Application of the Adam−Gibbs Equation to the Non-Equilibrium Glassy State

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Received December 1, 1999; Revised Manuscript Received March 21, 2000

ABSTRACT: The Tool−Narayanaswamy−Moynihan (TNM) equation for the temperature (T) and fictive temperature (T_f) dependence of the relaxation time in glassy materials is compared with the usual nonlinear form of the Adam−Gibbs (AG) equation. It is shown that the relationship derived between the Narayanaswamy parameter x and the temperature T_2 at which the configurational entropy reduces to zero, namely $x \approx 1 - T_2/T_f$, leads to unrealistic values of T_2 for many polymer glasses. This problem is resolved by expressing the configurational entropy as a function of both T and T_f, with a partitioning parameter x_s ($0 \le x_s \le 1$) controlling their respective contributions. Comparing TNM with this new nonlinear AG expression incorporating $S_c(T,T_f)$ leads to an explicit relationship between x and x_s involving T, T_2, and T_f, from which a number of predictions may be made. (1) For $T \approx T_f$, i.e., for relaxations close to equilibrium, the quantity $1 - T_2/T_f$ is identified as the *minimum* possible value for x, implying that $T_2 \ge T_f(1 - x)$, by an amount depending on the value of x_s. This resolves the apparently anomalous values of T_2. (2) For relaxations further from equilibrium, the TNM equation with constant x becomes increasingly inappropriate. (3) With increasing annealing temperature and increasing annealing time, the analysis predicts increasing values of x, as has often been reported in the literature. The origin of the dependence of S_c on T and T_f is considered from the theory of Gibbs and DiMarzio, and it is argued that typical values of x observed experimentally may be associated with the freezing-in of only a certain fraction of either flexed bonds and/or vacant lattice sites (holes) at the glass transition. Thus, it is possible to identify x_s, and indirectly x, with the relative contributions of physically meaningful parameters, such as intermolecular and intramolecular bond energies, to the freezing-in process.

1. Introduction

It has been known since the pioneering work of Tool[1−3] over half a century ago that the relaxation kinetics of glasses are determined not only by the thermodynamic temperature (T) but also by the instantaneous structure of the glass, and it was Tool who first introduced the concept of the fictive temperature (T_f) as a means of characterizing this structure. This idea is integral to several theoretical models which are able, often with remarkable success, to describe the response of glasses to thermal treatments in the vicinity of the glass transition temperature, T_g. One such approach which has been widely used is to separate the contributions of T and T_f to the relaxation time(s) τ according to the equation

$$\tau(T,T_f) = \tau_o \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \qquad (1)$$

in which the first term represents the temperature dependence and the second term represents the structure dependence, and Δh^* is the apparent activation energy defining the temperature dependence of τ in equilibrium ($T_f = T$). This equation has come to be known as the Tool[1−3]−Narayanaswamy[4]−Moynihan[5] (TNM) equation after the original contributions of these workers, and introduces the parameter x ($0 \le x \le 1$), most commonly referred to as the nonlinearity or Narayanaswamy parameter, which controls the relative contributions of T and T_f to the relaxation time(s).

Despite the rather wide application of this equation to many polymeric and inorganic glass-forming systems and the reasonable success it has enjoyed in describing experimental data (see, for example, the reviews in refs 6−8), there are a number of criticisms that have been leveled against it. Foremost among these is that the nonlinearity parameter x appears essentially as just a fitting parameter, and therefore it lacks any real physical significance. Likewise, the reduction of eq 1 to an Arrhenius equation in equilibrium is often viewed as a drawback since it is well-known that the temperature dependence is better described by, for example, a Vogel[9]−Tammann[10]−Fulcher[11] (VTF) type expression

$$\tau = A \exp\left(\frac{B}{T - T_2}\right) \qquad (2)$$

where A, B, and T_2 are positive constants for any given glassy system, T_2 being the temperature at which the relaxation time in equilibrium becomes infinite.

In addition to the above criticisms, a more pragmatic assessment of the usefulness of x also reveals some inadequacies in view of the fact that there is often considerable uncertainty in the value of x and that a significant spread of values from different authors is not uncommon (for example, see Table 1 in ref 7). In part this is due to the alternative methods for the evaluation

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10.1021/ma992015r CCC: $19.00

Table 1. Values of T_2 Derived for Several Polymer Glasses as Follows:[a] T_2^a, from Eq 9, Assuming a Hyperbolic Temperature Dependence for ΔC_p; T_2^b, from Eq 11, Assuming ΔC_p = Constant

material	T_g/K	x	T_2^a/K	T_2^b/K	ref
poly(vinyl acetate) (PVAc)	310	0.41	183	155	23
		0.27	226	214	21
poly(styrene) (PS)	373	0.49	190	143	21
		0.46	201	159	24
		0.43	213	175	25
poly(vinyl chloride) (PVC)	353	0.10	318	316	21
		0.27	258	244	26
poly(carbonate) (PC)	415	0.19	336	328	21
		0.46	224	177	27
poly(methyl methacrylate) (PMMA)	375	0.19	304	297	21
		0.20	300	292	28
		0.37	326	208	29
poly(methyl α-*n*-alkyl acrylates) (PMnAA)					
$n = 3$	324	0.35	211	189	30
$n = 5$	296	0.52	142	100	30
$n = 8$	260	0.58	109	65	30
poly(dipropylene terephthalate)	300	0.26	222	211	31
poly(ethylene terephthalate)	350	0.46	189	149	31
poly(propylene terephthalate)	361	0.57	155	96	31
poly(propylene isophthalate)	344	0.61	134	72	31

[a] The calculations are made assuming $T_f' = T_g$.

of x, namely the curve-fitting and peak-shift methods (see ref 7 for a concise discussion and references therein for further details). The former requires the simultaneous determination of a number of parameters, including x and a nonexponentiality parameter β characterizing the breadth of the distribution of relaxation times, whereas the latter evaluates x essentially independently of the distribution of relaxation times. Although x and β are independent parameters of the theory, it is an interesting observation that they appear to be correlated, with small values of x (highly nonlinear relaxation) being associated with small values of β (wide distribution of relaxation times). If indeed there is actually such a correlation, for whatever physical or molecular reason, then the curve-fitting evaluation of x will clearly be sensitive to the distribution of relaxation times. Not only is this a further complication in the interpretation of these results but also the widely observed correlation of x and β has yet to receive a really satisfactory explanation, despite considerable discussion (see ref 7 for example).

An alternative approach to that involving the TNM equation, and one which does not suffer from the aforementioned inadequacies related to the fitting parameter and Arrhenius temperature dependence, is based upon the original analysis of Gibbs and DiMarzio[12] (GDM), who considered the configurational entropy in the glass transition region. This was later developed by Adam and Gibbs[13] (AG) to derive an expression for the temperature dependence of the relaxation time in equilibrium for cooperative relaxation processes in glass-forming liquids, which may be written

$$\tau = A\ \exp\left(\frac{N_A s_c^* \Delta\mu}{kTS_c}\right) \tag{3}$$

where N_A is Avogadro's number, s_c^* is the configurational entropy of the smallest cooperatively rearranging region (CRR) that permits the transition of a molecular segment (for polymer glasses) from one state to another (and simultaneously the only CRR that contributes significantly to τ), $\Delta\mu$ is the elementary activation energy per segment, k is Boltzmann's constant, and S_c is the macroscopic configurational entropy of the sample. If a simple hyperbolic temperature dependence for ΔC_p, the increment in specific heat capacity between the glassy (C_{pg}) and liquidlike (C_{pl}) states, is assumed

$$\Delta C_p = C\frac{T_2}{T} \tag{4}$$

where C is the value of ΔC_p at $T = T_2$, then it can easily be shown[7] that eq 3 reduces to the VTF equation (eq 2) with

$$B = \frac{N_A\ s_c^* \Delta\mu}{kC} \tag{5}$$

It can likewise be shown[7] that if an alternative assumption is made that ΔC_p = constant = C, then the relaxation time is given by an expression quite similar to the VTF equation:

$$\tau = A\ \exp\left[\frac{B}{T\ \ln(T/T_2)}\right] \tag{6}$$

The temperature T_2 at which the relaxation time in the VTF equation becomes infinite is thus identified from the AG model as the Kauzmann temperature, T_K, where the configurational entropy S_c becomes zero. The temperatures T_2 and T_K are formally equal when ΔC_p has a hyperbolic temperature dependence, and they are approximately equal when other reasonable dependences, such as that expressed by ΔC_p = constant, are used. Indeed, several careful experimental studies have been made in the past in order to assess the equivalence of these two temperatures. For this purpose, T_K is evaluated by matching the area between the crystal and the supercooled liquid heat capacity curves to the area representing the combined fusion and solid-state transition energies, while T_2 is derived by fitting the VTF equation to equilibrium viscosity data over a range of temperatures. Thus, for example, Angell and Rao[14] find generally good agreement between T_K and T_2 for several low molecular weight and inorganic glasses, as do Angell and Smith[15] for various polyalcohols, in this latter case evaluating T_2 from VTF fits to both viscosity and dielectric data. More recently, Dixon[16] determined T_K and compared it with T_2, evaluated both from dielectric data and by specific heat spectroscopy, and found T_2 to be some 20 K below T_K. Dixon goes on to suggest that values of T_2 lying typically 5−20 K below T_K is a feature of many glass formers, though given the extrapolation involved in the evaluation of these temperatures this should be regarded as only a small difference.

The situation in polymer glasses is perhaps slightly less clear; values of T_2 and T_K may be found tabulated in refs 7 and 17. Here, however, care must be exercised in selecting the appropriate temperatures for comparison. Although T_2 is defined from an equilibrium temperature dependence of the relaxation time by eq 2 above, it may also be found less directly from nonequilibrium relaxation (usually enthalpy relaxation) data through a relationship (given shortly below as eq 9) between T_2 and the nonlinearity parameter x. This relationship depends on how the fictive temperature influences the configurational entropy in the glassy state, which is the subject of the present paper, and values of T_2 found in this way should therefore be considered in the light of the subsequent discussion in this paper.

Nevertheless, there remains one interesting anomaly from the realm of polymer glasses, namely polystyrene. For this polymer, it appears that reliable equilibrium-derived values of T_2 and T_K are significantly different, and out of the bounds of experimental and extrapolation uncertainties. This was noted some time ago by Miller,[18] who suggested that this may be due to a contribution to ΔC_p, but not to the configurational entropy S_c, from the onset of rotation of the bulky phenyl substituent about its own axis.

In the equations for τ derived according to the AG approach, therefore, there are no arbitrary parameters lacking physical significance, and the temperature dependence is non-Arrhenius. However, thus far the analysis treats only equilibrium conditions. The extension of its application to the nonequilibrium glassy state is usually achieved[7,19,20] by associating the configurational entropy S_c in eq 3 with the fictive temperature T_f

$$\tau(T,T_f) = A \exp\left[\frac{N_A\, s_c^*\, \Delta\mu}{k\, T\, S_c(T_f)}\right] \tag{7}$$

where $S_c(T_f)$ is given by

$$S_c(T_f) = \int_{T_2}^{T_f} \frac{C_p(T)}{T}\, dT \tag{8}$$

and can be evaluated simply for any given assumption about the temperature dependence of ΔC_p.

Hodge, in particular, has examined the equivalence, in a relatively narrow temperature interval around the glass transition, of the TNM expression (eq 1) and the so-called nonlinear AG expression (eq 7), and has derived approximate relationships between their respective parameters.[7,21] For the hyperbolic temperature dependence of ΔC_p given by eq 4, these inter-relationships may be summarized as

$$x \approx 1 - \frac{T_2}{T_f'} \quad \text{or} \quad \frac{T_2}{T_f'} \approx 1 - x \tag{9}$$

and

$$\frac{\Delta h^*}{R} \approx \frac{B}{x^2} \quad \text{or} \quad B \approx x^2 \frac{\Delta h^*}{R} \tag{10}$$

whereas for the case of ΔC_p = constant they become

$$\ln\left(\frac{T_f'}{T_2}\right) \approx \frac{x}{1 - x} \tag{11}$$

and

$$B \approx \frac{x^2}{1 - x} \frac{\Delta h^*}{R} \tag{12}$$

In these equations, eqs 9–12, relating the TNM and AG parameters, T_f' is the fictive temperature at which the glass is frozen in on cooling at an arbitrary rate. This is, of course, the same as the glass transition temperature, T_g.

The AG approach seems, therefore, to have much to commend it, and to have the additional advantage that it allows, through the inter-relationships above, an interpretation of the parameters of the TNM equation to be made. It is Hodge, again, who has examined this in some detail, and recently reviewed some of these ideas.[17] However, we believe that there are a number of inconsistencies introduced by the manner in which the nonlinearity has been included in eq 7, in other words by the assumption that $S_c(T_f)$ is a function only of the fictive temperature. For example, the values of T_2 = 180, 210, or 260 K found, variously, for polystyrene[17,21] are much lower than the WLF value of $T_g - C_2{}^g$ = 321.4 K obtained using T_g = 373 K and $C_2{}^g$ = 51.6 K, the "universal" constant.[22] Indeed, this discrepancy between the values of T_2 found from eq 9 and from the WLF equation increases as the Narayanaswamy parameter x increases, leading ultimately to quite unrealistic values for T_2, which are summarized in Table 1. Conversely, when realistic values for T_2 are obtained, the Narayanaswamy parameter x appears to be too small [≤ 0.2, e.g. for poly(vinyl chloride), poly(carbonate), and poly(methyl methacrylate)[21]] to be consistent with, for example, the KAHR model,[32–34] as will be shown below. We propose to show in the present paper that a small modification to the way in which the fictive temperature dependence, in other words the nonlinearity, is introduced into the AG equation removes these discrepancies, rationalizes their observation, and allows a more meaningful interpretation of the Narayanaswamy parameter x to be made.

2. Configurational Entropy

A concept that has gained increasing acceptance in the domain of glass-forming systems is that of fragility, first proposed by Angell[35] some years ago. Since then, attempts have been made to associate the Narayanaswamy parameter x with the fragility of glass-formers, with small values of x being correlated with fragile liquids and a highly nonlinear dependence of ln τ on reciprocal temperature.[29,36,37] Thus, from eqs 9 and 11, this argument would associate fragile liquids with values of T_2 rather close to T_f'. The values presented in Table 1 clearly show that for many of the polymers T_2 is very much lower than T_f', often by about 100 K and sometimes by as much as 150 K or even 200 K. Inasmuch as the difference between T_f' (or T_g) and T_2, or alternatively the ratio T_2/T_g, determines where a glass-former lies within the strong-fragile spectrum, with small differences and ratios close to unity indicative of greater fragility, it would appear that this analysis ranks these polymers as being rather strong glass-formers; this is contrary to the usual perception that most polymers lie toward the fragile limit of the spectrum.

An alternative viewpoint, however, may be gained by a closer examination of the fictive temperature dependence of the configurational entropy in eq 7. If S_c in the nonequilibrium glassy state were not, in fact, dependent entirely on T_f, then the assumption of $S_c(T_f)$ in eq 7 would automatically introduce too much nonlinearity, or in other words too much fragility. To compensate for this excessive nonlinearity inherent in the theoretical assumption of S_c (T_f), the values of T_2 obtained from experimental data (via the parameter x) are driven to lower temperatures and hence imply reduced fragility. These ideas are developed in the analysis that follows.

Consider the variation of the configurational entropy as a glass-forming liquid is cooled at a constant rate,

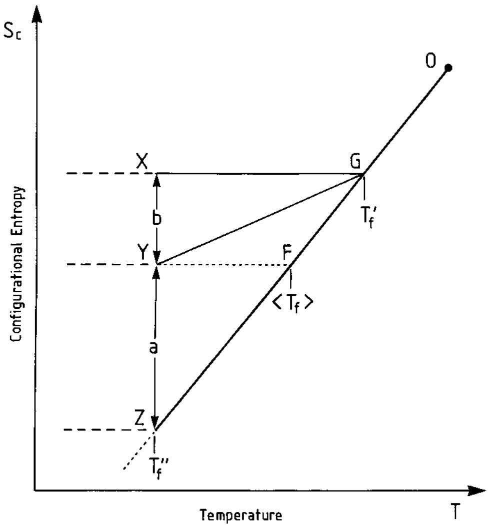

Figure 1. Schematic illustration of the variation of configurational entropy with temperature on cooling at an arbitrary constant rate. Path OGZ represents the equilibrium liquid line. Path GX represents the complete freezing-in of the configurational entropy at temperature T_f' on cooling; path GY represents the partial freezing-in according to eq 13, leading to state Y with an average fictive temperature $<T_f>$.

as illustrated schematically in Figure 1. At a certain temperature, namely the glass transition temperature T_g or the fictive temperature T_f', both of which are dependent on the cooling rate, conventional wisdom has it that the configurational entropy is frozen in at its value at T_f', denoted by $S_c(T_f')$, following the line OGX on further cooling. However, in the light of the discussion immediately above, let us suppose instead that, on reaching the temperature T_f' during cooling, the configurational entropy is not completely frozen in, but is only partially frozen in, following the line OGY. Had this freezing in process, either total or partial, not occurred, for example for an infinitely slow cooling rate, then the configurational entropy would have followed the equilibrium line OGZ. Thus, in the temperature interval between points G and Y in Figure 1, the configurational entropy is a function of both temperature T and fictive temperature T_f'. We may partition their relative contributions as

$$S_c(T,T_f') = x_s S_c(T) + (1 - x_s) S_c(T_f') \tag{13}$$

where x_s ($0 \leq x_s \leq 1$) is an entropic nonlinearity parameter analogous to the Narayanaswamy parameter x, and $S_c(T)$ and $S_c(T_f')$ are given by the appropriate integrals as in eq 8.

The physical meaning of the path OGY may be understood as follows, where a limiting condition is considered. Suppose the glass transformation is governed by two quite separate processes, one being a slow process, with a glass transition temperature at T_f', and the other being a much faster process, with a glass transition temperature much lower, at T_f''. Between T_f' and T_f'', the configurational entropy will therefore follow a path determined by the relative proportions of the slow and fast processes, lying somewhere between all slow processes ($x_s = 0$) and all fast processes ($x_s = 1$). The assumption of a linear temperature dependence for the configurational entropy in equilibrium means that we can identify x_s from the schematic illustration in Figure 1 as

$$x_s = \frac{b}{a+b}; \quad 1 - x_s = \frac{a}{a+b} \tag{14}$$

where a and b are the configurational entropy differences between states Y and Z, and between states X and Y, respectively.

Of course, such a limiting condition of two separate processes with widely different fictive temperatures is unrealistic. However, it is mathematically convenient, as it allows a derivation of a relationship between the entropic nonlinearity parameter x_s and the usual Narayanaswamy nonlinearity parameter x, as will be shown shortly (see section 3 below). More realistically, there will be a distribution of fictive temperatures corresponding to the distribution of relaxation times characterizing the relaxation process, with the long time end of the distribution freezing in at T_f', the short time end of the distribution freezing in at T_f'', and all the intermediate processes freezing in at temperatures between T_f' and T_f''. For a distribution that is 8 decades wide, for example, and for an apparent activation energy $\Delta h^* = 650$ kJ mol^{-1}, typical of glassy polymers, with $T_f' = 373$ K, then T_f'' would appear more than 30 K below T_f'. For a wider distribution and/or a smaller apparent activation energy, T_f'' would appear even further below T_f'. Thus, a significant distribution of fictive temperatures of width 30 K or greater is perfectly reasonable.

Indeed, a model for the glass transition in which the glassy state is characterized by a broad distribution of fictive temperatures was proposed several years ago by Rekhson.[38] Using a discrete distribution of 54 separate mechanisms covering almost 7 decades of time, for example, Rekhson modeled the behavior of an inorganic glass cooled slowly or quenched from an equilibrium liquid state. For the glass cooled slowly at 3 K min^{-1} to room temperature, for example, the average fictive temperature of 784 K was bounded by extremes of 627 and 824 K for the fastest and slowest processes, respectively, representing a fictive temperature range of nearly 200 K. The concept of a distribution of fictive temperatures is not new, therefore; what does appear new, though, is its introduction into the configurational entropy in the nonequilibrium state, expressed in simplified form through eq 13. Thus, we can consider the path OGY in Figure 1 to represent the *average* configurational entropy of a system with a distribution of relaxation times, and a corresponding distribution of fictive temperatures, with this average being characterized quantitatively through the entropic nonlinearity parameter x_s.

Clearly, the average configurational entropy cannot continue without limit to decrease with temperature, following the gradient defined by GY in Figure 1, otherwise the catastrophe corresponding to the Kauzmann temperature would be encountered. Accordingly we assume here that, on cooling further below T_f'', where the last (fastest) process has frozen in, the configurational entropy of all processes, and hence also the average configurational entropy, remains constant. This is indicated in Figure 1 by the horizontal dashed lines. In the analysis that follows, therefore, we confine ourselves to the temperature region between T_f'' and T_f', which may, as we have already seen, represent as much as 30 K or more below the glass transition temperature T_g. This is a typical temperature interval within which enthalpy relaxation studies are frequently made, and is therefore of particular interest in the present context.

It may appear at first sight that there is some inconsistency between eq 13, the usual definition of fictive temperature, and the meaning of the configurational entropy. At constant fictive temperature T_f', such as would occur during an ideal instantaneous temperature jump from state G in Figure 1, for example, the configurational entropy should remain constant, apparently in contradiction with the idea that S_c depends on both T and T_f'. However, it should be recalled that eq 13 describes the dependence of $S_c(T, T_f')$ during cooling at constant rate. An instantaneous temperature jump from equilibrium at T_f' to the temperature T_f'' would follow GX, displacing both slow and fast processes from equilibrium. In the time corresponding to whatever cooling rate defines path OGY, the fast processes will relax to equilibrium, with their fictive temperature T_f'' such that the average configurational entropy is defined by state Y.

Likewise, an instantaneous temperature jump from state Y to the equilibrium line will follow path YF, defining the average fictive temperature at state Y as $\langle T_f \rangle$, situated between T_f'' and T_f' in the same relative position as Y is situated between Z and X, assuming a linear equilibrium dependence of configurational entropy on temperature.

Having reached state Y on cooling at constant rate (or more generally having reached any intermediate state between G and Y), isothermal recovery will cause the configurational entropy to decrease from that of state Y toward equilibrium at state Z, by virtue of a decrease in T_f' as the slow processes are activated, and hence also with a corresponding decrease in the average fictive temperature from $\langle T_f \rangle$ toward T_f''. At any temperature T above T_f'' therefore, the configurational entropy of any state may be expressed by eq 13 in which T_f' is replaced by T_f, the instantaneous fictive temperature of the slowest processes. The implications of this new expression for the configurational entropy will now be considered in respect of the parameter correlations such as those derived earlier in eqs 9 to 12.

3. New Parameter Correlations

We adopt the same approach as was used earlier to derive the inter-relationships given in eqs 9–12, using as a starting point the temperature and structure (configurational entropy) dependence of the relaxation time given by the AG equation (eq 3), in which the configurational entropy S_c is replaced by the expression in eq 13, with T_f' replaced by T_f for the reasons explained immediately above

$$\tau(T,T_f) = A \exp\left[\frac{N_A s_c^* \Delta\mu}{kT\{x_s S_c(T) + (1 - x_s) S_c(T_f)\}}\right] \tag{15}$$

First, in equilibrium, when $T_f = T$, we can differentiate eq 15 to obtain

$$\left.\frac{\partial(\ln \tau)}{\partial\left(\frac{1}{T}\right)}\right|_{T=T_f\ \text{equilibrium}} = \frac{N_A s_c^* \Delta\mu}{k S_c(T_f)} + \frac{N_A s_c^* \Delta\mu}{k T_f [S_c(T_f)]^2} T_f^{\,2} \left.\frac{\partial S_c(T)}{\partial T}\right|_{T=T_f} \tag{16}$$

where $\partial S_c(T)/\partial T$ at $T = T_f$ is found from the equivalent of eq 8 to be $\Delta C_p(T_f)/T_f$. Hence

$$\left.\frac{\partial(\ln \tau)}{\partial\left(\frac{1}{T}\right)}\right|_{T=T_f\ \text{equilibrium}} = \frac{N_A s_c^* \Delta\mu}{k S_c(T_f)}\left[1 + \frac{\Delta C_p(T_f)}{S_c(T_f)}\right] \tag{17}$$

Similarly, at constant T, we can differentiate eq 15 to obtain

$$\left.\frac{\partial(\ln \tau)}{\partial\left(\frac{1}{T_f}\right)}\right|_T = \frac{N_A s_c^* \Delta\mu}{kT[S_c(T,T_f)]^2} T_f^{\,2} \left.\frac{\partial S_c(T,T_f)}{\partial T_f}\right|_T \tag{18}$$

where $\partial S_c(T, T_f)/\partial T_f$ is found from eqs 8 and 13 to be $(1 - x_s)\,\Delta C_p(T_f)/T_f$. Hence

$$\left.\frac{\partial(\ln \tau)}{\partial\left(\frac{1}{T_f}\right)}\right|_T = \frac{N_A s_c^* \Delta\mu}{k S_c(T,T_f)}(1 - x_s)\frac{T_f \Delta C_p(T_f)}{T\, S_c(T,T_f)} \tag{19}$$

Comparing eqs 17 and 19 with the equivalent dependences from TNM, which are

$$\left.\frac{\partial(\ln \tau)}{\partial\left(\frac{1}{T}\right)}\right|_{T=T_f\ \text{equilibrium}} = \frac{\Delta h^*}{R} \tag{20}$$

and

$$\left.\frac{\partial(\ln \tau)}{\partial\left(\frac{1}{T_f}\right)}\right|_T = (1 - x)\frac{\Delta h^*}{R} \tag{21}$$

we find

$$1 - x = (1 - x_s)\frac{T_f\ S_c(T_f)}{T\, S_c(T,T_f)}\ \frac{\Delta C_p(T_f)/S_c(T,T_f)}{1 + \Delta C_p(T_f)/S_c(T_f)} \tag{22}$$

Assuming the hyperbolic temperature dependence for ΔC_p given in eq 4, this becomes

$$\frac{1 - x_s}{1 - x} = \frac{T}{T_2}\left[1 - x_s\frac{T_2(T_f - T)}{T(T_f - T_2)}\right]^2 \tag{23}$$

or, for ΔC_p = constant, it becomes

$$\frac{1 - x_s}{1 - x} = \frac{T}{T_2}\left[1 + \ln\left(\frac{T_f}{T_2}\right)\right]\left[1 - x_s\frac{\ln(T_f/T)}{\ln(T_f/T_2)}\right]^2 \tag{24}$$

Thus, we can see that the entropic nonlinearity parameter x_s and the TNM parameter x are related, and they depend also in a rather complex way, to be discussed further (see below), on the temperature T_2 (equivalent to the Kauzmann temperature T_K) and the fictive temperature T_f. If we consider, for the present, relaxation close to equilibrium, then we can make the approximation $T \approx T_f$, and eqs 23 and 24 simplify to

$$1 - x_s \approx (1 - x)\frac{T_f}{T_2} \tag{25}$$

and

$$1 - x_s \approx (1 - x)[1 + \ln(T_f/T_2)] \tag{26}$$

respectively. Now, the minimum value of x_s in eq 13 is zero, and hence the minimum value of x is found as

$$x_{\min} \approx 1 - \frac{T_2}{T_f} \tag{27}$$

from eq 25, or

$$x_{\min} \approx \frac{\ln(T_f/T_2)}{1 + \ln(T_f/T_2)} \tag{28}$$

from eq 24. Thus, it can be seen that, for this approximation, i.e., for temperatures close to the fictive or glass transition temperature, the inter-relationships expressed by eqs 9 and 11 now, in fact, represent the *minimum* possible values for x. Alternatively, for a given value of x determined experimentally, we may express the equality of eq 27 as the inequality

$$T_2 \geq T_f\,(1 - x) \tag{29}$$

and the equality of eq 28 as the inequality

$$\ln\left(\frac{T_f}{T_2}\right) \leq \frac{x}{1 - x} \tag{30}$$

According to eqs 29 and 30 respectively, therefore, the values of T_2^a and T_2^b calculated using eqs 9 and 11, respectively, and listed in Table 1 represent, approximately, the *minimum* possible values for T_2, which correspond to $x_s = 0$ in eq 13, and hence a purely fictive temperature dependence for $S_c(T,T_f)$. This has some significant implications, as follows.

If we take a typical value of $T_f \approx T_g \approx 373$ K for polymers and assume $T_2 = T_g - 51.6$ K, following the universal WLF equation, we find $x_{\min} \approx 0.14$ as being representative of the minimum possible value of x for polymers. Table 1 shows one value (for PVC) which is less than $x_{\min}$ and others (for PC and PMMA) which are only slightly greater, while there are many other examples of values of x less than 0.14 in the literature (see, for example, Table 1 in ref 39). These were all obtained by the curve-fitting method, and one must ask how values lower than $x_{\min}$ can be reconciled with the above analysis.

Interestingly, in the peak-shift method[32−34] for the evaluation of x, values of x less than 0.2 were not included in the analysis, as they were considered to be unrealistic.[33] In fact, this can clearly be seen from the master curve used for the evaluation of x by the peak-shift method, which is reproduced in Figure 2. The function $F(x)$, which is given by

$$F(x) = \Delta C_p\left(\frac{\partial T_p}{\partial \bar{\delta}_H}\right) = \frac{\Delta h^*}{R{T_g}^2}\left(\frac{\partial T_p}{\partial(\ln q_2)}\right) - 1 = -\frac{\Delta h^*}{R{T_g}^2}\left(\frac{\partial T_p}{\partial(\ln|q_1|)}\right) \tag{31}$$

represents the limiting normalized (dimensionless) shift of the peak endothermic temperature T_p, observed during heating of an aged sample, as a function of the experimental variables defining the three-step thermal cycles: $\bar{\delta}_H$ is the enthalpy lost during aging at the annealing temperature, q_2 is the heating rate, and q_1 is the prior cooling rate. Most experimental data for polymers are found to give values of $F(x)$ quite close to unity. What is clear from Figure 1 is that values of x less than 0.2 give unrealistically large values for $F(x)$, and more so as x decreases, in agreement with the analysis above, which yields a typical minimum possible value of $x_{\min} \approx 0.14$.

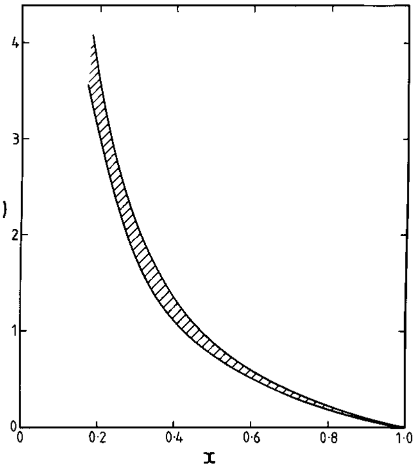

Figure 2. Master curve for the dependence of $F(x)$ on x. The shaded region represents the small effect of different distributions of relaxation times, from a single relaxation time to a double-box distribution over four decades of time.[33]

A similar conclusion was also reached when the single parameter KAHR model[32] was applied to the response of glasses to temperature modulated differential scanning calorimetry.[40] This relatively novel thermal analysis technique superimposes a periodically modulated signal (usually sinusoidal) on the constant heating rate of conventional DSC, and allows a complex specific heat capacity $C_p{}^*$ to be evaluated from the modulated heat flow by a Fourier transformation process.[41] The complex specific heat capacity can be separated into real (in-phase) and imaginary (out-of-phase) components, $C_p{}'$ and $C_p{}''$, respectively, by means of a phase angle ϕ between the heat flow and the heating rate. It has been suggested[42] that $C_p{}''$ provides information about internal entropy changes in the sample during the periodic cycles. We have shown, though, from a theoretical analysis of TMDSC in the glass transition region,[40] that a value of x as low as 0.2 leads to $C_p{}''$ values that are inconsistent with the thermodynamic interpretation suggested by Schawe,[42] and it was concluded that this may imply the existence of forbidden values of x at the lower end of the range, consistent with the present analysis.

In addition to considering the approximations defined by eqs 25 and 26, applicable to situations close to equilibrium, for which $T \approx T_f$, it is interesting to examine in more detail the general inter-relationships defined by eqs 23 and 24. In particular, these show that the correspondence between x_s and x involves the actual temperature T as well as the fictive and equivalent Kauzmann temperatures, T_f and T_2, respectively. Thus, if x_s is a material parameter, whose physical significance will be considered below, then one might anticipate that the Narayanaswamy parameter x would depend on the experimental conditions. This would clearly be inconsistent with the fundamental assumption of the TNM approach that x is a material constant. Nevertheless, it is an observation that is quite often reported in the literature that the value of x found by the curve-fitting method can depend on the values of the experimental parameters. The argument here would be that, if the assumption that x is a constant is not in fact correct, but the TNM theory with constant x is used to curve-fit

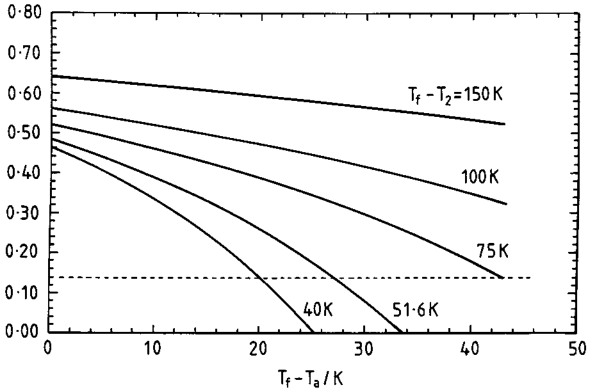

Figure 3. Illustration of the effect of annealing temperature relative to fictive temperature, $T_f - T_a$, on the value of x derived from eq 23 and corresponding to $x_s = 0.4$. Several different values of $T_f - T_2$ have been used, and are indicated against each curve. The dashed line indicates the minimum value of x from eq 27 for $T_f - T_2 = 51.6$ K. In all cases, we take $T_f = 373$ K.

experimental data, then the value of x obtained will be some complicated average value that is influenced by the actual conditions defining the experimental curve. The relationships expressed by eqs 23 and 24 can be used to explain such observations.

For example, it is commonly found experimentally that the value of x decreases as the annealing temperature T_a decreases. O'Reilly[39] shows values of x for poly(carbonate) decreasing, for relatively short annealing times, from the range 0.35−0.40 for $T_a = 415$ K to the range 0.10−0.15 for $T_a = 395$ K. Similarly, Tribone et al.[28] find x for atactic poly(methyl methacrylate), again for relatively short annealing times, decreases from about 0.3 for $T_a = 370$ K to about 0.2 for $T_a = 362$ K. This decrease in x with decreasing T_a is predicted from eqs 23 and 24 if x_s is maintained constant and one considers typical values for T_2 and T_f. For example, for $T_f = 373$ K and $T_2 = T_f - 51.6$ K as before, and taking $x_s = 0.4$, we find $x = 0.44$ or 0.43 from eq 23 and eq 24, respectively, at $T_a = 368$ K, i.e., 5 K below T_f, whereas we find $x = 0.33$ or 0.31, respectively, at $T_a = 358$ K, i.e., 15 K below T_f. Similarly, it may be shown from eqs 23 and 24 that x increases as T_f decreases isothermally, in other words as the isothermal aging time increases. This observation has also been reported commonly in the literature (e.g., see refs 28 and 39).

A further implication of the reduction in x as T_a decreases provides the answer to a question posed earlier: how can experimentally determined values of x which are less than $x_{\min}$ (defined by eqs 27 and 28) be reconciled with the present analysis? The answer is that the value of x derived from eqs 23 or 24 may decrease below the minimum values defined by eqs 27 and 28 if T_a is sufficiently far below T_f. This is illustrated in Figure 3 for $x_s = 0.4$ and several values of $T_f - T_2$. For example, using eq 23 and for the values of T_f and T_2 used above, ($T_f - T_2 = 51.6$ K) and for $x_s = 0.4$ again, we find $x = 0.18$ for $T_a = 348$ K, i.e., 25 K below T_f, and $x = 0.08$ for $T_a = 343$ K, i.e., 30 K below T_f. Thus, the minimum values of x defined by eqs 27 and 28 should be considered only as approximations when the temperature of the sample remains close to T_f. On the other hand, when the sample temperature is very different from T_f, not only do eqs 27 and 28 no longer hold, but also x becomes significantly temperature dependent. The closer is T_2 to T_f, the greater becomes this temperature dependence. Indeed, for relatively small values of $T_f - T_2$, x can apparently become negative when T_a is sufficiently far below T_f. However, this situation would be unlikely to arise in practice, since the curve-fitting algorithm would seek a lower value of T_2 instead. Furthermore, the present analysis is confined to a range of T_a between T_f' and T_f'' (refer to Figure 1), implying that T_a cannot be reduced indefinitely without the analysis becoming invalid. In respect of the location of T_2, on the other hand, for lower values of T_2, hence for larger $T_f - T_2$, the dependence of x on $T_f - T_a$ becomes less important, at least within the range of $T_f - T_a$ values (with $x_s = 0.4$) in Figure 3. This temperature dependence of x could explain why it has been noted, by Moynihan et al.[43,44] among others, that the TNM model fails to produce acceptable fits to experimental data when the sample is far from equilibrium, that is when T and T_f are significantly different. The present analysis predicts that such failure would be more likely in apparently fragile glass formers, for which T_f and T_2 are relatively close.

In summary, therefore, the assumption that the configurational entropy is a function of both T and T_f in the glassy state, with $S_c(T,T_f)$ given by eq 13, leads to a number of implications which are consistent with previous observations. These are as follows: (i) that for samples annealed at temperatures not too distant from T_g there is a minimum value for x, typically of the order of 0.14; (ii) that the temperature T_2 at which $S_c = 0$ is related to x by an inequality, eq 29 or 30 depending on the temperature dependence of ΔC_p, and that it is therefore inappropriate to evaluate T_2 from the equality given by eq 9 or eq 11; (iii) that the value of x will increase with aging time at constant temperature; (iv) that as the annealing temperature is decreased further below T_f, the parameter x evaluated experimentally will decrease, and more so the closer T_f and T_2 are, thus making it impossible to reconcile, with the same set of parameter values, experiments conducted close to and far from equilibrium.

The rationale for the assumption implicit in eq 13 will now be examined in the light of the theory of Gibbs and DiMarzio.[12]

4. Rationale for S_c (T, T_f) Based upon the Theory of Gibbs and DiMarzio

The starting point for this development is the statistical mechanical quasi-lattice theory of the glass transition and the glassy state of Gibbs and DiMarzio[12] (GDM), which is the basis for the Adam−Gibbs[13] (AG) theory used above. The GDM theory allows for chain stiffness, by introducing an energy difference $\Delta\epsilon$ between reasonably low energy bond orientations and higher energy flexed bonds, and for free volume effects, by designating by n_o the number of vacant lattice sites in a system consisting of n_y linear polymer chains of y segments each, and defines a van der Waals bond energy (α) between nearest neighbor segments. GDM show that, for a polymer with a carbon−carbon backbone chain, the configurational entropy in equilibrium above T_2 is given by

$$S_c(T > T_2) = kyn_y\left(\ln\left(\frac{V_o}{S_o}\right) + \frac{n_o}{yn_y}\ln\left(\frac{V_o}{S_o{}^2}\right) + \frac{\ln[3(y+1)]}{y} + \left(\frac{y-3}{y}\right)\left\{\frac{f\Delta\epsilon}{kT} - \ln(1-f)\right\}\right) \quad (32)$$

where

$$f = \frac{2e^{-\Delta\epsilon/kT}}{1 + 2e^{-\Delta\epsilon/kT}} \tag{33}$$

represents the fraction of bonds in the higher energy, flexed orientation, V_o is the fraction of vacant lattice sites

$$V_o = \frac{n_o}{yn_y + n_o} \tag{34}$$

and S_o is a fraction characterizing the "best" amorphous packing of the system of segments and holes

$$S_o = \frac{2n_o}{(y + 1)n_y + 2n_o} \tag{35}$$

There is a transcendental equation relating V_o and S_o, which depends on the intermolecular energy α and the temperature:

$$\ln\left(\frac{V_o}{S_o^{\,2}}\right) = \frac{2\alpha}{kT}(1 - S_o)^2 \tag{36}$$

The thermodynamic second-order transition temperature T_2 is defined by

$$\lim_{T \to T_2} [S_c(T > T_2)] = 0 \tag{37}$$

where $S_c(T > T_2)$ is given by eq 32, and T_2 is identified by GDM as T_g since the theory considers only equilibrium states, or "slow" experiments. Below T_2, the hole fraction n_o is "frozen-in" at its value at T_2, such that the difference in volumetric thermal expansion coefficient $\Delta\beta$ between the liquidlike and glassy states, above and below T_2 respectively, may be obtained from the volume of a lattice site and the temperature dependence of n_o:

$$\Delta\beta = \left(\frac{\partial n_o/\partial T}{yn_y + n_o}\right)_{T_2} = \left[\frac{\dfrac{2\alpha}{kT_2^{\,2}}V_o(1 - S_o)^2}{2(1 - S_o) - \dfrac{4\alpha}{kT_2}S_o(1 - S_o)^2 - (1 - V_o)}\right]_{T_2} \tag{38}$$

For a given value of T_2 for a polymer consisting of a known number of y-mers, the intermolecular energy α is found from eqs 36 and 38, while $\Delta\epsilon$ is obtained by the application of eqs 32 and 37. The configurational entropy in equilibrium at any temperature higher than T_2 is then obtained simply from eq 32. By way of a numerical illustration, we take the values for poly(styrene) of molecular weight 85 000 given by GDM

$$\Delta\beta = 2.90 \times 10^{-4}\ \mathrm{K}^{-1}$$

$$T_2 = 373\ \mathrm{K}$$

$$\frac{2\alpha}{k} = 887.7\ \mathrm{K}$$

$$\frac{\Delta\epsilon}{k} = 839.3\ \mathrm{K}$$

and evaluate S_c $(T > T_2)$ from eq 32 for temperatures from T_2 to $T_2 + 50$ K. The result is shown by the full line in Figure 4, where an approximately (but not strictly) linear variation is seen over this temperature range. At T_2, where $S_c = 0$, the value of V_o, which may be considered from eq 34 to be a measure of the fractional free volume, is 0.033; this may be compared with the "universal" value of 0.025 at T_g. With increasing temperature, V_o increases and reaches a value of 0.049 at $T_2 + 50$ K. The fraction f of flexed bonds also increases from 0.174 at T_2 to 0.216 at $T_2 + 50$ K.

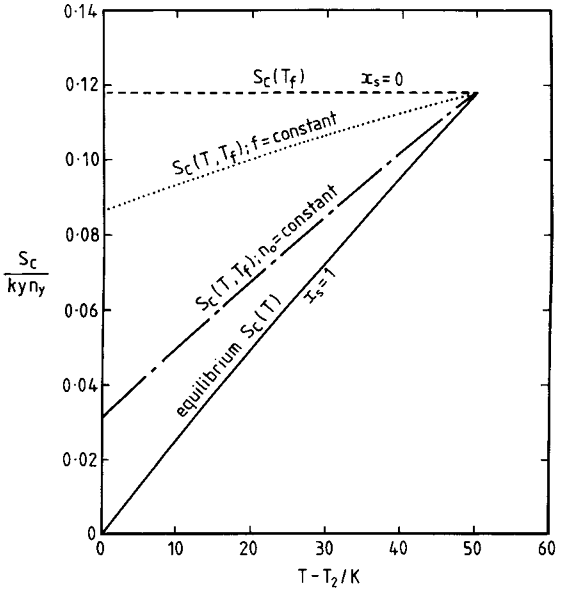

Figure 4. Dependence of S_c/kyn_y on temperature, calculated from eq 32, for the poly(styrene) data given by Gibbs and DiMarzio:[12] full line, equilibrium conditions; dashed line, nonequilibrium state on cooling defined by $S_c(T_f)$; dash−dotted line, nonequilibrium state on cooling assuming n_o remains constant; dotted line, nonequilibrium state on cooling assuming f remains constant.

The original GDM theory was expressed in terms of the volume of an ensemble of lattice sites, which is frozen-in at temperature T_2 such that there is a discontinuity in the thermal expansivity, defined by $\Delta\beta$ in eq 38. An analogous theoretical treatment may be made for the heat capacity.[45] The equivalent hyopthesis is that, under "ideal" conditions of infinitely slow cooling, the change in specific heat at T_2 at constant pressure, ΔC_p, is due to the freezing-in of conformational and free volume components. Making use, instead, of the specific heat at constant volume, ΔC_v, O'Reilly[46] estimated values of the equivalent conformational energy difference $\Delta\epsilon$ for 14 polymers and found satisfactory agreement with literature data, concluding that the basic premise is confirmed that the change in ΔC_v at T_2 is due to the conformational contribution. Shortly thereafter, Roe and Tonelli[47] found that ΔC_p not only consisted of conformational and free volume components but also contained a "miscellaneous" component arising from heat capacity changes due to, for example, changes in the vibrational frequency or amplitude or from changes in the average nearest neighbor coordination number. Such miscellaneous contributions are included in the flex energy $\Delta\epsilon$ derived by O'Reilly.[46]

To extend the argument in the present paper, however, we return to the formalism of the original GDM paper, and recall that the full line in Figure 4 represents the change in configurational entropy under equilibrium conditions, equivalent to infinitely slow cooling. The usual extension to the nonequilibrium state assigns a purely fictive temperature dependence to $S_c(T_f)$ as in eq 7, which would imply that, on cooling, the configurational entropy is frozen-in and remains constant (on continued cooling) at its value at the experimental glass transition temperature. Supposing that, for arbitrary experimental conditions, this transition occurs at $T_2 + 50$ K, then the configurational entropy would remain constant at the value $S_c/kyn_y = 0.118$, as indicated by the dashed line in Figure 4.

However, the configurational entropy given by eq 32 from the GDM theory shows a dependence on the number n_o of holes or vacant lattice sites (and hence also on V_o and S_o) and on the fraction f of flexed bonds. The assumption above that $S_c = S_c(T_f)$ implies, therefore, that both n_o and f are frozen-in at the glass transition. We could imagine, though, that only the hole fraction is frozen-in at the glass transition. This may be a somewhat unrealistic limiting situation, and indeed there may also be an interdependence between the number of holes and the fraction of flexed bonds, but it nevertheless serves a useful illustrative purpose. On this basis, the first three terms on the right-hand side of eq 32 remain constant in the nonequilibrium glassy state on cooling, while the last term, which involves f, decreases as f decreases from 0.216 at $T_2 + 50$ K to 0.174 at T_2. The resulting temperature dependence of the configurational entropy is shown as the dash−dotted line in Figure 4. This clearly corresponds to a combination of temperature dependence, $S_c(T)$, and fictive temperature dependence, $S_c(T_f)$, as proposed in eq 13. The parameter x_s in eq 13 is readily obtained using eq 14 and the location of the dash−dotted $S_c(T,T_f)$ line in Figure 3 relative to those for $S_c(T)$ and $S_c(T_f)$, and one finds $x_s \approx 0.74$. Taking $T_f = T_2 + 50\ \mathrm{K} = 423$ K and considering a temperature $T = T_f - 20\ \mathrm{K} = 403$ K, typical for studies of enthalpy relaxation behavior in polymers, a value of $x \approx 0.54$ is obtained; reducing the temperature to $T = T_f - 25\ \mathrm{K} = 398$ K reduces x to approximately 0.43. These values for x are not untypical of experimentally determined values, and in fact closely span the range given by Hodge[7] for poly(styrene). Of course, the exact value of x found from x_s will depend on the choice of T, as was noted earlier, but it is encouraging to find that consideration of typical experimental conditions leads to realistic values for x.

The origin of values of x rather smaller than 0.4 or 0.5 now needs to be considered, and may arise from another way of freezing-in the structure at the experimental glass transition. For example, if, instead of freezing-in n_o as was considered above, it were the fraction f of flexed bonds which froze in at T_g, then it would be the last term on the right-hand side of eq 32 which remained constant on cooling below T_g, while the first three terms would display a temperature dependence due to that of n_o, the number of vacant lattice sites, corresponding to a decrease of V_o from 0.049 to 0.033 over the 50 K range of temperature. This would lead to the variation of the configurational entropy shown in Figure 4 by the dotted line. Again comparing this with the dependence of $S_c(T,T_f)$ given by (13), we find $x_s \approx 0.26$, which, for the same choice of T_f and T as before gives $x \approx 0.16$ for $T = T_f - 20$ K and $x \approx 0.10$ for $T = T_f - 25$ K. These values of x are not untypical of some of those reported for poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA), for example (see Table 1); although the calculations presented here apply nominally to poly(styrene), almost the same values for T_2 and T_f could have been used for PVC and PMMA.

We note here that it was recently drawn to our attention that the philosophy of the present approach, encapsulated in the schematic illustration of Figure 4, was in fact suggested over 30 years ago by Eisenberg and Saito.[48] These authors carefully evaluated the intermolecular and intramolecular contributions, $2\alpha/k$ and $\Delta\epsilon/k$, respectively, to the GDM theory for a wide variety of polymer systems, and found a rather close correlation between them; indeed, within reasonable limits of experimental uncertainty they appear identical. The only possibility that seemed plausible to Eisenberg and Saito for this rather remarkable observation lay in the fact that, while the temperature T_2 of the GDM theory is thermodynamic in nature, T_g is not. Their suggestion is that, since T_g depends strongly on kinetic factors, “the intermolecular energy might be far more important than the chain stiffness in some cases, while the opposite may be true in others”, and they go on to state that if one applies the GDM theory to the experimental glass transition, “one apparently finds that one of the two parameters [$2\alpha/k$ and $\Delta\epsilon/k$] strongly overshadows the other”. This is in essence what is proposed here as the molecular basis for the dependence of configurational entropy on both thermodynamic and fictive temperatures, expressed by eq 13.

In a rather general way, the present analysis allows the introduction of less nonlinearity in the glassy state than is inherent in the usual nonequilibrium extension of the AG equation described by eq 7. It appears that this permits the rationalization of a number of experimentally observed problems associated with the TNM/AG equations, and would imply that an improved description of experimental data would be obtained with the use of eq 13, resulting also in more realistic parameter values. Interestingly, an apparently similar, but fundamentally different, approach proposed by Gomez-Ribelles and co-workers[49−51] (GR) also seems to provide a better description of experimental differential scanning calorimetry (DSC) data. The similarity lies in the fact that GR also reduces the extent of nonlinearity in the glassy state; the fundamental difference lies in their doing so by assigning a “limit” state, with a configurational entropy S_c^{lim} greater than that of equilibrium. In the present work, therefore, the nonlinearity is associated with $S_c(T, T_f) - S_c(T)_{\mathrm{equilibrium}}$, with either f = constant or n_o = constant (or some combination of both) defining the exact contribution of T_f to $S_c(T, T_f)$, while in GR it is associated with $S_c(T_f) - S_c^{\mathrm{lim}}$; both of these approaches introduce less nonlinearity than that associated with $S_c(T_f) - S_c(T)_{\mathrm{equilibrium}}$ implicit in the usual nonequilibrium extension of the AG model. What is interesting is that reduced nonlinearity is the theme common to the improved modeling of both GR and the present analysis, and suggests that this is an avenue worth pursuing further.

It is also interesting to return to the observation, mentioned briefly in the Introduction, that the TNM nonlinearity parameter x and the nonexponentiality parameter β are correlated. The present model could be argued to provide a possible explanation for this. It is indisputable that glassy state relaxation involves a distribution of relaxation times, which may be characterized by β. The present model does not explicitly introduce the parameter β or any other distribution function; it does, however, explicitly introduce a distribution of fictive temperatures, which *implies* a distribution of relaxation times. We may imagine, therefore, an overall distribution of relaxation times which combines the distribution of fictive temperatures with an "intrinsic" distribution function characterized by β. Then, for a given overall distribution, the smaller x_s is, the narrower is the distribution of fictive temperatures, and the wider must be the "intrinsic" distribution function to compensate. Thus, small x_s would associate with small β. Since the TNM parameter x decreases as x_s decreases (eq 25, for example), this implies that by ignoring the distribution of fictive temperatures one automatically couples small values of x with small values of β (or, in an analogous way, large values of x with large values of β) in order to obtain an optimum fit to the experimental data.

In summary, the analysis presented here shows that quite different, but reasonable, values for x are obtained by the choice of the type of freezing-in process that affects the configurational entropy. In practice, though, it is likely that the glass transformation process will involve some combination of the freezing-in of both holes and flexed bonds, and hence of both intermolecular (α) and intramolecular ($\Delta\epsilon$) energies. Indeed, a similar idea was proposed by Cortés and Montserrat in their work on linear polyesters,[31] where they argued that the values of x derived by the peak-shift method for their different polyesters could be rationalized in terms of the solubility parameter. One possible approach to develop these ideas would be to consider glass-forming systems in which the relative contributions of intermolecular and intramolecular energies could be controlled; this will be the subject of further work.

Finally, one is left with the question of whether there is the possibility of evaluating x_s from relaxation data. We believe that indeed there is and believe that the same approach as was adopted earlier in the peak-shift method[32−34] could be used again here. The relaxation time in the nonequilibrium glassy state is given by eq 15, instead of eq 7 as has been used hitherto, and this together with an appropriate constitutive equation and distribution of relaxation times permits the response of the glass to any prescribed thermal history to be followed. In particular, therefore, for three-step thermal cycles involving cooling from the equilibrium liquid, isothermal annealing, and subsequent reheating, an endothermic peak will appear at a temperature T_p which will depend on the experimental variables and, among other parameters, the entropic nonlinearity parameter x_s. In the same way as was done earlier,[32−34] a comparison of experimental and theoretical dependences (shifts) of T_p on a suitable experimental variable (most conveniently, the amount of annealing) should allow an independent evaluation of x_s. This work is currently in progress.

5. Conclusions

A comparison of the Tool−Narayanaswamy−Moynihan (TNM) equation for the temperature and structure dependence of the relaxation time with the usual nonlinear form of the Adam−Gibbs (AG) equation equation leads, for many polymer glasses, to unrealistically low values for T_2, the thermodynamic second-order transition temperature at which the configurational entropy reduces to zero. An alternative nonlinear extension of the AG equation, in which the configurational entropy is dependent on both thermodynamic temperature and fictive temperature $S_c(T, T_f)$, with an entropic partitioning parameter x_s, rationalizes these unrealistic values for T_2 and predicts a number of effects often reported in the literature, including apparently unreasonably low values for the Narayanaswamy parameter x, a decrease in x with decreasing annealing temperature below T_g, and an increase in x with increasing annealing time, as well as the inability of the TNM or AG equation to describe adequately the nonlinearity for glasses far from equilibrium.

The rationale for expressing the configurational entropy in the glassy state as $S_c(T, T_f)$ is based upon the statistical mechanical lattice theory of Gibbs and DiMarzio in which the contributions of vacant lattice sites (holes) and of different bond conformations can be identified. By considering the glass transition as a freezing-in process for the fraction of holes and/or the fraction of flexed bonds, it is shown that realistic and physically meaningful values of x_s can lead to the typical values of Narayanaswamy parameter observed experimentally.

Acknowledgment. The authors are very grateful to Professor Jose Lluis Gómez-Ribelles for his careful reading of, and comments on, a first draft of this manuscript. J.M.H. acknowledges a grant from the Royal Society (U.K.) which facilitated this collaboration. The support of the CICYT Project No. MAT 97-0634-102-02 is also acknowledged.

References and Notes

(1) Tool, A. Q.; Eichlin, C. G. *J. Am. Ceram. Soc.* **1931**, *14*, 276.
(2) Tool, A. Q. *J. Am. Ceram. Soc.* **1946**, *29*, 240.
(3) Tool, A. Q. *J. Am. Ceram. Soc.* **1948**, *31*, 177.
(4) Narayanaswamy, O. S. *J. Am. Ceram. Soc.* **1971**, *54*, 491.
(5) Moynihan, C. T.; Easteal, A. J.; DeBolt, M. A.; Tucker, J. *J. Am. Ceram. Soc.* **1976**, *59*, 12.
(6) McKenna, G. B. in *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon: Oxford, U.K., 1989; Vol 2, Polymer Properties, p 311.
(7) Hodge, I. M. *J. Non.-Cryst. Solids* **1994**, *169*, 211.
(8) Hutchinson, J. M. *Prog. Polym. Sci.* **1995**, *20*, 703.
(9) Vogel, H. *Phys. Z.* **1921**, *22*, 645.
(10) Tammann, G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245.
(11) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(12) Gibbs, J. H.; DiMarzio. E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(13) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(14) Angell, C. A.; Rao, K. J. *J. Chem. Phys.* **1972**, *57*, 470.
(15) Angell, C. A.; Smith, D. L. *J. Phys. Chem.* **1982**, *86*, 3845.
(16) Dixon, P. *Phys. Rev.* **1990**, *B42*, 8179.
(17) Hodge, I. M. *J. Res. Natl. Inst. Stand. Technol.* **1997**, *102*, 195.
(18) Miller, A. A. *Macromolecules* **1970**, *3*, 674.
(19) Howell, F. S.; Bose, R. A.; Macedo, P. B.; Moynihan, C. T. *J. Phys. Chem.* **1974**, *78*, 639.
(20) Scherer, G. W. *J. Am. Ceram. Soc.* **1984**, *67*, 504.
(21) Hodge, I. M. *Macromolecules* **1987**, *20*, 2897.
(22) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(23) Sasabe, H.; Moynihan, C. T. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1447.
(24) Hutchinson, J. M.; Ruddy, M. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2341.
(25) Privalko, V. P.; Demchenko, S. S.; Lipatov, Yu. S. *Macromolecules* **1986**, *19*, 901.
(26) Pappin, A. J.; Hutchinson, J. M.; Ingram, M. D. *Macromolecules* **1992**, *25*, 1084.
(27) Hutchinson, J. M.; Smith, S.; Horne, B.; Gourlay, G. M. *Macromolecules* **1999**, *32*, 5046.
(28) Tribone, J. J.; O'Reilly, J. M.; Greener, J. *Macromolecules* **1986**, *19*, 9, 1732.
(29) Hutchinson, J. M. *Polym. Int.* **1998**, *47*, 56.

(30) Godard, M.-E.; Saiter, J.-M.; Cortés, P.; Montserrat, S.; Hutchinson, J. M.; Burel, F.; Bunel, C. *J. Polym. Sci., Polym. Phys. Ed.* **1998**, *36*, 583.
(31) Cortés, P.; Montserrat, S. *J. Polym. Sci., Polym. Phys. Ed.* **1998,** *36*, 113.
(32) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097.
(33) Ramos, A. R.; Hutchinson, J. M.; Kovacs, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1655.
(34) Hutchinson, J. M. *Lect. Notes Phys.* **1987**, *277*, 172.
(35) Angell, C. A. In *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; US Department of Commerce: Springfield VA, 1984; p 3.
(36) Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.
(37) Hodge, I. M. *J. Non-Cryst. Solids* **1996**, *202*, 164.
(38) Rekhson, S. M. *J. Non-Cryst. Solids* **1986**, *84*, 68.
(39) O'Reilly, J. M. *CRC Crit. Rev. Solid State Mater. Sci.* **1987**, *13*, 259.
(40) Hutchinson, J. M.; Montserrat, S. *Thermochim. Acta* **1997**, *304*/*305*, 257.
(41) Schawe, J. E. K. *Thermochim. Acta* **1995**, *260*, 1.
(42) Schawe, J. E. K. *Thermochim. Acta* **1997**, *304*/*305*, 111.
(43) Moynihan, C. T.; Crichton, S. N.; Opalka, S. M. *J. Non-Cryst. Solids* **1991**, *131*−*133*, 420.
(44) See also the Discussion Session on p 528 ff of ref 43.
(45) Di Marzio, E. A.; Gibbs, J. H.; Fleming, P. D.; Sanchez, I. C. *Macromolecules* **1976**, *9*, 763.
(46) O'Reilly, J. M. *J. Appl. Phys.* **1977**, *48*, 4043.
(47) Roe, R.-J.; Tonelli, A. E. *Macromolecules* **1978**, *11*, 114.
(48) Eisenberg, A.; Saito, S. *J. Chem. Phys.* **1966**, *45*, 1673.
(49) Gómez-Ribelles, J. L.; Monleón-Pradas, M. *Macromolecules* **1995**, *28*, 5867.
(50) Gómez-Ribelles, J. L.; Monleón-Pradas, M.; Vidaurre-Garayo, A.; Romero-Colomer, F.; Más-Estellés, J.; Meseguer-Dueñas, J. M. *Macromolecules* **1995**, *28*, 5878.
(51) Montserrat, S.; Gómez-Ribelles, J. L.; Meseguer-Dueñas, J. M. *Polymer* **1998**, *39*, 3801.

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