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Volume and Enthalpy Relaxation Rate in Glassy Materials

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ABSTRACT: Volume and enthalpy relaxation in glassy materials subjected to a temperature jump $\Delta T = T_0 - T$ can conveniently be compared on the basis of the fictive relaxation rate $R_f = -(dT_f/d \log t)_i$. It has been shown that within the current phenomenological model, involving the stretched exponential relaxation function and the reduced time integral, the R_f can be described by a simple equation $R_f = 2.303/[e/\Delta T\beta + \sigma]$. A remarkable feature of this equation is that it separates the contribution of nonexponentiality (β) and nonlinearity (σ). The nonlinearity contribution corresponds to structural changes during the relaxation process. It can be expressed for the Narayanaswamy−Moynihan (NM) model as $\sigma = (1 - x)\Delta h^*/RT_g^2$ and for the Adam−Gibbs (AG) model as $\sigma = BT_2/T(T_g - T_2)^2$. This equation for $R_f(\Delta T)$ predicts an increasing fictive relaxation rate with the magnitude of the temperature jump and it has been tested by using reported NM and AG parameters and experimental volume and enthalpy relaxation data reported for various glassy materials, such as As_2S_3, As_2Se_3, polystyrene, poly(vinyl acetate), polycarbonate, poly(methyl methacrylate), poly(vinyl chloride), epoxy, etc. The R_f data for volume and enthalpy relaxation are very similar (within the limit of experimental errors) for all materials examined. The prediction of the $R_f(\Delta T)$ for the NM and AG models agrees well with experimental data at moderate temperature departures ($\Delta T \leq 10$ K). Discrepancies observed at higher temperature departures $\Delta T >$ 10 K are discussed.

I. Introduction

It is well established that glassy materials below the glass transition temperature T_g exist in a nonequilibrium state characterized by excess thermodynamic quantities (volume, enthalpy, etc.). These systems undergo a structural relaxation process which reduces excess quantities toward equilibrium values. A clear demonstration of such relaxation behavior is a temperature jump experiment well described by Tool[1] and Kovacs.[2] If a glassy material is equilibrated at temperature T_0 (usually near T_g) and then suddenly cooled to temperature T, the volume will change as shown in Figure 1. During this temperature jump the vibrational response causes an instantaneous change of volume corresponding to $V\alpha_g(T - T_0)$ because the structure of the glass does not change. Substantial structural changes then take place during the isothermal hold at T, and the volume will change gradually toward its equilibrium value at this temperature. The structural changes during the relaxation process can be conveniently characterized by means of *fictive temperature* T_f introduced by Tool.[1] T_f is defined as the temperature at which the specimen volume would be equal to equilibrium volume at T_f. Thus the fictive temperature decreases from T_0 to T in a manner that characterizes the particular relaxation process (as shown in Figure 1).

Isothermal volume relaxation following the temperature jump experiment can be described by means of relative departure δ_V of actual volume V from equilibrium volume V_∞ (see Figure 1) and defined[2] as

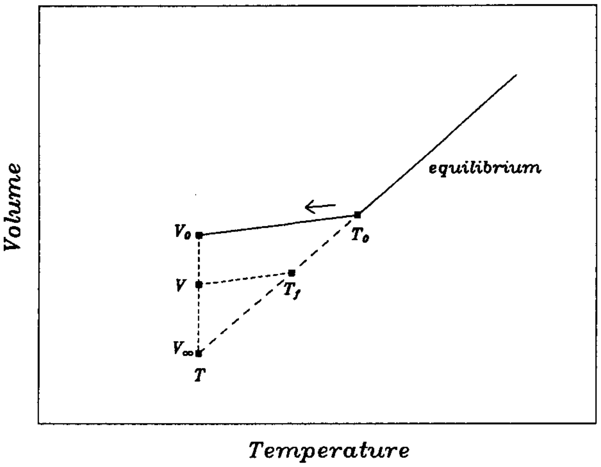

Figure 1. Schematic illustration of the volumetric changes of a equilibrated glassy material subjected to a temperature jump from temperature T_0 to T.

$$\delta_V(t) = \frac{V(t) - V_\infty}{V_\infty} \tag{1}$$

Initial departure from equilibrium δ_V^0 can be related to the magnitude of temperature jump $\Delta T = T_0 - T$ and it is defined[2] as

$$\delta_V{}^0 = \Delta\alpha\Delta T \tag{2}$$

where $\Delta\alpha$ is the difference between the volume thermal expansion coefficient of the equilibrium undercooled liquid and volume thermal expansion coefficient of the glass. Isothermal enthalpy relaxation following the temperature jump experiment is usually described by means of the excess enthalpy[3] defined as

$$\delta_H = \Delta H_\infty - \Delta H(t) \tag{3}$$

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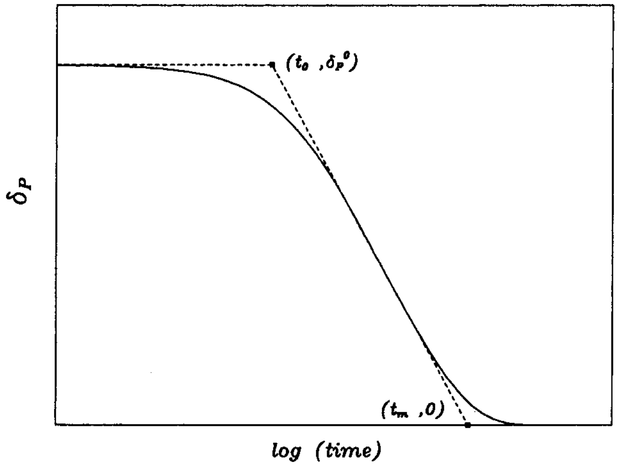

Figure 2. Isothermal relaxation curve corresponding to the thermal history depicted in Figure 1.

where ΔH is the relaxation enthalpy corresponding to the net area under the DSC peak of the annealed sample in comparison to the enthalpy change of the quenched sample taken as the reference. The value of $\delta_H{}^0$ can be related to the magnitude of temperature jump ΔT and expressed[2] as

$$\delta_H{}^0 = \Delta H_\infty \cong \Delta C_p \Delta T \tag{4}$$

where ΔH_∞ is the limiting long time (equilibrium) value of $\Delta H(t)$ and ΔC_p is the heat capacity change at T_g. It is often more convenient to describe the excess enthalpy of a glassy material using T_f rather than δ_H.[3]

Time dependence of δ_P function (where P refers to particular macroscopic property such as volume, enthalpy, etc.) is usually plotted on a logarithmic time scale as shown in Figure 2. The broken line corresponds to an inflectional tangent, and its slope $-(\mathrm{d}\delta_P/\mathrm{d}\log t)_i$ is usually referred to as the relaxation rate. This parameter introduced by Kovacs[2,4] became quite popular and it is often used to compare the volume[4-8] and enthalpy[9-11] relaxation kinetics in various glassy materials. There was also an attempt made to compare both volume and enthalpy relaxation rates for various glassy polymers.[12] The main problem of such comparison is that $-(\mathrm{d}\delta_V/\mathrm{d}\log t)_i$ and $-(\mathrm{d}\delta_H/\mathrm{d}\log t)_i$ are not fully comparable quantities because the $\Delta\alpha$ and ΔC_p may be different for many materials. Therefore, observed changes in the relaxation rate can be partially caused by these differences. It has been shown recently[13,14] that a possible solution is the *fictive relaxation rate* R_f defined as the change of the fictive temperature per decade of time:

$$R_f = -(\mathrm{d}T_f/\mathrm{d}\log t)_i \tag{5}$$

where subscript i refers to the inflection point. This parameter is very useful when the relaxation response in different materials is compared.

The aim of this paper is to analyze available isothermal volume contraction data and their enthalpy equivalent for some organic polymers and inorganic glassy materials. The rate-controlling factors for such isothermal experiments are analyzed for the most frequently used phenomenological models,[3] i.e., Narayanaswamy−Moynihan and Adam−Gibbs. It is shown that mathematical analysis of the condition for the inflectional slope of the relaxation curve yields a simple equation relating the fictive relaxation rate and kinetic parameters characterizing the relaxation process. This equation can be used for prediction of the isothermal enthalpy and volume relaxation rate in different glassy materials. In light of this analysis we examine previously reported isothermal volume relaxation data and enthalpy relaxation data for arsenic selenide (As_2Se_3) and arsenic sulfide (As_2S_3) glasses, polystyrene (PS), poly(vinyl acetate) (PVA), bisphenol A polycarbonate (PC), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and some other materials.

II. Phenomenological Model

It is well established[3] that the structural relaxation is both nonexponential and nonlinear. The *nonexponential* behavior means that the relaxation toward equilibrium following a single temperature jump ΔT is described by a nonexponential decay function $\delta_P(t)$. This is formally equivalent to a distribution of relaxation times. An empirical function which has been found to give a reasonably accurate fit to the structural relaxation process in a large variety of amorphous materials is a stretched exponential function[3,15]

$$\delta_P(t) = \delta_P{}^0 \exp[-(t/\tau)^\beta] \tag{6}$$

where τ is a characteristic time and β ($0 < \beta \leq 1$) is a direct measure of nonexponentiality. The parameter β is inversely proportional to the width of corresponding distribution of relaxation times and therefore it is also related to the cooperativity inherently associated with the structural relaxation in glassy state.[16]

It should be stressed, however, that although eq 6 describes well $\delta_P(t)$ data for a small temperature jumps (i.e., near equilibrium), it fails for a temperature jumps higher than $\Delta T > 1$ K. This *nonlinear* behavior was studied and explained by Tool.[1] He established that τ cannot depend only on temperature and suggested that it should depend in addition upon the instantaneous structure of a glass characterized by T_f. Therefore, τ will vary with t during the isothermal hold after the temperature jump. Narayanaswamy[17] argued that since the nonlinearity of structural relaxation arises from the time dependence of τ, linear behavior can be restored by using the reduced time defined by

$$\xi = \int_0^t \frac{\mathrm{d}t'}{\tau(T, T_f)} \tag{7}$$

The normalized relaxation function then can be expressed as[17]

$$\frac{\delta_P(\xi)}{\delta_P{}^0} = \exp(-\xi^\beta) = \frac{T_f - T}{\Delta T} \tag{8}$$

The most frequently used expression for $\tau(T,T_f)$ in eq 7 is the Narayanaswamy equation[17] as modified later by Moynihan et al.[18] (referred to as NM):

$$\tau(T, T_f) = A \exp\left[x\frac{\Delta h^*}{RT} + (1 - x)\frac{\Delta h^*}{RT_f}\right] \tag{9}$$

where A is the preexponential constant, x is the nonlinearity parameter ($0 < x \leq 1$), and Δh^* is the effective activation energy. An equivalent but much less used expression for $\tau(T,T_f)$ is the KAHR equation.[19] The TN formalism has been extensively tested on many glassy materials and it was found that it describes the glass transition and glassy state relaxation very well (for details, see, e.g., ref 3). Nevertheless, it should be recognized that eq 9 is purely empirical and therefore the NM parameters A, Δh^*, and x have no clear physical interpretation.[3]

Another formulation of nonlinearity is based on the entropic Adam-Gibbs equation[20] for τ which was originally derived from a generalization of the transition state expression:

$$\tau = A\ \exp\left(\frac{z^*(T)\Delta\mu}{k_B T}\right) \tag{10}$$

where k_B is the Boltzmann constant, $\Delta\mu$ is the potential barrier hindering rearrangement, and $z^*(T)$ is temperature dependent number of cooperatively rearranging entities. The temperature dependence of $z^*(T)$ is determined by the macroscopic configurational entropy S_c:[20]

$$z^*(T) = \frac{N_A s_c^*}{S_c} \tag{11}$$

where s_c^* is entropy of the smallest number of rearranging entities and N_A is Avogadro's number. Equations 10 and 11 then yield

$$\tau = A\ \exp\left(\frac{B'}{TS_c}\right) \tag{12}$$

where $B' = N_A\Delta\mu s_c^*/k_B$. The fictive temperature is introduced into eq 12 through the expression for the macroscopic configurational entropy S_c as[21-23]

$$S_c = \int_{T_2}^{T_f} \frac{\Delta C_p(T)}{T}\, \mathrm{d}T \tag{13}$$

where $\Delta C_p(T)$ is configurational heat capacity and T_2 is the temperature at which S_c extrapolates to zero; i.e., it is conceptually identical with the thermodynamic Kauzmann temperature T_K. Equation 13 suggests that the fictive temperature of a glass is a measure of its configurational entropy during the relaxation process. Usually it is assumed that the entropic and enthalpic fictive temperatures are the same, since the integrals of $\Delta C_p(T)$ and $\Delta C_p(T)/T$ are nearly proportional in narrow range of $T_f - T$ for the most relaxation experiments.[23]

An explicit expression for $\tau(T,T_f)$ can be derived from eqs 12 and 13, and it depends on the temperature dependence of $\Delta C_p(T)$. For the first time these equations were applied to enthalpy relaxation by Scherer[22] who assumed a linear temperature dependence $\Delta C_p(T) = c_0 + c_1 T$. Then from eqs 12 and 13 it follows that

$$\tau(T,T_f) = A\ \exp\left[\frac{Q/T}{\ln(T_f/T_2) + c(T_f - T_2)}\right] \tag{14}$$

where $Q = N_A\Delta\mu S_c^*/k_B c_0$ and $c = c_1/c_0$. In similar way we can obtain a simple equation for constant $\Delta C_p(T) = c_0$:

$$\tau(T,T_f) = A\ \exp\left[\frac{Q}{T\ln(T_f/T_2)}\right] \tag{15}$$

Hodge[23] used a hyperbolic expression for configurational heat capacity $\Delta C_p(T) = \Delta C_p(T_2)T_2/T$ and obtained a simple expression (here referred to as the AG equation):

$$\tau(T,T_f) = A\ \exp\left[\frac{B}{T(1 - T_2/T_f)}\right] \tag{16}$$

where $B = N_A\Delta\mu S_c^*/k_B\Delta C_p(T_2)$. Note that the well-known Vogel–Tamman–Fulcher (VTF) equation is obtained[21] from eq 16 for $T_f = T$. The AG formalism provides a valuable insight into structural relaxation of glasses, using the concept of cooperatively rearranging regions. The nonlinearity then can be associated with the difference between the kinetic glass transiton temperature T_g and the thermodynamic Kauzmann temperature.[3,23,24] It has been hypothesized[3] that the potential barrier $\Delta\mu$ determines the T_g/T_2 ratio and thus a positive correlation between B and T_g/T_2 is expected. Such types of correlations were found[24] for different classes of materials.

III. The Fictive Relaxation Rate

The fictive relaxation rate R_f is introduced[13,14] by eq 5. The time dependent volume relaxation response to the temperature jump is $\delta_V(t) = \Delta\alpha[T_0 - T_f(t)]$. Therefore, the R_f for volume relaxation can be written as follows

$$R_f = -\frac{1}{\Delta\alpha}\left(\frac{\mathrm{d}\delta_V}{\mathrm{d}\log t}\right)_i \tag{17}$$

and similarly the fictive rate for the enthalpy relaxation response is

$$R_f = -\frac{1}{\Delta C_p}\left(\frac{\mathrm{d}\delta_H}{\mathrm{d}\log t}\right)_i \tag{18}$$

For simplicity the temperature dependence of $\Delta\alpha$ and ΔC_p is neglected. These fictive relaxation rates can easily be obtained from the experimental $\delta_P(\log t)$ data. The main advantage of this definition of the relaxation rate is that the value of R_f should depend only on the magnitude of the temperature jump and the parameters of the phenomenological model described in section II.

Differentiation of eq 8 with respect to ln t at the inflection point then yields

$$-\left(\frac{\mathrm{d}\delta_P}{\mathrm{d}\ln t}\right)_i = \frac{\delta_{Pi}\beta\xi_i^\beta}{1 + \sigma(\mathrm{d}T_f/\mathrm{d}\delta_P)_i\delta_{Pi}\beta\xi^\beta{}_i} \tag{19}$$

where

$$\sigma = -\left(\frac{\partial\ln\tau}{\partial T_f}\right)_i \tag{20}$$

By numerical simulations it was found[13] that at the inflection point $\delta_{Pi} \cong (\delta_P^0/e)\xi_i^{-\beta}$. Then from eqs 8 and 19 one can obtain the following expression

$$-\frac{\Delta T}{\delta_P{}^0}\left(\frac{\mathrm{d}\delta_P}{\mathrm{d}\ln t}\right)_i = \left[\frac{e}{\Delta T\beta} + \sigma\right]^{-1} \tag{21}$$

By comparison of eqs 2, 4 and eqs 17, 18 is evident that the left-hand side of eq 21 corresponds to $R_f/\ln(10)$. Therefore we can write the following expression for the parameter R_f:

$$R_f = 2.303\left[\frac{e}{\Delta T\beta} + \sigma\right]^{-1} \tag{22}$$

This equation predicts increasing fictive relaxation rate with the magnitude of the temperature jump, which agrees well with experimental observations.[2] The nonexponentiality parameter β has a similar effect and, therefore, for a constant ΔT one can expect decreasing relaxation rate with broadening of the distribution of relaxation times (i.e., decreasing of β). The influence of the parameter σ on the $R_f(\Delta T)$ plot and $R_f(10)$ vs β plot is shown in Figure 3. This parameter corresponds to the degree of nonlinearity of the particular relaxation response. In a linear case ($\sigma = 0$) there is no structural contribution of the relaxation time and, therefore, we can expect the maximum fictive relaxation rate $R_f^{\max} = 0.847\Delta T\beta$. However, for most glassy systems $\sigma > 0$, which means that they relax more slowly. For $\sigma > 0.6$ the fictive relaxation rate is very slow and is nearly independent of ΔT and β, and its particular value is mainly determined by the parameter σ.

Equation 22 apparently separates the contribution of nonexponentiality (β) and nonlinearity (σ). This feature is remarkable as it is usually believed[12] that these two contributions seems to be inextricably bound together by the reduced time, relaxation function, and nonlinearity expression (equations 7, 8, and 9 or 16). The separation of these two aspects of relaxation behavior suggests the possibility of evaluation of parameters β and σ from $R_f(\Delta T)$ data. The problems related to such an evaluation procedure are discussed elsewhere.[13]

From eqs 20 and 9 we can find the parameter σ for the NM model:

$$\sigma \cong (1 - x)\frac{\Delta h^*}{R{T_g}^2} \tag{23}$$

Similarly, from eqs 20 and 16 the parameter σ for the AG model yields

$$\sigma \cong \frac{T_2 B}{T(T_g - T_2)^2} \tag{24}$$

In both cases the approximation $T_{f,i} \cong T_g$ has been used. Similar expressions for σ can be easily obtained for another formulation of nonlinearity defined by eqs 14 and 15. The relationships between NM and AG parameters derived by Hodge[3,21,23] can also be obtained from the condition d ln τ/d($1/T$) and eqs 23 and 24, assuming that $T_f \cong T \cong T_g$

$$1 - x \cong \frac{T_2}{T_g} \tag{25}$$

and

$$\frac{\Delta h^*}{RT_g^2} \cong \frac{B}{(T_g - T_2)^2} \tag{26}$$

The left-hand side of eq 26 is a reduced effective activation energy, θ, first introduced in the KAHR model.[19] This is a characteristic constant for a particular glassy material,[3] generally close to 1 (or higher) for polymeric materials and 0.1−0.3 for inorganic glasses. Equation 26 indicates that θ and x are inversely correlated,[3] since $\theta = B/(xT_g)^2 \approx 1/x$. Therefore, one can expect considerably higher values of parameter σ and thus slower relaxation rates for polymeric materials. On the other hand, relative fast relaxation (low value of σ) is expected for inorganic glasses.

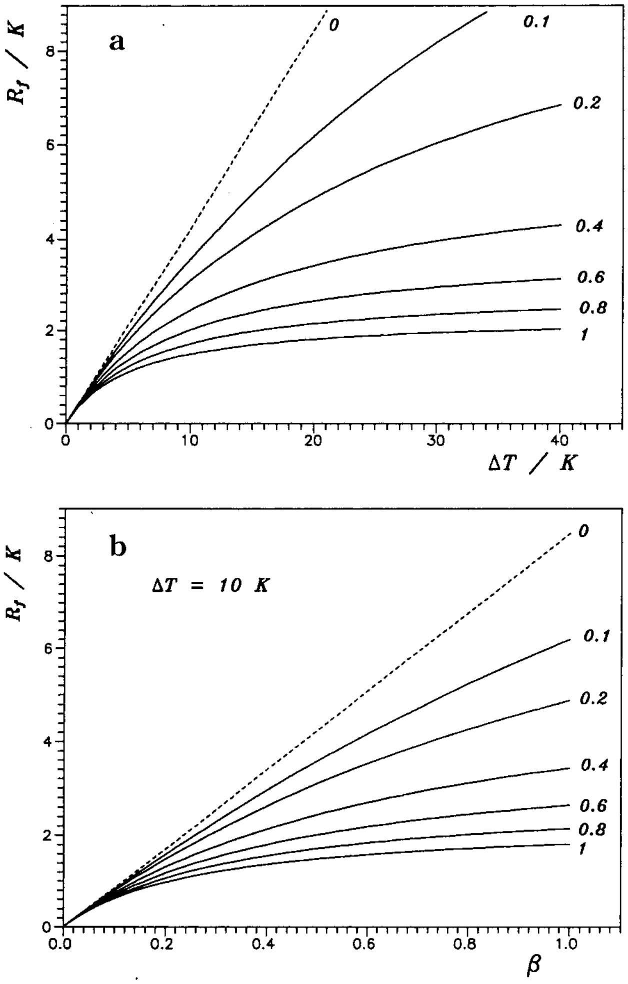

Figure 3. (a) The dependence of the fictive relaxation rate R_f on the magnitude of temperature jump calculated using eq 22 for $\beta = 0.5$. (b) $R_f(10)$ as a function of the nonexponentiality parameter β. The values of parameter σ are shown next to the curves.

It should be recognized that alhough NM and AG parameters are related through eqs 25 and 26, the nonlinearity contribution σ is defined in substantially different ways for both models. According to eq 23 the parameter σ is temperature independent, being a characteristic constant for given material. Therefore, in this case eq 22 predicts that for the NM model $R_f(\Delta T)$ increases even for very high-temperature departures (see Figure 3). In contrast, the parameter σ is temperature dependent for the AG model. Thus, one can expect practically constant or even slightly decreasing R_f for sufficiently high ΔT. This point will be addressed in more detail later when the $R_f(\Delta T)$ data obtained by dilatometric and calorimetric experiments for various glassy materials are compared with predictions of both NM and AG models.

IV. Discussion

In assesssing the applicability of the concept of fictive relaxation rate we consider first some problems related to correct determination of ΔT. Following this we discuss the quality of reported $\delta_P(\log t)$ and $-(d\delta_P/d \log t)_i$ data for volume and enthalpy relaxation and the reliability of $R_f(\Delta T)$ determined from eqs 17 and 18. Finally, the $R_f(\Delta T)$ data obtained by dilatometric and calorimetric experiments are compared with predictions of eq 22 for NM and AG parameters of various glassy materials. The influence of rate-determining factors (parameters β and σ) is discussed.

Equation 22 predicts an increasing fictive relaxation rate with the magnitude of the temperature jump $\Delta T = T_0 - T$. Implicitly it is assumed that $T_f(0) = T_0$. In fact, it is rather difficult to change the temperature so quickly (in particular for polymer samples) and there is always finite initial time t_{ini} needed to reach thermal equilibrium of a real sample.[2,6,12] If T_0 is too high ($T_0 \gg T_g$) then the relaxation response during the thermal equilibration will be very fast and an important part of the relaxation occurs before t_{ini} is reached. In this case the first part of the relaxation curve will be truncated and a true inflectional slope as well as a $\delta_P{}^0$ value cannot be determined correctly. Consequently, the fictive temperature of the sample may change considerably during this thermal equilibration. Therefore, it seems to be more correct if ΔT is defined as the temperature departure from the fictive temperature after t_{ini} has elapsed, i.e., $\Delta T = T_f(t_{ini}) - T$. The $T_f(t_{ini})$ can be calculated by using eq 8 for a given set of NM or AG parameters. To simplify this problem, it is assumed here that $T_f(t_{ini})$ is essentially close to T_g provided that $T_0 \geq T_g$. On the other hand one can expect that the change in fictive temperature is small immediately after the temperature jump if $T_0 < T_g$. Thus the temperature departure may be defined as follows

$$\Delta T = T_g - T \qquad \text{for} \qquad T_0 \geq T_g$$

$$\Delta T = T_0 - T \qquad \text{for} \qquad T_0 < T_g$$

Dilatometric T_g is then defined as the temperature where the relaxation response apparently corresponds to the exponential relaxation[3,14] (i.e., $\log(t_m/t_0) = e/\ln(10) \cong 1.18$). The value of dilatometric T_g can also be estimated by extrapolating the temperature dependence of the inflectional slope $-(d\delta_P/d \log t)_i$ to zero. For calorimetric experiments ΔT corresponds to $T_g - T$. The glass transition temperature T_g for enthalpy relaxation should be obtained from the cooling DSC scan by using the integration procedure described by Richardson and Savill[25] and Moynihan et al.[18] Nevertheless, it is quite common in the literature that the T_g value is obtained from the heating DSC scan. Such a definition is rather problematic since T_g is affected by the previous thermal history of a glassy material. It should be also pointed out that calorimetric and dilatometric T_g need not have necessarily the same value. These facts should also be taken into consideration when normalized volume and enthalpy relaxation rates are compared.

For any practical application of the concept of fictive relaxation rate it is essential to consider how the experimental R_f value was obtained. In an ideal case, the R_f value can directly be obtained from the slope of the $T_f(\log t)$ plot according to eq 5. Figure 4 shows such plots for volume and enthalpy temperature jump experiments for As_2S_3 glass.[28] The fictive temperature for volume relaxation was calculated by $T_f = T + \Delta T(\delta_V/\delta_V{}^0)$, and for enthalpy relaxation it was obtained by using the method described by Moynihan et al.[29]

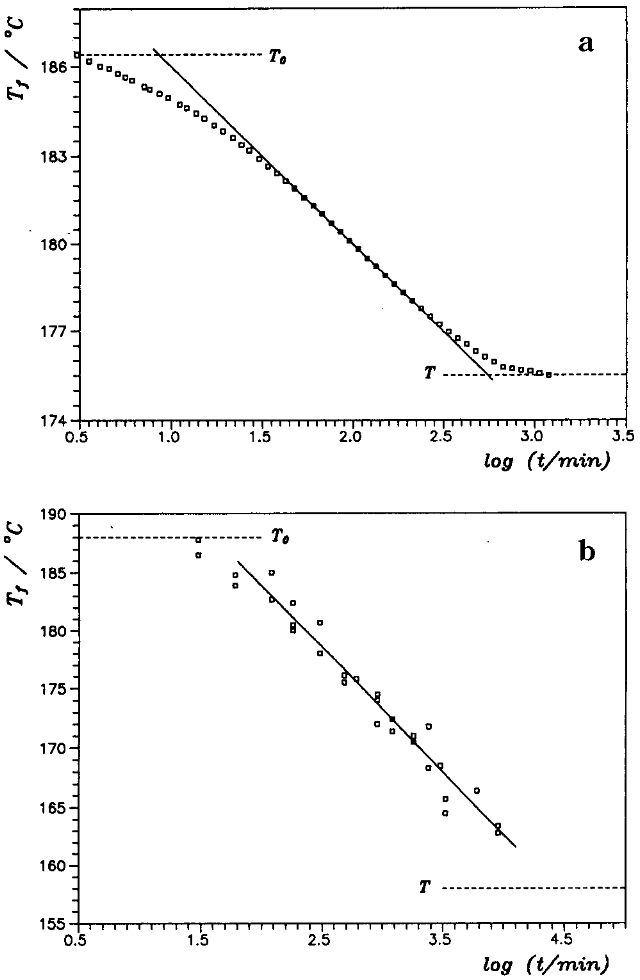

Figure 4. Fictive temperature as a function of time for As_2S_3 glass subjected to temperature jump experiments: (a) Volume relaxation data T_0 = 186.4 °C, T = 175.5 °C. (b) Enthalpy relaxation data T_0 = 188 °C, T = 158 °C.

These data, however, are not always available. If the R_f is determined from the slope of the isothermal relaxation curve $\delta_P(\log t)$ (according eqs 17 and 18), it is important to be sure that it corresponds to a truly inflectional tangent. There is always an initial curvature observed on the relaxation curves (see Figure 2), which may be extended to several decades of time, particularly for higher temperature departures ΔT. Consequently, if an insufficiently long experimental time scale, t_e, is used, then the slope of the $\delta_P(\log t)$ curve and thus also R_f values can easily be underestimated.[6,12] Similar problems may also occur due to curvature of the $\delta_P(\log t)$ plot for very long times close to equilibrium ($t \approx t_m$). For these reasons, it is very difficult to estimate the reliability of frequently reported $-(d\delta_P/d \log t)_i$ data unless the original $\delta_P(\log t)$ plots or at least t_e are known. Therefore, care needs to be exercised in the interpretation of the R_f defined in terms of $-(d\delta_P/d \log t)_i$ data, especially for short t_e and higher temperature departures ΔT. It should be also mentioned that experimental error is generally larger in the measurement of δ_H than δ_V, which causes some difficulties in the identification of enthalpic equilibrium.[12] With increasing time more samples must be scanned and this procedure is repeated until no furher change in δ_H is observed. There are a number of difficulties associated with this procedure. On the other hand, the equilibrium is clearly seen when there is no further change in volume with log time.

The temperature dependence of $\Delta\alpha$ and ΔC_p in eqs 17 and 18 is neglected. Such an approximation is

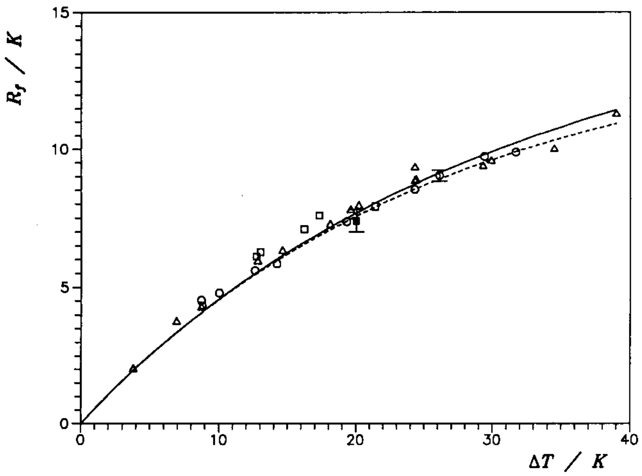

Figure 5. Fictive relaxation rate as a function of temperature departure from T_g for As_2Se_3 glass. Points correspond to dilatometric data [Málek[28] $T_0 = 166$ °C (□), $T_0 = 173$ °C (△), $T_0 = 177$ °C (○)] and to calorimetric data [Moynihan et al.[29] (■)]. The solid and dotted lines were calculated by using eqs 22–24 for NM parameters (Table 2) and AG parameters (Table 3), respectively.

acceptable for dilatometric measurements because $\Delta\alpha$ is nearly temperature independent.[12] Nevertheless, the approximation is more problematic for calorimetric experiments. It is well-known that the value of ΔC_p generally decreases with increasing thermodynamic temperature.[22,26,27] Therefore, ΔC_p increases with the magnitude of temperature departure ΔT. Consequently, the related value of R_f may be in fact slightly lower than obtained from a simplified eq 18 neglecting temperature dependence of ΔC_p. From data reported in refs 22 and 26, it is possible to estimate that the error introduced by such a simplification is about 5% for ΔT =10 K. On the other hand, it is rather difficult to estimate the error for higher temperature departures, because an extrapolation of $\Delta C_p(T)$ data from temperatures $T > T_g$ far below T_g is uncertain.

Experimental errors in $\delta_V(\log t)$ plots for dilatometric temperature jump experiments increase considerably if the initial part of isothermal relaxation curve is truncated. As already noted, this occurs particularly if the temperature T_0 is too high ($T_0 \gg T_g$), leading to $\delta_V{}^0 < \Delta\alpha\Delta T$, which is a well-known fact[2] to all experimentalists working in this field. In this case it becomes quite difficult to construct a true inflectional slope correctly and therefore the R_f values can be seriously in error. Such problems may be also important for the calorimetric experiments if the fast temperature jump ("quench") is replaced by a slower cooling rate. It is not so easy to assess reliable error limits in R_f data due to the factors mentioned above. However, comparing reported dilatometric[2,4–8] and calorimetric[9–12] data the experimental error in R_f is estimated to be about ±0.2 K for dilatometric and ±0.4 K for calorimetric data.

Figure 5 shows the fictive relaxation rate R_f as a function of temperature departure ΔT for arsenic selenide (As_2Se_3) glass. The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of $T_f(\log t)$ plots reported by Málek[28] for different temperature jump experiments: $T_0 = 166$ °C, □; $T_0 = 173$ °C, △; $T_0 = 177$ °C, ○. Dilatometric T_g (174 °C) was obtained by extrapolation of $\log(t_m/t_0)$ vs $1/T$ plot [$(\log(t_m/t_0) = 1.18$]. The datum for enthalpy relaxation (■) was obtained from the inflectional slope of $T_f(\log t)$ plot reported by Moynihan et al.[29] for temperature jump $\Delta T = 20$ K. The solid line in Figure 4 was calculated by using eqs 22 and 23 for NM parameters obtained by curve fitting of calorimetric data[29] (see Table 2). The dotted line was calculated for AG parameters using eqs 22 and 24 (see Table 3). These predictions agree quite well with dilatometric and calorimetric data up to $\Delta T = 30$ K. However, it is evident that AG formalism provides a better account for the fictive relaxation rate at higher temperature departures as a consequence of temperature-dependent parameter σ. Due to a very small nonlinearity contribution ($\sigma = 0.10$) the fictive ralaxation rate at $\Delta T = 10$ K, $R_f(10)$, is relatively high, being about 5.5 K [i.e., $R_f(10) \cong 0.97R_f{}^{max}$].

Table 1. Summary of T_g, $\Delta\alpha$, and ΔC_p Values

material	T_g/K	$\Delta\alpha \times 10^4$/K^{-1}	ΔC_p/J g^{-1} K^{-1}	ref
As_2Se_3[a]	464	2.53	0.21	30, 28
As_2S_3[a]	461	2.22	0.34	13, 28
PS	373	3.3	0.31	6, 35
PVA	310	4.5	0.46	2, 41
PC	415	3.9	0.23	6, 9
PMMA	381	3.3	0.27	6, 48
PVC	353	4.30	0.34	6, 50

[a] In this case the value of $\Delta\alpha$ was calculated from the $\Delta\alpha_L$ obtained by length dilatometry ($\Delta\alpha \cong 3\Delta\alpha_L$).

Table 2. Naraynaswamy–Moynihan Parameters[a]

material	$(\Delta h^*/R)$/kK	x	β	σ/K^{-1}	ref
As_2Se_3	40.9	0.49	0.67	0.10	29
As_2S_3	32.4	0.31	0.82	0.11	31
PS	110	0.41	0.47	0.47	33
PVA	88	0.27	0.51	0.67	23
PC	150	0.19	0.46	0.71	23
PMMA	138	0.19	0.35	0.77	23
PVC	225	0.10	0.23	1.63	23

[a] These parameters (except for As_2S_3) were obtained from nonisothermal calorimetric data. Parameters for As_2S_3 were obtained from isothermal dilatometric data. For details see corresponding references.

Table 3. Adam–Gibbs Parameters[a]

material	B/kK	T_2/K	β	σ/K^{-1}	ref
As_2Se_3[b]	9.82	237	0.67	0.10	23
As_2S_3[b]	3.11	318	0.82	0.11	
PS[b]	18.51	220	0.47	0.47	
PVA	6.23	225	0.55	0.63	23
PC	7.03	325	0.54	0.68	23
PMMA	3.43	325	0.34	0.93	23
PVC	2.61	320	0.28	2.17	23

[a] The parameter σ corresponds to $\Delta T = 0$. [b] Obtained from NM parameters by using eqs 25 and 26.

Figure 6 shows the fictive relaxation rate R_f as a function of temperature jump ΔT for arsenic sulfide glass (As_2S_3). The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of $T_f(\log t)$ plots reported by Málek for different temperature jump experiments: $T_0 = 188$ °C, □;[31] $T_0 = 186$ °C, △;[28] $T_0 = 177$ °C, ○.[28] Dilatometric T_g (188 °C) was obtained by extrapolation of the $\log(t_m/t_0)$ vs $1/T$ plot. Data for enthalpy relaxation (■) were obtained from the inflectional slope of the $T_f(\log t)$ plot.[28] It is clear that the dilatometric and calorimetric relaxation data for As_2S_3 glass give comparable values of R_f within the limits of experimental errors. The solid line in Figure 6 was calculated by using eqs 22 and 23 for NM parameters obtained by curve fitting of isothermal dilatometric data[31] (see Table 2). The dotted line was calculated for AG parameters by using eqs 22 and 24 (see Table 3). In

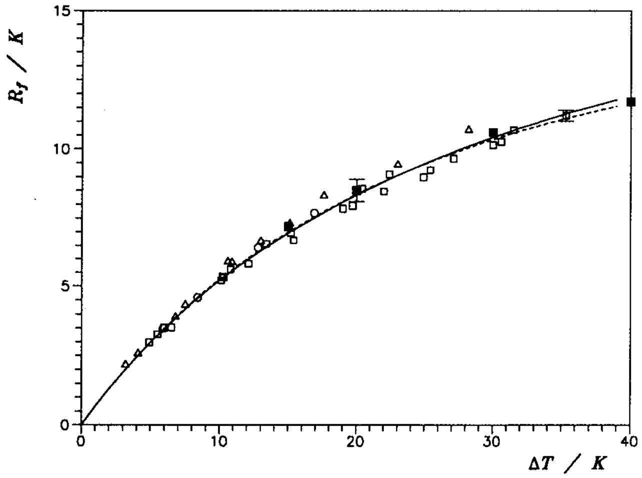

Figure 6. Fictive relaxation rate as a function of temperature departure from T_g for As_2S_3 glass. Points correspond to dilatometric data [Málek[28,31] $T_0 = 188$ °C (□), $T_0 = 186$ °C (△), $T_0 = 180$ °C (○)] and to calorimetric data [Málek[28] (■)]. The solid and dotted lines were calculated by using eq 22−24 for NM parameters (Table 2) and AG parameters (Table 3), respectively.

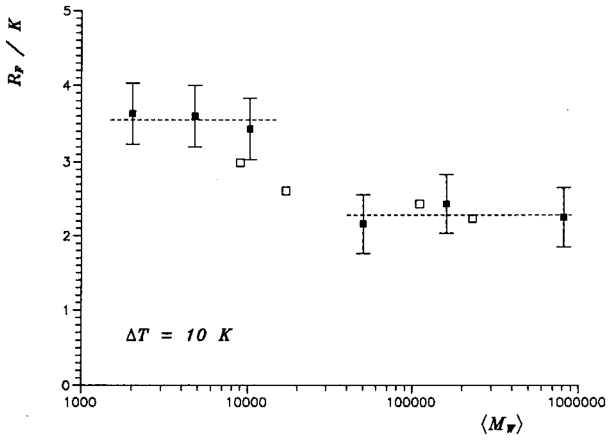

Figure 7. $R_f(10)$ as a function of molecular weight for enthalpy relaxation of PS. Points represent data reported by Marshall and Petrie[32] (■) and R_f calculated by using eq 22 for NM parameters reported by Privalko et al.[33] (□). The dotted lines are drawn as a guide to eye.

this case the prediction of R_f for NM and AG models agrees well for both dilatometric and calorimetric data up to $\Delta T = 40$ K. It is evident that the relaxation rate $R_f(10)$ for As_2S_3 is high, being about 5.0 K [i.e., $R_f(10) \cong 0.72 R_f^{max}$], as a consequence of a relatively narrow distribution of relaxation times ($\beta = 0.82$) and a very small nonlinearity contribution ($\sigma = 0.11$).

One of the most studied materials from the point of view of volume nad enthalpy relaxation is perhaps atactic polystyrene (PS). It is well-known that $\delta_H(\log t)$ plots,[32] as well as the NM parameters[33] of PS, depend on the molecular weight. Figure 7 shows the $R_f(10)$ data obtained from the inflectional slope of $\delta_H(\log t)$ plots reported by Marshall and Petrie[32] for different molecular weight (■). These data are compared with $R_f(10)$ calculated from eqs 22 and 23 for NM parameters reported by Privalko et al.[33] (□). Both data sets clearly demonstrate that higher molecular weight PS ($M_n \geq 5 \times 10^4$) relaxes more slowly ($R_f \cong 2.3$) than lower molecular weight PS ($M_n \leq 1 \times 10^4$) samples ($R_f \cong 3.6$). Observed differences in the fictive relaxation rate are higher than the expected uncertainties in the measured and calculated R_f.

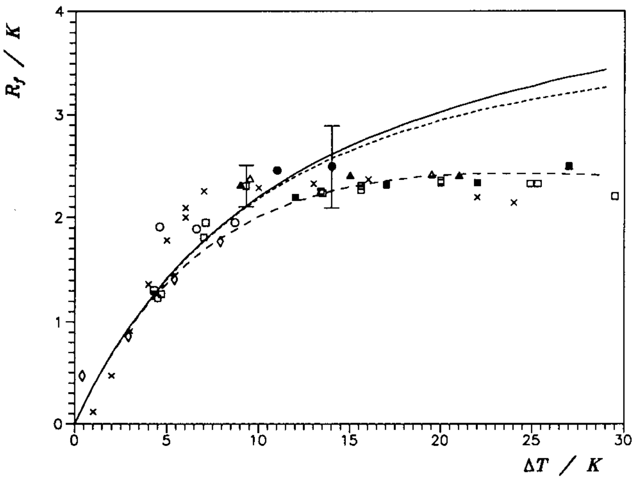

Figure 8. Fictive relaxation rate as a function of temperature departure from T_g for PS ($M_n > 50\,000$). Points correspond to dilatometric data [Greiner and Schwarzl[6] (□); Kovacs[4] (△); Hutchinson[12] (◇); Adachi and Kotaka[34] (○); Struik [5,7] (×)] and calorimetric data [Petrie[35] (■); Marshall and Petrie[32] (▲); Roe and Millman[36] (●); Chang and Li[37] (⊖)]. The solid and dotted lines were calculated by using eqs 22−24 for NM parameters (Table 2) and AG parameters (Table 3), respectively. The dashed line was calculated by using eqs 22 and 29 with $k = 5 \times 10^{-3}$ K^{-2}.

Therefore, for any quantitative comparison of volume and enthalpy relaxation rates it is important to compare data corresponding to PS samples of similar molecular weights. Such comparison of the $R_f(\Delta T)$ data for PS ($M_n > 5 \times 10^4$) is shown in Figure 8. The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of $\delta_V(\log t)$ plots reported by Greiner and Schwarzl[6] (□), Hutchinson[12] (◇), and Adachi and Kotaka[34] (○) for $\Delta\alpha$ shown in Table 1. The values obtained from $-(d\delta_V/d \log t)_i$ data of Kovacs[4] (△) are similar. Dilatometric T_g (100 °C) was obtained by extrapolation of $\log(t_m/t_0)$ vs T plot for data of Greiner and Schwarzl.[6] Higher values were found for data of Adachi and Kotaka[34] ($T_g = 101$ °C) and Hutchinson[12] ($T_g = 103$ °C). The $R_f(\Delta T)$ obtained from $-(d\delta_V/d \log t)_i$ data of Struik[5,7] (×) are very similar. In this case the dilatometric T_g (91 °C) has been estimated by extrapolating the temperature dependence of the inflectional slope $-(d\delta_V/d \log t)_i$ to zero. In this case the $\delta_V(\log t)$ plots are not available and, therefore, the dilatometric T_g cannot be determined by extrapolation of $\log(t_m/t_0)$ vs T plot. The $R_f(\Delta T)$ values for enthalpy relaxation were obtained from the inflectional slope of $\delta_H(\log t)$ plots reported by Petrie[35] (■), Marshall and Petrie[32] (▲), and Roe and Millman[36] (●) for ΔC_p shown in Table 1 and calorimetric $T_g = 104$ °C. The value of R_f obtained from the inflectional slope of $\delta_H(\log t)$ plot reported by Chang and Li[37] (⊖) is similar if a lower value of T_g (100 °C) is taken. It is evident that dilatometric and calorimetric relaxation data for PS give comparable values of R_f within the limits of experimental errors. Therefore, it seems that enthalpy and volume relaxation in PS ($M_n > 5 \times 10^4$) are very similar. This result agrees well with experimental finding of Takahara[38] who reported probably the first data for the simultaneous measurement of the enthalpy and volume relaxation in PS near T_g and demonstrated that volume and enthalpy relaxation functions are similar within the experimental errors. The solid line in Figure 8 was calculated by using eqs 22 and 23 for NM parameters (obtained by curve fitting of calorimetric data) reported by Privalko et al.[33] (see Table 2). The

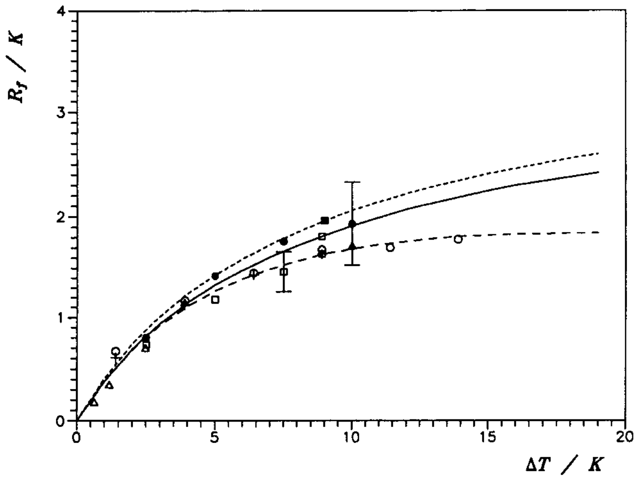

Figure 9. Fictive relaxation rate as a function of temperature departure from T_g for PVA. Points correspond to dilatometric data [Kovacs[2,39] $T = 30$ °C (□), $T = 35$ °C (△), $T_0 = 40$ °C (○); Delin et al.[40] (+)] and calorimetric data [Bair et al.[41] (■); Cowie et al.[42] (▲); Wang and Filisko[43] (●)]. The solid and dotted lines were calculated by using eqs 22−24 for NM parameters (Table 2) and AG parameters (Table 3), respectively. The dashed line was calculated by using eqs 22 and 29 with $k = 8 \times 10^{-3}$ K^{-2}.

dotted line was calculated for AG parameters using eqs 22 and 24 (see Table 3). These predictions are relatively good for both dilatometric and calorimetric data at $\Delta T < 10$ K but there are substantial discrepancies for higher temperature departures ($\Delta T > 10$ K). It seems that in this case the temperature dependence of the parameter σ for the AG model is not sufficient to provide a quantitative account for $R_f(\Delta T)$. This observation will enter into later discussion concerning the limits of applicability of eq 22 and alternative formulation of nonlinearity. The $R_f(10)$ for PS is considerably lower than for As_2Se_3 or As_2S_3 glass being about 2.2 K [i.e., $R_f(10) \cong 0.55R_f^{max}$]. This is mainly due to a higher value of the nonlinearity contribution ($\sigma = 0.47$) in comparison with inorganic glasses.

Figure 9 shows a comparison of volume and enthalpy fictive relaxation rates for poly(vinyl acetate) (PVA). The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of the $\delta_V(\log t)$ plots reported by Kovacs for different temperature jump experiments ($T_0 = 40$ °C, $25 \le T \le 37.5$ °C, ○),[2] ($T = 30$ °C, $32.5 \le T_0 \le 60$ °C, □),[2] and ($T = 35$ °C, $35.6 \le T_0 \le 40$ °C, △)[39] for Δα shown in Table 1. Dilatometric T_g (39 °C) was obtained by extrapolation of the $\log(t_m/t_0)$ vs $1/T$ plot for data of Kovacs[2] ($T_0 = 40$ °C, $25 \le T \le 37.5$ °C). Practically identical $R_f(\Delta T)$ values are obtained from the inflectional slope of the $\delta_V(\log t)$ plots reported by Delin et al.[40] ($T_0 = 40$ °C, $30 \le T \le 37.5$ °C, +) for the same Δα and T_g. The $R_f(\Delta T)$ values for enthalpy relaxation were obtained from the inflectional slope of the $\delta_H(\log t)$ plots reported by Bair et al.[41] (■), Cowie et al.[42] (▲), and Wang and Filisko[43] (●) for ΔC_p shown in Table 1 and calorimetric[42] T_g (40 °C). Bair et al.[41] have shown that calorimetric T_g for dry PVA sample is considerably higher ($T_g = 43.5$ °C) than for the sample containing 1.8% water ($T_g = 30$ °C). Nevertheless, the values of fictive relaxation rates for both these samples are very close for a constant ΔT. It is seen that dilatometric and calorimetric relaxation data for PVA give comparable values of R_f within the limits of experimental errors. The solid line in Figure 9 was calculated by using eqs 22 and 23 for NM parameters obtained by curve fitting of calorimetric data reported by Hodge[23] (see Table 2). The dotted line was calculated from eqs 22 and 24 for AG parameters obtained by curve fitting of the same data set [23] (see Table 3). The calculated $R_f(\Delta T)$ plots differ within the limit of experimental errors because there are differences in β and σ parameters for NM and AG formulation of nonlinearity. The prediction of NM and AG models agrees well with experimental R_f data for $\Delta T < 10$ K but, similarly as observed for PS, there are systematic deviations for higher temperature departures ΔT. These discrepancies are discussed in more detail below. The $R_f(10)$ for PVA is lower than the value observed for PS, being about 1.7 K [i.e., $R_f(10) \cong 0.39R_f^{max}$].

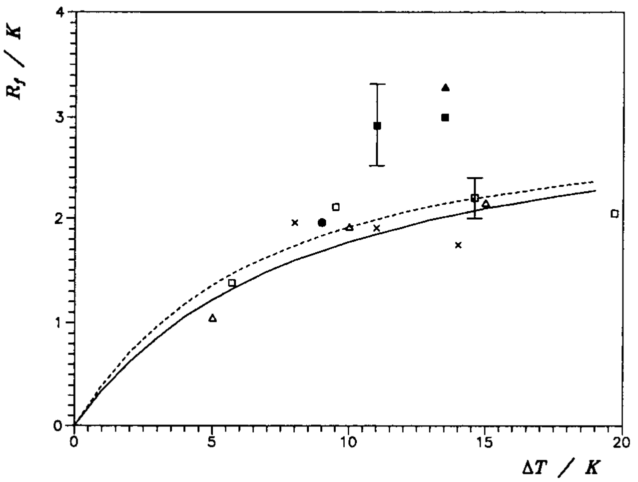

Figure 10. Fictive relaxation rate as a function of temperature departure from T_g for PC. Points correspond to dilatometric data [Greiner and Schwarzl[6] (□); Bartos et al.[8] (△); Struik[7] (×)] and calorimetric data [Bauwens[9] (■); Steer and Rietsch[44] (▲); Cheng et al.[45] (●)]. The solid and dotted lines were calculated by using eqs 22−24 for NM parameters (Table 2) and AG parameters (Table 3), respectively.

A comparison of volume and enthalpy fictive relaxation rates for bisphenol A polycarbonate (PC) is shown in Figure 10. The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of the $\delta_V(\log t)$ plots reported by Bartos et al.[8] (△) for Δα shown in Table 1 and dilatometric $T_g = 145$ °C. The values obtained from $-(d\delta_V/d \log t)_i$ data reported by Greiner and Schwarzl[6] (□) and Struik[7] (×) are very similar. A higher value of T_g (148 °C) was assumed for data of Struik.[7] The $R_f(\Delta T)$ data for enthalpy relaxation were obtained from the inflectional slope of the $\delta_H(\log t)$ plots reported by Bauwens[9] (■), Steer and Rietsch[44] (▲), and Cheng et al.[45] (●), for ΔC_p shown in Table 1 and calorimetric $T_g = 144$ °C. The $R_f(\Delta T)$ for enthalpy relaxation data of Cheng et al.[45] agrees well with data obtained from volume relaxation experiments. In contrast, the enthalpy relaxation data reported by Bauwens[9] and Steer and Rietsch[44] give higher values of the fictive relaxation rate. The differences are evidently higher than the expected experimental uncertainty. Nevertheless, it is not clear whether they really correspond to some differences in kinetics of enthalpy relaxation of the sample used by authors[9,44] or can be attributed to particular details of the experimental setup and evaluation procedure. In this respect it should be pointed out, however, that the prediction of eqs 22−24 based on the parameters obtained by curve fitting of calorimetric data[23] (solid line for NM parameters (Table 2), dotted line for AG parameters (Table 3)) agrees within the experimental errors with the

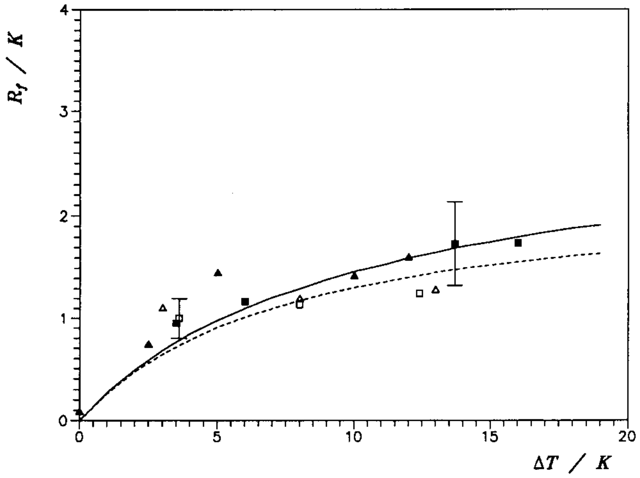

Figure 11. Fictive relaxation rate as a function of temperature departure from T_g for PMMA. Points correspond to dilatometric data [Greiner and Schwarzl[6] (□); Hutchinson and Bucknall[46] (△)] and calorimetric data [Cowie and Ferguson[47] (■); Perez and Cavaille[48] (▲)]. The solid and dotted lines were calculated by using eqs 22−24 for NM parameters (Table 2) and AG parameters (Table 3), respectively.

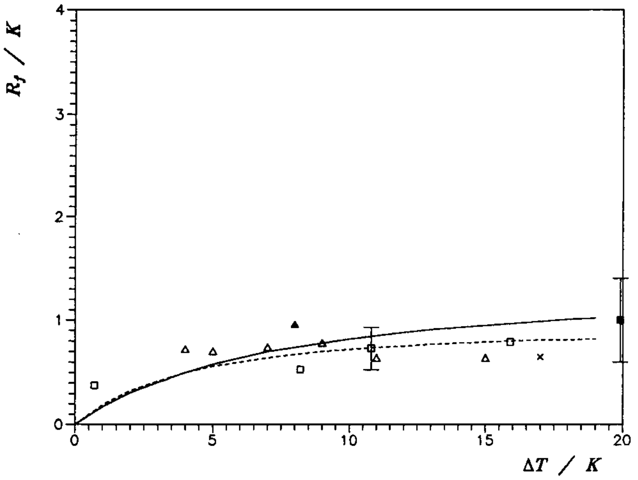

Figure 12. R_f as a function of temperature jump for PVC. Points correspond to dilatometric data [Greiner and Schwarzl[6] (□); Lee and McGarry[49] (△); Struik[7] (×)] and calorimetric data [Pappin et al.[50] (■); Gomez Ribelles et al.[51] (▲)]. The solid and dotted lines were calculated by using eqs 22−24 for NM parameters (Table 2) and AG parameters (Table 3), respectively.

$R_f(\Delta T)$ data obtained from dilatometric experiments (see Figure 10). The $R_f(10)$ for PC is comparable to the corresponding value for PS, being about 2.1 K [i.e., $R_f(10) \cong 0.54R_f^{max}$].

Figure 11 shows a comparison of volume and enthalpy fictive relaxation rates for poly(methyl methacrylate) (PMMA). The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of the $\delta_V(\log t)$ plots reported by Hutchinson and Bucknall[46] (△) for Δα shown in Table 1 and dilatometric $T_g = 108$ °C. The values obtained from $-(\mathrm{d}\delta_V/\mathrm{d}\log t)_i$ data of Greiner and Schwarzl[6] (□) are similar. The $R_f(\Delta T)$ data for enthalpy relaxation were obtained from the inflectional slope of the $\delta_H(\log t)$ plots reported by Cowie and Ferguson[47] (■) and Perez and Cavaille[48] (▲) for ΔC_p shown in Table 1 and calorimetric T_g 118 and 115 °C, respectively. Both dilatometric and calorimetric relaxation data for PMMA give comparable values of R_f within the limits of experimental errors. The solid line in Figure 11 was calculated by using eqs 22 and 23 for NM parameters obtained by curve fitting of calorimetric data reported by Hodge[23] (see Table 2). The dotted line corresponds to AG parameters obtained by curve fitting of the same data set [23] (see Table 3). The difference between predictions of NM and AG models is very small in comparison with estimated experimental error in R_f. The $R_f(10)$ for PMMA is lower than the value observed for PVA, being about 1.3 K [i.e., $R_f(10) \cong 0.44R_f^{max}$].

A comparison of volume and enthalpy fictive relaxation rates for poly(vinyl chloride) (PVC) is shown in Figure 12. The $R_f(\Delta T)$ values for volume relaxation were obtained from the inflectional slope of the $\delta_V(\log t)$ plots reported by Lee and McGarry[49] (△) for Δα shown in Table 1 and dilatometric $T_g = 85$ °C. The values obtained from $-(\mathrm{d}\delta_V/\mathrm{d}\log t)_i$ data reported by Greiner and Schwarzl[6] (□) and Struik[7] (×) are very similar. In this case, however, a lower value of T_g (76 °C) was assumed. The $R_f(\Delta T)$ data for enthalpy relaxation were obtained from the inflectional slope of the $\delta_H(\log t)$ plots reported by Pappin et al.[50] (■) and Gomez-Ribelles et al.[51] (▲) for ΔC_p shown in Table 1 and calorimetric $T_g = 80$ °C. It is seen that dilatometric and calorimetric relaxation data for PVC give comparable values of R_f within the limits of experimental errors. It should be pointed out that the value of R_f for PVC, PMMA, and PC can also be obtained from $\delta_H(\log t)$ plots reported by Ott;[52] however, these data give R_f very much larger than other authors. The reason for these discrepancies is not clear but for Ott's data $\delta_H^0 > \Delta C_p \Delta T$, which may indicate some problems in the determination of δ_H. The solid line in Figure 12 was calculated by using eqs 22 and 23 for NM parameters obtained by curve fitting of calorimetric data reported by Hodge[23] (see Table 2). The dotted line corresponds to AG parameters obtained by curve fitting of the same data set[23] (see Table 3). The calculated $R_f(\Delta T)$ plots differ within the limit of experimental errors because there are differences in β and σ parameters for NM and AG formulation of nonlinearity. The $R_f(10)$ for PVC is lowest among all materials examined, being about 0.7 K [i.e., $R_f(10) \cong 0.36R_f^{max}$].

It was found that the fictive relaxation rate R_f for volume and enthalpy relaxation agrees within the experimental error for all materials examined in this paper. Some discrepancies were found for enthalpy relaxation data of PC.[9,44] The origin of these discrepancies is not known. However, it is only the inflectional slope that is being compared. The fact that the R_f for volume and enthalpy relaxation appear to be very similar for many glasses does not mean necessarily that the time scales are identical. The validity of eq 22 was verified for different values of T_0 and T as shown, e.g., for As_2Se_3 (Figure 5), As_2S_3 (Figure 6), and PVA (Figure 9). The prediction of the $R_f(\Delta T)$ plot based on eq 22 agrees quite well with experimental data for moderate temperature departure ΔT, particularly for matereials with a lower contribution of nonlinearity ($\sigma < 0.4$). At higher temperature departures from T_g, eq 22 overestimates R_f values. This can be caused by the fact that t_m rapidly increases for higher ΔT and consequently the true inflectional tangent is not necessarily reached within the experimental time scale. Such an explanation is plausible for R_f obtained from $-(\mathrm{d}\delta_P/\mathrm{d}\log t)_i$ data. However, it can hardly be used for PS (see Figure 8) or PVA (see Figure 9), where eq 22 overestimates considerably the experimental value of R_f obtained from $\delta_V(\log t)$ plots for $\Delta T > 10$ K. In these cases the R_f

Table 4. Calculated and Measured Fictive Relaxation Rate

	calculated			measured			
material[a]	β	σ/K^{-1}	R_f/K	P	ΔT/K	R_f/K	ref
NBS 710	0.63	0.06	10.6	*n*	27.9	10.1	22
ZBLA	0.54	0.36	5.2	*H*	60	4.3	53, 54
ZBLALiPb	0.54	0.34	4.9	*H*	41	4.5	54
epoxy FRD50	0.30	0.53	2.4	*H*	20	2.4	11
epoxy CY070	0.30	0.42	2.6	*H*	20	2.4	11
epoxy CY100	0.30	0.55	2.3	*H*	20	3.0	11
epoxy[b]			0.5	*V*	2.5	0.5	56
glycerol	0.51	0.49	3.4	*H*	27	3.6	57, 58

[a] For explicit composition see corresponding references. [b] In this case the R_f was calculated for $\beta = 0.3$ and $\sigma = 0.5$.

values were obtained from dilatometric data of Greiner and Schwarzl[6] and Kovacs[2] measured for quite a long experimental time scale ($t_e \cong 290$ and 100 h), and thus there are no doubts about the reliability of $R_f(\Delta T)$ data. In fact observed differences can be even slightly higher due to neglecting the temperature dependence of $\Delta\alpha$ and ΔC_p in eqs 17 and 18. Table 4 summarizes experimentally determined R_f data obtained from different relaxation experiments (enthalpy, *H*; volume, *V*; and refractive index, *n*) for various glassy materials. A reasonable prediction is obtained for the relaxation of refractive index data reported by Scherer[22] for NBS 710 glass. In this case the diffrence between R_f obtained from a $T_f(\log t)$ plot and the prediction of eq 22 is not higher than 6% for $\Delta T \cong 28$ K. In contrast, there are considerable discrepancies in the prediction of eq 22 and enthalpy relaxation data reported by Moynihan et al.[53] for ZBLA glass far from equilibrium. The quality of these data obtained from a $T_f(\log t)$ plot again leaves no doubt that eq 22 really overestimates R_f at higher temperature departures from equilibrium.

It is not probable that failure of eq 22 for higher temperature departures lies in the approximation $\delta_{Pi} \cong (\delta_P{}^0/e)\xi_i{}^{-\beta}$ used in its derivation. This can easily be demonstrated[28] by analyzing theoretical $\delta_P(\log t)$ plots calculated by using methods described by Scherer[15] and Hodge and Berens.[55] Therefore, it seems that the discrepancies between calculated and experimentally observed R_f probably come from limitations of the phenomenological description. A rather speculative explanation of observed discrepancies could be that some glassy systems become thermorheologically complex for higher ΔT and therefore the nonexponentiality parameter β may be temperature dependent.[3,59] However, this would explain perhaps a slight variation in R_f for materials with lower σ (inorganic glasses), but it can hardly be acceptable, e.g., for PVA ($\sigma = 0.63-0.67$), where a rather low sensitivity of R_f with respect to β is expected. Another possible solution could be the change of the formulation of the nonlinearity expression for τ to make it more sensitive to T_f. The ratio of the nonequilibrium ($T_f \neq T$) to the equilibrium ($T_f = T$) relaxation time at the same temperature is given by eq 9 as

$$\ln(\tau/\tau_{eq}) = \frac{(1-x)\Delta h^*}{R}(1/T_f - 1/T) \cong \frac{(1-x)\Delta h^*}{RT_f^{\,2}}(T - T_f) \quad (27)$$

Moynihan[60] suggested that the next order of approximation to account for nonlinearity for large departures from equilibrium would be to add a quadratic term to the above expression. The expression for $\tau(T,T_f)$ then can be written as

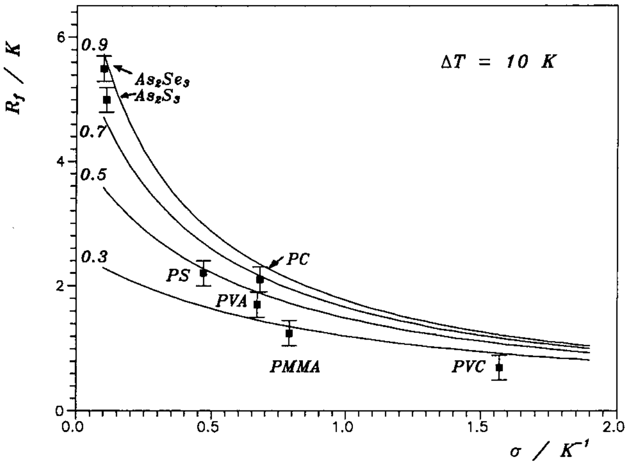

Figure 13. $R_f(10)$ as a function of parameter σ. Full lines were calculated by using eq 22 for different values of parameter β (shown next to the curves). Points correspond to the $R_f(10)$ data of various glassy materials obtained from volume relaxation measurements.

$$\tau(T,T_f) = A\exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f} + k(T_f - T)^2\right] \quad (28)$$

where *k* is a constant. From eq 20 the nonlinearity contribution can be expressed as

$$\sigma \cong (1-x)\frac{\Delta h^*}{RT_g^{\,2}} + 2k\Delta T \quad (29)$$

where the approximation $T_{f,i} \cong T_g$ has been used. This formulation of nonlinearity provides a very good fit of experimental $R_f(\Delta T)$ data for higher temperature departures. It is shown by a dashed line in Figure 8 for PS ($k = 5 \times 10^{-3}$ K^{-2}) and in Figure 9 for PVA ($k = 8 \times 10^{-3}$ K^{-2}), calculated by using eqs 22 and 29 for the NM prameters shown in Table 2. Therefore, it seems that the improved structure dependent formulation of nonlinearity is more adequate for the desription of the relaxation behavior far from equilibrium. It should be stressed, however, that in most cases NM or AG formulations of nonlinearity as defined by eqs 9 and 16 are sufficient and eq 22 then gives reasonable predictions for moderate ΔT. This allows one to compare relaxation rates of various properties and the predictions for NM and AG models.

In section III it has been anticipated that the fictive relaxation rate R_f decreases considerably with the nonlinearity contribution σ. This prediction seems to be confirmed experimentally as shown in Figure 13 where the $R_f(10)$ vs σ plots (for $0.3 \leq \beta \leq 0.9$) calculated by using eqs 22 and 23 are compared with experimental $R_f(10)$ data obtained from dilatometric temperature jump experiments. It is evident that particularly for low values of σ the $R_f(10)$ depends also on the nonexponentiality parameter β. On the other hand, this effect seems to be within the experimental errors for materials with high values of σ ($\sigma \geq 0.8$). An inspection of Tables 2−4 reveals that there is an inverse correlation between the parameters σ and β. This type of correlation seems to be confirmed also for NM and AG parameters collected for many materials in Hodge's excellent review paper.[3] Therefore, for materials with low values of parameter σ (e.g., for inorganic glasses), relatively high relaxation rates can be expected. In contrast, very slow relaxation response is observed for materials with higher values of parameter σ (e.g., vinylic polymers), where the R_f becomes practically independent of the magnitude of temperature departure, as well as of the parameter β (for $\Delta T > 10$ K).

V. Concluding Remarks

The fictive relaxation rate $R_f = -(\mathrm{d}T_f/\mathrm{d}\log t)_i$ provides a basis for a comparison of volume and enthalpy relaxation kinetics in various materials subjected to a temperature jump ΔT. It has been shown that within the current phenomenological model, involving the stretched exponential relaxation function and the reduced time integral, the R_f can be described by a simple equation $R_f = 2.303/[e/\Delta T\beta + \sigma]$. A remarkable feature of this equation is that it separates the contribution of nonexponentiality (β) and nonlinearity (σ). The nonlinearity contribution corresponds to structural changes during the relaxation process. It can be expressed for the NM model as $\sigma = (1 - x)\Delta h^*/RT_g^2$ and for the AG model as $\sigma = BT_2/T(T_g - T_2)^2$. This equation predicts an increasing fictive relaxation rate with the magnitude of the temperature jump and it has been tested by using volume and enthalpy relaxation data reported for various glassy materials (As_2Se_3, As_2S_3, PS, PVA, PC, PMMA, PVC, epoxy, etc.). A reasonable prediction is obtained for moderate ΔT, but the R_f values are underestimated for temperature departures far from equilibrium. The origins of these discrepancies are not known exactly. Nevertheless, it is probable that they come from limitations of the current phenomenological description of the relaxation process and that the nonlinearity formulation should be more structure dependent.

Within the limit of experimental error it seems that the R_f data for volume and enthalpy relaxation are very similar for all materials examined. A very slow relaxation rate is observed for materials where $\sigma > 0.6$ (vinylic polymers), which is nearly independent of ΔT and β, and its particular value is mainly determined by the parameter σ. In contrast, relatively fast relaxation rates are observed for materials where $\sigma < 0.3$ (inorganic glasses). This behavior can be explained by the inverse correlation between the parameters σ and β. A more detailed study is needed to verify these findings at higher ΔT for other glassy materials, particularly for inorganic glasses, where a relatively large influence of the parameters σ and β is expected, and therefore problems related to thermorheological simplicity or temperature dependence of σ can probably be resolved.

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