducted at constant pressure, not constant volume.

The important feature of Figure 6, for our purposes, is that this system shows what was also true for the W-L model OTP behavior discussed in our introduction. That is the finding that the higher the temperature the more low frequency modes are present in the real density of states. They are produced at the expense of high frequency modes.
and in concert with unstable modes. The same can be seen in the CS$_2$ simulations of Ji et al\textsuperscript{11}, who suggest that the imaginary mode DoS be added back at positive values for purposes of comparison with experiment. There is a proviso here (T. Keyes, private communication): instantaneous structures in positively correlated systems must be more expanded than the corresponding inherent structures and, for this reason alone, have lower frequency modes. It is therefore not certain from Fig. 6 that the inherent structures of CS$_2$ along an isobar in this system have an excess vibrational heat capacity. On the other hand, Saito and Ohmine\textsuperscript{32} studied CS$_2$ in a slightly modified version of the Moore-Keyes model, and obtained the VDoS at 300K by all three approaches, instantaneous normal modes, normal modes of the inherent structure, and Fourier transform of velocity autocorrelation function. In their Figure 1 comparing the three cases, the VDoS of the inherent structure, which of course has no imaginary frequency modes, is actually the richest in low frequency modes.

Thus the observed behavior in Figure 6, increase of lower frequency VDoS as temperature rises, is likely to be found also in the inherent structures behavior for increasing effective temperature, and is exactly the behavior that leads to an excess vibrational heat capacity and, consequently, a rush to the top of the potential energy landscape. It is this aspect of the behavior of a fragile liquid that has been discussed in the introduction and that is now documented for CS$_2$ in Figure 5. It is interesting that Madan and Keyes\textsuperscript{33} long ago proposed a direct connection between the density of imaginary modes and an increment in the heat capacity above $T_g$, which we would now see as a vibrational excess heat capacity. An isobaric study of the inherent structure density of states for this system carried out for a range of effective temperatures, would be rewarding.

If we were to plot the total VDoS for CS$_2$ in the form $g(\omega)/\omega^2$ that is used to compare with light scattering data, as done by Angell et al\textsuperscript{19} for the case of Mossa’s VDoS for W-L OTP\textsuperscript{17}, we would find the presence of a strong “boson peak” which moves to higher intensities and lower frequencies with increasing fictive (effective) temperature. In the model OTP case the increase in the vibrational heat capacity at $T_g$ associated with the changing VDoS\textsuperscript{19} proved equal to the missing fraction of the total excess heat capacity that was deduced in the independent Goldstein\textsuperscript{20, 34}, and Wang and Richert\textsuperscript{22}, analyses. To recall briefly, Goldstein’s discussion was based on the careful assessment of residual entropies (0 K), and excess entropies at $T_g$, for glasses by Chang and Bestul\textsuperscript{35}, which in 2002 was extended to 33 glasses by Johari\textsuperscript{36}. Each paid particular attention to OTP. In a discussion of the possible alternative sources of excess heat capacity over configurational, Goldstein provided criteria for distinguishing the effect of changes in the VDoS from (i) anharmonicity or (ii) secondary relaxations. VDoS effects were indicated for the fragile OTP\textsuperscript{20, 36} but anharmonicity was indicated for others. Indeed, the most fragile non-polymeric liquids yet studied, decalin and decahydro-isoquinoline\textsuperscript{28, 37, 38} prove to be extremely anharmonic in neutron scattering studies, even in the glassy state\textsuperscript{39, 40}. In the Wang-Richert case, the configurational specific heat could be determined via the absorption of energy directly into the slow configurational modes (as in microwave heating) and the associated heat capacity then compared with the measured increase at $T_g$. It was always less than the excess quantity by an amount that increased with fragility, but there was no information on the nature of the difference (i.e. whether it resided in VDoS changes, anharmonicity or secondary relaxations). What was
clear, though, was that this component remained decoupled from the fast modes until the structure relaxed.

Combining these observations with those of Li and Keyes on CS$_2$, and our present demonstration of high fragility for this simple laboratory system, it might seem that a strong, if not conclusive, argument for the importance of the vibrational manifold in determining the fragility of a key group of molecular liquids can be made. However, there is a problem due to the recent insertion, by Johari and co-authors in two publications$^{41, 42}$, of the idea that such a vibrational excess heat capacity would have to be detectable by a high frequency, or low temperature, heat capacity effect in ac heat capacity studies. Since they failed to find any such effect, they were lead to conclude that the heat capacity jump observed at $T_g$ was entirely configurational in origin. This conclusion effectively denied their own and Goldstein’s earlier demonstrations to the contrary, and also contradicted a more recent re-examination of the Chang-Bestul data by Goldstein$^{34}$ in the light of the Mossa et al studies discussed in our introduction.

Unfortunately, a number of authors (and reviewers) seem to have accepted this notion, failing to recognize that the vibrational excess heat capacity, (being related to the shape of the higher energy basins on the energy landscape that are accessed by relaxation above $T_g$), can only be accessed on the timescale of the alpha relaxation. Fortunately, the correctness of this latter viewpoint has been recognized by Wyart$^{21}$, who emphasizes the importance of higher order effects at the boson peak, but notes also a connection of VDoS changes under different thermodynamic conditions to differences between constant volume and constant pressure fragilities. The finding of lower fragility in systems studied at constant volume has been demonstrated by several laboratories$^{43-45}$ and now seems to be recognized as established phenomenology.

Clearly, there is a need for further analyses of both the VDoS, and anharmonicity, effects in appropriate simulated systems, and in laboratory glasses that have been, alternatively, hyperquenched or well-annealed. While the idea that anharmonicity of the boson peak modes controls the ability of an amorphous solid to relax, i.e. of the glass transition to occur, has been around for some time$^{46, 47}$, the notion that these modes, through softening and anharmonicity, also determine the fragility of the liquid$^{48, 49}$ is a less obvious$^{50}$ - even unexpected - twist because it implies that fragility is determined in the vibrational, rather than the configurational, manifold of microstates.

**Concluding remark**

Because it is an excellent light scatterer, the possibility of Raman scattering studies of the boson peak and low frequency VDoS, using vapor-deposited samples of pure CS$_2$, suggests itself. Here, though, there is an unexpected problem. Vapor deposition of glassformers usually leads to vitreous phases with a close relation to the glass formed from the liquid, but for CS$_2$ this appears not to be the case. Careful vapor deposits of pure CS$_2$ have been made and studied by Yamamuro and coworkers$^4$, and the $T_g$ they observe is dramatically different from (much lower than) the value obtained from Figure 4. Yet the value from Figure 4 leads to relaxation time plots for the pure liquid that seem very consistent with the behavior of the CS$_2$-rich solutions, see Figure 5. From the finding that CS$_2$ in microemulsions yields a glass temperature$^2$ that is even higher than the value extrapolated in Figure 4, the behavior of the vapor deposit seems anomalous. Clearly, in view of the lower $T_g$, it is not to be explained by the “ultrastable glass” phenomenon
discovered recently in glasses that have been vapor-deposited near the normal liquid $T_g$, since they have much longer relaxation times than normal glasses$^{51,52}$. Attempts should probably be made to hyperquench pure CS$_2$ liquid to obtain a liquid-derived glass to compare with the results from ref. 4. An alternative possibility is to undertake a study of the three-atom molecule SCl$_2$ which is shaped like ozone and, according to the Turnbull-Cohen criterion, should be a glassformer by itself. Although difficult to prepare pure, and prone to slow disproportionation to S$_2$Cl$_2$ and chlorine, this substance might prove to be the simple glassformer par excellence that, through neutron scattering, heat capacity, and dielectric relaxation studies, will clarify some basic features of glassformer phenomenology.

References