

ADAM-GIBBS FORMULATION OF NONLINEAR ENTHALPY RELAXATION

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ABSTRACT

The Adam-Gibbs (AG) expression linking relaxation times with configurational entropy gives an excellent account of the nonlinearity 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 , Δh^* , and the KWW exponent β 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 nonexponential and nonlinear. Nonexponentiality is very common in condensed media, but nonlinearity 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 nonequilibrium glassy state relative to the equilibrium glass, that results in appreciable structural relaxation on human timescales, i.e. annealing occurs. A correct description of nonlinearity is therefore essential for the accurate prediction of annealing behavior. The physical origin of nonlinearity is also of theoretical interest, and it is this aspect that is addressed here.

Most methods used to describe nonlinearity 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 nonlinearity 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 [5], has been used mostly for enthalpy relaxation and is the starting point for the present considerations:

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

where R is the ideal gas constant and A , x , and Δh^* are empirical constants. The constant Δh^* is the activation energy in the equilibrium state above T_g , and $x \cdot \Delta h^*$ 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

$$\ln \tau = A + \frac{B}{(T - T_0)} \quad (2)$$

where A , B , and T_0 are empirical constants. The effective activation energy is

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

The nonexponentiality of glassy state relaxations is well described by the Kohlrausch - Williams - Watt equation

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

and is used for all the calculations considered here. Enthalpic values of the parameter β 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 ± 0.05 .

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 1
Narayanaswamy Parameters

Material	$\Delta h^*/R$	x	β	Reference
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
	127	0.13	0.30	21
iPMMA	80	0.22	0.42	13
	82	0.14	0.40	21
sPMMA	115	0.20	0.36	13
	183	0.12	0.33	21
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
	38.5	0.40	0.70	18
5P4E	38.5	0.40	0.70	18
LiOAc	200	0.17	0.56	22
Ca/K NO ₃	70	0.31	0.46	14
B ₂ O ₃	45	0.40	0.65	17
As ₂ Se ₃	40.9	0.49	0.67	18
NaKSi ₂ O ₇	49	0.70	0.66	16
NBS710	73.6	0.44	0.63	23
NBS711	45	0.65	0.65	24
ZBLA	168	0.23	0.43	25
	165	0.19	0.50	19
ZBLALiPb	124	0.23	0.53	25
ZBLALi	132	0.30	0.55	25
ZBLAN	112	0.35	0.56	25
ZBL	184	0.27	0.54	25
BZnYbT	137	0.35	0.48	25

Table 1. A striking feature of these results is the strong correlation between the parameters x , Δh^* , and β . The correlation between x and Δh^* is shown in figure 1.

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. The accuracy of eq. (4) for describing nonexponentiality is well established, and we therefore focus our attention on eq. (1). Both the successes and failures of this equation raise a number of issues:

(1) The equation is empirical, and the partitioning between T and T_f is *ad hoc*.

(2) The values of Δh^* are usually far too large to be considered as simple transition state activation energies.

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

(4) The correlations between Δh^* , x , and β , are not understood.

The second of these issues, that of the large values of Δh^* 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 nonexponentiality is associated with cooperative behavior, this can also rationalize the observed correlation between Δh^* and β [9]. This qualitative argument can be quantified using the heuristic 1965 entropic theory of Adam and Gibbs [20]. In the present paper, we demonstrate that a natural extension of this theory, together with a few plausible ancillary hypotheses, can resolve all the issues listed above. A pleasing and compelling self consistency emerges that 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 nonlinear 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 excitation energy corresponding to the activation energy per particle. 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 effective activation energy, Δh^* , is written as

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

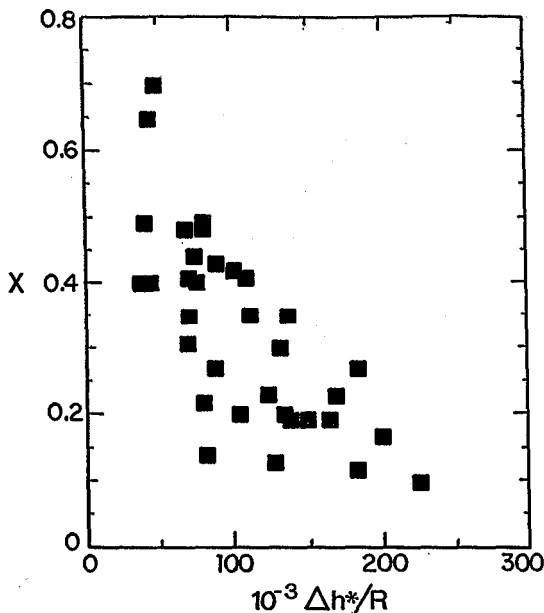


Figure 1.

Correlation between x and Δh^* for the materials listed in Table 1.

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

$$z^*(T) = \frac{N_A \cdot s^*}{S_c(T)} \quad (6)$$

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

$$\begin{aligned}\tau &= A \exp \left[\frac{z^* \Delta \mu}{kT} \right] \\ &= A \exp \left[\frac{N_{AS}^* \Delta \mu}{kT S_c(T)} \right]\end{aligned}\quad (7)$$

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 temperature dependence of S_c is given by

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

where ΔC_p is the configurational heat capacity and T_2 is the temperature at which S_c extrapolates to zero, i.e. the Kauzmann temperature.

For the temperature dependence of $\Delta C_p(T)$ it is convenient to use the approximate hyperbolic form

$$\Delta C_p(T) = \frac{CT_2}{T} \quad (9)$$

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

$$B = \frac{N_{AS}^* \Delta \mu}{kC} \quad (10)$$

The nonlinear extension of eq. (7) is obtained by noting that the nonequilibrium value of S_c is determined by T_f rather than T . This is simply a statement that S_c includes the excess entropy associated with the nonequilibrium glassy state. Replacing the upper limit of integration in eq. (8) with T_f , and using the hyperbolic form for ΔC_p , produces the relation

$$\tau = A \exp \left[\frac{B}{T(1-T_2/T_f)} \right] \quad (11)$$

where B is given by eq. (10). Equation (11) is the desired expression for τ as a function of T and T_f . 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

$$x \approx \left(1 - \frac{T_2}{T_f'}\right) \quad (12)$$

$$\frac{\Delta h^*}{R} \approx \frac{B}{(1 - T_2/T_f')^2} \approx \frac{B}{x^2} \quad (13)$$

where T_f' is the value of T_f in the glassy state. Equations (12) and (13) have been confirmed for polymers [19] by fitting eqs. (1) and (11) to the same data. Equations (1) and (11) also give comparably good best fits to experimental heat capacity data [19].

3. DISCUSSION

Equation (12) indicates that the nonlinearity 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 to suppose that $\Delta\mu$ is 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 simplify the analysis by assuming that B is proportional to $T_f'/T_2 - 1$, which is almost indistinguishable from B being proportional to $1 - T_2/T_f' \approx x$. In this case eq. (13) predicts that Δh^* is proportional to $1/x$, or that $x \cdot \Delta h^*$ is approximately constant:

$$B = K_1 \Delta\mu \approx K_2 \left(\frac{T_f'}{T_2} - 1\right) \approx K_2 \left(1 - \frac{T_2}{T_f'}\right) \approx K_2 x \quad (14)$$

$$\frac{\Delta h^*}{R} \approx \frac{B}{x^2} \approx \frac{K_2}{x} \quad (15)$$

Thus x and Δh^* are predicted to be inversely correlated, as observed (fig. 1). However, $x \cdot \Delta h^*/R$ is found to be variable because K_2 varies between different classes of material. This manifests itself as a series of correlation lines when $T_f'/T_2 = T_g/T_2$ is plotted against B , as shown in fig. 2.

The values of T_2 obtained from AG analyses of enthalpy relaxation data [19] agree with the Kauzmann temperatures T_K for some materials. This is shown in Table 2. With the notable exception of PS the agreement is within 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

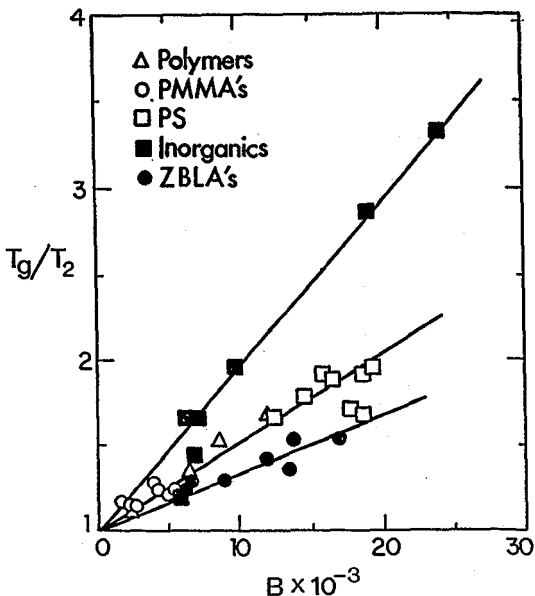


Figure 2.

Plot of the eq. (11) B parameter as a function of $T_f/T_2 \approx (1-x)^{-1}$ for the materials listed in Table 1.

relaxation data obtained above T_g (238 K) [19]. The values of T_2 and T_0 also agree for several other materials. These results indicate that the AG formulation of nonlinearity is consistent with the well-documented relation between the kinetic and thermodynamic aspects of the glass transition phenomenon.

Values for $\Delta\mu$ can be estimated from the observed values of B [19], once a value of s^* is specified. It is defined by $s^* = k \ln W$, where for polymers W is the minimum number of Wunderlich beads able to rearrange. Because the smallest scale nonvibrational 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 3. They are of the order of rotational energy barriers, consistent with intersegmental motion being the primary relaxation event for polymers.

TABLE 2
Adam-Gibbs T_2 and Kauzmann T_K Temperatures

Material	x	T_2	T_K
As ₂ Se ₃	0.49	237	236
B ₂ O ₃	0.40	336	335
PVC	0.10	320	290
aPMMA	0.19	325	330
PS	0.49	210	280

TABLE 3
Estimated Values for $\Delta\mu$

Polymer	No. of 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

As indicated above, larger values of Δh^* correspond to larger values of z^* , more cooperativity, and smaller values of the KWW parameter β . Low values of β are therefore expected to be associated with low values of T_f'/T_2 , since these produce large values of z^* , and as T_f'/T_2 approaches unity it is reasonable to suppose that β would approach zero. At the other extreme, as T_f'/T_2 increases to high values and z^* approaches a limiting low value of unity, relaxation would be simply exponential and $\beta = 1$. An empirical function that satisfies these limiting conditions is

$$\frac{T_f'}{T_2} = \frac{1}{(1-x)} = \frac{1}{(1-\beta)} \quad (16)$$

and this relation is observed experimentally. It is consistent with the approximate proportionality between x and β [7].

The correlations between T_f'/T_2 , β , $\Delta\mu$ and Δh^*_{eff} are all consistent with the classification of liquids above T_g into degrees of "strong" and "fragile" behavior, proposed by Angell [26]. In this scheme "strong" materials exhibit Arrhenius temperature dependences with small values of Δh^*_{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 Δh^*_{eff} , and have large values of $\Delta C_p(T_g)$ and pronounced nonexponential response functions. The polymers studied here, with the apparent exception of PS, have lower values of T_g/T_2 and are therefore more non-Arrhenius near T_g , and have more nonexponential 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 in contrast with inorganic and simple molecular glasses there is no correlation between ΔC_p and either T_f'/T_2 or β for polymers.

The correlations observed here suggest that a single causative factor is determining both the nonlinearity and the nonexponentiality 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. 2) and also therefore x , β , and how non-Arrhenius eq. (11) is for $T \approx T_g$. If it is assumed that ΔC_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 ΔC_p and strength (high T_g/T_2) can also be rationalized. Thus the fact that ΔC_p is small for strong silicate liquids can be attributed to the large values of $\Delta\mu$ and T_g/T_2 . 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 nonlinear 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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