

Fragility in Liquids and Polymers: New, Simple Quantifications and Interpretations

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In order to provide a firmer base for efforts to interpret the different fragilities of liquids (i.e., the different deviations from simple Arrhenius temperature dependence of relaxation processes), a new and simple one-scan method of quantifying fragility is described and verified. It is based on detecting, by simple differential thermal analysis (DTA), the temperature of maximum energy dissipation during temperature scanning under single-frequency excitation (electrical or mechanical) of the liquid. The frequency is chosen so that the DTA signal indicates directly not only T_g but also the temperature $T_{1/2}$ (where the relaxation time reaches 10^{-6} s) of the new and unambiguous fragility metric $F_{1/2}$,¹ which is defined by $F_{1/2} = 2(T_g/T_{1/2}) - 1$. The measurement is verified against dielectric data for liquids of widely varying fragility. The usefulness of such rapid scan methods in confirming or denying a vibrational density of states origin of fragility in liquids is considered.

Introduction

Fragility, a qualitative concept related to the manner in which temperature affects the properties of liquids, has become a much discussed subject in connection with viscous liquid and glass phenomenology.^{2–4} It is currently also being found of interest in fields as diverse as drug and food preservation^{5,6} and polymer rheology.^{7–9} In the latter it is recognizable as a key factor controlling the energy dissipation in flexing rubbers and the kinetics of aging in glassy polymers.⁹ Yet there is so far little understanding of its molecular origin. A problem impeding progress is that the quantification of fragility has been ambiguous, as inconsistencies in the values reported for fragilities of the same material, using different methods, testify. In this report, after a brief review of the concept, we examine the sources of ambiguity in its quantification and then demonstrate a simple and unambiguous way to define the quantity and an equally simple (differential thermal analysis, DTA-based) method for its measurement.

Fragility has both relaxational and thermodynamic manifestations. In the relaxational (and mass transport) case it is manifested by different levels of departure from Arrhenius kinetics. In thermodynamics, it is manifested by the different rates (with respect to temperature) at which the excess entropy of the liquid relative to crystal diminishes upon supercooling.¹⁰

The deviations from Arrhenius behavior can vary systematically from cases like SiO_2 , BeF_2 , and P_2O_5 in which deviations are barely detectable (“strong” liquid extreme) to cases with such pronounced deviations that the low-temperature Arrhenius slope translates to an (apparent) activation energy many times the vaporization energy—the “fragile” liquid extreme. Thermodynamically, strong liquids like SiO_2 and GeO_2 show such small differences in heat capacity, ΔC_p , between liquid and glass^{2,11,12} that supercooled liquid entropies approach the crystal values only slowly. Fragile liquids, on the other hand, have such high heat capacities relative to their crystals that a natural extrapolation of liquid entropy below the melting point indicates disappearance of the excess over crystal at a temperature far above 0 K, and in some cases as little as ~30% below the

melting point.¹⁰ This is, of course, the Kauzmann entropy catastrophe,¹⁰ which is avoided only by the adventitious intervention of the glass transition.¹³ The source of this diversity of behavior and, in particular, of the apparently diverging relaxation times and vanishing excess entropy [at T_o (or T_K) not far below T_g] in very fragile liquids is seen as an outstanding unsolved problem in condensed matter theory.¹⁴

While the term “fragility” connotes the sensitivity to temperature of the structural state of the liquid, the fragility has so far been quantified by reference to the temperature dependence of the transport constants (particularly viscosity) or relaxation times (particularly dielectric τ_D). The relaxation time, which has a theoretical infinity at T_K , decreases, with increasing temperature to the value 200 s at the “normal” glass temperature,¹⁵ where ergodicity is restored in laboratory studies and then continues to fall as $T > T_g$ in a manner which is usually predictable over much of the range from the Vogel–Fulcher–Tammann (VFT) equation,

$$\tau = \tau_o \exp(DT_o/[T - T_o]) \quad (1)$$

where τ_o , D , and T_o , are constants, and $T_o \sim T_K (< T_g)$ ¹⁶ is the divergence temperature. A number of other temperature dependences have been suggested.¹⁷

The proximity of the divergence temperature T_o to the “normal” T_g ($0 < T_o/T_g < 1.0$) provides one measure of the fragility,^{18,19} but of course its value will depend on the appropriateness of the data from which T_o is assessed. This constitutes a major source of ambiguity if the VFT equation is used, since the accord of data with this equation is quite variable. The ambiguity is reduced if the pre-exponential constant in the equation is assigned the physical value of 10^{-14} s,¹⁶ but then the fit to the equation will be worse. The same considerations apply to the use of the fragility measure $(1 - C_2/T_g)$ for polymers²⁰ where C_2 is the Williams–Landel–Ferry equation parameter,^{21,22} and also to the use of the parameter D of eq 1 as a “strength” index.^{2,16}

The dependence of the fragility number on the particular equation used to determine it is avoided by using the other common way of quantifying the fragility. This is to measure

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the slope of the Arrhenius plot at the glass transition temperature, and write²³

$$m = (T_g)^{-1} d(\ln \tau)/d(1/T) \quad (2)$$

m has been called both the “fragility”²³ and the “steepness index”.²⁴

m values for a large number of substances have been tabulated in ref 25. The value $m = 16$ corresponds to Arrhenius behavior.^{23,26} The difficulties with this fragility metric are many. Firstly, it is difficult to determine accurately the slope of a rapidly varying function near T_g , given the usual uncertainties in sample temperature and relaxation time. Secondly, liquids near their T_g may develop eccentricities in their behavior due to decoupling of the relaxation process under study being measured from the fundamental structural relaxation process (the entropy equilibration), or to rapidly increasing differences between most probable and average relaxation times as deviations from exponential relaxation become larger, or to other causes such as increasing microheterogeneity, etc.^{27–29}

These can all lead the slope of τ at T_g to differ from that which represents best the overall deviation from Arrhenius behavior. Most lead to an underestimate of the fragility in the case of very fragile liquids, and since the high fragility liquids are the most provocative and interesting, this is a matter of concern.

New Reduced Ambiguity Definition of Fragility. In light of the above we will here (a) advocate the adoption of a new and unambiguous measure of the fragility,¹ designated $F_{1/2}$ and (b) describe a method of measuring it which requires nothing more than a simple DTA setup and a single-frequency dielectric or piezoelectric driver, tuned to the frequency $10^6/2\pi$ (i.e., $10^{5.2}$) Hz.

$F_{1/2}$ is a direct measure of the deviation of the measured system from Arrhenius behavior. It measures how much more quickly than Arrhenius, the relaxation time decreases, relative to an ideal Arrhenius case with the same T_g and τ_0 , by comparing the temperature intervals needed to change τ from 100 s at T_g to the designated value, 10^{-6} s.

Its determination from relaxation time plots in the T_g -scaled Arrhenius representation is illustrated in Figure 1. It is called $F_{1/2}$ because it is determined at a relaxation time (10^{-6} s) which is half way in log units between that at the reference temperature T_g (where the relaxation time is $\sim 10^2$ s) and the high-temperature (phonon) limit 10^{-14} s. We claim it is free of ambiguity, since (a) it does not depend on any equation, and (b) it is measured at a point where the deviation from the reference Arrhenius behavior is large so that the sensitivity to differences in fragility between different substances should be approximately optimal. There will, however, be a residual ambiguity stemming from the possibility of different temperature dependences for different properties (dielectrics, viscosity, diffusivity, etc.).

The $F_{1/2}$ value is then defined by

$$F_{1/2} = 2[T_g/T_{1/2} - 0.5] \quad (3)$$

(where the quantity inside the brackets is the length ℓ in Figure 1), so as to have values lying between 0 and 1. Analysis shows that for a 1% uncertainty in the τ measurement, $F_{1/2}$ would be in error by less than 0.05%, if T_g/T were error-free. However, the T_g measurement is probably the greatest source of uncertainty, in which case $F_{1/2}$ is determined by our method within only 1%.

There are a number of possible ways of obtaining the quantities needed to obtain the fragility according to this definition.

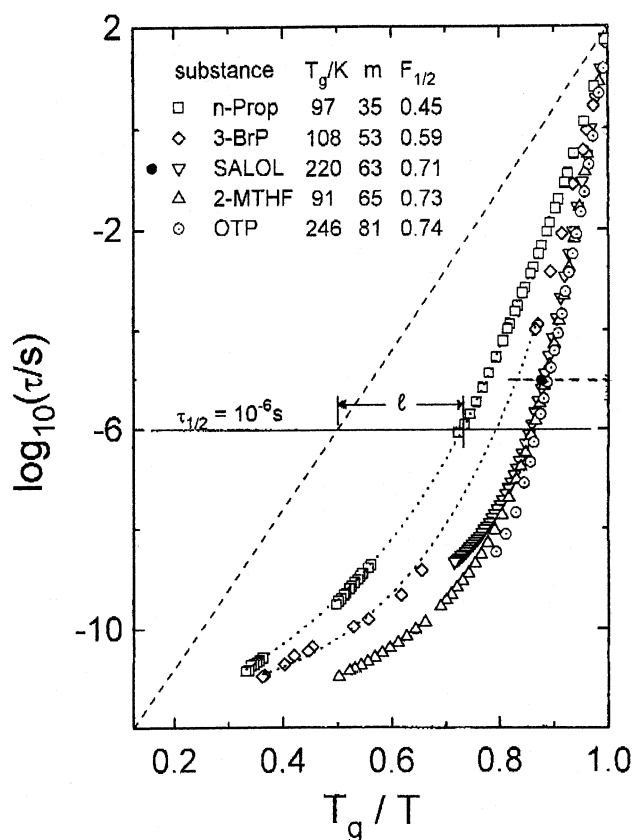


Figure 1. T_g -scaled Arrhenius plot of the dielectric relaxation times for several molecular liquids¹ showing how the fragility $F_{1/2}$ is defined. $F_{1/2} = 2\ell = 2(T_g/T_{1/2})^{-1}$. The liquids are, in order, *n*-propanol, 3-bromopentane, salol (phenylsalicylate) 2-methyltetrahydrofuran, and ortho-terphenyl. Values obtained for OTP and salol are quoted in the text. Shown as a solid symbol is the value of the temperature at which the structural relaxation time of salol reaches $10^{-5.1}$ s, according to work described herein. The horizontal dotted line above the $\tau_{1/2}$ line corresponds to the 20 kHz excitation frequency of the ultrasonic generator used in this study. (Adapted from ref 1 by permission.)

We will describe here a particularly simple version, suitable for laboratories with minimal equipment, and then suggest how such measurements can be combined with others available in many labs to reveal the molecular thermodynamic origin of fragile behavior in liquids and polymers.

Experimental Section

To determine $F_{1/2}$ in a single measurement using only a differential thermal analysis setup for detection, we make use of the relation between the imaginary part of a frequency-dependent response and energy dissipation. The energy dissipated from a fluctuating field, in a material which the field is perturbing, is a maximum when the field frequency (in radians/s) is the inverse of the most probable relaxation time of the material. This is the condition $\omega\tau = 1$ for an exponentially relaxing material in which τ is the single time constant, or $\omega\tau^* = 1$ for the non-exponentially relaxing case (τ^* being the most probable relaxation time in the distribution). Therefore, during a temperature scan, the temperature difference between a sample under irradiation at $10^{5.2}$ Hz, and a reference sample of the same substance, will pass through a maximum when the relaxation time of the sample is 10^{-6} s. Thus, $T_{1/2}$ of eq 3 is obtained as the temperature at the ΔT maximum. This method of determining the dielectric relaxation time was demonstrated in 1976 by Matsuo et al.^{30,31} but little utilized since. We re-apply it here, and show also, with the help of a commercial ultrasonic agitator

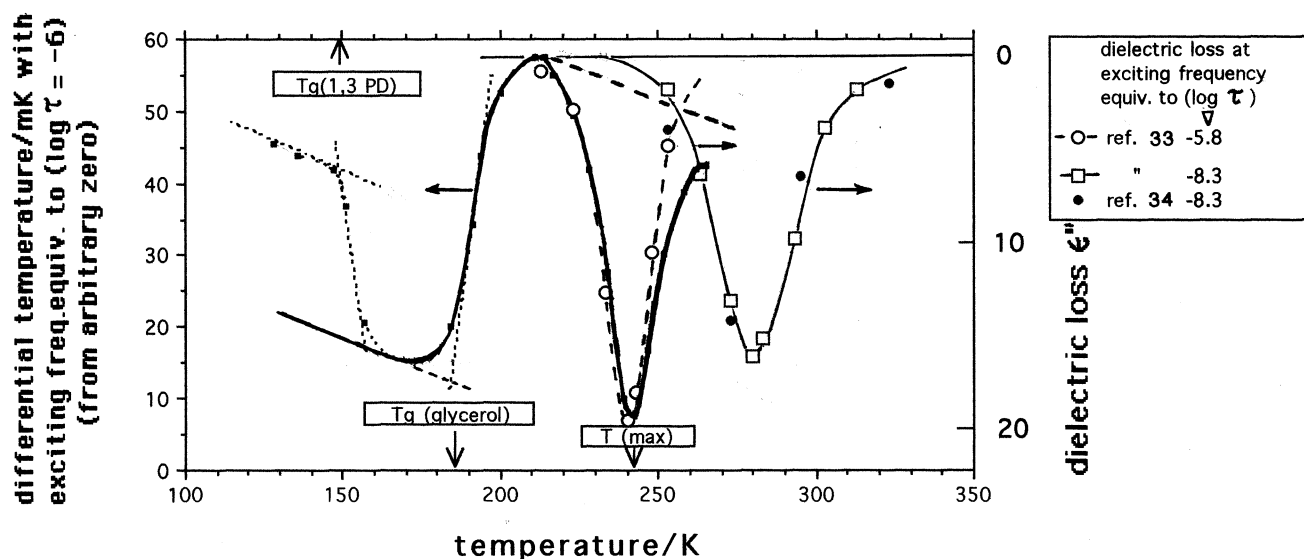


Figure 2. DTA trace of a sample of glycerol scanned at 10 K/min under steady $10^{5.2}$ Hz irradiation, referenced to 1,2 propanediol (PD). The maximum in the differential temperature (ΔT_{\max}) at -31 °C indicates a (most probable) relaxation time for glycerol of 10^{-6} s at this temperature. The dashed line passing through the open circles is a trace from the dielectric relaxation study of Morgan³³ in which temperature scans at a constant frequency of 20 kHz were made. Morgan's work was pioneering in high-frequency dielectric studies, as the surprisingly good agreement with the current measurements of Lunkenheimer et al.³⁴ at 32 MHz ($\tau = 10^{-8.3}$ s) shows.

operating at 20 kHz, that a similar effect can be obtained for the mechanical relaxation. For the dielectric case, the temperature at which the differential temperature is a maximum will be the $T_{1/2}$ of the $F_{1/2}$ definition, eq 2. For the mechanical case using 20 kHz excitation it will be a lower temperature.

If the reference is calorimetrically inert then the glass transition will be recorded in the same scan. If the scan is conducted at 10 K/min, the value of T_g will correspond to $T_{(\tau=200\text{s})}$, and the scan will record *both* the temperatures needed to define the $F_{1/2}$ fragility. $T_{1/2}$ will not be affected by the scan rate in principle, since the liquid is in equilibrium at this temperature, though distortion could follow from differences in heat flow. To avoid these we used, as the reference, a liquid with similar heat capacity but lower T_g , (in which case both glass T_g s are recorded during the scan).

The energy dissipation in $\text{Joules s}^{-1} \text{cc}^{-1}$ from an electric field of RMS voltage E_0 acting on a medium of dielectric loss ϵ'' is given by^{30,31}

$$W = E_0^2 \epsilon'' \omega \epsilon_0 \quad (4)$$

(where ϵ_0 is the permittivity of free space), and a quick calculation shows that voltages between 20 and 200 V (still well within the linear response regime) are sufficient to generate the heat necessary to detect with a standard DTA setup. We use a two-pen millivolt recorder and include a low-noise operational amplifier (earthed to the recorder) to boost the microvolt DTA differential signal. To produce up to 1200 V(rms) at $10^{5.2}$ Hz we used a FET Hartley oscillator with a one-stage buffer followed by several stages of amplification.³² The field is introduced either externally to the sample via two Al foil electrodes on the outside of the sample tube (as described in ref 31) or internally via two metal electrodes attached to the thermocouple sheath.

It is clear from eq 4 that our dielectric loss-based determination of $F_{1/2}$ will encounter difficulties with liquids of very small dielectric constant. Furthermore, with some liquids such as the normal alcohols, the maximum in the dielectric loss is determined by dipole clusters or other complexities in the liquid and does not correspond to the structural relaxation time which

is required for the determination of $F_{1/2}$. For such cases an alternative to the dielectric technique is needed. Energy dissipation from a fluctuating mechanical stress in principle offers an alternative equivalent method for obtaining $F_{1/2}$.

High-intensity, high-frequency, mechanical energy is available from the piezoelectric drivers used in a variety of ultrasonic agitators. While these generally produce too much energy to be suitable for our purposes we may use the results for illustrative purposes. We adapted a Sonics vibracell agitator, originally purchased for preparation of emulsions, by mechanically coupling a 0.5 mm tungsten wire to the 2.5 mm end section of the agitator in such a way as to transmit only a fraction of the available energy. This was inserted into the sample contained in a 4 mm i.d. DTA sample tube. The frequency of the agitator is 20 kHz which will give maximum energy dissipation when the mechanical relaxation time is $10^{-5.1}$ s.

Results

Results are illustrated for the case of anhydrous glycerol in Figure 2. The solid line is the DTA scan. To avoid confusion, the reference sample glass transition has been omitted in drawing the solid line (but is shown by the dotted line). Figure 2 shows a glass transition at 185 K and a sharp ΔT maximum at 242 K, which is therefore $T_{1/2}$ for this substance. Our ac field-induced DTA peak at 242 K is compared with the dielectric loss peak obtained during temperature scan at a constant 100 kHz probe frequency by Morgan.³³ This frequency will give rise to a maximum loss when $\log \tau = -5.8$, close to our chosen value. The close similarity to our DTA trace is a consequence of eq 4 for the energy dissipation. The additional curves in Figure 2 are reliability checks of Morgan's early work discussed in the figure caption.

In the case of a fragile liquid like propylene carbonate, the $T_{1/2}$ energy dissipation peak must occur much closer to T_g , and overlap with the T_g endotherm could become a problem. This can be dealt with by adjusting the exciting field voltage to provide $T_{1/2}$ loss peaks of different magnitudes relative to the pen displacement at T_g . This is illustrated for applied peak-to-peak voltages 0, 87.4, and 176.8 V, in Figure 3. Equation 4 shows that the heat output should vary as the square of the

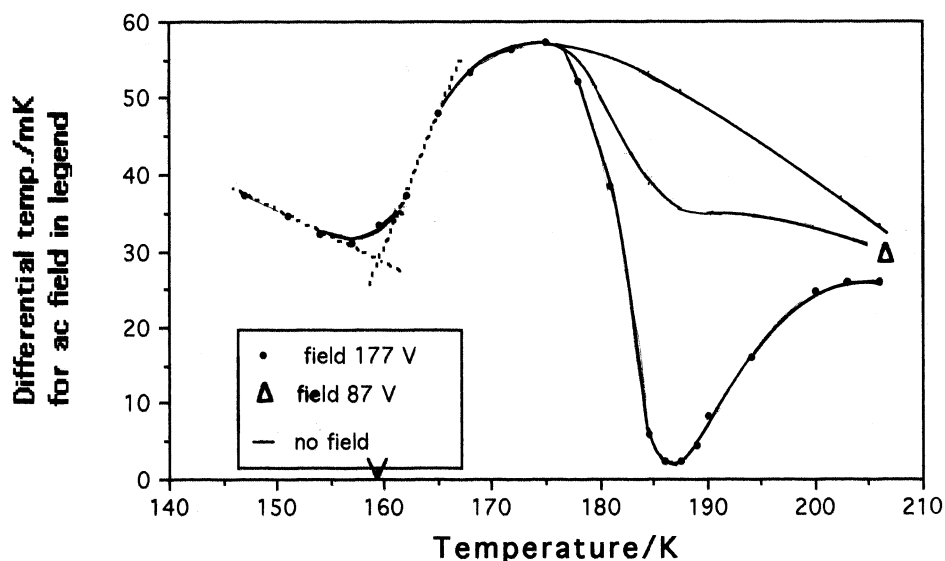


Figure 3. DTA traces for propylene carbonate under $10^{5.2}$ Hz irradiation, (using inert reference DMSF) at three different fields settings (0, 87, and 177 V). The $T_{1/2}$ values are little affected by change of voltage. T_g is seen at 159 K.

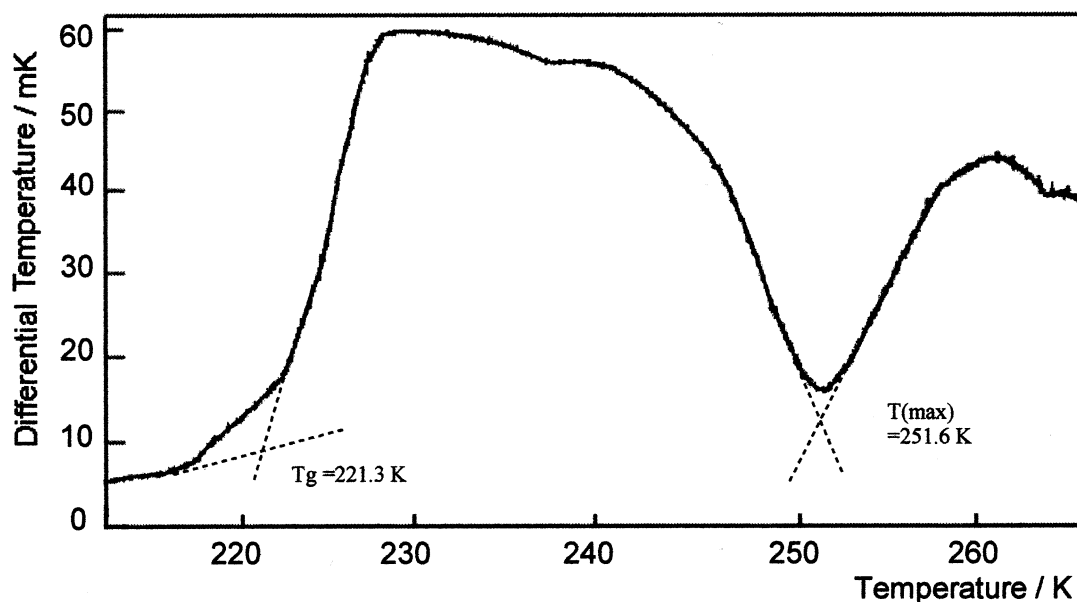


Figure 4. DTA trace for salol under 20 kHz ultrasonic excitation, showing the temperature at which the structural relaxation time is $1/2\pi(20 \text{ kHz})$, i.e., $10^{-5.1}$ s. While this datum is in good agreement with literature data, results for other liquids using the present simple technique have been of indifferent reliability and refinements are needed.

applied field, though we see less than a factor of 4 difference in ΔT .

The $F_{1/2}$ fragilities of glycerol and propylene carbonate obtained from Figures 2 and 3 are 0.55 and 0.72, respectively. These are to be compared with values of 0.56 and 0.74 obtained from previous dielectric studies in which T_g has been taken as the temperature at which $\tau = 100$ s.^{1,25} This may lead to small difference from our values since T_g obtained at scan rates of 10 K/m in from DTA or DSC tend to occur at 200–500 s.¹⁵ The values which would be predicted from the recorded m values,²⁵ by eq 1 are 0.54 and 0.73, an agreement which is quite pleasing.

Mechanical Excitation. In our crude application of the DTA-based fragility determination using the adapted ultrasonic oscillator we invariably obtained a peak in the differential output. However, the shapes of the peak and often also the peak temperatures were unreliable. We associate this, with uncontrolled overtone and subsidiary frequency generation in the exciting wire. In the case of propylene carbonate we also

consistently obtained two peaks which may be significant. Such problems could be avoided if an appropriately chosen piezoelectric crystal (oscillating at $10^{5.2}$ Hz) could be immersed in the sample or mechanically coupled to the sample tube.

Figure 4 shows the DTA recording, obtained using the present excitation method, for the case of salol which has too small a dielectric constant to be studied effectively by the dielectric technique. The example shown in Figure 4 shows an appropriate peak shape. Since the frequency 20 kHz does not correspond to a time of 10^{-6} s we cannot quote a $F_{1/2}$ fragility directly from the peak temperature. Rather, the peak differential temperature should occur when the relaxation time is $10^{-5.1}$ s. However, the temperature at which the relaxation time reaches $10^{-5.1}$ s indicated by the peak at 251.6 K corresponds well with the value obtained from the conventional dielectric relaxation times plotted in Figure 1.

The ultrasonic excitation method for determination of $F_{1/2}$ has the advantage that it can be used to determine the fragility

for any liquid, polar or otherwise. A disadvantage is that high-frequency mechanical agitation tends to promote crystal nucleation and so may cause the experiment to terminate prematurely.

Discussion

First, we point out that an even simpler, though intrinsically less reliable, method of assessing fragility than the present one has recently been described.³⁵ It involves only the determination of the width of the glass transition in temperature measured during scanning within a well-defined cool/heat protocol. The disadvantage of this simple method is that, while the width is controlled mainly by the relaxation time temperature dependence, it is also affected by the non-exponentiality of relaxation, and by the presence or otherwise of composition fluctuations. Thus some empiricism must be invoked in its use and care taken with its application. For reliable studies of fragility, the present method or one based on comparable fixed frequency dielectric scans such as that of Morgan in Figure 1, must be considered more desirable.

At this time, the factors that determine whether a given liquid will be strong or fragile are very imperfectly understood, and the subject deserves to be the focus of much attention from the liquids community. We believe the present rapid method of scanning an assortment of molecular liquids to determine their relative fragilities can be of much help in this endeavor. We justify this statement by the following line of thought.

For a while it seemed that there were major discrepancies in fragility assignments by relaxation and thermodynamic (heat capacity jump) criteria for cases like the alcohols. However, the recent demonstration that fragilities determined from purely thermodynamic (scaled excess entropy) temperature dependences³⁵ follow essentially the same order as those determined from relaxation data directs our attention back to thermodynamic factors and their molecular origin. Simple two-state models which seem physically reasonable for glass-formers in which the behavior is dominated by the breaking of covalent bonds, suggest³⁶ that the fragility is determined directly by the entropy change accompanying bond breaking. Whether this entropy of "elementary excitation" resides in the vibrational density of states or in the configurational density of states is a key question, which can be answered experimentally by neutron- or light-scattering studies.

If it is due to an entropy $R \ln \nu_1/\nu_2$, due to the generation of low-frequency quasi-lattice modes on the creation of broken bond sites in the quasi-lattice, then this should be detectable in the low-frequency vibrational density of states. Indeed, there is a strong evidence, in the work of Phillips et al.,³⁷ for such a population buildup in the case of selenium as temperature increases above T_g .

The density-of-states observations of Phillips et al. on selenium have been used by Granato³⁹ in his interesting attempts to extend theories of interstitials in crystal to the glass-forming liquids problem. We see much in common between his approach and our own, even to the similar estimates of the fraction of excitations frozen in at the glass transition (0.03³⁹ vs 0.04⁴⁰ for intermediate glass-formers NiZr₂ (metallic glass) on the one hand^{39,41} and ZnCl₂ (ionic-covalent glass) on the other.⁴⁰ Such an interpretation then is consistent with Goldstein's analysis of the problem⁴² based on the difference in thermal behavior of quenched vs annealed glasses. In his analysis, Goldstein found that Se lost a great deal of the excess entropy of glass over crystal measured at T_g during cooling from T_g to 0 K—which implies an origin for much of this excess in the vibrational manifold.

Selenium is the most fragile composition in the selenium-based chalcogenide glass systems,³⁸ and the fragility decreases dramatically as the content of Ge or [Ge + As] builds up. Our expectation would be that the population buildup would be much less obvious in the Ge-containing glasses and would be unobservable at the "rigidity percolation" threshold where the average number of bonds per particle is 2.4.³⁶

To relate this behavior to that of the molecular liquids of the present study, we first note that even more pronounced losses of glass entropy over crystal during cooling to 0 K were found for the most fragile liquid in Goldstein's study, orthoterphenyl. This suggests that packing excitations in van der Waals liquids can play a phenomenological role indistinguishable from that of bond-breaking excitations in covalent liquids. This was certainly the implication of the comparable "excitation profiles" demonstrated for covalent and van der Waals glass-formers recently.³⁶ This being the case, the present method could be used to assess rapidly the relative fragilities of a series of molecular liquids in which systematic changes in molecular structure are introduced. The same liquids would then be examined by low-frequency Raman scattering for a correlating rate of buildup of low-frequency intensity at $\nu < \nu_{\text{boson}}$. There is already piece-meal evidence for this correlation in the work of Sokolov et al.,⁴³ for which we here provide a thermodynamic interpretation. This correlation needs to be systematized.

If the origin of the low-frequency scattering is indeed the static excitation of the quasi-lattice, then the resolution of a conundrum is at hand. The conundrum⁴⁴ is that it seems possible to detect the occurrence of the glass transition from the increase in diffusivity-related mean-square particle displacements (MSD) observed in picosecond time scale measurements, even though the glass transition onset is known to occur when relaxation times reach 10² s. The resolution lies in recognizing that the MSD is determined by the number of excitations with modes of low frequency, hence large amplitude, and that this number becomes frozen in at T_g during cooling. On reheating, the number begins to increase immediately T_g is passed and new excited configurations are generated. The relevant time scale is the temperature equilibrium time (sample preparation time), not the probe time scale. The break in MSD vs temperature is in this case no more surprising than that in the spectroscopic observables such as the UV spectra in CKN,⁴⁵ the visible spectra for divalent cobalt ions in chloride melts,⁴⁶ or the —OH overtone IR spectra which were shown to duplicate the calorimetric glass transition in the case of sorbitol.⁴⁶

The proof of this notion would lie in the observation of a decrease in MSD during annealing of quenched glasses below T_g —an experiment not yet reported, to our knowledge. This latter experiment and one other key annealing experiment need to be made. The second key annealing experiment is a study of the annealing effects on the sub-boson peak scattered light (or neutron) intensity. This should approach an equilibrium value at each temperature below T_g , and these values should be consistent with the frozen-in excitation fraction predicted from measurements made above T_g . This would prove the structural origin of the low-frequency quasi-elastic scattering, and confirm its role in promoting the structural collapse as $T > T_g$. It would also establish a spectroscopic signature for the configurational excitation⁴⁰ (or "defect").^{39,47} The role of intermediate range order in producing non-fragile behavior² would then have to lie in its "protection" of the system against generation of frequencies below ν_{boson} during structural excitation.

Note Added in Proof: J. B. Suck has alerted us to his neutron scattering-based observation of a decrease in the low

frequency density of states of a quenched NiZr metglass during annealing below T_g ; Suck, J. B. In *Dynamics of Amorphous Materials*; Richter, D., Dianoux, A. J., Petry, W., Teixeira, J., Eds.; Springer: Berlin, 1989; p 182.

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