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COMPARISON BETWEEN VOLUME AND ENTHALPY RELAXATIONS IN NON-CRYSTALLINE SOLIDS BASED ON THE FICTIVE RELAXATION RATE

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Abstract

The volume and enthalpy relaxation rate of inorganic glasses and organic polymeric materials subjected to temperature jump ΔT has been analyzed. It is shown that the relaxation behavior in isothermal conditions can be compared on the basis of the fictive relaxation rate defined as $R_f=(dT_f/d\log t)_i$. No significant difference between volume and enthalpy relaxation rate has been found for all materials examined. A simple equation relating the R_f and parameters of Tool-Naraynaswamy-Moynihan (TNM) phenomenological model has been derived. This equation predicts increasing R_f with the magnitude of temperature jump. It seems that correct determination of TNM parameters might be problematic for slowly relaxing polymers as the effect of these parameters becomes comparable with experimental uncertainty.

Keywords: enthalpy relaxation, glasses, polymers, volume relaxation

Introduction

It is well known that non-crystalline solids exist in a non-equilibrium state below the glass transition temperature (T_g). The molecular rearrangements slow down to such extent that they require time scale considerably longer than corresponds to T_g (i.e. about 100 s). When a glass-forming liquid is subjected to a sudden change in temperature, it undergoes a process that is called structural relaxation. This process, can be followed by the change in thermodynamic property P characterizing the state of the material (volume, enthalpy etc.) as it approach towards its equilibrium value during the annealing. The time scale for equilibration become very long rapidly as the annealing temperature is reduced, so that many decades in time are necessary to achieve equilibrium far from T_g.

The most simple structural relaxation experiment involves monitoring of the isothermal change of property P following a temperature jump from equilibrium state

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in supercooled liquid at temperature T_0 to a non-equilibrium state in solid at the annealing temperature T (Fig. 1a). The structural changes following the temperature jump experiment can be described by means of departure δ_P of actual property P from its equilibrium value P_∞ and defined as:

$$\delta_P(t) = P(t) - P_\infty \tag{1}$$

Initial departure from equilibrium δ_P^o can be related to the magnitude of temperature jump $\Delta T=T_0-T$ and it is defined as

$$\delta_P^o = \left[\left(\frac{dP}{dT}\right)_{liquid} - \left(\frac{dP}{dT}\right)_{solid}\right]\Delta T \tag{2}$$

For volume relaxation the term in brackets in Eq. (2) is $V_o\Delta\alpha$, where $\Delta\alpha$ is the difference between the thermal expansion coefficient of the equilibrium supercooled liquid and thermal expansion coefficient of solid. Similarly, for enthalpy relaxation this term equals to the heat capacity change ΔC_p at T_g. Time dependence of $\delta_P(t)$ is usually plotted on a logarithmic time scale as shown in Fig. 1b. The broken line corresponds to an inflectional tangent, and its slope $-[d\delta_P(t)/d\log t]_i$ is usually referred to as the relaxation rate. This parameter introduced by Kovacs [1, 2] for volume relaxation has been used to compare both volume and enthalpy relaxation rate for various non-crystalline solids [3]. However, there are some problems inherent to such a comparison as $-(d\delta_V/d\log t)_i$ and $-(d\delta_H/\log t)_i$ are not fully comparable quantities as $\Delta\alpha$ and ΔC_p might be different between materials. It has been shown recently [4–6] that the fictive relaxation rate R_f can be conveniently used for a such comparison. It is defined as the change of the fictive temperature per decade of time:

$$R_f = \left[\frac{dT_f}{d\log t}\right]_i \tag{3}$$

The fictive temperature T_f was introduced by Tool [7] to characterize the structural changes during the isothermal annealing. It is defined as the temperature at which the material property would be equal to equilibrium one (Fig. 1a). Therefore, the fictive temperature decreases as the equilibrium is approached:

$$T_f(t) = T + \left[\frac{\delta_P(t)}{\delta_P^o}\right]\Delta T \tag{4}$$

The fictive relaxation rate for volume relaxation data then can be written as

$$R_f = -\frac{1}{V_o\Delta\alpha}\left(\frac{d\delta_V}{d\log t}\right)_i \tag{5}$$

and for the enthalpy relaxation as

$$R_f = -\frac{1}{\Delta C_p}\left(\frac{d\delta_H}{d\log t}\right)_i \tag{6}$$

The aim of this paper is to analyze reported volume and enthalpy relaxation data for non-crystalline materials. These data are then compared on the basis of fictive relaxation rate. The rate controlling factors are analyzed and discussed for the Tool-Narayanaswamy-Moynihan phenomenological model.

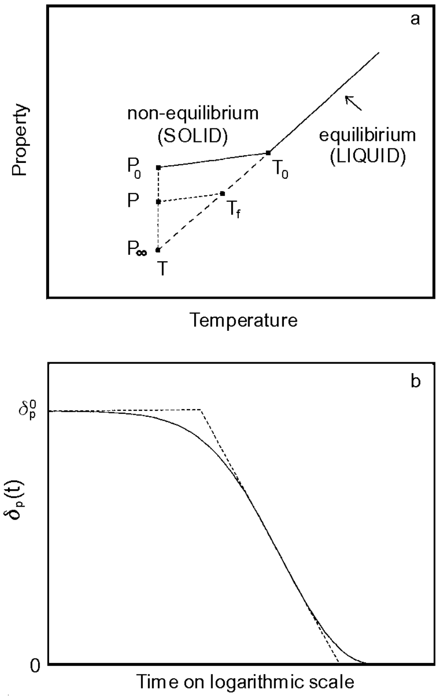

Fig. 1 a – The macroscopic property of an equilibrated non-crystalline material subjected to a temperature jump $\Delta T=T_o-T$. During an isothermal annealing at T the property relaxes from its initial value P_o toward its equilibrium value P_∞. b – Isothermal relaxation curve corresponding to the thermal history depicted above

Theory

It is well known that the function $\delta_P(t)$ obtained from volume or enthalpy relaxation data for a non-crystalline solid is non-exponential. This behavior can be explained by assuming the distribution of relaxation times and formally it can be expressed by a stretched exponential function [8, 9]:

$$\delta_P(t) = \delta_P^0\exp[-(t/\tau)^\beta] \tag{7}$$

where τ is a characteristic time and the exponent $\beta(0<\beta\leq 1)$ is inversely proportional to the width of corresponding distribution of relaxation times. Equation (7) describes well experimental data for a small temperature jump ($\Delta T<1$ K), however, at larger departures from equilibrium the $\delta_P(t)$ function becomes non-linear which means that the kinetics of isothermal structural relaxation do not scale linearly with the magnitude of the departure from equilibrium. Therefore, the responses expressed by Eq. (7) for different temperature jumps ΔT cannot be superposed to a single master curve by any linear transformation in time. This behavior was explained by Tool [7] assuming that τ depends on temperature as well as the instantaneous structure of a non-crystalline material characterized by T_f. Later it was shown by Naraynaswamy [10] that the linearity can be restored by introducing the reduced time ξ defined by

$$\xi = \int_0^t \frac{\mathrm{d}t}{\tau(T,T_f)} \tag{8}$$

The fictive temperature then can be expressed as

$$T_f = T + \Delta T\exp(-\xi^{\beta}) \tag{9}$$

The most frequently used expression for $\tau(T,T_f)$ in Eq. (8) is the Tool-Narayanaswamy formulation [10] as modified later by Moynihan *et al.* [11] (referred to as TNM):

$$\tau(T,T_f) = A\exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f}\right] \tag{10}$$

where A is the preexponential constant, x is the non-linearity 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 [12]. Equation (10) is purely empirical and therefore the parameters A, Δh^* and x have no clear physical interpretation. Nevertheless, it has been extensively tested on many non-crystalline materials and it was found that it describes the glass transition and their relaxation behavior quite well [8].

By differentiation of Eq. (9) with respect to log$t$ at the inflection point one can obtain the following equation [5, 6]:

$$R_f = 2.303\left[\frac{e}{\Delta T\beta} + \sigma\right]^{-1} \tag{11}$$

where the parameter σ for the TNM model can be written as

$$\sigma = -\left(\frac{\partial \ln\tau}{\partial T_f}\right)_i \cong (1-x)\frac{\Delta h^*}{RT_g^2} \tag{12}$$

Equations (11) and (12) predict increasing fictive relaxation rate even for large ΔT which agrees well with experimental data [2]. One can expect decreasing relaxation rate with broadening of the distribution of relaxation times (low values of β). The parameter σ corresponds to the non-linearity contribution. In a linear case (σ=0) the relaxation time is a function of temperature only and the maximum relaxation rate can be expected ($R_f^{max}=0.847\Delta T\beta$). Nevertheless, the relaxation behavior for the most non-crystalline materials is non-linear ($\sigma>0$) which means that they relax more slowly. For $\sigma>0.6$ the relaxation rate is very slow being nearly temperature independent and its value is mainly determined by the non-linearity contribution σ.

Results and discussion

For any quantitative comparison of volume and enthalpy relaxation, it is important to consider thoroughly the quality of reported $\delta_P(\log t)$ and $-(d\delta_P/d\log t)_i$ data. The related problems have been addressed elsewhere [5, 6]. In an ideal case the R_f value can directly be obtained from the slope of $T_f(\log t)$ plot according to Eq. (3). Figure 2 shows such plots for isothermal volume and enthalpy relaxation experiments for As_2S_3 glass subjected to a temperature jump experiment of 10.9 and 30.0 K, respectively [6]. The fictive temperature was calculated from volume and enthalpy loss data by using Eq. (4). As there are well defined temperature limits for T_f it is quite easy to construct the inflectional slope correctly. It is evident that experi-

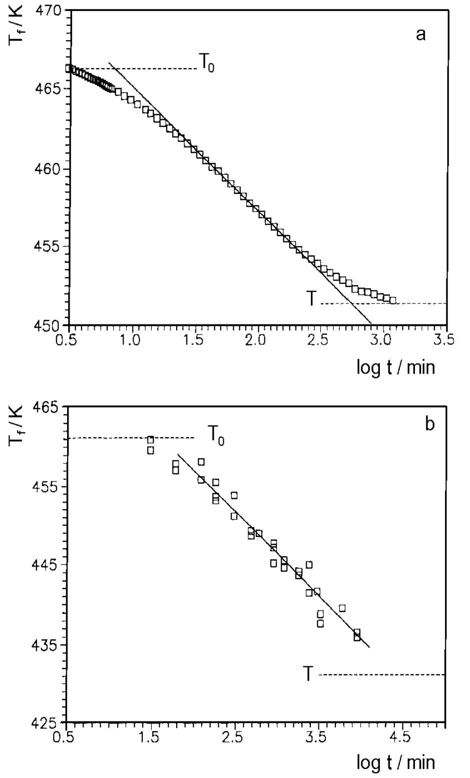

Fig. 2 Fictive temperature as a function of logarithm of time for As_2S_3 glass subjected to temperature jump experiments [6]: a – Volume relaxation data ΔT=10.9 K. b – Enthalpy relaxation data ΔT=30.0 K

mental errors for enthalpy relaxation are higher than for similar volume relaxation experiment. The error limits in R_f is estimated to be about ±0.2 K for volume and ±0.4 K for enthalpy relaxation.

Figure 3 shows the fictive relaxation rate as a function of temperature jump for As_2S_3 glass reported by Málek [6]. The $R_f(\Delta T)$ values for volume relaxation were obtained from the slope of $T_f(\log t)$ plots for different starting temperatures: $T_0=461.2$, $T_0=459.2$ and $T_0=453.2$ K [6]. Enthalpy relaxation data ($T_0=461.2$ K) were obtained in the same way. It is evident that the volume and enthalpy relaxation experiments give the R_f values that appear to be identical within the limits of experimental errors. It should be also noted that, as anticipated by Eq. (11), temperature T_0 has no measurable effect within the change between 450 and 461 K on the relaxation rate and only magnitude of the temperature jump is relevant for the fictive relaxation rate. The solid line in Fig. 3 was calculated by using Eq. (11) for TNM parameters $\beta=0.82$, $\sigma=0.11$ K^{-1} [13, 14]. In this case the theoretical prediction for the fictive relaxation rate agrees well for both enthalpy and volume relaxation data up to $\Delta T=40$ K.

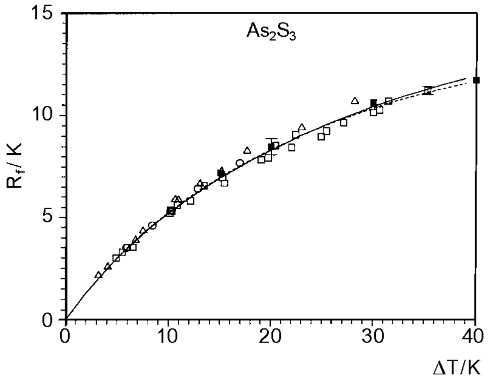

Fig. 3 Fictive relaxation rate for As_2S_3 glass as a function of magnitude of the temperature jump ΔT. Points correspond to volume relaxation data for different starting temperatures T_0: 461.2 K (□), 459.2 K (△), 453.2 K (○) and to enthalpy relaxation data (■) [6]. The solid line was calculated by using Eq. (11) for the TNM parameters $\beta=0.82$, $\sigma=0.11$ K^{-1} [13, 14]

However, the $T_f(\log t)$ data are not always available. If the R_f value is calculated from the slope of isothermal $\delta_P(\log t)$ plot (from Eqs (5) and (6), respectively), it is important to be sure that it corresponds to a truly inflectional tangent. If an experimental time scale is short then the slope of the $\delta_P(\log t)$ plot and thus also R_f value can easily be underestimated [3, 6]. Therefore, 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 the experimental time scale are known.

Taking into account these suggestions it is possible to find reported data obtained from different relaxation experiments (enthalpy, H; volume, V; and refractive index, n) for some non-crystalline materials and calculate the R_f value as shown in Table 1.

Data from several sources are given, in particular, for polystyrene (PS), polyvinyl acetate (PVA), polycarbonate (PC), polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC). These values are compared with fictive relaxation rate calcu-

Table 1 Measured and calculated fictive relaxation rate for non-crystalline materials

Material^a	Measured				Calculated			
	Ref.	P^b	ΔT/K	R_f/K	R_f/K	β	σ/K^{-1}	Ref.
NBS 711	[15]	*n*	27.9	10.1	10.58	0.63	0.06	[15]
As_2Se_3	[16]	*H*	20	7.4	7.60	0.67	0.10	[16]
	[6]	*V*	21.4	7.9	7.95			[16]
As_2S_3	[6]	*H*	30	10.6	10.44			[14]
	[6]	*V*	16.9	7.7	7.52	0.82	0.11	[14]
ZBLALiPb	[17]	*H*	41	4.5	4.98	0.54	0.34	[17]
ZBLA	[18]	*H*	60	4.3	5.19	0.54	0.36	[17]
Se	[19]	*H*	10	2.9	>2.80	>0.60	0.37	[19]
Ps	[20]	*H*	12	2.2	2.42	0.47	0.47	[21]
	[22]	*H*	11	2.4	2.31			[21]
	[23]	*V*	7	1.8	1.78			[21]
	[1]	*V*	9.5	2.4	2.13			[21]
	[24]	*V*	8.7	2.0	2.03			[21]
glycerol	[25]	*H*	27	3.6	3.35	0.51	0.49	[26]
epoxy DGEBA	[27]	*H*	20	2.4	2.4	0.30	0.55	[28]
epoxy EPON	[29]	*V*	2.5	0.5	0.55			[28]
PVA	[30]	*H*	10	1.7	1.91	0.51	0.67	[31]
	[32]	*H*	9	1.9	1.82			[31]
	[33]	*H*	10	1.9	1.91			[31]
	[2]	*V*	6.4	1.5	1.53			[31]
	[34]	*V*	6.4	1.4	1.53			[31]
PC	[35]	*H*	13.5	3.0	2.01	0.46	0.71	[31]
	[36]	*H*	9	1.9	1.69			[31]
	[37]	*H*	13.5	3.3	2.01			[31]
	[23]	*V*	5.7	1.4	1.32			[31]

Table 1 Continued

Material[a]	Measured				Calculated			
	Ref.	P^b	ΔT/K	R_f/K	R_f/K	β	σ/K^{-1}	Ref.
PMMA	[40]	*H*	13.7	1.7	1.72	0.35	0.77	[31]
	[41]	*H*	10	1.4	1.49			[31]
	[23]	*V*	8	1.1	1.32			[31]
	[42]	*V*	8	1.2	1.32			[31]
PVC	[43]	*H*	19.9	1.0	1.04	0.23	1.63	[31]
	[44]	*H*	8	1.0	0.74			[31]
	[45]	*V*	9	0.8	0.78			[31]
	[23]	*V*	10.8	0.7	0.85			[31]

[a] For explicit composition see corresponding references
[b] Property: enthalpy, *H*; volume, *V*; and refractive index, *n*

lated by using Eq. (11) for reported TNM parameters obtained mainly from enthalpy relaxation data (Table 1). It is seen that the R_f for volume and enthalpy relaxation of these materials is practically identical within the limits of experimental errors specified above. Somewhat higher discrepancies are observed far from equilibrium for some multicomponent fluoride glasses (ZBLA, ZBLALiPb) where Eq. (11) overestimates R_f values for about 20%. It seems that these differences probably come from limitations of the phenomenological model and that non-linearity formulation defined by Eq. (10) should be more structure dependent [6]. Some enthalpy relaxation data reported by Bauwens [35] and Steer and Rietsch [36] give considerably higher value for R_f than it is expected from Eq. (11) for reported NM parameters [31]. The reason for these discrepancies is not known.

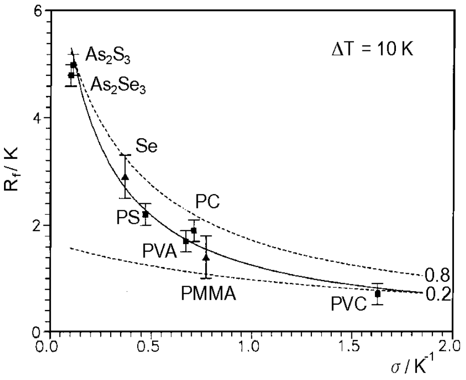

Fig. 4 The fictive relaxation rate corresponding to a temperature jump of 10 K as a function of parameter σ for volume (■) and enthalpy (▲) relaxation data. Full line represents the best fit to these data (see text). Broken lines were calculated by using Eq. (11) for different values of parameter β (shown next to the curves)

According to Eq. (11) one can expect fast decrease of the fictive relaxation rate for higher values of non-linearity contribution. Figure 4 shows experimental data for $R_f(\Delta T=10\text{ K})$ as a function of non-linearity contribution σ. Full line represents the best fit of a simple hyperbolic function $[R_f=1/(a+b\sigma)]$ to these data. Broken lines correspond to Eq. (11) for $\beta=0.2$ and 0.8, respectively. It seems that there is an inverse correlation of parameters β and σ. Similar type of correlation has been also proposed by Hodge [8]. It is evident that for higher values of non-linearity contribution ($\sigma>1$) the effect of parameter β is negligible and it becomes comparable with experimental error. Therefore, it might be rather difficult to separate non-exponentiality and non-linearity effects for these slowly relaxing materials.

Conclusions

The volume and enthalpy relaxation rate of inorganic glasses and organic polymeric materials has been analyzed. It is shown that the relaxation behavior can be compared on the basis of the fictive relaxation rate defined as $R_f=(\mathrm{d}T_f/\mathrm{dlog}t)_i$. A simple equation relating the R_f and parameters of Tool-Naraynaswamy-Moynihan (TNM) phenomenological model has been derived. This equation has been tested by using volume and enthalpy relaxation data reported for various glassy materials. The R_f data for volume and enthalpy relaxation are very similar within the limits of experimental errors. It seems that correct determination of TNM parameters might be problematic for slowly relaxing polymers as the effect of these parameters becomes comparable with experimental uncertainty.

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