

# Strong and fragile liquids – a brief critique

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Received 6 December 1994; revised 4 October 1995

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## Abstract

The classification scheme of strong and fragile liquid relaxation behavior introduced by Angell is examined, and the relations between the different fragility parameters are derived and discussed. The relation between fragility and non-linear relaxation behavior within and below the glass transition temperature range is explored. It is suggested that the minimum value of the fragility parameter,  $m$ , is proportional to the quotient of the glassy state activation enthalpy and  $T_g$ , and implications of this interpretation are discussed. It is argued that  $T_g \Delta C_p(T_g)$  is an inappropriate measure of the thermodynamic contribution to the Angell strength parameter,  $D$ , because it contains the kinetic quantity,  $T_g$ .

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## 1. Introduction

The classification of liquids as having different degrees of ‘strong’ and ‘fragile’ behavior has been advocated by Angell [1–8] as a framework for describing relaxation in liquids. In this paper, I collect and discuss the different metrics of fragility, propose alternative interpretations of some observed trends, and suggest a new physical interpretation of the minimum value,  $m_{\min}$ , of the fragility parameter,  $m$ .

Fragile liquids were originally so named because of an inferred rapid breakdown of their configurational structure with increasing temperature near and above the glass transition temperature,  $T_g$ , i.e., the structure is thermally fragile [1]. The structures of strong liquids do not change much with temperature. In this context, configurational structure is associated with the nearest neighbor coordination number and

the intermediate range order lying between the first coordination shell (as defined by the first maximum in the radial distribution function for example), and the long range randomness that defines amorphousness [3]. An immediate consequence of the different temperature dependences of structure is that fragile liquids have large configurational heat capacities, resulting from their configurational entropy changing rapidly with temperature, whereas strong liquids have small configurational heat capacities. More recently, however, fragility has become identified with a non-Arrhenius temperature dependence of the structural relaxation time, using the glass temperature as a scaling factor. This method of classification can be traced to Uhlmann [9] and can also be linked to temperature dependent structures using the concept of potential energy hypersurfaces in configurational space. For the non-Arrhenius definition of fragility, however, not all liquids having large heat capacity change at  $T_g$  are highly fragile (some hydrogen bonded liquids, for example).

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The non-Arrhenius version of fragility is usually discussed [6] in terms of the Vogel–Tammann–Fulcher (VTF) equation [10]:

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right), \quad (1)$$

where  $\tau_0$ ,  $B$ , and  $T_0$  are positive constants. Eq. (1) simplifies to the Arrhenius equation as  $T/T_0 \rightarrow \infty$ , obtained either by  $T \rightarrow \infty$  or  $T_0 \rightarrow 0$ . The high temperature limit is clearly inappropriate near  $T_g$ , and Arrhenius behavior is recovered only in the limit  $T_0 \rightarrow 0$ . This is also evident from the VTF expression for the temperature dependence of the effective activation enthalpy,  $\Delta h_{\text{eff}}$ :

$$\frac{\Delta h_{\text{eff}}}{R} \equiv \frac{d \ln \tau}{d(1/T)} = \frac{B}{(1 - T_0/T)^2}. \quad (2)$$

It has been suggested that  $B$  be expressed as  $DT_0$  [2–5,7,8], so that

$$\tau(T) = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (3)$$

and

$$\frac{\Delta h_{\text{eff}}}{R} = \frac{DT_0}{(1 - T_0/T)^2}. \quad (4)$$

It would appear that Eq. (3) does not converge to the Arrhenius equation in the limit  $T_0 \rightarrow 0$ , but rather to the unphysical result  $\tau = \tau_0$ , resulting from  $DT_0 \rightarrow 0$  noted by Johari [11]. However, it is always observed experimentally that  $B = DT_0$  is non-zero, even in the Arrhenius limit  $T_0 \rightarrow 0$ , and to ensure this (and other consistencies noted later), it is necessary that  $D = B/T_0 \rightarrow \infty$  as  $T_0 \rightarrow 0$ . This pathology must be regarded as a disadvantage of  $D$ .

## 2. Measures of fragility

The VTF equation is not accurate for all materials. This is indicated by the parameter,  $T_0$ , sometimes varying with the temperature range selected for fitting, or by a return to Arrhenius behavior as

$T \rightarrow T_g^{-1}$ . To eliminate the dependence of fragility on the VTF equation, a ‘fragility parameter’,  $m$ , has been defined in terms of the effective activation enthalpy at  $T_g$  [5,6,13],

$$m \equiv \left. \frac{d \log \tau}{d(T_g/T)} \right|_{T=T_g} = \left( \frac{1}{T_g} \right) \left. \frac{d \log \tau}{d(1/T)} \right|_{T=T_g} \\ = \frac{\Delta h_{\text{eff}}(T_g)}{(\ln 10) RT_g}. \quad (5)$$

In terms of the VTF equations,

$$m = \frac{B/T_g}{(\ln 10)(1 - T_0/T_g)^2} \quad (6)$$

$$= \frac{D(T_0/T_g)}{(\ln 10)(1 - T_0/T_g)^2}. \quad (7)$$

The minimum value of  $m$ ,  $m_{\text{min}}$ , is given by [13]

$$m_{\text{min}} \equiv \log\left(\frac{\tau(T_g)}{\tau_0}\right), \quad (8)$$

which for the VTF equations is

$$m_{\text{min}} = \frac{B/T_g}{(\ln 10)(1 - T_0/T_g)} \quad (9)$$

$$= \frac{D(T_0/T_g)}{(\ln 10)(1 - T_0/T_g)}. \quad (10)$$

Eqs. (9) and (10) result from inserting  $T = T_g$  into the VTF Eqs. (1) and (3), respectively [6,13]. If  $\tau_0$  is identified with vibrational lifetimes,  $\sim 10^{-14}$  s, then  $m_{\text{min}} \approx 16$  for all materials if  $\tau(T_g) \approx 10^2$  s [6]. Note that the expressions for  $m$  and  $m_{\text{min}}$  in terms of  $D$  remain non-zero in the Arrhenius limit,  $T_0 \rightarrow 0$ , only when  $D \rightarrow \infty$ , so that  $DT_0 = B$  remains non-zero. The mathematical inconvenience of using  $D$  is again evident.

The scaling parameter for temperature in the non-Arrhenius version of the strong/fragile scheme is  $T_g$ . Since  $T_0/T$  determines in part the departure from Arrhenius behavior, fragility is also a function

<sup>1</sup> The return to Arrhenius behavior could be an artifact. Some high viscosity data obtained near  $T_g$  may be incorrect because the measuring frequency was not low enough to ensure a limiting low frequency (Newtonian) viscosity, i.e., viscoelasticity may not have been properly accounted for. In other cases the shear rate may have been sufficiently high that non-linear viscoelasticity became significant [12].

of  $T_o/T_g$  [3,5,6,13–15]. This ratio conveniently lies between 0 (strong) and 1 (fragile), and the suggestion that it is related to fragility is implicit in an early publication by Donth [16]. Donth observed that smaller values of the complementary function  $1 - T_o/T_g$ , i.e., larger values of  $T_o/T_g$ , correspond to greater values of  $\Delta h^*/RT_g$  and, thus, to greater fragility (although Donth's contribution predates the introduction of the fragility terminology). The ratio,  $T_o/T_g$ , has also been discussed within the context of fragility elsewhere [2,5,6,13], in some cases with the kinetic, VTF  $T_o$ , parameter replaced by the thermodynamic Kauzmann temperature,  $T_K$  (at which the configurational entropy extrapolates to zero). Eqs. (6) and (7) indicate that  $T_o/T_g$  and  $m$  are equivalent measures of fragility.

Elimination of  $B$  between Eqs. (6) and (9), or of  $D$  between Eqs. (7) and (10), yields

$$(1 - T_o/T_g) = \frac{m_{\min}}{m}, \quad (11a)$$

or [5]

$$T_g/T_o = \frac{1}{1 - m_{\min}/m}. \quad (11b)$$

Similarly, elimination of  $T_o/T_g$  between Eqs. (6) and (9), or between Eqs. (7) and (10), yields [13]

$$B = \frac{T_o m_{\min}^2 (\ln 10)}{m - m_{\min}}, \quad (12a)$$

and

$$D = \frac{m_{\min}^2 (\ln 10)}{m - m_{\min}}. \quad (12b)$$

Thus,

$$m = m_{\min} + \frac{T_o m_{\min}^2 (\ln 10)}{B} = m_{\min} + \frac{m_{\min}^2 (\ln 10)}{D}, \quad (12c)$$

$$= 16 + \frac{589.5}{D} = 16 + \frac{589.5T_o}{B} \quad \text{for } m_{\min} = 16. \quad (12d)$$

The inverse relation between  $m$  and  $D$  expressed in Eqs. (12b) and (12d) is plotted in Ref. [6] and is the origin of  $D$  being referred to as a strength parameter. Note again that as  $D \rightarrow \infty$  in the strong (Arrhenius) limit  $T_o \rightarrow 0$ ,  $m \rightarrow m_{\min}$  as it should.

### 3. Configurational heat capacity

The relationship between the non-Arrhenius definition of fragility and the heat capacity change at  $T_g$ ,  $\Delta C_p(T_g)$ , is usually discussed in terms of the Adam–Gibbs theory [17] because this yields an explicit relationship between  $\tau(T)$  and  $\Delta C_p(T_g)$ . Thus, the evolution in meaning of the term ‘fragility’, from that describing a highly temperature dependent configurational structure and large  $\Delta C_p(T_g)$  to that of  $T_g$ -scaled non-Arrhenius behavior, is in large measure predicated on the validity of the Adam–Gibbs theory. For the purpose of discussing the connection between  $\tau(T)$  and  $\Delta C_p(T_g)$  in terms of the Adam–Gibbs theory, it is convenient to express  $\Delta C_p(T)$  by the hyperbolic relations

$$\Delta C_p(T) = \frac{CT_o}{T} = \frac{T_o \Delta C_p(T_o)}{T}, \quad (13)$$

$$= \frac{C'T_g}{T} = \frac{T_g \Delta C_p(T_g)}{T}, \quad (14)$$

$$= \frac{K}{T} = \frac{T_g \Delta C_p(T_g)}{T}, \quad (15)$$

which are good approximations for inorganic and monomeric organic glasses, but tend to overestimate the temperature dependence for organic high polymers [14,15]. The resulting Adam–Gibbs relations [17] between  $\Delta C_p(T)$ ,  $B$  and  $D$ , are

$$B = \frac{N_A s^* \Delta \mu}{k_B \Delta C_p(T_o)} \quad (16)$$

$$= \left( \frac{N_A s^* \Delta \mu}{k_B \Delta C_p(T_g)} \right) \left( \frac{T_o}{T_g} \right), \quad (17)$$

and

$$D = \frac{N_A s^* \Delta \mu}{k_B T_o \Delta C_p(T_o)} \quad (18)$$

$$= \frac{N_A s^* \Delta \mu}{k_B T_g \Delta C_p(T_g)}, \quad (19)$$

where  $N_A$  is Avogadro's number,  $k_B$  is Boltzmann's constant,  $\Delta \mu$  is the activation energy per rearranging

particle, and  $s^*$  is the minimum entropy required for rearrangement (often equated to  $k_B \ln 2$ , but probably larger for polymers [14,15]). The appearance of  $T_0$  in the numerator of Eq. (17), and the implicit assumption that  $K = T_g \Delta C_p(T_g)$  is a material constant, were the original rationales for replacing  $B$  with  $DT_0$  [8].

Eq. (19) has been interpreted in terms of  $D$  having kinetic ( $\Delta\mu$  and  $s^*$ ) and thermodynamic ( $K = T_g \Delta C_p(T_g)$ ) contributions [3,4] (the same factors clearly contribute to  $B$ ). The logical consistency of using  $T_g \Delta C_p(T_g)$  as a thermodynamic measure seems questionable, however, since  $T_g$  is a kinetically determined quantity. This concern is vindicated by analysis of the compilation of  $\Delta C_p(T_g)$ ,  $T_g$ , and  $T_K$  data for 37 non-polymeric materials by Privalko [18]. Such an analysis indicates that  $T_g \Delta C_p(T_g)$  has twice the variability (standard deviation =  $\sigma = 72\%$  of the mean) of that of  $\Delta C_p(T_g)$  alone ( $\sigma = 35\%$ ). This results entirely from the significant range in  $T_g$  for these materials (60–540 K,  $\sigma = 55\%$ ) because the percentage standard deviation for  $T_g \Delta C_p(T_g)$  is essentially that calculated for uncorrelated variabilities in  $\Delta C_p(T_g)$  and  $T_g$ :  $(35^2 + 55^2)^{1/2} = 65\%$ . Thus, when comparing the ‘thermodynamic’ contribution  $T_g \Delta C_p(T_g)$  to  $D$  or  $B$  for different classes of non-polymeric materials, any differences will as likely be due to  $T_g$  as to  $\Delta C_p(T_g)$ <sup>2</sup>. The case against  $T_g \Delta C_p(T_g)$  is more difficult to establish for organic polymers, however, because of their smaller range in  $T_g$  (150–480 K,  $\sigma = 32\%$ ). Regarding  $\Delta C_p(T_K)$  as the thermodynamic factor [14,15] is logically even more satisfactory, but does not appear to have any practical advantage over  $\Delta C_p(T_g)$  because the variability in  $T_K/T_g \approx T_0/T_g$  is much smaller than that in  $\Delta C_p(T_g)$ . It is concluded that, to the extent that the data in Ref. [18] are representative and accurate, there is no objective experimental criterion for choosing between  $\Delta C_p(T_g)$  or  $\Delta C_p(T_0)$  as a measure of the thermodynamic contribution to  $D$  or  $B$ , but that both are preferable to  $T_g \Delta C_p(T_g)$ .

According to the original definition of fragility given in the Introduction,  $\Delta C_p(T_g)$  increases with increasing fragility. This has been discussed by Angell [3,4,19] in terms of the number and depths of the potential energy hypersurface minima in configuration space, described earlier by Gibbs [20] and Goldstein [21]. Another interpretation can be inferred from the correlation between  $\Delta C_p(T_g)$  and  $T_0/T_g$ , and the approximate constancy of the residual entropy at  $T_g$ ,  $S_c(T_g)$  [18]. For the hyperbolic heat capacity relation expressed in Eq. (13), for example,

$$S_c(T_g) = \int_{T_0}^{T_g} \frac{T_0 \Delta C_p(T_0) dT}{T^2} \tag{20}$$

$$= T_0 \Delta C_p(T_0) \left( \frac{1}{T_0} - \frac{1}{T_g} \right) \tag{21}$$

$$= \Delta C_p(T_0) \left( 1 - \frac{T_0}{T_g} \right) \tag{22}$$

$$= \Delta C_p(T_g) \left( \frac{T_g}{T_0} - 1 \right). \tag{23}$$

Eq. (23) demonstrates that  $\Delta C_p(T_g)$  increases with increasing  $T_0/T_g$ , and thus increasing fragility, provided  $S_c(T_g)$  is approximately constant. It has been speculated that this trend in  $\Delta C_p(T_g)$  might also result from  $\Delta C_p(T_0)$  being material invariant [22], so that  $\Delta C_p(T_g) \approx \Delta C_p(T_0)(T_0/T_g) \approx (\text{constant})(T_0/T_g)$ . However, Eq. (22) is inconsistent with both  $\Delta C_p(T_0)$  and  $S_c(T_g)$  being independent of  $T_0/T_g$ . Rather,  $\Delta C_p(T_0)$  can be expected to vary appreciably between materials and, therefore, provide truly thermodynamic information on the relation between the VTF parameters,  $B$  and  $D$ , as a function of material type (assuming again that  $T_0 \approx T_K$ ).

#### 4. Non-linearity

The ratio  $T_0/T_g$  is related to the non-linear relaxation behavior observed in the glass transition temperature range and glassy state [14,15], suggesting that glassy state behavior can be incorporated into the strong/fragile scheme. A relationship between

<sup>2</sup> These estimates could be made more rigorous if analyses of variance were performed. However, such improved estimates would not change the conclusion that the variabilities in  $T_g$  and  $\Delta C_p(T_g)$  make comparable contributions to the variability of  $T_g \Delta C_p(T_g)$ .

non-linearity and fragility is implicit in the non-linear Adam–Gibbs equation, which for the hyperbolic expression for  $\Delta C_p(T)$  is [14,15]

$$\tau(T, T_f) = \tau_0 \exp\left(\frac{B}{T(1 - T_0/T_f)}\right), \quad (24)$$

where the fictive temperature,  $T_f$ , is the temperature at which the value of an observed excess non-equilibrium property would be the equilibrium one. In the equilibrium state above  $T_g$ ,  $T_f = T$  and Eq. (24) reduces to the VTF equation. The value of  $T_f$  frozen in after cooling through the glass transition temperature range,  $T_f'$ , is one measure (and the best [15]) of the glass transition temperature. The glassy-state activation enthalpy is obtained by partial differentiation of  $\tau(T, T_f)$  with respect to  $1/T$  for  $T_f = T_f' = T_g$ :

$$\Delta h_{\text{eff, glass}} = \frac{BR}{1 - T_0/T_g} = m_{\text{min}} RT_g (\ln 10). \quad (25)$$

The non-linear Adam–Gibbs equation, therefore, predicts Arrhenius behavior in the glassy state. As noted above, the same *mathematical* result for  $m_{\text{min}} RT_g (\ln 10)$  in terms of  $B$  and  $T_0/T_g$  (rearrangement of Eq. (9)) is obtained by inserting  $T = T_g$  directly into the VTF equation [6,13]. However, there is a *physical* distinction between these two derivations because the VTF equation refers only to the equilibrium state above  $T_g$ , and cannot admit the interpretation of  $m_{\text{min}}$  as a measure of the non-equilibrium glassy-state activation enthalpy (nor of any other activation enthalpy, since no derivative with respect to  $1/T$  is taken).

Another expression for  $\tau(T, T_f)$  that, despite appearances, is essentially equivalent to Eq. (24)<sup>3</sup> is the Narayanaswamy–Moynihan expression [15,23,24]

$$\tau(T, T_f) = \tau_0 \exp\left(\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right), \quad (26)$$

where  $x$  is a measure of non-linearity. Above  $T_g$ ,  $\Delta h_{\text{eff}}(T_g) = \Delta h^*$  in the equilibrium state and in the

non-equilibrium glassy state where  $T_f$  is constant  $\Delta h_{\text{eff}}(\text{glass}) = x\Delta h^*$ . Eqs. (11) and (24)–(26) yield [14,15]

$$x = \frac{x\Delta h^*(T = T_g)}{\Delta h^*(T = T_g)} = \frac{\Delta h_{\text{eff}}(\text{glass})}{\Delta h_{\text{eff}}(\text{liquid})} = \frac{m_{\text{min}}}{m} \approx (1 - T_0/T_g). \quad (27)$$

According to Eq. (27), the observed range in values of  $x$  (0.11 to 0.70 [15]) corresponds to  $T_0/T_g$  values of 0.30 to 0.89. For  $m_{\text{min}} = 16$ , the corresponding range in  $m$  is 23 to 160, and in  $D$  the range is 4 to 84. The range in  $m$  corresponds closely to that given in [6], but it is difficult to assess the numerical accuracy of Eq. (27) because of uncertainties in the data (particularly in  $x$ ). What evidence there is points to there being a problem with Eq. (27) because the values of  $m$  tabulated in Ref. [6] and those calculated from Eq. (27) using the  $x$  values listed in [15] are in poor agreement for all of the five polymeric and six non-polymeric materials for which both  $m$  and  $x$  are known. It is possible that  $m_{\text{min}}$  does not equal 16 for all materials, but it is inconceivable that it is different by the factor of 2 needed to force agreement with Eq. (27). The discrepancies for the polymers might be associated with  $m$  being obtained from viscoelastic data, which are not very reproducible at low compliances and may also be uncertain for the higher compliances selected from [25]. For the non-polymeric materials, the discrepancies could arise from the activation energies for non-linear enthalpy relaxation being different from those obtained from linear relaxation data (dielectric or mechanical relaxation and light scattering). Such differences can arise from a decoupling of the fundamental enthalpy (structural) relaxation processes from more localized relaxations that may be probed by other techniques [3]. This complication does not arise for two materials for which linear activation enthalpies were obtained from ac calorimetry, but the results for these materials are equivocal. For glycerol, the value of  $m = 53$  tabulated in [6] agrees very well with that calculated from Eq. (27) using the value of  $x$  cited in [15] ( $m = 55$ ). For the fused salt  $\text{K}_3\text{Ca}_2(\text{NO}_3)_7$ , on the other hand, the value of  $m = 93$  calculated from ac calorimetry data is almost twice the value  $m = 52$  calculated from the average

<sup>3</sup> Eq. (26) can be regarded as a non-linear Arrhenius equation. The range in  $T$  and  $T_f$  in the glass transition region is sufficiently small (typically 10 K) that the non-linear Adam–Gibbs equation is well approximated by the Arrhenius analog.

value of  $x$  (0.31). The situation is not improved if the smallest value of  $x$  (0.24) for the three histories studied [26] is used, since this gives a value for  $m$  (67) that is still far outside any reasonable experimental uncertainty in the ac calorimetric value. The numerical accuracy of Eq. (27) remains an open question.

To the extent that the non-linear Adam–Gibbs equation (Eq. (24)) is accurate, the constancy of  $m_{\min}$  associated with constant  $\tau_0$  carries the provocative implication that the glassy-state activation enthalpy is proportional to  $T_g$  for all materials. This can be tested using the compilation of  $T_g$ ,  $\Delta h^*$  and  $x$  data tabulated in Ref. [15]. These data provide no support for  $x\Delta h^*$  being proportional to  $T_g$ . For the 25 materials listed (organic high polymers, inorganic oxides, zirconium–barium–lanthanum–aluminum (ZBLA) fluorides, silver molybdates, and aqueous solutions), the standard deviation in  $x\Delta h^*/RT_g$  (27% of the mean) is the same as that for  $x\Delta h^*/R$  alone (26%). Although enthalpy relaxation parameters have large (and correlated) uncertainties arising from the necessarily intricate phenomenology of non-linear and non-exponential relaxation in the glass transition temperature range, the experimental uncertainty in  $x\Delta h^*$  is less than the individual uncertainties in  $x$  and  $\Delta h^*$  [15]. Thus, the evidence against glassy-state activation energies, being proportional to  $T_g$ , is stronger than might be supposed. However, it cannot yet be considered definitive because the validity of the non-linear Adam–Gibbs equation is not yet firmly established.

## 5. Origins of fragility

Angell has interpreted fragility in terms of the number and depths of minima in the multidimensional potential energy configurational hypersurface [3,19]. Here, we restrict the discussion to a question posed by the issues raised above: what factors determine  $T_0/T_g$ ? Hodge [14,15] and Sethna [27] have suggested that the Adam–Gibbs primary activation energy,  $\Delta\mu$ , determines how close  $T_g$  can get to  $T_0$ . The value of  $\Delta\mu$  has also been used to rationalize the exceptional heat capacities of alcohols referred to above [3]. Hodge explored the consequences of assuming, for simplicity, that  $T_g/T_0$  is a linear func-

tion of  $\Delta\mu$ . His results are discussed below, but first we briefly address the claim [3] that “... [the VTF equation] requires  $T_g/T_0$  to be linearly related to  $D$  ... [if  $\tau_0$  and  $\tau(T_g)$  are fixed]” (italics added). This statement is mathematically indisputable but, as has been argued elsewhere, [15] it could equally well be true that the near constancy of  $\tau(T_g)/\tau_0$  is a *consequence* of the reasonable hypothesis that  $\Delta\mu$  (and, therefore,  $D$  and  $B$ ) determines  $T_g/T_0$  in an approximately linear fashion.

The assumed linear relation between  $T_g/T_0$  and  $\Delta\mu$  can be expressed as

$$B = K_1\Delta\mu = K_2(T_g/T_0 - 1), \quad (28)$$

which produces the desired limit,  $T_g \rightarrow T_0$ , as  $\{B, D, \Delta\mu\} \rightarrow 0$ <sup>4</sup>. From Eq. (16), the proportionality constant,  $K_1$ , is  $N_A s^*/[k_B \Delta C_p(T_0)]$ . Eq. (28) finds experimental support in the linearity of plots of  $B$  as a function of  $T_g/T_0 \approx (1-x)^{-1}$  [14,15]. Separate lines are observed for different types of material (all of which extrapolate to  $T_g/T_0 \rightarrow 1$  as  $B \rightarrow 0$ , however), implying that  $K_2$  is constant only within particular classes of materials. This is consistent with the thermodynamic factor,  $\Delta C_p$ , contributing to  $B$  and  $D$  (Eqs. (16)–(19)). It is also possible that the minimum entropy for rearrangement,  $s^*$ , could vary systematically with material type, particularly if materials are classified by their molecular geometry rather than chemical type. For example, Hodge [14,15] has suggested that  $s^* = k_B(\ln 2^3)$  for polymers, since a minimum of three chain segments with two possible orientations between each are required for small scale rearrangements (the so-called crankshaft motions). Sales [28] has also given an excellent account of the possible effects of coordination geometry in phosphate glasses on the non-linear Adam–Gibbs parameters.

Further insight into the relation between non-linearity and fragility can be gained by applying the approximation,  $x \approx (1 - T_0/T_g) \approx a(T_g/T_0 - 1) + b$ , where  $x$  is the non-linearity parameter of Eq. (26)

<sup>4</sup> As noted in Ref. [14], the limits  $D \rightarrow 0$  and  $B \rightarrow 0$  correspond uniquely to  $\Delta\mu \rightarrow 0$ , because both  $s^*$  and  $\Delta C_p$  are finite and non-zero (with the exception of  $\Delta C_p \sim 0$  for  $\text{SiO}_2$ ).

and  $a$  and  $b$  are constants. For  $0.2 < x < 0.5$  (a range that encompasses most known values), this approximation is accurate to about 15% for  $a = 0.42$  and  $b = 0.1$ , which is adequate for the present discussion. Then, neglecting  $b$  for the moment,

$$B \approx K_2 x \Rightarrow \frac{\Delta h^*}{R} \approx \frac{B}{x^2} \approx \frac{K_2}{x} \quad (29)$$

$$\Rightarrow \frac{x\Delta h^*}{R} \approx K_2. \quad (30)$$

Eq. (30) is consistent with the smaller variability of  $x\Delta h^*$  (standard deviation 26% of the mean) compared with that of  $\Delta h^*$  (56% of the mean). This consistency is unaffected by reintroduction of the constant,  $b$ . Equivalently, Eq. (30) is consistent with the inverse correlation observed between  $x$  and  $\Delta h^*$  [14,15].

These findings provide a molecular level rationalization of the generally observed correlation between  $\Delta C_p(T_g)$  and  $T_o/T_g$  or fragility, discussed in macroscopic terms in Section 3. Consider two materials at the extremes of fragility:  $\text{SiO}_2$  and o-terphenyl. In the very strong liquid,  $\text{SiO}_2$ , the three-dimensional network structure requires the breaking of covalent bonds, and the value of  $\Delta\mu$  is very large, preventing  $T_g$  from approaching  $T_o$  and, therefore, producing small values of  $T_o/T_g$  and  $\Delta C_p(T_g) \approx (T_o/T_g)\Delta C_p(T_o)$  (provided  $\Delta C_p(T_o)$  is not abnormally large). This is observed experimentally for  $\text{SiO}_2$ , for which  $\Delta C_p(T_g)$  is too small to be measured. For the hydrocarbon o-terphenyl, on the other hand, molecular rearrangement requires only the surmounting of non-directional dispersion (van der Waals) energy barriers, and  $\Delta\mu$  can reasonably be expected to be small. Thus, it is predicted that  $T_o/T_g$  and  $\Delta C_p(T_g)$  are larger, consistent with the greater fragility of o-terphenyl. This line of reasoning leads to the result that smaller values of the ‘primary’ activation energy,  $\Delta\mu$ , correspond to larger values of  $\Delta h_{\text{eff}}$  and  $m$ , and vice versa (at least for materials of similar  $T_g$  such as polymers). This apparent paradox arises from  $\Delta h_{\text{eff}}/\Delta\mu \sim \Delta h_{\text{eff}}/B = \Delta h_{\text{eff}}/DT_o$  being an inverse quadratic function of  $(1 - T_o/T_g)$  (Eqs. (5)–(7)), that is stronger than the observed nominally linear proportionality between  $\Delta\mu$  and  $(1 - T_o/T_g)$ .

## 6. Non-exponentiality

Fragile liquids are often (but not always) characterized by broader distributions of relaxation and retardation times, or more non-exponential decay functions, than are strong liquids [6]. This trend can also be rationalized in terms of  $T_o/T_g$  as a measure of fragility, by appealing again to the Adam–Gibbs vision of cooperative relaxation near  $T_g$ . Larger values of the fragility ratio,  $T_o/T_g$ , imply larger cooperatively rearranging groups ( $z^*(T_g) \propto (1 - T_o/T_g)^{-1}$ ) [17], and these larger rearranging groups would be expected to relax in a more cooperative and, therefore, more non-exponential manner. Thus, a positive correlation can be anticipated between  $x$  and the fractional exponent,  $\beta$ , in the ubiquitous fractional exponential expression for the enthalpy retardation decay function,  $\phi(t)$ :

$$\phi(t) = \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right). \quad (31)$$

This expectation is supported by the nearly linear relation between  $\beta$  and  $x^5$  [14] and is broadly consistent with equilibrium relaxation data near  $T_g$  that exhibit an approximately linear relationship between  $\beta$  and  $m = m_{\text{min}}/x$  [6] with negative slope<sup>6</sup>. It seems reasonable that for  $x = 0$ , corresponding to  $T_g/T_o = 1$ , the Adam–Gibbs cooperatively rearranging region would be of macroscopic dimensions and, therefore, relax with an exponent  $\beta \approx 0$ , giving an effectively infinite average relaxation or retardation time ( $\langle \tau \rangle$ ) even when  $\tau$  is finite and non-zero<sup>7</sup>. The limit,  $\beta \rightarrow 0$  as  $T \rightarrow T_o$ , is also consistent with some equilibrium relaxation data [29–32]. For  $x = 1$ , corresponding to  $T_o/T_g \rightarrow 0$ , relaxation is expected to be localized and, therefore, exponential ( $\beta = 1$ ). The simplest relation with these hypothesised boundary conditions is a direct proportionality between  $x$  and  $\beta$  with a proportionality constant near unity, as is observed experimentally.

<sup>5</sup> Two datapoints for high silica glasses, which have exceptionally large values of  $x$  but not unusual values of  $\beta$ , lie off this linear correlation line. These exceptions are discussed in Ref. [15].

<sup>6</sup> The range in  $x$  is sufficiently narrow that inverse functions can be approximated as linear. The important point is that a well-defined positive correlation between  $x$  and  $\beta$  is observed.

<sup>7</sup> This occurs because  $\langle \tau \rangle = (\tau/\beta)\Gamma(1/\beta)$ , where  $\Gamma$  is the gamma function.

