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Fragility thy name is glass*

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Abstract

Fragility is a novel concept to understand the behaviour of glass-forming liquids. Several approaches have been made to quantify fragility. In this paper, some important formulae have been briefly introduced. A new approach has been made, in which the ionicity of bonding and a distance parameter have been introduced on the basis of intuitive arguments. An expression has been proposed on a heuristic basis, which seems to give fragilities in good agreement with the reported $F_{1/2}^{\mathrm{Relx}}$ fragilities.

Keywords: Fragility, glass-forming liquids, ionicity of bonding.

1. Introduction

Fragility is a new concept which has influenced profoundly our understanding of glass-forming liquids. In order to capture a few glimpses of the rapid developments in this area, we very briefly summarize some relevant and basic concepts of glass science.

Glasses are best understood with reference to a volume vs temperature plot. Consider a solid which has been heated to well above its melting point. When such a melt is gradually cooled its volume decreases continuously down to its freezing point, T_m. At T_m, the volume generally decreases abruptly due to crystallization. Upon further cooling, the volume again decreases continuously but with a reduced slope, which is characteristic of a crystalline solid. On the contrary, if the melt is cooled very fast so as to bypass crystallization, the volume below T_m continues to decrease at the same rate as above T_m. But at a low enough temperature, about two thirds of T_m, a change occurs in slope of variation of the volume and the now-rather-viscous melt solidifies. The expansivity of this solid known as 'glass' is similar to that of the crystalline solid.

The temperature of the change of slope is known as 'glass transition temperature', T_g. But this T_g (Fig. 1) is not a unique temperature and it depends on the rate of cooling; the slower the cooling, the lower the T_g. From Fig. 1, one can also see that the volume of the glass is slightly higher than that of the parent crystal and this is almost always the case.

The regime of temperature between T_m and T_g is referred to as 'supercooled region'. Above T_m the entropy of the melt is largely configurational, arising out of numerous energetic-

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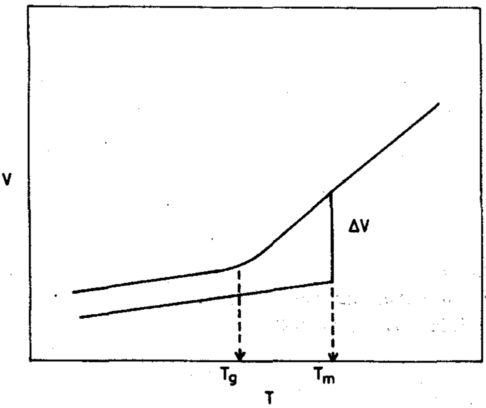

FIG. 1. Volume vs temperature plot.

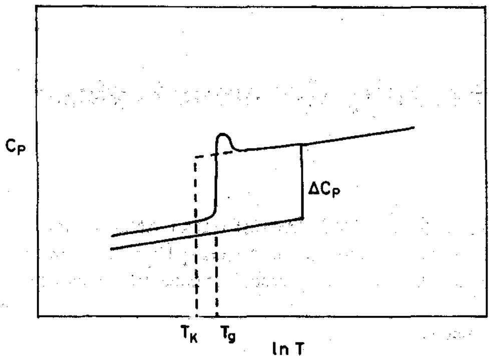

FIG. 2. Heat capacity plot.

cally equivalent arrangements in which the system can be realized. The configurational entropy of the molten state is generally lost, but never completely, as the melt is cooled towards T_g. Because of this reason, fewer and fewer configurational states become available to the supercooled melt as it nears T_g and even these states are accessed only through highly cooperative rearrangements. Therefore, the viscosity increases very rapidly and the system is eventually frozen into a state which corresponds to one of the many local free energy minima.

Let us examine the heat capacity plot (C_p vs ln T, Fig. 2) for the same general case as in Fig. 1. On cooling the melt, its C_p decreases very little till when at T_m it drops abruptly to the C_p value of the crystal. But when so cooled as to bypass crystallization, the supercooled melt continues to follow the same heat capacity behaviour of the melt above T_m. The supercooled melt, therefore, always has a higher heat capacity than the crystal. On cooling further, however, the supercooled melt exhibits an almost abrupt decrease in C_p at T_g where it solidifies into a glass. The glassy state heat capacity is only slightly higher than that of the crystal. This drop appears inevitable when we consider the following. Since the heat capacity of the melt is higher in the supercooled region, it loses more entropy than the crystal upon cooling from T_m to T_g. The melt can afford this extra loss of entropy because at T_m the melt had acquired entropy, $\Delta S_m = \Delta H_m/T_m$, which manifests largely as it is configurational entropy.

But this extra entropy would be lost completely at some temperature, T_K, subject to the constraint,

$$\Delta S_m = \int_{T_K}^{T_m} \Delta C_p \ln T \qquad (1)$$

(ΔH_m is the melting enthalpy and ΔS_m the melting entropy. $\Delta C_p = C_p(\text{melt}) - C_p(\text{crystal})$). But T_K is never attained by the supercooled melt and before that at $T_g > T_K$, it becomes a glass, because the melt becomes so viscous ($\geq 10^{13}$ poises) that configurational changes cannot occur on ordinary time scales. Supposing that the viscosity did not become a limiting parameter, could the melt be supercooled further? Equation (1) suggests that it cannot be cooled below T_K because there would be a paradoxical situation of supercooled liquid having lower entropy

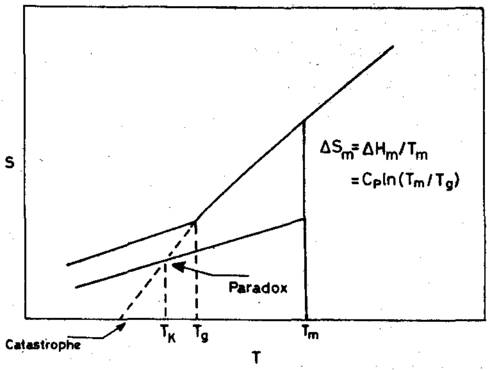

FIG. 3. Kauzmann Paradox and entropy catastrophe.

than the parent crystal. This is more clearly represented in Fig. 3, where entropy, S, itself is plotted as a function of temperature, T, for the same system as in Figs 1 and 2.

Upon cooling the melt, if crystallization occurs, entropy drops discontinuously at T_m to the value characteristic of the crystal. When crystallization is bypassed, entropy decreases down to T_g where it is close to, but slightly higher than, the entropy of the crystal. If the cooling rate is slow, the slope changes at temperatures still closer to the entropy curve of the crystalline solid. But it never crosses the entropy curve of the crystal itself because that would be a thermodynamic absurdity, whereby a supercooled melt would possess lower entropy than the crystalline solid itself. This is referred to as 'Kauzmann Paradox'. The limiting temperature, where the entropy of the glass and crystal become equal is called as Kauzmann temperature, T_K, which we have used in eqn (1) to represent the lower temperature limit for integration. If glass transition did not occur and the supercooled liquid continued to lose entropy at the same rate, then at some temperature greater than ^{0}K, the entropy of the supercooled liquid would become zero, which is the unacceptable thermodynamic catastrophe.

The behaviour of viscosity (η) of the melt for the same temperature history as in Figs 1–3 is shown in Fig. 4. η increases rapidly in the supercooled region. It attains values of the order of 10^{13} poises at T_g and therefore behaves as a solid. Viscosity can be plotted as ln η vs $1/T$ also. Such a plot is very interesting for the present purpose. Such plots reveal generally two types of behaviour. One is a simple Arrhenius behaviour, a linear variation of ln η as a function of $1/T$, described by the relation,

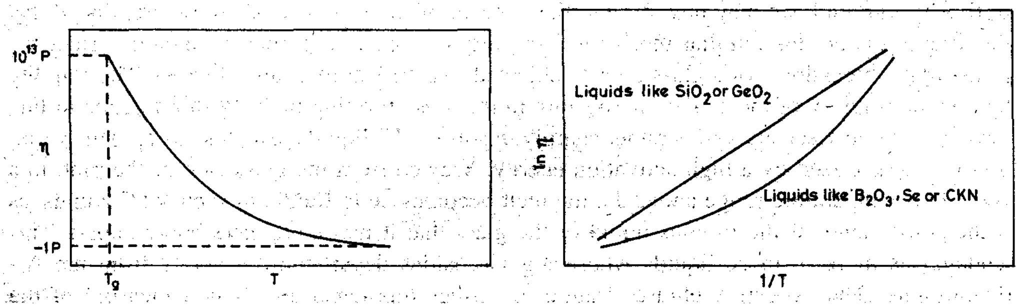

FIG. 4. Viscosity behaviour of a glass-forming liquid.

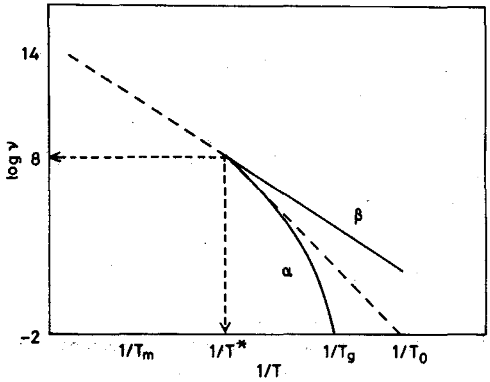

FIG. 5. Relaxation behaviour of glass-forming liquids.

$$\eta = \eta_0 \exp\left[-\frac{E}{RT}\right] \tag{2}$$

The second is the more interesting Vogel–Tammann–Fulcher (VTF) behaviour, a nonlinear variation of ln η vs $1/T$. This nonlinearity is removed when η is plotted as a function of $(1/(T - T_0))$ instead of $1/T$ and the viscosity is described by the relation:

$$\eta = \eta_0 \exp\left[-\frac{DT_0}{T - T_0}\right]. \tag{3}$$

Glass-formers like SiO_2, GeO_2 exhibit Arrhenius behaviour, while liquids like B_2O_3, Se or ionic glass-forming liquids of the type 60 KNO_3.40 $Ca(NO_3)_2$ (CKN) exhibit VTF behaviour.

Behaviour of the relaxation times of the glass-forming liquids for the same region of temperature as the above is even more complex and very revealing. A plot of log ν vs $1/T$ is shown in Fig. 5. The relaxation times vary from 10^{-14} s (vibrational) to 10^2 s (viscous) in the supercooled region. The variation of the relaxation times appears quite nonlinear and several Arrhenius-like branches appear to split off from the main curve. The principal ones of interest to glass science are described as α, β and γ relaxations.

2. Fragility of glass-forming liquids

In this background, we may now discuss the concept of fragility. One should be reminded that this fragility is not the familiar mechanical fragility of a glass, a property which describes the catastrophic breakdown of a glass object subjected to a critical mechanical stress. The fragility here is the fragility of molecular architecture in the glass-forming melt. With reference to Fig. 6 we notice that viscosity varies rather sharply in some VTF liquids just close to T_g. This variation is characterized by a high activation energy. Viewed from the glass side of the plot, in a very short temperature range above T_g, the melt becomes quite fluidic in such VTF liquids, as if the constituents of the viscous liquid or the glass that it was at T_g have broken apart. This tendency is more in those liquids whose log viscosities depart more severely from the Arrhenius line. The evocative phrase ‘fragile’ describes this departure. It is a measure of the steepness in viscosity drop above T_g; greater the steepness, higher the fragility.

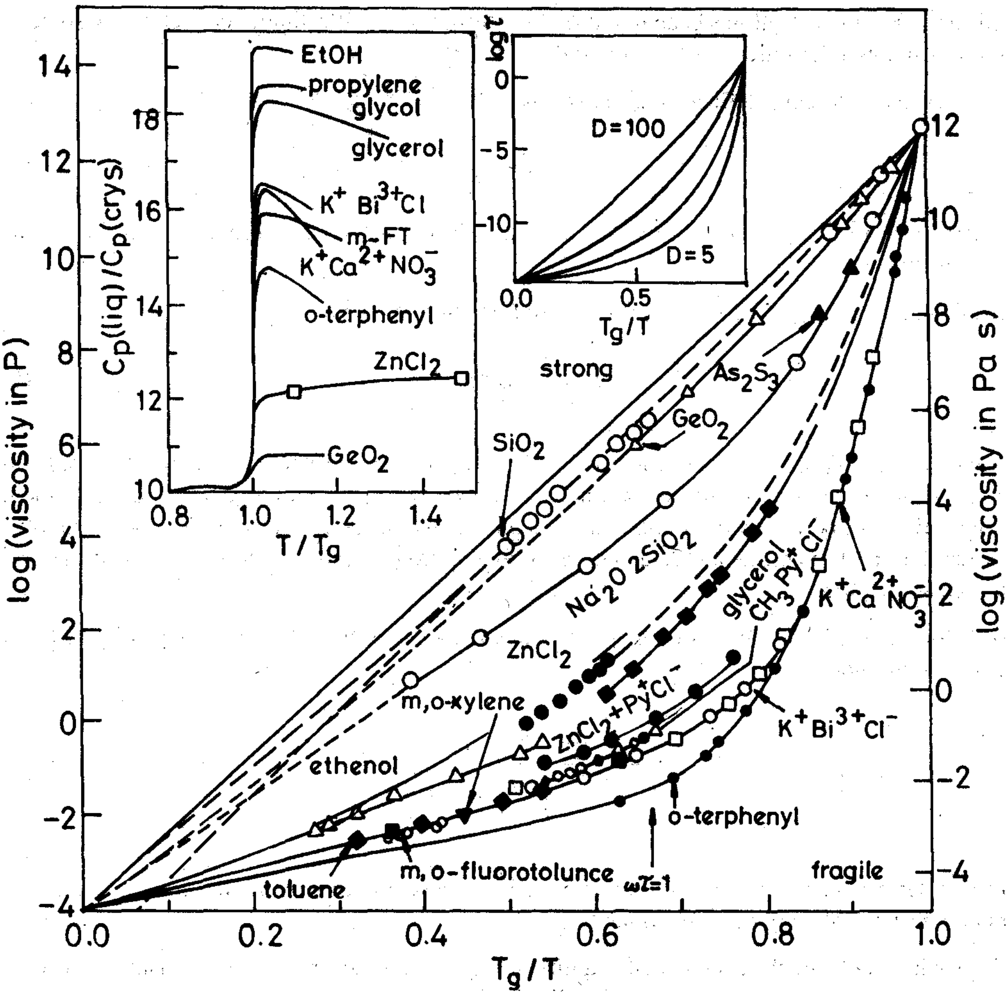

Fig. 6. Plot of log viscosity as a function of scaled temperature (from Angell[3]).

A plot of log viscosity as a function of scaled temperature (T_g/T) is more useful in visualizing comparative fragilities. Angell[1, 2] classified glass-forming liquids as 'strong' and 'fragile' on the basis of such a plot. Arrhenius liquids are described as strong while those following the VTF equation are fragile. In contrast to strong liquids, viscosities of fragile liquids exhibit a pronounced divergence near T_g. In a very short range of temperature above T_g, η drops by about 6 to 7 orders of magnitude in typically fragile liquids like CKN. Therefore, a glass formed from a fragile liquid becomes quite fluidic and capable of accessing a large number of configurational states in just a short range of temperature above T_g.

The concept of fragility has opened a new window which provides insights into the behaviour of glass-forming liquids. In just under a decade much research work has been reported in this area. Fragility itself has been quantified in various ways. We simply collect below some of the well-known definitions of fragility to date.

(i) Very early, Angell[4] defined fragility (F) as;

$$F = \frac{1}{D} \tag{4}$$

where D is from VTF equation (eqn 3). D is a measure of the departure of ln η from the Arrhenius linearity.

(ii) Donth[5] and Hodge[6] related fragility (F) to transition temperatures as

$$F = \frac{T_K}{T_g} \text{ or } F = \frac{T_0}{T_g} \tag{5}$$

where T_K and T_0 are the Kauzmann and VTF temperatures, respectively. Since viscosity increases rather steeply towards T_g in a narrow regime, T_K or T_0 get closer to T_g itself in more fragile liquids and this is the implied argument. But measurements of both T_K and T_0 involve extrapolation of experimental data and hence assumptions regarding the behaviour of the system in this region.

(iii) Zhu[7] defined fragility as the steepness index itself, as measured from the viscosity-reduced temperature plots.

$$F = \frac{\partial \ln\left(\frac{\eta}{\eta_0}\right)}{\partial\left(\frac{T_g}{T}\right)} = \frac{E_\eta}{RT_g}. \tag{6}$$

In this definition, F represents the most directly evident property of fragile liquids and its implications have already been mentioned.

(iv) Richert and Angell[8] also related fragility to relaxation times in an indirect manner. Accordingly, a more convenient $F_{1/2}$ (not F) fragility is given by

$$F_{\frac{1}{2}}^{\text{Relx}} = \left[2\left(\frac{T_g}{T_{\frac{1}{2}}}\right) - 1\right] \tag{7}$$

where $T_{1/2}$ corresponds to the temperature at which the relaxation time on a logarithmic scale is halfway between its value at the high temperature (~ 10^{-14} s) and at T_g (~ 10^2 s). It is evidently the temperature where $\tau = 10^{-6}$ s.

(v) A corresponding thermodynamic $F_{1/2}$ fragility was also defined by Angell[8] as

$$F_{\frac{1}{2}}^{\text{Therm}} = \frac{T_{\frac{1}{2}}}{T_m} \tag{8}$$

where $T_{1/2}$ is now the temperature at which entropy lost by the supercooled melt is $\Delta S_m/2$ and ΔS_m is the melting entropy.

Definitions (4) and (5) are both logical and intuitive. In the first, a large increase of η over narrow range of temperature can only mean that the initial half (high temperature side) of the increase of relaxation time has been slow and has occurred over more than half of the temperature regime. This results in a quicker increase of τ in the other half (lower temperature half) of the temperature regime. The second is a bit more involved since ΔS is defined in terms of logarithmic difference in temperature but has similar basis.

(vi) Xia and Wolynes[9] arrived at a fragility relation involving the magnitude of the change in heat capacity at T_g.

$$F = \frac{\Delta C_p}{32R} \tag{9}$$

where ΔC_p is the difference in heat capacities of the liquid and glass at T_g. This complies with the fact that ionic glasses like CKN exhibit large ΔC_p at T_g and are quite fragile.

(vii) Rault[10] has recently discussed a more involved fragility expression:

$$F = \frac{T_0}{T^*} \approx 1 - \left(\frac{BR}{E_\beta} \right). \tag{10}$$

Here, $B = (E_\beta/R)[(T - T_0)/nT]$ is obtained from the relaxation time expression, $\tau = \tau_0 \exp \left\lfloor \frac{B}{T - T_0} \right\rfloor$ (temperature dependence) and n from the stretched exponential function (frequency dependence) $\phi(t) = \phi(0) \exp\left[-\left(\frac{t}{\tau}\right)^n \right]$.

(viii) Moynihan[11] related fragility to experimentally observed width of the glass transition as: On the basis of the observation that $E_a(T_g)$ scale with T_g in several glass-forming liquids.

$$F = \frac{E_a}{RT_g} \sim \frac{\Delta T_g}{T_g} = \frac{c\Delta T_g}{T_g}. \tag{11}$$

This relation was used later by Ito, Moynihan and Angell (IMA),[12] who examined the relation between $\Delta T_g/T_g$ and $F_{1/2}^{\mathrm{Relx}}$. A plot of $\Delta T_g/T_g$ vs $F_{1/2}^{\mathrm{Relx}}$ obtained by IMA is represented in Fig. 7. In fact, $\Delta T_g/T_g$ is well represented by the function (the smooth line in Fig. 7).

$$\frac{\Delta T_g}{T_g} = 0.151 \left[\frac{1 - F_{1/2}}{1 + F_{1/2}} \right]. \tag{12}$$

From eqn (12), $F_{1/2}^{\mathrm{Relx}}$ can itself be reformulated as:

$$F_{1/2}^{\mathrm{Relx}} = \left[\frac{0.151 - x}{0.151 + x} \right] \tag{13}$$

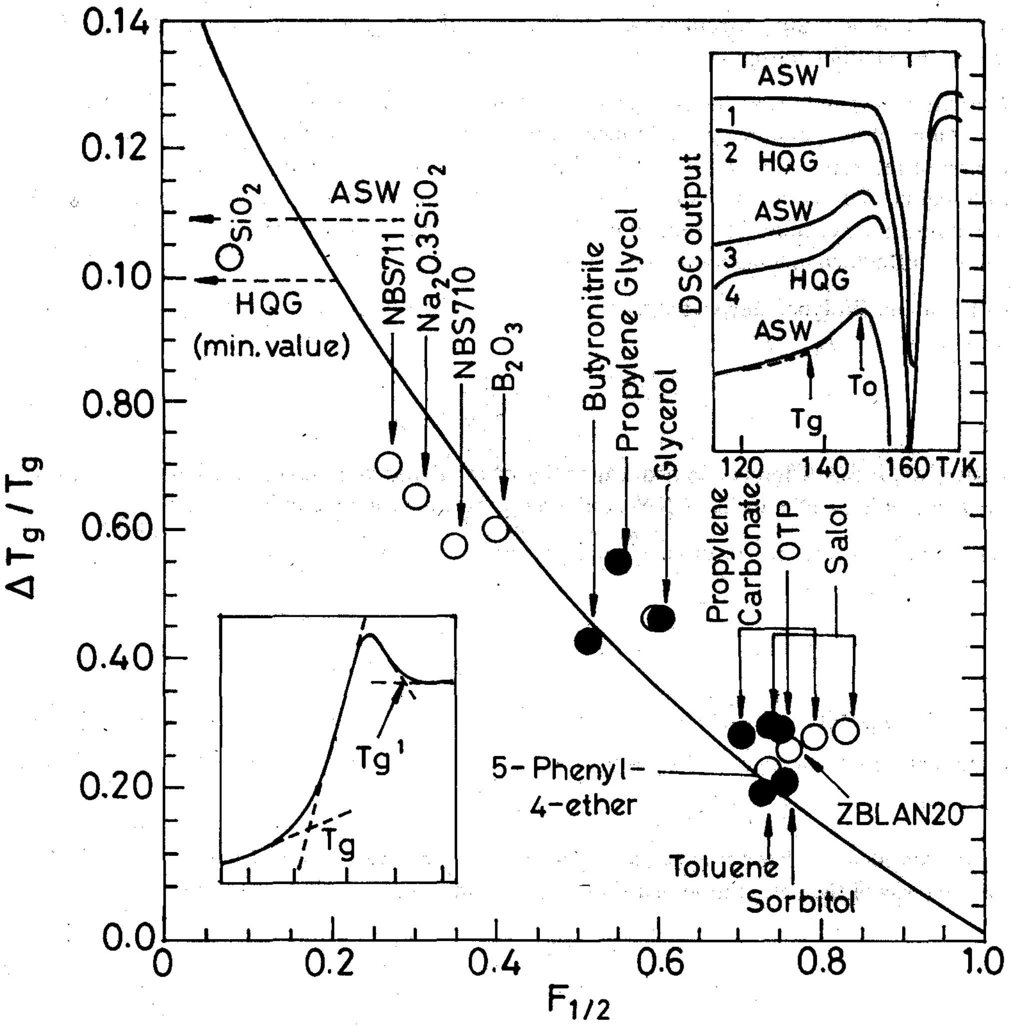

FIG. 7. IMA[12] plot $\Delta T_g/T_g$ vs $F_{1/2}^{\mathrm{Relx}}$. The smooth line is function in eqn (12).

where $x = \Delta T_g/T_g$.

The preceding compilation of fragility definitions is a telling summary of the intensity of the activities in this area. But the most surprising feature is that no effort appears to have been made to relate fragility to the more fundamental quantities, which determine variations in either viscosity or entropy. In order to make progress in this direction, we take note of the following commonly observed features of fragile and strong liquids well established experimentally.

The fragilities of ionic melts such as CKN in general are high while those of highly covalently bonded materials like SiO_2 are low. This implies that fragility is related to the ionicity of bonding. Ionicity of bonding is determined by a $\langle \Delta\chi \rangle^2$ term, where $\Delta\chi = \chi_A - \chi_C$ is the difference in electronegativities of A and C which constitute the anionic (more electronegative) and cationic (less electronegative) elements in the material.[13] Although in terms of total cohesive energy ionic bonding is superior to covalent bonding, it is a long-range interaction and nondirectional. Therefore, its contribution to the local 'grip' between the constituents is rather low compared to the same in a covalently bonded compound. Since fragility is quintessentially breaking apart of the molecular architecture into smaller bits—weaker 'grip' should make them more fragile. These are the locally weak ionic bonds. Such weak local bonds can be simply Van der Waals' type like in *ortho*-terphenyl. When such weak bonds are excited and a loss of 'grip' or resistance to shear occurs, their viscosities rapidly plummet above T_g. It is intuitively obvious that it cannot happen easily in covalently bonded materials.

Whatever the nature of these weaker links, their numbers should also matter. Their numbers determine the distance, r, between them. This parameter should influence the fragility. We anticipate that this r may correspond to the size of the cooperatively rearranging region (CRR), which is known to consist of only a few molecules near T_g. This aspect of CRR near T_g is evident in the work of various authors like Donth[5], Moynihan[11], Rault[10], Hodge[6], Johari[14], Plazek and Ngai[15] and others in recent literature. Cluster model of glass transition,[16] in fact, recognizes the presence of such weak links between small clustered regions, which exist in the glass around T_g. The weak links result from the highly anharmonic potentials in the cluster model.

Therefore, we recognize that there are at least two important physical quantities governed by ionic-covalent bonding in glass-forming liquids, which determine their fragilities. One is the ionicity, which is a $\Delta\chi^2$ term and the other is the inverse of a characteristic distance, r, which represents the size of the eventually broken down constituents of glass structure above T_g.

On a purely heuristic basis we suggest that $\Delta T_g/T_g$ is a function of $\langle \Delta\chi \rangle^2/r$, and for want of deeper insight simply use a scaling relation,

$$\frac{\Delta T_g}{T_g} \sim \frac{\langle \Delta\chi \rangle^2}{r} = c\left(\frac{\langle \Delta\chi \rangle^2}{r}\right) \tag{14}$$

where $\langle \Delta\chi \rangle$ is the compositional weighted average of electronegativity differences of all chemically meaningful pairs in a given glass-forming composition, c a constant of proportionality and is taken as 0.08 on the basis of IMA $F_{1/2}^{\text{Relx}}$ value of SiO_2. We may, therefore, recast the $F_{1/2}^{\text{Relx}}$ fragility relation of IMA in terms of $x' = 0.08\langle \Delta\chi \rangle^2/r$ instead of $x = \Delta T_g/T_g$ so that

$$F'_{1/2} = \left[\frac{0.151 - x'}{0.151 + x'}\right]. \tag{15}$$

We have considered a number of liquids whose $F_{1/2}$ values have been reported by IMA and calculated the x' values. The primary data are presented in Table I. Generally, it is found that r is simply the inter ionic (bond) distance (treating the material as ionic) and is only rarely that a multiple of the nearest neighbour distances is required to be used. For example, in SiO_2, $r = r_{si^{4+}(\text{IV})} + r_{o^{2-}}$, but in B_2O_3, r is the distance from the centre of boroxol ring to the nearest

Table I
Glass compositions, electronegativity differences ($\Delta\chi$), r, x', fragilities ($f_{1/2}$) and $\Delta T_g/T_g$ values

No	System	$\Delta\chi$	r	x'	$F_{1/2}$	$\Delta T_g/T_g$
1	SiO_2	1.54	1.62	0.117	0.13	0.1
2	$0.3\ K_2SO_4 : 0.7\ ZnSO_4$	1.85	4.46	0.061	0.42	0.062
3	$0.225\ K_2SO_4{:}0.075\ Na_2SO_4{:}0.7\ ZnSO_4$	1.84	4.46	0.061	0.43	0.067
4	$0.15\ K_2SO_4{:}\ 0.15\ Na_2SO_4{:}\ 0.7\ ZnSO_4$	1.83	4.46	0.060	0.43	0.066
5	B_2O_3	1.40	2.74	0.057	0.45	0.060
6	$PbO{:}PbF_2$	1.55	3.71	0.052	0.49	0.047
7	$PbO{:}PbCl_2$	1.29	2.77	0.048	0.52	0.065
8	As_2Se_3	2.37	4.54	0.099	0.21	0.105
9	As_2S_3	0.74	1.22	0.036	0.62	–
10	GeO_2	1.43	1.75	0.093	0.24	–
11	BeF_2	2.41	3.92	0.118	0.12	–
12	P_2O_5	1.25	1.53	0.082	0.30	–
13	$0.6Ca(NO_3)_2{:}\ 0.4KNO_3$	1.8	9.14	0.028	0.68	–
14	$0.2Li_2O{:}0.4GeO_2{:}0.4P_2O_5$	2.03	3.48	0.095	0.23	0.072
15	$0.15SnO{:}0.85NaPO_3$	2.06	3.91	0.087	0.27	0.102
16	$NaPO_3$	2.14	3.91	0.094	0.23	0.070
17	$K_2O{:}MoO_3{:}P_2O_5$	2.29	4.51	0.093	0.24	0.060
18	$K_2O{:}WO_3{:}P_2O_5$	2.31	4.52	0.094	0.23	0.076
19	$Pb_2P_2O_7{:}Li_4P_2O_7$	1.69	3.48	0.065	0.40	0.090
20	$Ag_4P_2O_7{:}Li_4P_2O_7$	1.66	3.48	0.063	0.41	0.063
21	$0.2Li_2SO_4{:}0.4Li_2O{:}0.4P_2O_5$	1.94	3.48	0.086	0.27	0.062
22	$0.2Li_2SO_4{:}0.4Li_2O{:}0.4B_2O_3$	2	3.43	0.093	0.24	–
23	$0.2PbO{:}0.4Li_2O{:}0.4B_2O_3$	1.86	4.5	0.061	0.42	–

oxygen outside the ring. Thus, r in B_2O_3 represents the linear dimension of the intermediate range order. Similarly, use of second or third neighbour distances in some chalcogenide glasses is also found necessary to obtain the $F'_{1/2}$ value in good agreement with the $F_{1/2}^{\text{Relx}}$. r seems to be roughly the Donth type of CRR radius in CKN glasses and has been used tentatively in Ta

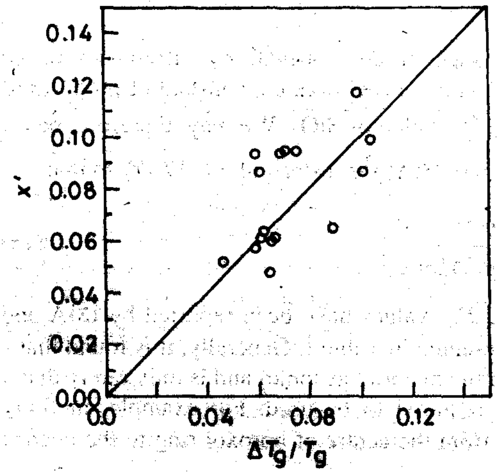

FIG. 8. Comparison between x' and x ($\Delta T_g/T_g$).

ble I without further justification. Table I suggests an agreement between $F_{1/2}$ (IMA) and $F'_{1/2}$ (RBK). A comparison is also made of x and x' in Fig. 8, which also suggests reasonably good correlation.

There is at present no *a priori* theory of fragility. This empirical RBK approach is, therefore, a modest first effort in this direction in search of deeper meaning of fragility. It may be noted that the use of x' (with the use of inter-ionic distance for r as a first guess) and not x, can be readily calculated. Therefore, RBK approach has a predictive capability because x' can be calculated without recourse to other measurements. The form of $F_{1/2}$ function used by IMA has been retained by us for purposes of comparison only. The stress in this work is to emphasize the need to develop $F_{1/2}$ or some other fragility function, which is dependent on quantities other than $\Delta T_g/T_g$. This is because ΔT_g is often dependent on heating and cooling rates employed in the experiments and hence basically unsatisfactory for the present purpose. The present approach stresses the relation of fragility to fundamental quantities like ionicity of bonding. It introduces in an intuitive way a length scale which in some cases is surprisingly similar to the dimensions of CRR. But there is at present significant arbitration in the choice of r. Further work is in progress to evaluate the ideas presented in this paper.

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