Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 6. Adam–Gibbs Formulation of Nonlinearity

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ABSTRACT: Alternatives to the Narayanaswamy expression (N) for nonlinearity, $\tau_0 = A \exp[x\Delta h^*/RT + (1-x)\Delta h^*/RT_f]$, were derived from the Adam–Gibbs (AG) theory and fitted to experimental data on five polymers. Two AG-derived expressions were evaluated: $\tau_0 = A \exp[B/RT \ln (T_f/T_2)]$ ("AGL") and $\tau_0 = A \exp[D/RT(1-T_2/T_f)]$ ("AGV"). The N and two AG expressions gave comparably good fits for most thermal histories, AGV giving somewhat better fits at the longest annealing times. Reported variations in N parameters with thermal history were shown to be qualitatively consistent with AG predictions. The N parameter, x, was shown to be a direct measure of T_f'/T_2 (T_f' = glassy state value of T_f); the N activation energy, Δh^*, was found to vary inversely with the AG parameters B and D. Correlations of B and D with T_f'/T_2 were observed and shown to be consistent with T_f' approaching T_2 as the AG primary activation energy decreased to zero. The Kohlrausch–Williams–Watt parameter, β, also decreased with decreasing T_f'/T_2, suggesting increased cooperativity as T_2 is approached. Variations in AG parameters, obtained directly for polymer glasses and indirectly from published N parameters for nonpolymeric glasses, were consistent with generally observed variatons in non-Arrhenius behavior above T_g. It was concluded that nonlinear behavior near and below T_g is determined by the same factors that influence equilibrium behavior above T_g.

Introduction

It is well established that relaxation in the glass-transition region and glassy state is nonexponential and nonlinear. Nonexponentiality is demonstrated by the well-known memory effect, in which relaxation from some initial state depends on how that state was reached. This has been discussed in detail by Goldstein[1] and is exemplified by the pioneering experimental studies of borosilicate glass by Ritland[2] and of poly(vinyl acetate) (PVAc) by Kovacs.[3] Nonlinearity is indicated by the assymmetry of relaxation following positive or negative departures from equilibrium. For temperature jumps, nonlinearity is observed for changes greater than about 2 K and gives rise to the characteristically rapid changes in relaxation time during heating through the glass-transition region. Indeed, the term "transition" originates from the sharpness of these changes with temperature. In this paper we formulate the nonlinear aspects of enthalpy relaxation in polymers by extending the Adams–Gibbs theoretical description of linear relaxation processes above T_g.

The most successful method for handling nonlinearity is due to Tool,[4] who expressed the average relaxation time as a function of the departure from equilibrium. With this approach it is convenient to use the fictive temperature T_f, introduced by Tool and Eichlin[5] as the "equilibrium temperature" and defined by them as the temperature at which the nonequilibrium value of some macroscopic property would be the equilibrium one. Thus departure from equilibrium is measured by $T_f - T$. This definition of T_f has several limitations, however, that have been discussed in detail by Ritland[2] and Narayanaswamy.[6] The most important limitation is the implicit assumption that a single equilibrium state can be associated with every nonequilibrium state, which is valid only for exponential relaxations that exhibit no memory effect. For nonexponential relaxations, the memory effect was interpreted by Narayanaswamy[6] to mean that some nonequilibrium states comprise several equilibrium states, each with its own fictive temperature. Narayanaswamy handled this intricate problem by assuming a single, thermorheologically simple, nonexponential relaxation mechanism. Changes in actual and fictive temperatures were assumed to shift the time scale only, and for simplicity the shift function was assumed to follow an Arrhenius form

$$\tau_0 = A \exp\left(\frac{H_g}{RT} + \frac{H_s}{RT_f}\right) \qquad (1)$$

where A, H_g, and H_s are constant parameters and R is the ideal gas constant. Relaxation can then be described by the usual methods of the linear response theory, modified by eq 1 to include changes in τ_0 as T_f relaxes. In particular, Boltzmann superposition of responses to any thermal history can be applied. This approach to structural relaxation was poineered by Mazurin, Rekhson, and Startsev.[7] Moynihan et al.[8] rewrote eq 1 as

$$\tau_0 = A \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \qquad (2)$$

where $1 \geq x > 0$, and it is in this form that the Narayanaswamy (N) expression is usually used. For nonpolymeric materials the parameter Δh^* usually equals the readily evaluated activation energy for shear viscosity above T_g. For polymers, however, entanglements determine the viscosity in the terminal region and other methods must be used. The method of choice is to determine the cooling-rate dependence of the glassy-state value of T_f, T_f',[8] obtained by integration of the normalized heat capacity measured on heating.

Although the N expression describes the glass transition and glassy-state relaxations very well, it has several shortcomings. As noted earlier,[9] these include the following:

1. The prediction of an Arrhenius temperature dependence for the equilibrium state ($T_f = T$), in conflict with the well-established Vogel[10] and WLF[11] expressions. Associated with this are unusually large values of $\Delta h^*/R$, as high as 225 kK.[12,13]

2. The expression is empirical, and the parameters x and Δh^* have no clear physical interpretation.

3. The physical origin of the inverse correlation between x and Δh^* [13] is obscure.

4. Systematic changes in N parameters with thermal history, particularly in x, have been reported by several groups.[14-16] These appear to be more pronounced at long annealing times and low annealing temperatures. It has been suggested by Chen and Kurkjian[17] that these indicate a qualitative distinction between glassy-state relaxations

and the glass transition. An alternative view[14,15] is that the problem resides in the N expression for the partitioning of T and T_f. It is our opinion that the correct formalism for the glass-transition kinetics has yet to be found and that the N expression for nonlinearity is indeed suspect.

In seeking a theoretical basis for nonlinearity it is natural to consider free-volume theories. However, although free volume, V_f, can be associated with a fictive temperature, there is no direct method for introducing the actual temperature. Macedo and Litovitz[18] have criticized the usual free-volume derivations for neglecting the thermal activation needed for a particle to move from one pocket of free volume to another and derived the hybrid expression

$$\tau_0 = A \exp(B/V_f + E/RT) \tag{3}$$

where A, B, and E are constant parameters. Putting $V_f \sim T_f - T_2$, where T_2 is the temperature of zero free volume, yields

$$\tau_0 = A \exp[B'/R(T_f - T_2) + E/RT] \tag{4}$$

whose linear form ($T_f = T$) was first proposed by Dienes.[19] Equation 4 correctly predicts an Arrhenius temperature dependence in the glassy state but does not produce the Vogel form at equilibrium. Nevertheless, the Dienes equation was found by Macedo and Litovitz to give a good account of the viscosity of B_2O_3, SiO_2, alkali silicates, alcohols, and poly(isobutylene). Note that B' and E in eq 4 are independent quantities, related to free-volume fluctuations and thermal activation barriers, respectively, so that eq 4 has the disadvantage of having an additional independent parameter compared with N.

Mazurin et al.[20] proposed the equation

$$\tau_0 = A \exp[Q_1/R(T_f - T_2) + (Q_2/R)(T^{-1} - T_f^{-1})] \tag{5}$$

where A, Q_1, Q_2, and T_2 are constant parameters. This is similar to eq 4 but produces the Vogel form in the equilibrium state. However, it shares with N the disadvantage of being empirical and like eq 4 has an additional independent parameter.

Entropy-based theories offer a more promising approach because they produce a natural separation of actual and fictive temperatures. The Adam–Gibbs theory[21] (AG) is the most familiar of these and provides the foundation for our treatment of nonlinearity. The AG expression for relaxation time τ_0 is

$$\tau_0 = A \exp\left(\frac{\Delta\mu s_c^*}{RTS_c}\right) \tag{6}$$

where A is a constant, $\Delta\mu$ is the free-energy barrier hindering rearrangement, s_c^* is the configurational entropy of the smallest group able to rearrange, and S_c is the macroscopic configurational entropy. The fictive temperature is introduced into the expression for S_c as

$$S_c = \int_{T_2}^{T_f} \Delta C_p / T \, dT \tag{7}$$

where ΔC_p is the configurational heat capacity and T_2 is the configurational ground-state temperature, conceptually identical with T_2 in the Gibbs–DiMarzio[22] thermodynamic theory of the glass transition. Equation 7 expresses the idea that the fictive temperature of a glass is a measure of its configurational entropy and that loss of excess entropy during annealing corresponds to relaxation of T_f toward the annealing temperature, T_e. In applying the AG expression to enthalpy relaxation, it must be assumed that the entropic and enthalpic fictive temperatures are the same. This is a good approximation, however, because the range in T and T_f for the glass-transition and annealing

processes is sufficiently narrow that the integrals of ΔC_p and $\Delta C_p/T$ are nearly proportional. For example, a range of 20 K produces a difference in entropic and enthalpic T_f on the order of 0.1 K.

Explicit expressions for $\tau_0(T, T_f)$ derived from eq 6 and 7 depend on the temperature dependence of ΔC_p. For constant ΔC_p,

$$\tau_0 = A \exp[B/RT \ln (T_f/T_2)] \tag{8a}$$

where

$$B = \Delta\mu s_c^* / \Delta C_p \tag{8b}$$

Plazek and Magill[23] observed that the experimental ratio of activation energies for creep recovery in 1,3,5-tri-α-naphthylbenzene, above and below T_g, was in excellent agreement with eq 8 with parameters determined above T_g. Magill[24] also found that log (viscosity) varied linearly with $(TS_c)^{-1}$ at low temperatures near T_g, in accordance with eq 6, but failed at high temperatures where the AG assumptions were probably inapplicable.

Approximate relations between the parameters of eq 2 and 8 can be derived from appropriate temperature derivatives (T_f = unannealed glassy state value of T_f):

$$\Delta h^* / R = \frac{d \ln \tau_0}{d(1/T)} \approx B(L^{-1} + L^{-2}) \tag{9a}$$

where

$$L \equiv \ln (T_f' / T_2) \tag{9b}$$

and

$$x \Delta h^* / R = \left.\frac{\partial \ln \tau_0}{\partial(1/T)}\right|_{T_f'} \approx B/L \tag{10}$$

from which

$$x \approx L/(1 + L) \tag{11}$$

Equations 9 and 10 were first derived by Plazek and Magill,[23] using a different notation. Because of the logarithmic term in T_f, we refer to eq 8 as AGL.

For ΔC_p with the temperature dependence

$$\Delta C_p = CT_g/T \tag{12}$$

where $C = \Delta C_p$ at T_g, it has been shown[9,25] that

$$\tau_0 = A \exp[D/RT(1 - T_2/T_f)] \tag{13}$$

from which

$$\Delta h^* / R \approx D/(1 - T_2/T_f')^2 \tag{14}$$

and

$$x \approx 1 - T_2/T_f' \tag{15}$$

where $D = \Delta\mu s_c^* T_2 / CT_g$. In the equilibrium state eq 13 assumes the Vogel form

$$\tau_0 = A \exp[D/R(T - T_2)] \tag{16}$$

and we therefore refer to eq 13 as the Adam–Gibbs–Vogel (AGV) equation. Equation 12 is the simplest expression of the experimental observation that ΔC_p decreases with increasing temperature, although it is recognized that the empirical form

$$\Delta C_p = a - bT \tag{17}$$

is generally more accurate.

The AG equation was also discussed by Howell et al.[26] in their study of the molten salt $0.4Ca(NO_3)_2$–$0.6KNO_3$. They derived the following general expressions for the effective activation energies above and below T_g:

$$\Delta h^* = E/S_c(T) + [ET/S_c{}^2(T)]\frac{dS_c(T)}{dT} \qquad (18)$$

$$x\Delta h^* = E/S_c(T_f') \qquad (19)$$

where $E = \Delta\mu s_c^*$. These investigators observed that S_c must always decrease with decreasing T_f ($\Delta C_p > 0$), and the value of $x\Delta h^*$ must therefore increase with decreasing T_f. In this respect both the AGL and AGV equations differ significantly from the empirical eq 4 and 5, both of which predict an Arrhenius activation energy in the glassy state that is independent of T_f'. Matsuoka[27] has shown that for dielectric and mechanical relaxaton in PVAc the parameter E in eq 4 varies with T_f' in a manner consistent with the AG theory.

The AG expression was first applied to structural relaxation by Scherer[28] in his analysis of NBS-710 soda-lime–silicate glass. He inserted eq 17 into eq 7, using calorimetrically measured values for the coefficients a and b, and obtained an excellent description of published viscosity,[29] refractive index,[30] and enthalpy[31] data.

We conclude this Introduction with a few brief comments on the parameter T_2, which appears in the AGL, AGV, and other expressions for τ_0 (T, T_f). The concept of a thermodynamically defined glass temperature T_2 originated with Kauzmann.[32] For many inorganic and some polymeric materials, T_2 can be calculated from the (temperature-dependent) difference in heat capacity of the liquid and crystal ($\approx$glass), ΔC_p, the enthalpy of melting, ΔH_m, and the melting temperature, T_m:

$$\Delta H_m/T_m = \int_{T_2}^{T_m} \Delta C_p/T \, dT \qquad (20)$$

It is assumed in this analysis that ΔC_p equals the configurational heat capacity, although this has been challenged by Goldstein,[33] who pointed out that ΔC_p can contain large vibrational and other contributions. For inorganics the calculation of T_2 from eq 20 is usually unambiguous, although care must be taken to properly include the entropy of solid-state transitions in some cases. For polymers, however, crystallizable forms usually have different tacticities from purely amorphous forms, and it must be assumed that ΔC_p, ΔH_m, and T_m do not change with tacticity, or change in a known way. It has also been argued[34] that the Kauzmann estimate of T_2 for polymers is an artifact of incorrect extrapolation of $\Delta C_p(T)$ below T_g, and the Gibbs–DiMarzio theory[22] has also been criticized.[35] Here, we assume that a configurational ground state for the amorphous state is conceptually possible, and that T_2 is physically relevant to relaxation behavior.

Calculation and Fitting Procedures

The method for calculating normalized heat capacities $C_p{}^N$ was similar to that described previously.[12] Nonexponentiality is described by the celebrated Kohlrausch–Williams–Watt function

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \qquad 1 \geq \beta > 0 \qquad (21)$$

with τ_0 expressed as a function of T and T_f according to the AGL or AGV expressions. Equation 21 was first applied to structural relaxation by Rekhson et al.[36] and is known to be quite accurate for a large number of relaxation processes in condensed media. The methods for dividing the annealing time, t_e, into subintervals, and for calculating high-heat-capacity overshoots, differed somewhat from earlier studies, however. First, t_e was divided into five subintervals per decade of time (in seconds), rather than a constant total of 10 subintervals. This produced more accurate values of T_f' for long t_e. Second, for large over-

Table I
Narayanaswamy Parameters

material	ln A, s	$\Delta h^*/R$, kK	x	β	ref
PVAc	−224.5	71	0.35	0.57	38
	−277.50	88	0.27	0.51	this work
PVC	−622.0	225	0.10	0.23	this work
PS	−211.20	80	0.49	0.74	this work
PMMA	−357.8	138	0.19	0.35	this work
PC	−355.8	150	0.19	0.46	this work
As_2Se_3	−85.5	40.9	0.49	0.67	39
B_2O_3	−75.6	45	0.40	0.65	40
5P4E	−153.1	38.5	0.40	0.70	39
Ca^{2+}–K^+–NO_3^-	−202.47	70	0.31	0.46	41
$NaKSi_3O_7$	−62.79	49	0.70	0.66	42
$ZBLA^a$	−282.6	165	0.19	0.50	43

[a] See ref 43 for explicit composition. Δh^* taken from ref 43.

shoots the usual constant-temperature step, ΔT_j, of 1 K was reduced in inverse proportion to $C_p{}^N$ calculated for the previous step, $C_{p,j-1}{}^N$:

$$\Delta T_j = 1/C_{p,j-1}{}^N \qquad C_{p,j-1}{}^N > 1$$
$$= 1.0 \qquad C_{p,j-1}{}^N \leq 1 \qquad (22)$$

This procedure ensured that changes in T_f did not exceed 2 K per step, for $C_p{}^N$ overshoots less than about 5 or 6. For higher overshoots, this procedure did not guarantee that $\Delta T_f < 2$ but was tolerated since only one set of data exhibited an overshoot of more than 6. The new procedure also generated values of $C_p{}^N$ at noninteger temperatures; values at integer temperatures, needed to fit experimental data, were obtained by linear interpolation. The Marquardt algorithm for obtaining best-fit parameters was described earlier.[37] As before,[13,37] one of the four parameters was fixed and the other three optimized. Initial studies indicated that fixing B (AGL) or D (AGV), eq 8 and 13, produced values of T_2, A, and β that depended on their starting values. Better behavior was found when T_2 was fixed. In this case starting values of B and D were calculated from T_2 and experimental values of T_f' and Δh^*, using eq 9 and 14. Starting values for ln A were calculated by placing $\tau_0 = 10$ s at $T = T_f = T_f'$ into the appropriate equation for τ_0, and starting values β were set equal to published N values.[13] Averaged sets of parameters were obtained for values of T_2 that gave the lowest overall residuals. Because the calculation procedure differed from earlier versions, new sets of N parameters were also obtained, with Δh^* fixed at the experimental values[12,13,37] determined from the cooling-rate dependence of T_f'.[8]

Results

The new N parameters for polystyrene PS, PVAc, poly(methyl methacrylate) (PMMA), and bisphenol A polycarbonate (PC) are collected in Table I, together with those obtained by others for nonpolymeric glasses. An additional set of parameters was obtained for PVAc with $\Delta h^*/R = 71$ kK, the activation energy reported by Sasabe and Moynihan.[38]

Best-fit AGL and AGV parameters for polymers, and those for nonpolymeric glasses estimated from published N parameters, are given in Tables II and III, respectively. Two sets of AGV parameters are given for PS (see Discussion). Experimental and calculated values of $C_{p,max}{}^N$ and T_{max} for poly(vinyl chloride) PVC are given in Table IV as a function of T_e and t_e (here $C_{p,max}{}^N$ is the maximum value of $C_p{}^N$ for the annealing-induced endotherm and T_{max} the temperature at which it occurs).

AGV fits for PS are shown in Figures 1–3, for PVAc in Figures 4 and 5, for PMMA in Figures 6 and 7, and for PC in Figures 8 and 9. The AGL and new N parameters gave similar fits in most cases and are compared with AGV fits