

## STRUCTURAL RELAXATION IN AMORPHOUS SOLIDS STUDIED BY THERMAL ANALYSIS METHODS

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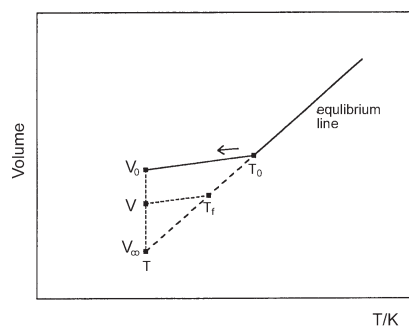
### Abstract

Structural relaxation for simple and more complex thermal histories is described by a phenomenological model based on a non-exponential relaxation function, the reduced-time concept and the non-linear structural contribution to the relaxation time. The history, development of experimental techniques and data analysis is described. It is shown that the volume and enthalpy relaxation response can conveniently be compared on the basis of a fictive relaxation rate,  $R_f$ . A simple equation relating  $R_f$  and the parameters of the phenomenological model is given. The calculated data for moderate departures from equilibrium are in good agreement with our experiments and data previously reported in the literature.

**Keywords:** amorphous materials, enthalpy relaxation, non-linearity, volume relaxation

### Introduction

The non-equilibrium thermodynamic state of an amorphous material was first recognized nearly 70 years ago by Simon [1]. When an equilibrium liquid is cooled, a transformation to a glass occurs at a temperature  $T_g$  when the molecular rearrange-



**Fig. 1** Schematic illustration of the volume changes of an amorphous material subjected to a temperature jump from equilibrium at temperature  $T_0$

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ments slow down to a such extent that they require time scale considerably longer than corresponds to an experimental time scale. The structure of such an amorphous material becomes 'frozen-in' and the glass will not be at equilibrium. Such a non-equilibrium state is obviously unstable and the amorphous material will search for an equilibrium structure. The approach of the structure towards equilibrium is usually called structural relaxation and this has been studied extensively, both for practical reasons and for a better theoretical understanding of the glass transition phenomena [2, 3].

If an amorphous 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 Fig. 1. The isothermal volume relaxation response is usually described [3] as the relative departure of the actual volume  $V$  from the equilibrium volume  $V_\infty$ , i.e.  $\delta_v = (V - V_\infty)/V_\infty$ . An alternative definition for the volume relaxation response is:

$$\Phi = \frac{V - V_\infty}{V_0 - V_\infty} = \frac{\delta_v}{\delta_v^0} \quad (1)$$

The initial departure from equilibrium,  $\delta_v^0$ , can be related to the magnitude of the temperature jump  $\Delta T = T_0 - T$  and is defined as  $\delta_v^0 = \Delta\alpha \cdot \Delta T$ , where  $\Delta\alpha$  is the difference between the volume thermal expansion coefficient of the equilibrium undercooled liquid and the volume thermal expansion coefficient of the solid. Similar expressions can be also written for the isothermal enthalpy relaxation.

Structural relaxation experiments are complicated by the fact that the structure of a glass is both time and temperature dependent. An analysis of such experimental data is difficult due to the non-linear character of the relaxation process as well as due to the memory effect. This paper describes the basic phenomenology and typical experiments. The volume and enthalpy relaxation data are analyzed and compared. Some thoughts for future research are given.

## A phenomenological model of structural relaxation

### *Non-exponentiality and the reduced-time concept*

It is well known that the normalized relaxation function  $\Phi(t)$ , obtained from volume or enthalpy data, is non-exponential. Such behavior can be explained by assuming a distribution of relaxation times. The relevant model of Kovacs, Hutchinson, Aklonis and Ramos [4] (referred to as KAHR) uses a discrete distribution. A continuous distribution is used in the 'stretched' exponential expression introduced by Moynihan *et al.* [5]:

$$\Phi(t) = \exp[-(t/\tau)^\beta] \quad (2)$$

where  $\tau$  is a characteristic time and the exponent  $\beta$  is inversely proportional to the width of corresponding distribution of relaxation times ( $0 < \beta \leq 1$ ).

Equation (2) describes experimental data well for small temperature jumps ( $\Delta T < 0.5$  K). At larger departures from equilibrium, however, the  $\Phi(t)$  function becomes non-linear which means that the kinetics of structural relaxation do not scale linearly with the magnitude of the departure from equilibrium. Therefore, the responses expressed by Eq. (2), corresponding to different temperature jumps  $\Delta T$ , cannot be superimposed on a single master curve by any linear transformation in time. This behavior was explained by Tool [6] by assuming that  $\tau$  depends on the instantaneous structure of an amorphous material characterized by the fictive temperature,  $T_f$  (defined as shown in Fig. 1), as well as on temperature  $T$ . Later it was shown by Narayanaswamy [7], in his excellent paper, that linearity can be restored by introducing the reduced-time integral defined by

$$\xi = \int_{T_0}^T \frac{dt}{\tau(T, T_f)} \quad (3)$$

The fictive temperature then can be expressed according to the Boltzmann superposition principle as:

$$T_f(t) = T_0 + \int_{T_0}^T [1 - \exp(-\xi^\beta)] dT \quad (4)$$

Both the Boltzmann and the reduced-time integral in Eq. (4) must be evaluated numerically, e.g. by the methods proposed by Mazurin [8], Moynihan *et al.* [5], Hodge and Berens [9] and Scherer [2] (Numerical simulation of structural relaxation).

#### *Non-linearity expressions*

The most frequently used expression for  $\tau(T, T_f)$  in Eq. (3) is the Tool–Narayanaswamy formulation [7] as modified later by Moynihan *et al.* [10] (referred to as TNM):

$$\tau(T, T_f) = A \exp \left[ x \frac{\Delta h^*}{RT} + (1-x) \frac{\Delta h^*}{RT_f} \right] \quad (5)$$

where  $A$  is the pre-exponential constant,  $x$  is the non-linearity parameter ( $0 < x \leq 1$ ) and  $\Delta h^*$  is the effective activation energy, which is essentially the same as that determined from viscosity data above  $T_g$  for most inorganic amorphous materials [11]. An equivalent, but much less-used, expression for  $\tau(T, T_f)$  is the KAHR equation [4]:

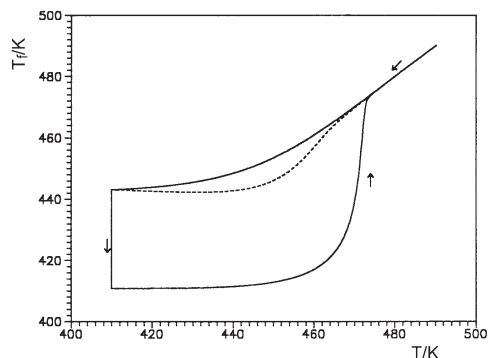
$$\tau(T, T_f) = \tau_0 \exp[-\theta(T - T_f) - (1-x)\theta\delta/\Delta\alpha] \quad (6)$$

where  $\tau_0$  is the value of  $\tau$  at equilibrium at the reference temperature  $T_f$  and  $\theta$  is a form of the effective activation energy. The relation between  $\theta$  and the TNM parameter,  $\Delta h^*$ , is derived by equating the temperature derivative of  $\tau$  in the equilibrium and assuming that  $T \cong T_f \cong T_g$ :

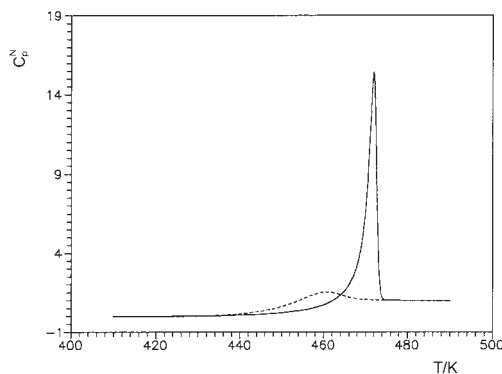
$$\theta = \frac{\Delta h^*}{RT_g^2} \quad (7)$$

The value of  $\theta$  is a characteristic constant for an amorphous material [11], generally being close to 1 for polymeric materials and in the range 0.1–0.3 for inorganic glasses. It should be pointed out that Eqs (5) and (6) are purely empirical. Equation (5) has been extensively tested on many amorphous materials and was found to describe the structural relaxation below  $T_g$  quite well [2].

Another formulation of non-linearity is based on the Adam–Gibbs equation [12] which assumes that the configurational entropy determines the average relaxation time. The functional form for  $\tau(T, T_f)$  is determined by the temperature dependence of the excess heat capacity used to calculate the configurational entropy. A non-linear Adam–Gibbs equation was applied for the first time to enthalpy relaxation by Scherer



**Fig. 2** The changes of the fictive temperature calculated using Eq. (4) during cooling ( $-10 \text{ K min}^{-1}$ ), annealing ( $T_a=410 \text{ K}$ ,  $t_a=10 \text{ days}$ ) and reheating ( $10 \text{ K min}^{-1}$ ) of an amorphous material characterized by the following TNM parameters:  $\Delta h^*/R=40 \text{ kK}$ ,  $\ln(A/s^{-1})=-85$ ,  $x=0.5$ ,  $\beta=0.7$ . The broken line corresponds to reheating without annealing



**Fig. 3** The normalized reheating heat capacity curves calculated using Eq. (9) for data shown in Fig. 2

[13]. Some time later, Hodge [14] used the hyperbolic form for  $\Delta C_p$  and obtained a simple non-linear expression (referred to as AGH):

$$\tau(T, T_f) = A_0 \exp \left[ \frac{B}{T(1 - T_2/T_f)} \right] \quad (8)$$

where  $B$  is a constant related to the potential barrier hindering rearrangement, and  $T_2$  is the temperature at which the configurational entropy extrapolates to zero; i.e. it is conceptually identical with the thermodynamic Kauzmann temperature.

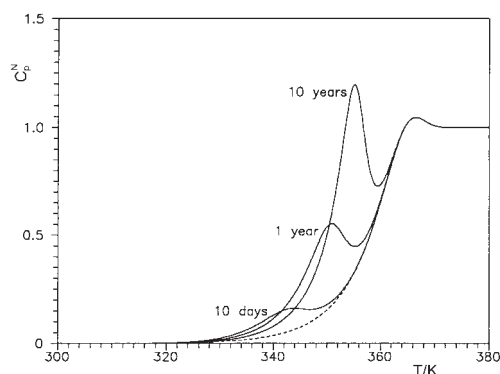
#### *Numerical simulation of structural relaxation*

Numerical simulation of structural relaxation is based on the Boltzmann superposition of responses that have been linearized using the reduced-time method of Narayanaswamy [7]. This method was first applied to thermal histories that included rate cooling and heating in 1975 by Mazurin *et al.* [8] and one year later by Moynihan *et al.* [5]. The evolution of the fictive temperature is calculated using Eq. (4). The zero time in the reduced-time integral is set when the amorphous material first departs from equilibrium. Starting the reduced-time 'clock' later can produce artifacts, arising from the memory effect associated with non-exponentiality. The relaxation from a particular state is determined not only by this state, but also by how it was reached [2]. Numerical evaluation of the Boltzmann integral is accomplished by expressing any thermal history  $T(t)$  as a series of temperature jumps that are small enough to ensure a linear response (usually 0.2 K). During annealing, the upper limit of the Boltzmann integral is fixed but the reduced-time integral summation continues.

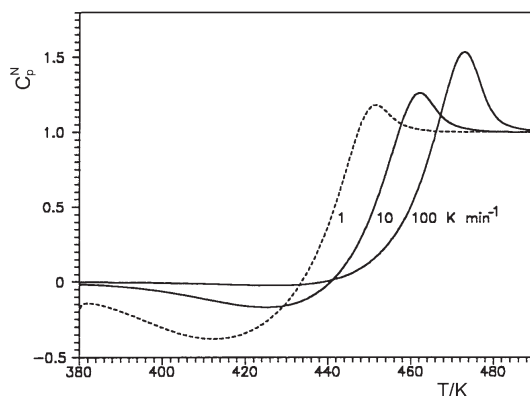
Figure 2 shows the changes of  $T_f$  calculated during cooling ( $-10 \text{ K min}^{-1}$ ), annealing ( $T_a=410 \text{ K}$ ,  $t_a=10 \text{ days}$ ) and reheating ( $10 \text{ K min}^{-1}$ ) of an amorphous material characterized by the following TNM parameters:  $\Delta h^*/R=40 \text{ kK}$ ,  $\ln(A/s^{-1})=-85$ ,  $x=0.5$ ,  $\beta=0.7$ . A dimensionless heat capacity is defined as [10, 11]:

$$C_p^N = \frac{dT_f}{dT} \quad (9)$$

which can be calculated by differentiating the  $T_f(T)$  dependence. Figure 3 shows the heat capacity curves calculated using Eq. (9) for reheating data in Fig. 2. In this case the relaxation behavior is characterized by a well known overshoot, superimposed on the glass transition heat capacity step. The intensity of this overshoot rapidly increases with annealing time. Quite different behavior is illustrated in Fig. 4 where the reheating data of an annealed amorphous material, characterized by a different set of TNM parameters:  $\Delta h^*/R=100 \text{ kK}$ ,  $\ln(A/s^{-1})=-275$ ,  $x=0.5$ ,  $\beta=0.3$ , are shown. There is a small overshoot which remains unchanged with annealing time. However, the most important feature is a time dependent, sub- $T_g$  peak, strongly affected by annealing. These sub- $T_g$  peaks are more pronounced for low  $\beta$  and  $x$  parameters [9] and they practically disappear for relatively narrow distributions of relaxation times (Fig. 3). If the amorphous material is rapidly quenched and then slowly reheated, there is an exo-



**Fig. 4** The heat capacity curves for reheating ( $10 \text{ K min}^{-1}$ ) of an amorphous material annealed at  $T_a=320 \text{ K}$  characterized by the TNM parameters:  $\Delta h^*/R=100 \text{ kK}$ ,  $\ln(A/s^{-1})=-275$ ,  $x=0.5$ ,  $\beta=0.3$ . The annealing times are shown next to the curves. The broken line corresponds to reheating without annealing



**Fig. 5** The normalized heat capacity curves for unannealed amorphous material reheated after cooling ( $-10 \text{ K min}^{-1}$ ), at different heating rates (shown next to the curves). The TNM parameters are the same as in Fig. 2

thermic dip in the heat capacity observed just before the heat capacity step at  $T_g$ . These dips are shown in Fig. 5 (the TNM parameters are the same as in Fig. 2) and are due to partial relaxation taking place during relatively slow reheating.

The TMN model, incorporating the distribution of relaxation times and the reduced-time concept, successfully predicts practically all experimentally observed phenomena. It has been extensively tested and shown to provide a satisfactory representation of the structural relaxation behavior of many amorphous materials [2]. Some experimental results are discussed in the following Section.

## Experimental techniques, history and development

### *Volume and length dilatometry*

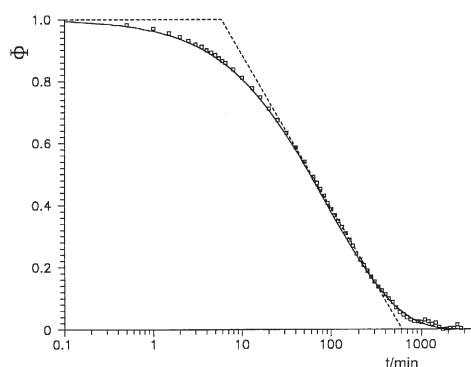
In volume dilatometry, the volume or length of an amorphous specimen which is subjected to a temperature jump is measured as a function of time. Because the volume changes due to structural relaxation are very small, accurate methods for detecting volume changes are required. One of the most widely used techniques is mercury dilatometry. This method is precise though time-consuming, because it requires careful sample preparation, degassing and delicate skills. Another shortcomings of this method are a restricted temperature range and the difficulty in its automation. Despite these limitations it has been used extensively in the study structural relaxation mainly in amorphous polymers. The precise experiments of Kovacs demonstrated all important aspects of structural relaxation [3].

On the other hand, length dilatometry is one of the simplest experimental methods. It has been used in the study of structural relaxation of inorganic materials. The pioneering dilatometric experiments made by Tool [6, 15, 16] on silicate glasses clearly show the non-linear nature of structural relaxation. It was established that isothermal annealing, following a temperature jump from an equilibrium state, could not be described by a kinetic equation in which the relaxation time depended only on the temperature. Tool assumed that  $\tau$  depended also on the instantaneous state or structure of the amorphous material, which could be characterized by means of a fictive temperature. This idea was one of the most important steps toward the understanding and quantitative description of the structural relaxation process. Nevertheless, it was shown later by Ritland [17], using his experiments on borosilicate crown glass, that the fictive temperature concept cannot account for all phenomena observed when more complicated thermal histories were applied. Kovacs [3] reported remarkable dilatometric experiments of some organic polymers and suggested that structural relaxation involves multiple processes characterized by different relaxation times. Similar results were obtained later by Spinner and Napolitano [18] and Macedo and Napolitano [19].

Isothermal volume relaxation has been studied on many amorphous materials [2, 3]. A typical volume relaxation isotherm is shown in Fig. 6 for  $\text{As}_2\text{Se}_3$  glass (points). Similar experimental data on amorphous polymers are usually interpreted within the free-volume theory [3, 21], or compared on the basis of the volume relaxation rate  $\beta_v$ . This parameter was introduced by Kovacs [3, 22] and its value has been used to compare the kinetics of volume relaxation in amorphous polymers [20, 21]. It is defined as the inflectional slope of the volume relaxation data, plotted on a logarithmic time scale:

$$\beta_v = -\frac{1}{V} \frac{dV}{d \log t} = -\delta_v^0 \frac{d\phi}{d \log t} \cong -\frac{d\delta_v}{d \log t} \quad (10)$$

The TNM model has been tested in numerous studies of inorganic materials. Much of this work has been reviewed by Mazurin [23]. The volume relaxation of a



**Fig. 6** Isothermal volume relaxation data for amorphous  $\text{As}_2\text{Se}_3$  subjected to a temperature jump from  $T_0=446.4$  K to  $T=433.6$  K (points). The full line corresponds to the best fit calculated for the TNM parameters:  $\Delta h^*/R=35.87$  kK,  $\ln(A/s^{-1})=-73.3$ ,  $x=0.51$ ,  $\beta=0.77$ . The slope at the inflection point is shown by the broken line

window glass was studied by Rekhson *et al.* [24]. The non-linearity parameter is found indirectly by fitting Eqs (2)–(5) to experimental data for temperature jumps, where  $T_f$  changes substantially. The curve in Fig. 6 has been calculated in this way for the TNM parameters:  $\Delta h^*/R=35.9$  kK,  $\ln(A/s^{-1})=-73.3$ ,  $x=0.51$  and  $\beta=0.77$ . The apparent activation energy is found from the temperature dependence of  $\tau$  near equilibrium and the value is very similar to the activation energy for the temperature dependence of viscous flow  $E_\eta/R=35.2$  kK [25, 26]. The very good agreement of the volume relaxation data (shown in Fig. 6) with the prediction of the phenomenological model is not surprising, because, the data were taken not too far from equilibrium ( $\Delta T=12.8$  K). Scherer [27], however, in his remarkable paper, successfully described the volume relaxation data of Hara and Suetoshi [28] within 100 K of  $T_g$ , using the Adam–Gibbs formulation of non-linearity.

#### *Differential scanning calorimetry*

In comparison with dilatometric experiments, differential scanning calorimetry (DSC) has been more frequently used for structural relaxation studies, both for amorphous polymers and for inorganic glasses. Probably the main reason for such popularity is the easy availability of DSC equipment. Enthalpy lost during annealing is usually recovered near  $T_g$ , producing the well-known overshoot. Early studies of this phenomenon were made by Volkenstein and Sharonov [29], Foltz and McKinney [30] and Petrie [31]. They used the area of the overshoot as a quantitative measure of the enthalpy that had relaxed during annealing at  $T_a$ . In fact, the difference in areas under the DSC curves for an annealed sample and the same sample for zero annealing time is the enthalpy lost on annealing. For a sufficient annealing time at  $T_a$ , the enthalpy relaxation will proceed to equilibrium, where the enthalpy is  $H_\infty$ . The departure from equilibrium is defined as  $\delta_H=H-H_\infty$ . The initial departure from equilibrium



is  $\delta_H^0 = \Delta C_p \Delta T$  for an instantaneous quench, where  $\Delta C_p$  is the difference between the heat capacity of the equilibrium undercooled liquid and the amorphous solid. The evolution of  $\delta_H$  or  $\Phi = \delta_H / \delta_H^0$  with time would give the enthalpy relaxation data, analogous to a volume contraction isotherm (Fig. 6). It is well known, however, that it is difficult to achieve an equilibrium enthalpy at about 20 K below  $T_g$  for polymers. For this reason, some authors used the enthalpy loss during annealing,  $\Delta H$ , referred to the initial state rather than the final equilibrium state. Such data were published for many amorphous polymers [32–35]. The enthalpy relaxation rate,  $\beta_H$ , is defined as:

$$\beta_H = -\delta_H^0 \frac{d\Phi}{d \log t} \cong -\frac{d\delta_H}{d \log t} \cong \frac{d\Delta H}{d \log t} \quad (11)$$

This parameter has been used to compare the kinetics of enthalpy relaxation of epoxy resins [36], polyesters [37] and chalcogenide glasses [38].

Considerably more attention has been devoted, however, to the analysis of heat capacity data for various thermal histories. The TNM or AGH parameters can be calculated using a curve fitting technique proposed by Moynihan *et al.* [5]. The literature in this area is voluminous. An excellent review of enthalpy relaxation and recovery in amorphous materials has been given by Hodge [11]. Figure 7 shows typical results for  $\text{As}_2\text{Se}_3$  glass for uniform cooling and reheating of an annealed and unannealed sample (points). The full lines were calculated for the same set of TNM parameters:  $\Delta h^*/R = 35.9$  kK,  $\ln(A/s^{-1}) = -74.46$ ,  $x = 0.51$  and  $\beta = 0.70$ . These parameters are practically identical, within the limits of experimental errors, with the results of curve fitting of isothermal dilatometric experiment (Section: Volume and length dilatometry). Moynihan *et al.* [5] have found very similar parameters,  $x = 0.49$  and  $\beta = 0.67$ , but somewhat higher values of  $\Delta h^*/R = 41.0$  kK,  $\ln(A/s^{-1}) = -85.5$ .

The application of the KAHR model differs significantly from the curve fitting approach. It is based on examining the peak temperature of the heat capacity overshoot as a function of the experimental conditions, in particular on the annealing time or heating rate [39]. This so-called peak shift method has been successfully used in analysis of some amorphous polymers [34–38].

#### *Comparison of calorimetric and dilatometric studies*

As anticipated above, the enthalpy relaxation rate  $\beta_H$  and the volume relaxation rate  $\beta_V$  are frequently used to characterize the relaxation kinetics in various materials [21, 22, 33]. In 1972, Petrie [31] raised the question as to whether the relaxation rates of different properties (volume, enthalpy, etc.) are identical or not. An attempt to compare both volume and enthalpy relaxation rates, as defined by Eqs (10) and (11), for various amorphous polymers, has been made by Hutchinson [20]. He concluded that there was no simple correlation between volume and enthalpy relaxation for the materials analyzed. The main problem of such a comparison is that  $\beta_V$  and  $\beta_H$  are not fully comparable quantities, because  $\Delta\alpha$  and  $\Delta C_p$  may be different for many materials. Observed changes in the relaxation rate can, therefore, be partially caused by these differences, which obscures the real changes in structural relaxation kinetics. It

has been shown recently [40, 41], that a convenient way to compare the volume and enthalpy relaxation kinetics is the fictive relaxation rate,  $R_f$ , defined as the change of the fictive temperature per decade of time:

$$R_f = - \left( \frac{dT_f}{d \log t} \right)_i \quad (12)$$

where the subscript  $i$  refers to the inflection point of the isothermal relaxation curve. This parameter is very useful when the relaxation responses in different materials are compared. The fictive relaxation rate for the volume relaxation rate can be written as  $R_f = \beta_v / \Delta \alpha$  and, for the enthalpy relaxation, as  $R_f = \beta_H / \Delta C_p$ . From Eq. (10) or Eq. (11) it then follows that:

$$R_f = \Delta T \left( \frac{d\Phi}{d \log t} \right)_i \quad (13)$$

It was found [40–42] that, for the phenomenological model of structural relaxation expressed by Eqs (2)–(4), the following equation can be expressed:

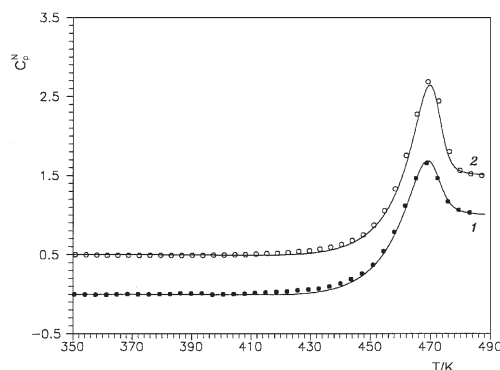
$$R_f = 2.303 \left[ \frac{e}{\Delta T \beta} + \sigma \right]^{-1} \quad (14)$$

where

$$\sigma = - \left( \frac{\partial \ln \tau}{\partial T_f} \right)_i \quad (15)$$

From Eqs (5), (7) and (15), the parameter,  $\sigma$ , for the TNM model can be expressed as  $\sigma \cong (1-x)\theta$ . Similarly, from Eqs (8) and (15) the parameter,  $\sigma$ , for the AGH model yields  $\sigma \cong T_2 B / [T(T_g - T_2)^2]$ . In both cases the approximation  $T_{fi} \cong T_g$  has been used.

Equation (14) predicts that the fictive relaxation rate increases with the magnitude of the temperature jump  $\Delta T$ . Similarly, one can expect an increasing  $R_f$  for a narrow distribution of relaxation times (i.e.,  $\beta \rightarrow 1$ ) [42]. The parameter  $\sigma$  corresponds to the degree of non-linearity of the particular amorphous material. In a linear case ( $\sigma=0$ ), there is no structural contribution to the relaxation time and, therefore, the maximum relaxation rate is expected:  $R_f^{\max} = 0.847 \Delta T \beta$ . Nevertheless, the parameter  $\sigma$  is greater than zero for most amorphous materials, which means that they relax more slowly. A remarkable feature of Eq. (14) is that it separates the contributions of non-exponentiality ( $\beta$ ) and non-linearity ( $\sigma$ ). It has been believed that these two contributions are inextricably bound together by the reduced-time [20]. All these predictions agree well with experimental observations [41, 42]. A very slow fictive relaxation rate is observed for materials where  $\sigma > 0.6$  (vinylic polymers), which is nearly independent of  $\Delta T$  and  $\beta$ , and its value is mainly determined by the parameter  $\sigma$ . In contrast, relatively fast relaxation rates are observed for materials where  $\sigma < 0.3$  (inor-



**Fig. 7** The reheating ( $10 \text{ K min}^{-1}$ ) heat capacity data for amorphous  $\text{As}_2\text{Se}_3$  obtained after cooling ( $-5 \text{ K min}^{-1}$ ) from equilibrium to 350 K (points): 1 – without annealing, 2 – 5 h annealing at 446.2 K (this curve is shifted by 0.5 units for clarity). The full lines correspond to the best fits calculated for the TNM parameters:  $\Delta h^*/R=35.9 \text{ kK}$ ,  $\ln(A/s^{-1})=-74.46$ ,  $x=0.51$ ,  $\beta=0.70$

ganic glasses). Such behavior can be explained by the inverse correlation between the parameters  $\sigma$  and  $\beta$  [42].

In assessing the applicability of the fictive relaxation rate, some problems related to a correct determination of the  $R_f$  and  $\Delta T$  should be mentioned. Implicitly it is assumed that  $T_f(0)=T_0$ . In fact, it is rather difficult to change the temperature instantaneously (for polymer samples in particular) and there is always a finite initial time,  $t_{\text{ini}}$ , needed to reach thermal equilibrium of a real sample [3, 20, 21]. If  $T_0$  is too high ( $T_0 \gg T_g$ ), then the relaxation response during thermal equilibration may be very fast and an important part of the relaxation takes place before  $t_{\text{ini}}$  is reached. In this case, the first part of the relaxation curve might be truncated and  $R_f$  cannot be determined correctly. Similarly, it seems to be more correct if  $\Delta T$  is defined as the temperature departure from the fictive temperature corresponding to  $t_{\text{ini}}$ , i.e.  $\Delta T=T_f(t_{\text{ini}})-T$ . The value of  $T_f(t_{\text{ini}})$  can be calculated using Eq. (4) for a particular set of TNM or AGH parameters. To simplify this problem, it is usually assumed [41, 42] that  $T_f(t_{\text{ini}}) \cong T_g$  provided that  $T_0 > T_g$ . On the other hand, if  $T_0 < T_g$  one can expect that the change in fictive temperature immediately after the temperature jump is negligibly small.

In an ideal case, the  $R_f$  value can be obtained directly from the slope of the plot of  $T_f$  vs.  $\log t$ , according to Eq. (12). These data, however, are not always available. If the  $R_f$  is determined from the slope of the isothermal relaxation curve  $\delta_v(\log t)$  or  $\delta_H(\log t)$ , it is important to make sure that it corresponds to a truly inflectional tangent [42]. Another source of errors may come, in this case, from the temperature dependence of  $\Delta\alpha$  and  $\Delta C_p$  which is usually neglected. The error limits in  $R_f$  data, due to these and other factors, was estimated to be about  $\pm 0.2 \text{ K}$  for dilatometric, and  $\pm 0.4 \text{ K}$  for calorimetric data.

One can expect reasonable agreement between experimentally determined  $R_f$  data and the values predicted by Eq. (14) for relaxation experiments not far from equilibrium. For example, the fictive relaxation rate obtained from the inflectional

slope of the volume relaxation data for  $\text{As}_2\text{Se}_3$  glass, shown in Fig. 6, was found to be  $R_f=6.3$  K for  $\Delta T=12.8$  K. This is very close to the value 6.28 K calculated using Eq. (14) for the TNM parameters reported above. The experimentally determined  $R_f$  values obtained from calorimetric and dilatometric data (evaluated for  $\Delta T \cong 10$  K) are shown in Table 1 for selected amorphous materials, in particular, for arsenic selenide glass ( $\text{As}_2\text{Se}_3$ ), amorphous selenium (Se), polystyrene (PS), polyvinyl acetate (PVA), polycarbonate (PC), polymethyl methacrylate (PMMA) and polyvinylchloride (PVC). These values are compared with the fictive relaxation rates calculated by using Eq. (14) for the parameters  $\beta$  and  $\sigma$  taken from previously reported enthalpy relaxation TNM fits (Table 1). It is seen that the  $R_f$  values for volume and enthalpy relaxations of these materials are practically identical, within the limits of experimental errors specified above. A reasonable prediction of the fictive relaxation rate is thus obtained for moderate  $\Delta T$ . In contrast, the  $R_f$  values are underestimated for temperature departures far from equilibrium [42]. It is probable that these discrepancies come from limitations of current phenomenological models.

**Table 1** Measured and calculated values of the fictive relaxation rates for amorphous materials, evaluated approximately 10 K below  $T_g$ . The parameters  $\beta$  and  $\sigma$  were taken from previously reported enthalpy relaxation TNM fits for organic polymers [14], amorphous Se [38] and  $\text{As}_2\text{Se}_3$  glass [5]

Material	Measured $R_f/\text{K}$		Calculated $R_f/\text{K}$	$\beta$	$\sigma/\text{K}^{-1}$	Ref.
	$V$	$H$				
$\text{As}_2\text{Se}_3$	4.7	–	4.55	0.67	0.10	[42, 25]
Se	–	2.9	>2.80	>0.60	0.37	[38]
PS	2.4	2.4	2.31	0.47	0.47	[22, 43]
PVA	1.9	1.9	1.91	0.51	0.67	[3, 44]
PC	1.9	1.9	1.85	0.46	0.71	[45, 46]
PMMA	1.2	1.4	1.32	0.35	0.77	[47, 33]
PVC	0.8	1.0	0.78	0.23	1.63	[48, 49]

## Future considerations

The current phenomenological model, based on the non-exponential relaxation function and the reduced-time concept, gives a very good prediction of both volume and enthalpy relaxations for moderate departures from equilibrium. So far, the most frequently used formulation of non-linearity is based on the TNM approach, although it is purely empirical and the corresponding parameters have no clear physical meaning. From this point of view, the AGH formulation of non-linearity should be more suitable because it corresponds to well known Vogel–Tamman–Fulcher equation in equilibrium. Curiously, the AGH approach does not provide for a better fit of experimental data, but it gives more meaningful parameters [11, 14]. These models treat the relaxation response as thermorheologically simple implying that the shape of relax-

ation function is invariant with respect to temperature. Strictly speaking, this is true only for a narrow temperature region. It was shown [50, 51], that the shapes of relaxation function and the spectrum of relaxation times broadened with decreasing temperature. Therefore, it seems to be promising to test thermorheologically complex models [52], particularly for inorganic materials (chalcogenide, halogenide and silicate glasses, etc.), where the relaxation responses can be measured far from equilibrium.

Volume and enthalpy relaxation responses can be quantitatively compared on the basis of the fictive relaxation rate. From comparison of previously reported data, it seems that the non-exponential and the non-linear contributions to the structural relaxation are mutually correlated [42]. It would be valuable to examine in more detail the origin and physical meaning of such correlation.

It seems that values of both volume and enthalpy fictive relaxation rates are very similar for many amorphous materials reported in the literature. The main problem of such comparisons is that relaxation data need not correspond to the same material measured under identical experimental conditions. To make sure whether the volume and enthalpy relaxation rates are really identical, it is necessary to perform simultaneous experiments on the same material. Such studies have been performed by adiabatic calorimetry [53, 54] at Osaka University and it was found that the volume and enthalpy relaxation responses for polystyrene were identical within the limits of experimental errors [54]. Unfortunately, due to spontaneous temperature drift inherent to adiabatic experiments, the concept of the fictive relaxation rate cannot be applied in this case. It would be interesting, however, to analyze these data using the current phenomenological model and to compare the calculated TNM or AGH parameters with those reported for scanning calorimetry or dilatometric experiments.

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