

# Adam–Gibbs formulation of non-linear enthalpy relaxation

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The Adam–Gibbs (AG) expression linking relaxation times with configurational entropy gives a good account of the non-linearity observed in enthalpy relaxation of amorphous polymeric, inorganic, and simple molecular materials near and below  $T_g$ . Data analyses yield zero-entropy temperatures that are comparable with available Kauzmann values. The AG formulation, when coupled with a few plausible ancillary assumptions, predicts correlations between the Arrhenius parameters  $x$ ,  $\Delta h^*$ , and the KWW exponent  $\beta$  that are observed experimentally. It is suggested that the AG primary activation energy,  $\Delta\mu$ , is the single causative factor that generates these correlations.

## 1. Introduction

Relaxation phenomena near and below the glass-transition temperature range are non-exponential and non-linear. Non-exponentially is very common in condensed media, but non-linearity in the glass transition is unusual because it is observed under normal experimental conditions using small temperature perturbations from equilibrium. Its most direct manifestation is the asymmetric approach to equilibrium following positive or negative departures from equilibrium. An important practical consequence is the shortening of relaxation times in the non-equilibrium glassy state relative to the equilibrium glass, that results in appreciable structural relaxation on human time-scale, i.e. annealing occurs. A correct description of non-linearity is therefore essential for the accurate prediction of annealing behavior. The physical origin of non-linearity is also of theoretical interest, and it is this aspect that is addressed here.

Most methods used to describe non-linearity are based on the pioneering work of Tool in 1945 [1], who expressed the relaxation time of an exponentially decaying process as a function of both temperature and departure from equilibrium. It is convenient to express the structural state of a relaxing system in terms of the fictive temperature,  $T_f$ , introduced by Tool and Eichlin as the ‘equilibrium temperature’ in 1924 [2], and defined

by them as the temperature at which the observed value of an intensive property would be the equilibrium one. Thus, the equilibrium state is defined by the condition  $T_f = T$ , and departure from equilibrium is measured by  $T_f - T$ . Annealing is described in terms of the isothermal time dependence of  $T_f$ , and non-linearity is defined by functions that partition the effects of  $T$  and  $T_f$ .

Two empirical expressions for the partitioning function for the average relaxation time are in general use. One, due to Kovacs [3], is used mainly for volume relaxation. The second expression, due to Narayanaswamy [4] and modified by Moynihan et al. [5], has been used mostly for enthalpy relaxation and is the one considered here:

$$\ln \tau(T, T_f) = \ln A + x \Delta h^*/RT + (1 - x) \Delta h^*/RT_f, \quad (1)$$

where  $R$  is the ideal gas constant and  $A$ ,  $x$  and  $\Delta h^*$  are empirical constants. The constant  $\Delta h^*$  is the activation energy in the equilibrium state above  $T_g$ , and  $x \Delta h^*$  is the activation energy in the glassy state at fixed  $T_f = T_f'$ . In the linear region above  $T_g$  the Arrhenius form is only accurate for small temperature ranges, a better fit being provided over wider temperature ranges by the empirical Vogel equation

$$\ln \tau = A + B/(T - T_0), \quad (2)$$

where  $A$ ,  $B$  and  $T_0$  are empirical constants. As is

well known, the Vogel equation is equivalent to the WLF equation, with  $T_0 = T_g - C_2$ . The effective activation energy is

$$\Delta h_{\text{eff}}^*/R = B/(1 - T_0/T)^2 > B. \quad (3)$$

The non-exponentiality of relaxations near structural equilibrium is well described by the Kohlrausch-Williams-Watt equation

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \quad (1 \geq \beta > 0). \quad (4)$$

Enthalpic values of the parameter  $\beta$  are generally weak functions of thermal history, and usually agree with those obtained by dielectric relaxation and other techniques in the linear response region above  $T_g$ , within the typical uncertainty of  $\pm 0.05$ . This is demonstrated in table 1. Equations (1) and (4) have been used by several groups to characterize enthalpy relaxation in polymers [6-13], and in ionic [14-16], covalent [17,18], and simple molecular [18] glasses. The results have been summarized by Hodge [19], and an extended list is shown in table 2. A striking feature of these results is the strong correlation between the parameters  $x$ ,  $\Delta h^*$ , and  $\beta$ . The individual correlations between  $x$  and  $\Delta h^*$ , and  $x$  and  $\beta$ , are shown in figs. 1 and 2, respectively.

The formalism outlined above provides good to excellent descriptions of enthalpy relaxation for a wide variety of materials, although systematic changes in  $x$  are often observed at long annealing times. Although the accuracy of eq. (4) for describing non-exponentiality near equilibrium is well established, the method for generalizing it to non-linear relaxations is not. We use the reduced

Table 2  
Narayanaswamy parameters

Material	$\Delta h^*/R$	$x$	$\beta$	Ref.	
PVAc	71	0.35	0.57	[19]	
	71	0.41	0.51	[6]	
	88	0.27	0.51	[19]	
PVC	225	0.10	0.23	[19]	
BPAPC	150	0.19	0.46	[19]	
aPMMA	138	0.19	0.35	[19]	
	105	0.20	0.38	[13]	
iPMMA	127	0.13	0.30	[24]	
	80	0.22	0.42	[13]	
	82	0.14	0.40	[24]	
sPMMA	115	0.20	0.36	[13]	
	183	0.12	0.33	[24]	
PS	68	0.48	-	[11]	
	75	0.44	0.66	[12]	
	80	0.49	0.74	[8]	
	76.1	0.40	0.63	[10]	
	88.1	0.43	0.53	[10]	
	101	0.42	0.51	[10]	
	110	0.41	0.47	[10]	
	80.5	0.48	0.58	[10]	
	5P4E	38.5	0.40	0.70	[18]
	LiOAc	200	0.17	0.56	[25]
Ca/K NO <sub>3</sub>	70	0.31	0.46	[26]	
B <sub>2</sub> O <sub>3</sub>	45	0.40	0.65	[17]	
As <sub>2</sub> Se <sub>3</sub>	40.9	0.49	0.67	[18]	
NaKSi <sub>2</sub> O <sub>7</sub>	49	0.70	0.66	[16]	
NBS710	73.6	0.44	0.63	[27]	
NBS711	45	0.65	0.65	[28]	
ZBLA	168	0.23	0.43	[29]	
	165	0.19	0.50	[19]	
ZBLALiPb	124	0.23	0.53	[29]	
ZBLALi	132	0.30	0.55	[29]	
ZBLAN	112	0.35	0.56	[29]	
ZBL	184	0.27	0.54	[29]	
BZnYbT	137	0.35	0.48	[29]	

Table 1  
Non-exponentiality parameters  $\beta$  from enthalpy and linear relaxation studies

Material	$\beta$ (enthalpy)	$\beta$ (linear)	Linear technique	Comments
PVC	0.23	~ 0.25	dielectric	
PVAc	0.51	0.55	dielectric	weak $T$ dependence
PMMA	0.35	0.31	dielectric	temp. dependence
PS	0.5-0.7	0.40	dielectric	H range from 4 groups
5P4E	0.70	0.65	stress relax	
B <sub>2</sub> O <sub>3</sub>	0.65	0.60	volume relax	pressure perturbation
		0.83	refractive index	$T$ perturbation
NaKSi <sub>3</sub> O <sub>7</sub>	0.66	0.57	stress relax	

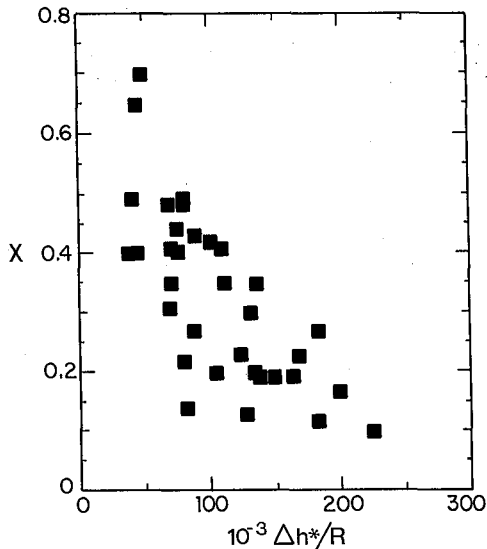


Fig. 1. Correlation between  $x$  and  $\Delta h^*$  for the materials listed in table 2.

time method of Tool–Narayanaswamy, as described by Moynihan et al. [5], but other methods have also been suggested [20]. Here, we focus our attention on the reduced time phenomenology and the non-linearity as expressed in eq. (1). Both the successes and failures of this equation raise a number of issues:

(1) The equation is empirical. Although the Arrhenius equation, of which eq. (1) is a generalization, can be derived from transition state theory, it is not clear how partitioning between  $T$  and  $T_f$  results from this theory.

(2) The values of  $\Delta h^*$  are often far too large to be considered as simple transition state activation energies. They are comparable with the effective activation energies derived from the Vogel equation (eq. (2)), but eq. (1) transforms to the Arrhenius equation above  $T_g$ , not to the Vogel equation. Thus, the physical interpretation of  $\Delta h^*$  is uncertain.

(3) There is no physical interpretation of the empirical partitioning parameter  $x$ .

(4) The correlations between  $\Delta h^*$ ,  $x$  and  $\beta$ , are not understood.

(5) Systematic changes in  $x$  with thermal history are often observed. The value of  $x$  usually increases with increasing annealing times and higher annealing temperatures.

Answers to the first two of these questions are available from the familiar phenomenology of linear relaxation processes above  $T_g$ . First, the Arrhenius equation is adequate over a small temperature range and, since the glass transition extends over only 10 K or so, it is not surprising that the generalized Arrhenius equation embodied in eq. (3) is reasonably accurate. The issue then becomes one of consistency, between the true non-Arrhenius behavior of linear relaxation processes above  $T_g$ , and the rigorously Arrhenius behavior in the glassy state. The second issue, that of the large values of  $\Delta h^*$  above  $T_g$ , has been rationalized in terms of the cooperative motions of many atoms so that the activation energy is shared by a large number of relaxing species. Since non-exponentiality is associated with cooperative behavior, the observed correlation between  $\Delta h^*$  and  $\beta$  is not unexpected, and this was noted when the correlations were first observed [9].

These qualitative arguments can be quantified using the heuristic 1965 entropic theory of Adam and Gibbs [21]. In the present paper, we demonstrate that a natural extension of this theory, together with a few plausible ancillary hypotheses, can resolve the other issues listed above. A pleasing and compelling self-consistency emerges that

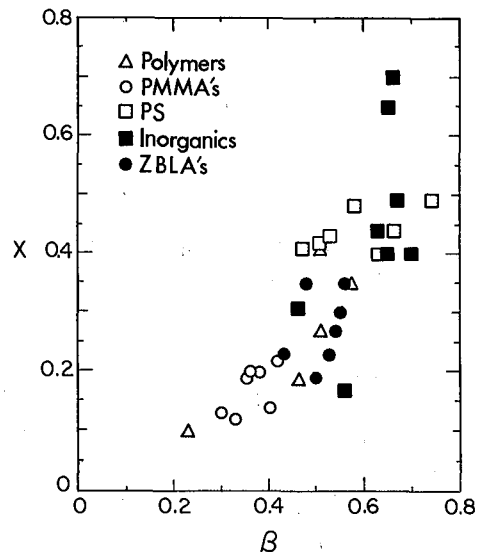


Fig. 2. Correlation between  $x$  and  $\beta$  for the materials listed in table 2.

retains the important connection between kinetic and thermodynamic properties that characterizes the glass transition.

## 2. Adam–Gibbs theory

We first give an abbreviated derivation of the linear form of the Adam–Gibbs equation, and then extend it to the non-linear form that is the focus of this paper. The central idea of the theory is that the number of particles that cooperatively rearrange increases with decreasing temperature, and that the observed activation energy is the product of this number and an elementary energy corresponding to the activation energy per particle (the definition of ‘particle’ is discussed below). The effective activation energy for the relaxation time therefore has a temperature dependence determined by the temperature dependence of the number of cooperatively rearranging species. The observed activation energy,  $\Delta h^*$ , is written as

$$\Delta h^* = z \Delta\mu, \quad (5)$$

where  $\Delta\mu$  is the elementary excitation energy and  $z$  is the number of rearranging particles. It is assumed that only the minimum value of  $z$ ,  $z^*$  contributes to the relaxation time, because processes associated with larger  $z$  values produce exponentially longer average relaxation times that are short circuited by the fastest relaxations (since the groups of  $z$  particles must rearrange independently for the definition of  $z$  to be meaningful). Thus, the problem is transformed to finding the temperature dependence of  $z^*$ . This is given by

$$z^*(T) = N_A s^* / S_c(T), \quad (6)$$

where  $N_A$  is Avogadro’s number,  $s^*$  is the entropy of the minimum number of particles able to rearrange, and  $S_c(T)$  is the macroscopic configurational entropy per mol of particles. Thus, the sought-after temperature dependence of  $z^*$  is determined by the experimentally measurable temperature dependence of the macroscopic entropy  $S_c$ . The transition state theoretical expression for the relaxation time then yields the result

$$\begin{aligned} \tau &= A \exp[z^* \Delta\mu / kT] \\ &= A \exp[N_A s^* \Delta\mu / kT S_c(T)], \end{aligned} \quad (7)$$

where  $k$  is Boltzmann’s constant and the temperature dependence of the pre-exponential has been suppressed because of its weakness relative to the exponential term. The final step is to determine the temperature dependence of  $S_c$ . Formally, this is given by

$$S_c = \int_{T_2}^T \Delta C_p / T \, dT, \quad (8)$$

where  $\Delta C_p$  is the configurational heat capacity and  $T_2$  is the temperature at which  $S_c$  extrapolates to zero. The temperature  $T_2$  is identical to the Kauzmann temperature  $T_K$ .

Assessment of the temperature dependence of  $\Delta C_p(T)$  requires some judgement. It is common to equate  $\Delta C_p$  with the difference between the liquid or rubber and glass heat capacities, on the assumption that this is totally configurational. This assumption has been challenged by Goldstein [22], who suggested that  $\Delta C_p$  has vibrational components and possible contributions from secondary relaxations. The temperature dependence of  $\Delta C_p$  is also uncertain because it must be obtained by extrapolation. Here, we assume that  $\Delta C_p$  is entirely configurational and accept as unavoidable the uncertainties of extrapolation. It is convenient to use the approximate hyperbolic form

$$\Delta C_p(T) = CT_2 / T, \quad (9)$$

where  $C$  is the heat capacity change at  $T_2$ , because this produces the Vogel equation when eq. (9) is inserted into eqs. (7) and (8), with

$$B = N_A s^* \Delta\mu / kC \quad (10)$$

The non-linear extension of eq. (7) was introduced by Scherer [27] who noted that  $S_c$  is determined by  $T_f$  rather than  $T$ , since  $S_c$  includes the excess entropy of the non-equilibrium glassy state. Replacing the upper limit of integration in eq. (8) with  $T_f$ , and using the hyperbolic form for  $\Delta C_p$ , produces the relation [19]

$$\tau = A \exp[B/T(1 - T_2/T_f)], \quad (11)$$

where  $B$  is given by eq. (10). Equation (11) is the desired expression for  $\tau$  as a function of  $T$  and  $T_f$ , and we shall refer to it as the Adam–Gibbs–Vogel (AGV) equation. If  $\Delta C_p$  is assumed constant, then

$$\tau = A \exp[B/T \ln(T_f/T_2)]. \quad (12)$$

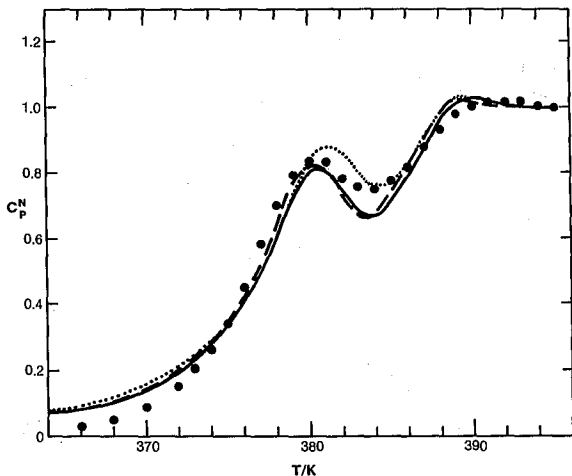


Fig. 3. Fits using eqs. (1) (.....), (11) (—), and (12) (---) to data for atactic PMMA. History: cooling at 40 K  $\text{min}^{-1}$ , annealing for 17 h at 350 K, heating at 10 K  $\text{min}^{-1}$ . See ref. [19] for full details.

This equation was first suggested by Plazek and Magill [30] (using a different notation), and has been referred to as the AGL equation [19] ( $L = \ln(T_f/T_2)$ ).

The parameters of eqs. (1) and (11) can be related to one another by appropriate differentiation with respect to temperature in the equilibrium and glassy states [19]. The results are

$$x \approx (1 - T_2/T_f'), \quad (13)$$

$$\Delta h^*/R \approx B/(1 - T_2/T_f')^2 \approx B/x^2, \quad (14)$$

where  $T_f'$  is the value of  $T_f$  in the glassy state. A result similar to eq. (13) was derived by Macedo and Napolitano [31]. Equations (13) and (14) have been confirmed for polymers [19] by fitting eqs. (1) and (11) to the same data. Equations (1) and (11) give comparable best fits to experimental heat capacity data, exemplified in fig. 3 for atactic PMMA.

### 3. Discussion

Equation (13) indicates that the non-linearity parameter  $x$  is a measure of how close  $T_f'$  is to  $T_2$ , and draws attention to the question of what determines  $T_f'/T_2$ . An intuitively attractive answer is

that the primary activation energy  $\Delta\mu$  determines this ratio, since it seems reasonable that  $\Delta\mu$  determines the barrier to  $T_f'$  approaching  $T_2$ . To assess this hypothesis, it is convenient to simplify the problem and assume that the parameter  $B$  is a direct measure of  $\Delta\mu$ , i.e. that  $C$  and  $s^*$  are relatively constant for different materials. We further assume that  $T_f'/T_2 - 1$  is directly proportional to  $B \sim \Delta\mu$ , which is almost indistinguishable from  $B$  being proportional to  $1 - T_2/T_f' \approx x$ . In this case, eq. (14) predicts that  $\Delta h^*$  is proportional to  $1/x$ , or that  $x \Delta h^*$  is approximately constant:

$$B \approx K_1 \Delta\mu \approx K_2 (T_f'/T_2 - 1) \approx K_2 (1 - T_2/T_f') \approx K_2 x, \quad (15)$$

$$\Delta h^*/R \approx B/x^2 \approx K_2/x. \quad (16)$$

Thus  $x$  and  $\Delta h^*$  are predicted to be inversely correlated, as observed (fig. 1). However,  $x \Delta h^*/R$  is found to be variable because  $K_2$  varies between different classes of material. This is shown in fig. 4.

The values of  $T_2$  obtained from AG analyses of enthalpy relaxation data [19] agree with the Kauzmann temperatures  $T_K$  for some of the materials listed in table 2; this is shown in table 3. With the notable exception of PS, the agreement is within

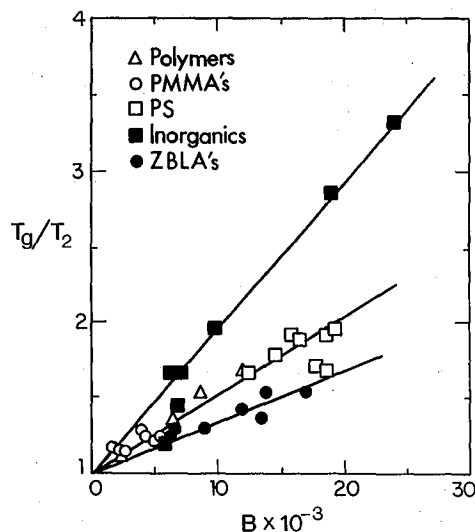


Fig. 4. Plot of the AGF  $B$  parameter as a function of  $T_f'/T_2 = (1 - x)^{-1}$  for the materials listed in table 2.

Table 3  
AGV  $T_2$  and Kauzmann temperatures,  $T_K$

Material	$x$	$T_2$ (K)	$T_K$ (K)	Comments
As <sub>2</sub> Se <sub>3</sub>	0.49	237	236	
B <sub>2</sub> O <sub>3</sub>	0.40	336	335	
PVC	0.10	320	290	$T_K$ uncertain due to thermal and tacticity uncertainties.
a-PMMA	0.19	325	330	$T_K$ for isotactic PMMA shifted by the difference in $T_g$
PS	0.49	210	280	

estimated uncertainties. For PVAc, which does not crystallize, the AG value of  $T_2$  (225 K) is the same within uncertainties as the Vogel  $T_0$  parameter determined from dielectric relaxation data obtained above  $T_g$  (238 K) [19]. The values of  $T_2$  and  $T_0$  also agree for other materials. These results indicate that the AG formulation of non-linearity is consistent with the well-documented relation between the kinetic and thermodynamic aspects of the glass-transition phenomenon.

Values of  $\Delta\mu$  can be estimated from the observed values of  $B$ , but to achieve this two details need to be addressed. First, a definition of what constitutes a 'particle' in the AG theory must be given. For polymers the appropriate moiety would appear to be the 'bead', introduced by Wunderlich. The heat capacity changes per bead at  $T_g$  given by Mathot [23] are used here. It is not clear what the most appropriate definition of a particle is for non-polymeric materials, and we do not discuss them here. A value of  $s^*$  must also be specified. It is defined by  $s^* = k \ln W$ , where  $W$  is the minimum number of beads able to be rearranged. Because the smallest scale non-vibrational motion in polymers is usually the crankshaft motion, involving 3 or 5 backbone segments,  $W$  must be larger than 2. If two rotational states are available to each segment and the crankshaft motion is assumed to involve 3 segments, then  $W = 2^3 = 8$  seems appropriate and  $s^*/k = 2.08$ . Values of  $\Delta\mu$  using this estimate of  $s^*$ , adapted from a recent compilation [19], are given in table 4. They are of the order of rotational energy barriers, consistent with intersegmental motion being the primary relaxation event for polymers.

As indicated above, larger values of  $\Delta h^*$  correspond to larger values of  $z^*$ , more cooperativity, and smaller values of the KWW parameter  $\beta$  (fig. 2). Low values of  $\beta$  are therefore expected to be associated with low values of  $T'_f/T_2$ , since these produce larger values of  $z^*$ , and as  $T'_f/T_2$  approaches unity it is reasonable to suppose that  $\beta$  would approach zero. At the other extreme, as  $T'_f/T_2$  increases to high values and  $z^*$  approaches a limiting low value of 1, relaxation would be simply exponential, i.e.  $\beta = 1$ . An empirical function that satisfies these limiting condition is

$$T'_f/T_2 = (1 - x)^{-1} = (1 - \beta)^{-1} \quad (17)$$

and this relation is observed experimentally. It is of course consistent with the approximate proportionality between  $x$  and  $\beta$  (fig. 2).

The correlations between  $T'_f/T_2$ ,  $\beta$ ,  $\Delta\mu$  and  $\Delta h_{\text{eff}}^*$  are all consistent with the classification of liquids above  $T_g$  into degrees of 'strong' and 'fragile' behavior, proposed by Angell [32]. In this scheme 'strong' materials exhibit Arrhenius temperature dependences with small values of  $\Delta h_{\text{eff}}^*$  near  $T_g$ , and tend to have low values of  $\Delta C_p(T_g)$  and nearly exponential response functions. 'Fragile' liquids exhibit non-Arrhenius behavior and high values of  $\Delta h_{\text{eff}}^*$ , and have large values of  $\Delta C_p(T_g)$  and pronounced non-exponential response functions. The polymers studied here, with the apparent exception of PS, have lower values of  $T'_f/T_2$  and are therefore more non-Arrhenius near  $T_g$ , and have more non-exponential response functions, than the inorganic and simple molecular glasses. Indeed, PVC appears to be the most fragile liquid yet encountered. However, the values of  $\Delta C_p(T_g)$  are not especially large for polymers, and

Table 4  
Estimated values for  $\Delta\mu$

Polymer	No. beads	$\Delta\mu/k$ (kK)
PVAc	4	2.2
PVC	2	1.2
PS	3	6.0
PMMA	3	1.6
	4	1.2
PC	5	4.0
	6	3.3

in contrast with inorganic and simple molecular glasses there is no correlation between  $\Delta C_p$  and either  $T_f'/T_2$  or  $\beta$  for polymers. This may result from their relatively weak temperature dependence for  $\Delta C_p$  (generally lying between the hyperbolic and constant forms), or perhaps to some more fundamental difference in their heat capacity behavior.

The correlations observed here suggest that a single causative factor is determining both the non-linearity and the non-exponentiality of the glass transition. A good candidate is the Adam-Gibbs primary activation energy  $\Delta\mu$ , since this evidently determines  $T_g/T_2$  (see fig. 4) and therefore  $x$  and  $\beta$ , and how non-Arrhenius the AGF equation is for  $T \approx T_f \approx T_g$ . If it is assumed that  $\Delta C_p$  is relatively constant at  $T_2$ , and that it has a negative temperature dependence (not necessarily of the hyperbolic form of eq. (9)), the identification of small  $\Delta C_p$  and strength (high  $T_g/T_2$ ) can also be rationalized. Thus the fact that  $\Delta C_p$  is small for strong silicate liquids can be attributed to the large values of  $\Delta\mu$  and  $T_g/T_2$ . This is also consistent with relatively constant residual entropies at  $T_g$  for different materials. We suggest therefore that the extremes of strong and fragile behavior, defined in terms of  $T_g/T$  in the linear region, arise from variations in  $T_g/T_2$ . Thus the observed correlations between the non-linear relaxation parameters and their consistency with the strong and fragile characteristics in the linear region above  $T_g$  can all be ascribed to the variability of the Adam-Gibbs primary activation energy  $\Delta\mu$ .

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