

Fragility and thermodynamics in nonpolymeric glass-forming liquids

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For nonpolymeric supercooled liquids, the empirical correlation $m=56T_g\Delta C_p(T_g)/\Delta H_m$ provides a reliable means of correlating dynamic and thermodynamic variables. The dynamics are characterized by the fragility or steepness index m and the glass transition temperature T_g , while thermodynamics enter in terms of the heat capacity step ΔC_p at T_g and the melting enthalpy ΔH_m . The combination of the above correlation with the 2/3 rule for the T_g/T_m ratio yields an expression, $m=40\Delta C_p(T_g)/\Delta S_m$, which was rationalized as the correlation of the thermodynamic and kinetic fragilities. Defining a thermodynamic fragility via $\Delta C_p(T_g)/\Delta S_m$ also reveals that the slopes in Kauzmann's original $\Delta S(T)/\Delta S_m$ versus T/T_m plot reflect the fragility concept [Chem. Rev. **43**, 219 (1948)], so long as $T_m/T_g=1.5$. For the many liquids whose excess heat capacity is a hyperbolic function of temperature, we deduce that the fragility cannot exceed $m=170$, unless the $T_g/T_m=2/3$ rule breaks down. © 2006 American Institute of Physics. [DOI: 10.1063/1.2244551]

I. INTRODUCTION

There has been considerable progress in recent years in understanding both the glass transition phenomenon and the structural relaxation dynamics of supercooled liquids. The concept of fragility categorizes a wide range of liquids in terms of three correlated quantities: the temperature dependence of the average relaxation time $\langle\tau\rangle(T)$, the deviation from exponential decay in the linear response to perturbations from the equilibrium state, and the nonlinearity of that response to thermodynamic perturbations.¹⁻⁴ These correlations have motivated many efforts to explore the origin of the strong-fragile pattern.⁵⁻⁸ The most widely used metric for quantifying fragility is the steepness index m ,

$$m = \left. \frac{d \log_{10} \langle \tau \rangle}{d(T_g/T)} \right|_{T=T_g}, \quad (1)$$

equivalent to the slope in a fragility plot, $\log_{10} \langle \tau \rangle$ vs T_g/T , evaluated at $T=T_g$. The m fragility is often, but not always, correlated with an alternative metric, $F_{1/2}=2(T_g/T_{1/2}-0.5)$, determined at a relaxation time intermediate (on a log scale) between the value of 10^2 s at T_g and the high-temperature limit of 10^{-14} s.⁹ The differences that are found will be of relevance to our findings reported herein; the former is sensitive to any imminent transition (liquid-liquid or ring-chain, for instance), while the latter, $F_{1/2}$, is not.

It has been proposed, controversially, that fragility reflects nontrivial thermodynamic properties. Accordingly, different approaches to dynamic and thermodynamic measures of fragility have been explored and compared.^{5,7,10,11} The initial attempt¹ to relate the thermodynamic aspect to the jump in heat capacity at T_g is clearly incorrect,^{10,12} even when scaled to take account of the number of rearrangeable units per mole of glass former. Alternatives, in which entropy at T_g is made the basis of scaling the increase in entropy at higher temperatures,⁵ are much more successful, but they require more data to implement, and the data are often not available.

A significant simplification was introduced by Wang and Angell,¹³ who used only readily available data to produce a correlation as convincing as any others. They correlated the fragility m with a dimensionless combination of the heat capacity step ΔC_p measured at the glass transition temperature T_g [$\Delta C_p(T_g)=C_p^{\text{liquid}}(T_g)-C_p^{\text{glass}}(T_g)$] and the melting enthalpy ΔH_m . The suggested relation reads

$$m = 56 \frac{T_g \Delta C_p(T_g)}{\Delta H_m}, \quad (2)$$

which has subsequently been derived from the random first-order transition (RFOT) theory,^{14,15} albeit with a factor of 52 instead of 56.^{16,17} In this paper, we will add additional cases of this correlation, provide a detailed description of the development of the equation, and derive an interesting consequence. We will show that Eq. (2) relates straightforwardly to the slopes of the original Kauzmann plots, assessed at T_g rather than at the melting points.

II. MODEL AND RESULTS

Figure 1 represents an updated graph of how the dynamic fragility m correlates with the thermodynamic properties for more than 50 nonpolymeric glass-forming liquids. Table I compiles the data and sources on which Fig. 1 is based. All the data for a given liquid are determined after a careful comparison within various relevant studies. Compared with the previous version of this plot,¹³ more data points have been provided and values have been updated where improved results became available.

The form of Eq. (2) has been initiated by a previous work,¹² where a calorimetric determination of the fragility index uses the relaxation enthalpy difference $\Delta H=H-H_s$ for glasses at fictive temperatures T_f and T_f^s obtained at two different cooling rates, Q and Q_s , respectively. The reference fictive temperature T_f^s is the same, within 0.5 K, as the T_g onset determined by scanning at 20 K/min (after cooling at the same rate). As the cooling rate Q approaches the refer-

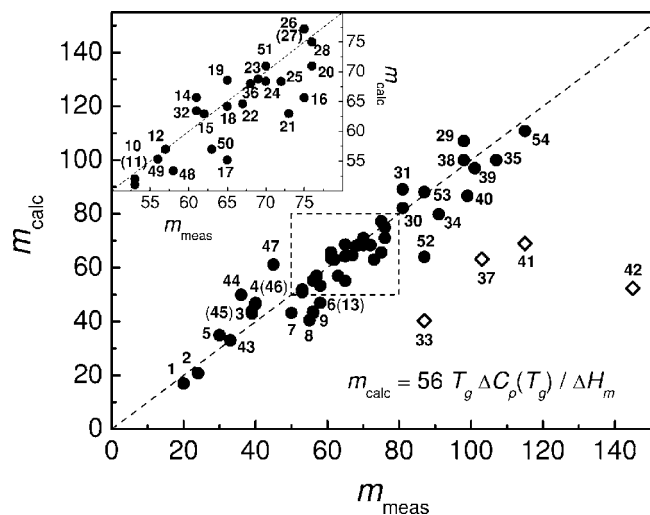


FIG. 1. Correlation of the calculated m_{calc} with the measured m_{meas} fragility index values for the 54 nonpolymeric glass-forming materials of Table I. Data in the $50 < m < 80$ range are also shown in the enlarged inset for clarity. The open diamonds (no. 33, 37, 41, and 42) are explained in the text. The dashed line represents the relation of Eq. (2), $m = 56 T_g \Delta C_p(T_g) / \Delta H_m$.

ence value Q_s , H tends towards H_s and T_f towards T_g^* , while the ratio $\Delta H^* = (H - H_s) / (\log Q - \log Q_s)$ remains constant. Therefore, ΔH^* is exclusively determined by the properties involved in the reference glass transition points: $T_g^* \Delta C_p(T_g) / m = \Delta H^*$. Because the above ratio ΔH^* is an energy-related term, a direct link to other measurable thermodynamic enthalpies is anticipated. Using the enthalpy of fusion ΔH_m and enthalpy of vaporization ΔH_v as trials, it turns out that the ΔH_m far better correlated with $T_g \Delta C_p(T_g) / m$ than ΔH_v . Other correlations between the glass transition properties and the enthalpy of fusion have been explored.¹⁸ Based on a large body of reliable experimental data the quantitative relation $\Delta H_m = 56 \Delta H^*$ is found.

Although Eq. (1) has been established empirically, the majority of data follow the predicted trend very accurately. The deviant points are the ones labeled 33, 37, 41, and 42 in Fig. 1. They correspond to selenium (Se), toluene, triphenylphosphite (TPP), and decalin [decahydronaphthalene (DHN)]. With respect to these four cases, we make the following relevant observations.

Decalin has an extremely high fragility for a molecular system, $m \approx 146$,^{12,19} but its $F_{1/2}$ value is close to that of *o*-terphenyl (OTP) which has a lower fragility, $m = 81$. Figure 1 shows that *o*-terphenyl (31) obeys the rule of Eq. (2) very well. The unusual high fragility of decalin might originate from the typical glass-forming material being a mixture (approximately 50/50) of *cis* and *trans* isomers.²⁰ The pure *cis*-decalin appears to have an intermediate fragility around $m = 60$ – 70 based on the dielectric activation energy of the α process at low temperatures of 141–146 K near its glass transition at 135 K.²¹ TPP is now known to show a transformation, near T_g , from the liquid to the so-called glacial phase,^{22–24} and this is likely to generate such an anomaly. The fragility of Se determined at T_g is quite high $m = 87$, while its $F_{1/2}$ value of 0.54 is very atypical for a fragile liquid.⁵ The anomaly is associated with the onset of a ring-chain equilibrium near T_g which, by introducing a new and

cooperative way of losing entropy, increases the m fragility but not the $T_{1/2}$ value. Therefore, it is not surprising that these liquids do not follow the relation of Eq. (2).

The high fragility of toluene is exceptional in its family since other alkyl-benzenes have significantly lower fragilities, m between 50 and 70.²⁵ Note that the other physical properties of toluene do not show any anomaly compared with those of these derivatives.

The sources of error in Fig. 1 originate mainly from uncertainties in determining the steepness index m and the heat capacity step ΔC_p at T_g . It is well known that various experiments such as viscosity, thermal, mechanical, and dielectric relaxations, and optical and nuclear magnetic resonance techniques lead to somewhat different values of fragility, an effect which becomes more pronounced for high fragility liquids (see the fragility data compilation in Refs. 3, 9, 10, 12, 26, and 27). The present data reflect mean values whenever multiple reliable results were available. Calorimetry results depend on the thermal history of the glasses, and for rapidly quenched glasses $\Delta C_p(T_g)$ will show larger values.²⁸

III. DISCUSSION

To interpret our findings and relate them to Kauzmann's original observations,²⁹ we invoke the well-known empirical relation between melting point and glass temperature ($T_g/T_m = 2/3$), but make the following cautionary observation. The “2/3 rule” is an empirical and approximate relation which can be understood as a consequence of the relation between the minimum crystallization time (the nose of the time-transformation-temperature curve) and the proximity of the melting point to the glass temperature.³⁰ Exceptions to the 2/3 rule exist, but these belong to the extremes of exceptionally good and exceptionally bad glass formers. As long as the glasses considered are those that vitrify on normal cooling rates (do not require hyperquenching or small sample techniques to obtain them), then the T_g/T_m rule applies well, as shown in the Fig. 2 inset.

The line through the points has a slope of 1.45, close to the value of 1.5 expected from the 2/3 law. As observed by Lubchenko and Wolynes in their development of the RFOT theory,¹⁶ combination of this T_m/T_g relation with Eq. (2) immediately yields

$$m = 40 \frac{\Delta C_p(T_g)}{\Delta S_m}, \quad (3)$$

which is demonstrated in Fig. 2, where the dashed line reflects the slope of 1/40. As in Eq. (2), this alternative description of fragility in terms of thermodynamic variables uses the glass-to-liquid heat capacity step $\Delta C_p(T_g)$. One might wonder why in Eq. (3) one variable, ΔS_m , relates to the crystal state, while all others do not. It has been pointed out that the volume density of the effective moving units in liquids might be extracted from the fusion entropy, and hence using the ratio of $\Delta C_p(T_g) / \Delta S_m$ in order to get a universal measure of the liquid configurational entropy.¹⁶ If the excess heat capacity $\Delta C_p^{\text{ex}}(T_g) = C_p^{\text{liquid}}(T_g) - C_p^{\text{crystal}}(T_g)$ were used instead of $\Delta C_p(T_g)$, the numerical factor would increase from

TABLE I. Dynamic and thermodynamic parameters of the 54 glass formers of this study. T_g is the onset glass transition temperature from heat capacity measurements, $\Delta C_p(T_g)$ and $\Delta C_p^{cx}(T_g)$ are the heat capacity differences of supercooled liquids relative to the glassy and crystalline state at T_g , respectively, m_{meas} is the fragility based on a relaxation time at 100 s or a viscosity at 10^{13} P, and ΔH_m and ΔS_m are the enthalpy and entropy of fusion, respectively.

	Materials	T_g (K)	$\Delta C_p(T_g)$ (J/K mol)	$\Delta C_p^{cx}(T_g)$ (J/K mol)	ΔH_m^a (kJ/mol)	m_{meas}	m_{calc}	$\Delta C_p(T_g)/\Delta S_m$	Refs.
1	GeO ₂	810	6.27	...	16.7	20	17	0.51	53 and 3
2	BeF ₂	590	~3	...	4.76	24	21	0.52	54, 55, and 10
3	Methanol	100	30	...	3.85	39 ^{b,c}	43	1.34	56–58
4	<i>n</i> -propanol	96.2	45	55	5.4	40	46	1.25	59 and 60
5	ZnCl ₂	378	17	...	10.24	30 ^c	35	0.98	61 and 3
6	Butyronitrile	97	40	45	5.02	56 ^c	43	1.28	62 and 63
7	Ethylene glycol	151	60	63	11.86	50	43	1.32	64 and 65
8	Ethanol	94	38	45.4	4.93	55	41	1.23	66, 1, and 10
9	<i>m</i> -xylene	125.5	72	79	11.56	56	44	1.40	33
10	Glycerol	190	90	91	18.3	53	52	1.44	12
11	3-bromopentane	106	72	78	8.4	53	51	1.43	67 and 68
12	<i>m</i> -cresol	198.6	54	62	10.57	57	57	1.46	33
13	2-methylpentane	78	68	77	6.26	58	47 ^c	1.30	69 and 58
14	β -D-fructose ^d	286	133	...	32.43	61	66	1.55	70–72
15	Phenolphthalein	363	146	...	47.15	62	63	1.65	71 and 73
16	Indomethacin	318	147	165	39.4	75 ^c	66 ^c	1.61	74 and 75
17	2-methyltetrahydrofuran	91	72	76	6.65	65	55	1.49	67 and 76
18	Hydrochloro-thiazide	385	92.3	...	31	65	64	1.63	77 and 78
19	Griseofulvin	364	127	...	37.75	65	69	1.66	77 and 78
20	1,3,5-tri- α -naphthylbenzene	340	124	145	33.3	76 ^c	71	1.77	79 and 80
21	Diethylphthalate	178	115	...	17.99	73 ^c	63	1.71	81 and 82
22	Probucol	295	139.5	150	35.66	67	65	1.56	83, 77, and 78
23	9-bromophenanthrene	224.8	77	...	14	69	69	1.82	12
24	Phenobarbital	319	106.8	...	27.9	70	68	1.71	77 and 78
25	D-glucose ^d	309	128	144	32.4	72	68	1.66	70, 27, and 72
26	Maltitol ^d	311	243.6	284	55	75	77	1.86	84–86
27	Glibenclamide	331	222.3	...	53.35	75	77	1.88	77 and 78
28	Salol	220	118	121	19.3	76	75	1.93	87 and 12
29	<i>m</i> -toluidine	187	90	91.5	8.8	98 ^c	107	2.55	33 and 88
30	Flopropione	335	127.5	...	29.1	81	82	1.98	77 and 78
31	<i>o</i> -terphenyl	246	112	116	17.2	81	89	2.13	89 and 12
32	α -phenyl-cresol	220	120	128	23.3	61 ^c	63	1.69	90 and 91
33	Selenium	308	14.4	...	6.16	87	40	1.16	92 and 3
34	Triphenylethene	246	117	121	20.35	91	80	1.96	93 and 94
35	Sorbitol ^d	268	201	240	30.2	107 ^c	100 ^c	2.44	83 and 95
36	H ₂ SO ₄ –3H ₂ O	158	186	195	24.22	68 ^c	68	1.82	96–98
37	Toluene	117	64	69.6	6.64	103 ^c	63	1.72	99 and 100
38	Sucrose ^d	345	215	260	41.4	98 ^c	100 ^c	2.44	101, 83, and 102
39	Ca(NO ₃) ₂ –4H ₂ O	217	250	...	31.17	101 ^c	97 ^c	2.54	103 and 104
40	Propylene carbonate	159.5	75.4	77.3	7.77	99	87	2.12	12
41	Triphenyl phosphite	200	155	171	25	115	69	1.83	105 and 106
42	<i>cis</i> -/ <i>trans</i> -decalin	137.4	64	81	9.46	145	52	1.56	12 and 19
43	As ₂ Te ₃	391	84.3	...	55.8	33	33	0.98	107 and 108
44	B ₂ O ₃	536	40	41	24	36	50	1.21	109 and 110
45	2-methyl-1-propanol	107	46	56	6.32	39	44	1.25	111 and 112
46	As ₂ Se ₃	453	75	...	40.76	40	47	1.18	107, 113, and 114
47	<i>m</i> -fluorotoluene	122.5	74	79	8.3	45 ^c	61	1.64	33 and 10
48	Ethylbenzene	115	76	84	9.17	58	53	1.48	99 and 115
49	3-methylpentane	77	68	72	5.3	56	55	1.41	116 and 117
50	<i>n</i> -butene	58	69	76	3.96	63 ^f	57	1.53	118 and 119
51	Isopropylbenzene	124.8	74.6	84.5	7.33	70	71	1.80	120 and 121
52	Xylitol ^d	244	155	...	34	87	62	1.63	122 and 123
53	PMS ^g	167	138	142	14.65	87	88	2.14	124 and 125
54	Li-acetate	401	62.7	...	12.7	115±10	111	2.73	53 and 104

^aDefault values are from National Institute of Standard and Technology (NIST) Chemical book.

^bThe fragility m values are based on the ratio T_0/T_g (see Ref. 58), and might not be stable.

^cData are updated from Ref. 13.

^dThe thermodynamic data of polyols and sugars are quite divergent. The entries chosen for use here are based on their proximity to the averages.

^eThe value is not reliable since there is no low-temperature viscosity or relaxation time data. Our latest dielectric relaxation measurement gives $m=65$ and $T_g=121.1$ K.

^fThe value is re-calculated at $T_g=T(\tau=100$ s) based on original temperature dependence of relaxation time of *n*-butene.

^gPMS is 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane.

40 to 43, but the quality of the correlation would remain unchanged. Therefore, using $\Delta C_p(T_g)$ vs $\Delta C_p^{\text{ex}}(T_g)$ does not affect our present discussion, and we will exploit the equivalence further below. The correlation coefficient of the solid symbols in Fig. 2 is $R=0.94$ (much higher than $R=0.22$ for the correlation between m and T_g), and $\Delta C_p(T_g)/\Delta S_m$ thus predicts m with a standard error of only 7.

It is necessary to discuss the physical meaning of the term $\Delta C_p(T_g)/\Delta S_m$ in Eq. (3). Although mentioned previously,³¹ this term has not yet been associated with dynamics, fragility, and related concepts. In Kauzmann's paper,²⁹ the scaled excess entropies of glasses and liquids are plotted as a function of the reduced temperatures, i.e., $\Delta S(T)/\Delta S_m$ vs T/T_m . This plot can be viewed as the thermodynamic equivalent of the kinetic fragility plot.³² Now, we will show that Eq. (3) quantitatively correlates the thermodynamic and kinetic fragilities. The slope of the $\Delta S(T)/\Delta S_m$ vs T/T_m plot at the glass transition T_g in the supercooled liquid region (not in the glass) can be derived as

$$\left. \frac{d(\Delta S(T)/\Delta S_m)}{d(T/T_m)} \right|_{T=T_g} = \frac{\Delta C_p^{\text{ex}}(T_g) T_m}{\Delta S_m T_g}. \quad (4)$$

It follows that the term $\Delta C_p(T_g)/\Delta S_m$ in Eq. (3), combined with a constant T_m/T_g , determines the slope in the thermodynamic plot of $\Delta S(T)/\Delta S_m$ vs T/T_m evaluated at T_g , when the glass-to-liquid entropy difference is replaced by the excess entropy. It thus appears that the definition of $\Delta C_p(T_g)/\Delta S_m$ as a slope in the thermodynamic plot is very analogous to the definition of the kinetic fragility m . When we define $\Delta C_p(T_g)/\Delta S_m$ as a thermodynamic fragility $m_t = \Delta C_p(T_g)/\Delta S_m$, Eq. (3) provides the quantitative correlation of thermodynamic and kinetic fragilities. The same equation also quantitatively explains the experimental observation of the thermodynamic correlation of kinetic fragilities, shown in Ref. 5, where the $F_{1/2}$ or $F_{3/4}$ values are used to connect them phenomenologically.

The consequence of Eqs. (2) and (3) regarding the kinetic versus thermodynamic manifestations of fragility is shown in Fig. 3, where the inset refers to $\Delta C_p(T_g)/\Delta S_m$ instead of $\Delta C_p(T_g)$. The example curves of this graph are based on a Vogel-Fulcher-Tammann (VFT) temperature dependence with a given fragility m and the fragility-plot constraints $\tau(T \rightarrow \infty) = 10^{-14}$ s and $\tau(T_g) = 100$ s:

$$\log_{10}(\tau/s) = A + \frac{B}{T - T_0} = -14 + \frac{m_{\min}^2}{m(T/T_g - 1) + m_{\min}}, \quad (5)$$

with $m_{\min} = 16$. The inset of Fig. 3 emphasizes the correlation between the scaled temperature dependence of relaxation times, $\tau(T_g/T)$, and the thermodynamic quantity, $\Delta C_p(T)/\Delta S_m$ near T_g . This is an improved plot of thermodynamic and kinetic manifestations of fragility over the original version presented in Ref. 1.

A. Upper bound for fragility of liquids

We will now discuss an interesting implication of Eq. (2). Since at the ideal glass transition temperature or Kauzmann temperature T_K , the excess entropy vanishes, the entropy of fusion can be written as

$$\Delta S_m = \frac{\Delta H_m}{T_m} = \int_{T_K}^{T_m} \frac{\Delta C_p^{\text{ex}}(T)}{T} dT, \quad (6)$$

where $\Delta C_p^{\text{ex}}(T) = C_p^{\text{liquid}}(T) - C_p^{\text{crystal}}(T)$ is the excess heat capacity of the liquid relative to its crystalline counterpart. For a number of glass-forming liquids, $\Delta C_p^{\text{ex}}(T)$ is observed to follow

$$\Delta C_p^{\text{ex}}(T) = \frac{k}{T^n} \quad (7)$$

quite well, where k is a material-specific constant and $0 \leq n \leq 2$. In many organic small molecule systems (especially the low T_g systems), $\Delta C_p^{\text{ex}}(T)$ was found to follow a k/T temperature dependence, i.e., $n=1$ in Eq. (7).³³⁻³⁵ Other cases with $n=0$ and $n=2$ are found to be more accurate in describing the excess heat capacities for some glass formers. The former case ($n=0$) is valid for many strong inorganic liquids such as GeO_2 and As_2Se_3 and moderately strong organic liquids such as glycerol.^{12,36,37} The latter case ($n=2$), although unusual, has been associated with some metallic systems.^{38,39} The $n=2$ case also applies to the heat capacity of the random energy model at constant volume,⁴⁰ but we emphasize that our discussion will not apply to the fragility of liquids under constant volume conditions.

The combination of Eqs. (6) and (7) will be able to predict an upper limit for the fragility of liquids, but the result depends on the choice of function ($n=0, 1$, or 2) for describing the excess heat capacity of liquids. In this study, most of our liquids belong to the category of organic small molecules. Therefore, we will use the $n=1$ case of Eq. (7) to demonstrate the derivation process, and then compare the result with the other two cases, $n=0$ and $n=2$. Using $\Delta C_p^{\text{ex}}(T) = k/T$, the constant k can be determined from $k = T_g \Delta C_p^{\text{ex}}(T_g)$ after setting $T = T_g$. From Eq. (6) and $\Delta C_p^{\text{ex}}(T) = k/T$ we obtain

$$\Delta S_m = \frac{\Delta H_m}{T_m} = \int_{T_K}^{T_m} \frac{\Delta C_p^{\text{ex}}(T)}{T} dT = \int_{T_K}^{T_m} \frac{k}{T^2} dT = \frac{k}{T_K} - \frac{k}{T_m}.$$

After inserting the result for the constant k this leads to

$$T_K = T_m \left(1 + \frac{\Delta H_m}{T_g \Delta C_p^{\text{ex}}(T_g)} \right)^{-1} \geq T_m \left(1 + \frac{\Delta H_m}{T_g \Delta C_p} \right)^{-1}, \quad (8)$$

where the inequality is based on $\Delta C_p(T_g) \leq \Delta C_p^{\text{ex}}(T_g)$.

The above inequality of Eq. (8) bears another interesting relation if combined with the near trivial requirement that $T_g > T_K$. Combining this into the first part of Eq. (8) yields

$$T_g > T_m \frac{m}{m + 56} \quad \text{or} \quad m < 56 \left(\frac{T_m}{T_g} - 1 \right)^{-1}. \quad (9)$$

Evidently, the resulting upper limit of the fragility m is exclusively dependent on the ratio of T_g/T_m . Here, T_m and T_g refer to properties of bulk liquids under standard conditions, where T_g is based on the conventional cooling and heating rates of 10 or 20 K/min. This temperature ratio is material specific and Eq. (9) thus implies an upper bound for m for

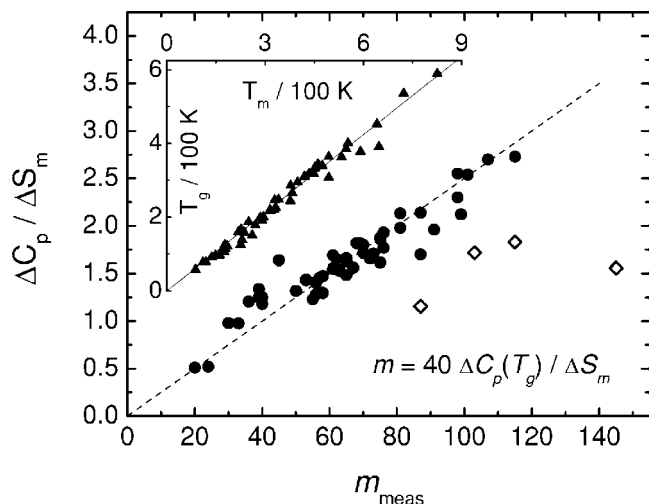


FIG. 2. Correlation of the heat capacity jump to melting entropy ratio $\Delta C_p/\Delta S_m$ with measured m_{meas} fragility index values for the 53 nonpolymeric glass-forming materials of Table I. The open diamonds are explained in the text. The dashed line represents the relation of Eq. (3), $m = 40\Delta C_p(T_g)/\Delta S_m$. The inset shows T_g vs T_m for the set of glass formers, with the line reflecting $T_m/T_g = 1.45$.

individual T_g/T_m values. According to our derivation, applicability of Eq. (9) is limited to materials following the relation of Eq. (2) and the reciprocal temperature dependence $\Delta C_p^{\text{ex}}(T) \propto k/T$. A more universal quantitative statement is obtained by observing that the inequality $T_g/T_m \leq 0.75$ captures practically all data of organic small molecule liquids in the inset of Fig. 2. Examples for reliable experimental data of some high T_g/T_m values in nonpolymeric liquids are *m*-toluidine 0.77, *o*-terphenyl 0.75, and di-*n*-butyl phthalate 0.75. Using 0.75 for the upper bound of the glass transition to melting temperature ratio based on the present set of data, a limit for the fragility index of $m < 170$ is found. The consequence in terms of a fragility plot is included in Fig. 3, suggesting that organic small molecular liquids are not expected to enter the range below the dashed line marked $m = 170$.

When we assume $\Delta C_p^{\text{ex}}(T) = k$ ($n=0$) and $\Delta C_p^{\text{ex}}(T) = k/T^2$ ($n=2$), the upper bound of fragility is calculated to be $m=96$ and $m=192$, respectively. It is evident that $m=96$ cannot be adopted to be the upper limit of fragility since the $n=0$ case applies to strong liquids. For the $n=1$ and $n=2$ modes, it is seen that the bound varies only from $m=170$ ($n=1$) to $m=192$ ($n=2$). It turns out that having used an excess heat capacity of the form of $\Delta C_p^{\text{ex}}(T) = k/T$ in Eq. (7) is not very restrictive regarding the present result when compared with $n=2$ power laws. However, we note that the $n=2$ situation is quite rare, and therefore the $m < 170$ can be used to express the upper limit of fragility for a large number of molecular systems.

An earlier study of the correlation of fragility m and stretching [Kohlrausch-Williams-Watts (KWW)] exponent β_{KWW} revealed a linear relation, $m = 250(\pm 30) - 320\beta_{\text{KWW}}$. This implies an upper limit of fragility of $m = 250$,³ which corresponds to a relaxation time distribution of infinite dispersion with $\beta_{\text{KWW}} \rightarrow 0$. However, it is unlikely that real liquids are able to approach this extreme case beyond β_{KWW}

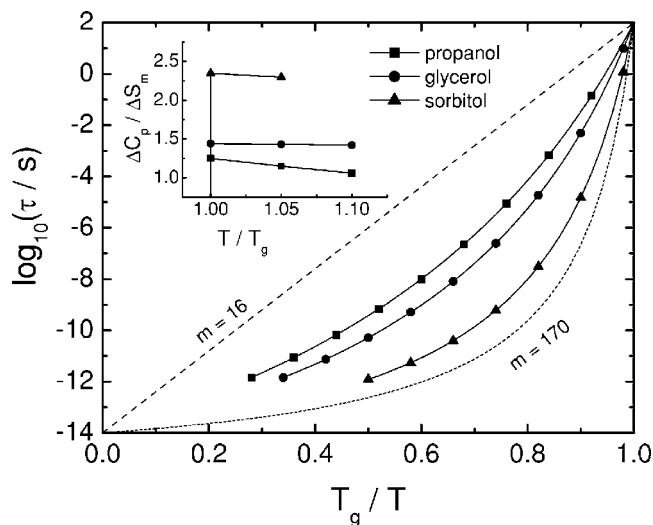


FIG. 3. Fragility plot, $\log(\tau)$ vs T_g/T , for three supercooled liquids [*n*-propanol ($T_g=96$ K, $m=40$), glycerol ($T_g=189$ K, $m=53$), and D-sorbitol ($T_g=266$ K, $m=107$)], which differ significantly in their fragilities. The $\tau(T)$ traces are calculated based on the m values and assuming VFT behavior with a common prefactor parameter of $A=-14$. The dashed lines display the lower and upper bounds for the fragility index, $m=16$ and $m=170$, respectively, as indicated. The inset shows the correlation with $\Delta C_p(T)/\Delta S_m$ evaluated near T_g .

≈ 0.25 . For nonpolymeric systems, very low KWW exponents around 0.3 have been reported, while $\beta_{\text{KWW}}=0.25$ corresponds to $m=170$ on the basis of the above linear $m-\beta$ relation. For the class of nonpolymeric liquids, the highest experimental fragility reported is around 150,^{13,19,41} consistent with our upper bound. A recent molecular dynamic simulation of a pure monoatomic glass former resulted in a value as high as $m \approx 200$.⁴²

It is interesting to observe that several alcohols also obey the present correlations of kinetic and thermodynamic fragilities. In the case of monohydroxy compounds, their dominant dielectric relaxation is a Debye-type peak which is not associated with a calorimetric transition, so that Eq. (3) cannot be applied. However, deriving the kinetic fragility from the true α process restores the correlation with the calorimetric properties.^{43,44}

Finally, note that the implication advanced here are not meant to apply to polymers, plastic crystals, or the liquid fragility scenario under constant volume condition. For the polymers, the fragilities, which may be as high as $m \approx 200$ (polyetherimide: 214,⁴⁵ polyvinyl chloride: 191,¹⁰ and poly(ethylene terephthalate): 156.^{10,46}), are associated with the dynamics of their segmental motion in glass-forming polymers, while thermodynamic data will reflect more global behavior (certainly $T_K \neq T_0$ in general). For plastic crystals, liquidlike dynamics are observed, but the lack of translational modes results in smaller heat capacity jumps relative to regular liquids.⁴⁷⁻⁴⁹ In the case of the fragility under constant volume, the simulation results show that low frequency vibrational modes are stronger at low temperature, and the vibrational entropy of the glasses is highest for the lowest fictive temperature glasses.^{50,51} So, the increase in heat capacity at T_g is much lower than that at constant pressure, but much of the decrease is due to the fact that now the vibrational con-

tribution is going in the opposite direction, which leads to the excess heat capacity being smaller than the configurational one, $C_v^{\text{ex}}(T) < C_v^{\text{conf}}(T)$.⁵² Therefore, the implication suggested in this paper will not apply to theoretical liquids.

IV. CONCLUSIONS

Through a simple equation, the kinetic fragility m of nonpolymeric liquids is correlated to thermodynamic properties involved at glass transition process. It is an empirical expression based on a large body of experimental data; however, a recent theoretical study has regenerated a similar expression with the constant 56 in Eq. (2) replaced by 52. Our results justify viewing the quantity $m_t = \Delta C_p(T_g) / \Delta S_m$ as a thermodynamic gauge for fragility, where $m = 40m_t$ correlated kinetic and thermodynamic fragilities accurately for over 50 nonpolymeric glass-forming materials, which cover a wide range of chemical compositions. The findings also imply that Kauzmann's plot of $\Delta S(T) / \Delta S_m$ vs T/T_m displays slopes which vary systematically with fragility m . An important implication is also derived: for a large class of glass-forming liquids, fragility is bound to an upper limit of $m_{\text{max}} \approx 170$, while excess heat capacities that differ from a k/T behavior and atypical T_g/T_m ratios will modify the numerical result.

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