Relaxation behaviour in the transition region of glassy systems

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Following the Adam–Gibbs procedure for describing the relaxation process of glass-forming liquids, a Vogel–Fulcher type equation has been obtained, determined by a new structural parameter called the isovolume fictive temperature, T_x. The resulting expression for the relaxation time has been applied satisfactorily to the experimental data of dielectric relaxation during physical ageing of poly(vinyl acetate). For testing the reliability of the proposed model, comparison with other phenomenological approaches has been made.

(Keywords: relaxation; transition; glassy polymer)

INTRODUCTION

During the past 30 years, much experimental and theoretical work has been carried out to describe the relaxation process of glass-forming substances. Although there has been considerable progress in understanding the phenomenology of relaxation of viscous liquids, there is not yet a generally accepted microscopic interpretation of structural relaxation. It is well known that vitreous materials, including glassy polymers, are not in thermodynamic equilibrium below their thermal glass transition temperature, T_g. These substances are hindered from reaching equilibrium in the glassy state by kinetic phenomena, and a possible second-order thermodynamic transition can never be attained in the timescale of a normal human life. The time dependence of any property (density, enthalpy, structure factor, optical properties, dielectric behaviour, stress response) lacks a diverging singularity when a critical temperature is approached, and much scientific work has been aimed at obtaining a complete description of the time–temperature dependence of these properties. Above T_g, this description is very well determined by the Williams–Landel–Ferry (WLF) equation[1], or by a Vogel–Fulcher formula[2], obtained either by free volume[3] theories or the Adam–Gibbs theory[4], based on a configurational entropy change at a true thermodynamic transition temperature, T_2. Below T_g, the relaxation time or viscosity diverges as the critical temperature is approached.

The introduction of a structural parameter, the 'fictive temperature', T_f, is an attempt to describe phenomenologically the structural recovery in glass-forming systems[5]. The time evolution of any property p may be given by the so-called Williams–Watt or Kohlrausch function[6], $\varphi(t)$:

$$\varphi_p(t) = \exp\left[-\left(\frac{t}{\tau}\right)^b\right] \tag{1}$$

where τ represents an average relaxation time and b is a positive constant less than unity. Narayanaswamy[7], who generalized the method developed by Tool[8], proposed an equation for τ, which divides the temperature- and structure-dependent parts in terms of T_f:

$$\tau = A \exp\left[\frac{xH}{RT} + \frac{(1-x)H}{RT_f}\right] \tag{2}$$

where x is an adjustable parameter, H expresses the activation energy of the relaxation process and A is a pre-exponential factor. Hodge[9] has recently introduced the following expression for the relaxation time τ, resulting from the Adam–Gibbs theory[4]:

$$\tau = A \exp\left[\frac{D}{RT(1 - T_2/T_f)}\right] \tag{3}$$

with

$$D = \mu S_c^*/\Delta c_p \tag{4}$$

where μ is the free energy barrier hindering cooperative rearrangement, S_c^* is the configurational entropy of the smallest group able to rearrange, Δc_p is the configurational heat capacity and T_2 is the configurational ground state temperature.

Matsuoka *et al.*[10] found a better fit to experimental data for poly(vinyl acetate) (PvAc) in the equilibrium and non-equilibrium state, by substituting the third therm in equation (2), which has the form of the equation proposed by Macedo and Litovitz[11]:

$$\ln \tau = C + \frac{H_a}{RT} + \frac{H_w}{R(T_f - T_2)} \tag{5}$$

where H_a and H_w express the activation energies of Arrhenius and Vogel–Fulcher formulae, respectively, and C is the logarithmic value of the pre-exponential factor. In the present study, a procedure analogous to that developed by Hodge has been followed. For the

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calculation of S_c, however, another structural parameter, T_x, has been introduced, corresponding to a temperature in the equilibrium state where the total volume of the recovering system is equal to the volume of the disturbed one. In this way, part of the configurational entropy due to volume changes between the two states may be avoided. This approach will be applied in dielectric measurements resulting in the temperature dependence of dielectric relaxation time of PvAc[12]. Comparison between the proposed equation and that of Hodge, equation (3), in respect of the experimental values of relaxation time, will also be made.

RELAXATION BEHAVIOUR IN THE NON-EQUILIBRIUM STATE

Structural recovery in glass-forming systems, or any change in properties during arbitrary thermal cycles, can be accurately described by phenomenological theories[5]. The first important step in the development of such models was by Tool[8], who proposed that structural relaxation should obey an equation analogous to that of the viscoelastic stress relaxation. Combining this assumption with the fact that fictive temperature, T_f, constitutes a single internal parameter used in practice for the description of the non-equilibrium state, a simple equation could be extracted, describing the relaxation of this internal parameter:

$$T_f = T - \int_0^{\xi} \varphi(\xi - \xi') \frac{dT}{d\xi'} d\xi' \qquad (6)$$

where ξ is the reduced time defined by:

$$\xi = \tau_r \int_0^{t} \frac{dt'}{\tau} \qquad (7)$$

and τ_r is the value of relaxation time τ at some reference temperature. By combining equations (1) and (6) with one of the equations (2), (3) or (5), the time evolution of fictive temperature is obtained.

Hodge[9] assumed that the change of the configurational entropy, S_c, between the characteristic temperature T_2 and a temperature T_f of the non-equilibrium state may be expressed by:

$$S_c = \int_{T_2}^{T_f} \frac{\Delta C_p}{T} dT = \Delta C_p\left(\ln \frac{T_f}{T_2}\right) \cong \Delta C_p\left(1 - \frac{T_2}{T_f}\right) \qquad (8)$$

where the Taylor expansion of the logarithmic function for $T_2 < T_f$ has been taken into account. T_f is the upper limit of integration replacing temperature T, with ΔC_p the configurational contribution to the isobaric heat capacity.

However, a volume change between states A and B exists, resulting in an excess configurational entropy, ΔS, for state B (*Figure 1*). This extra configurational entropy, ΔS, has been calculated and subtracted from equation (8) as follows. At temperature T, the total volume of the system, V_T, is occupied by a number, N, of subsystems, and the probability of finding such a subsystem in volume V_T is considered to be proportional to the volume: $W_1 = CV_T$, where C is a constant. The probability, W_T, of finding N subsystems simultaneously in volume V_T is the N-fold product of W_1, that is:

$$W_T = W_1^N = (CV_T)^N \qquad (9)$$

State B is characterized by the fictive temperature T_f and a volume V_{Tf}, with corresponding probability, W_{Tf}, given by:

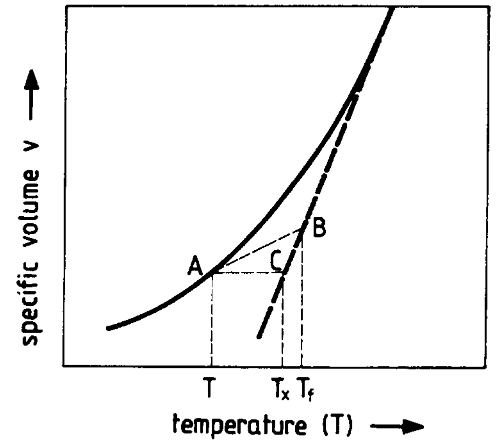

Figure 1 Schematic presentation of the temperature dependence of volume in the glassy and liquid states

$$W_{Tf} = (CV_{Tf})^N \qquad (10)$$

Hence the difference in configurational entropy between a state of volume V_T and a state of volume V_{Tf} is:

$$\Delta S = K(\ln W_T - \ln W_{Tf}) = KN \ln(V_{Tf}/V_T) \qquad (11)$$

Following the extrapolation of *Figure 1*, the ratio V_{Tf}/V_T could be calculated by the thermal expansion equation:

$$V_{Tf}/V_T = [1 + a_g(T_f - T)] \qquad (12)$$

Substituting this form in equation (11) and taking the Taylor expansion of the logarithmic function, we obtain:

$$\Delta S = KNa_g(T_f - T) \qquad (13)$$

By subtracting this amount from equation (8), another expression for the configurational entropy will be extracted:

$$S'_C = S_C - KNa_g(T_f - T) \qquad (14)$$

The above calculations may be avoided if a new position in the equilibrium state is adopted, characterized by a temperature T_x, where the entropy contribution due to volume changes should be eliminated. Point C of *Figure 1* is selected to represent such a state in equilibrium, and the corresponding amount of excess entropy is:

$$\Delta S = KNa_1(T_f - T_x) \qquad (15)$$

Equating this term with the second part of equation (13), temperature T_x may be evaluated:

$$T_x = T_f - \frac{a_g}{a_1}(T_f - T) \qquad (16)$$

where a_1 is the thermal expansion coefficient of the equilibrium state. Parameter T_x, which will be called the isovolume fictive temperature, is obtained by extrapolating a line of the non-equilibrium state A parallel to the T-axis to intersect with the equilibrium curve. T_x could be used as the upper limit of integration in equation (8). The configurational entropy is then found to be:

$$S'_C = \int_{T_2}^{T_x} \frac{\Delta C_p}{T} dT = \Delta C_p\left(1 - \frac{T_2}{T_x}\right) \qquad (17)$$

The resulting form of relaxation time will then be given by:

$$\tau = A \exp\left[\frac{D}{RT\left(1 - \frac{T_2}{T_x}\right)}\right] \qquad (18)$$

For describing the time evolution of T_x in terms of equation (16), two choices could be adopted. The first involves accepting the glassy thermal expansion coefficient, $a_g(t)$, as a time-dependent physical property, which varies from an initial value, $a_g(0)$, up to an equilibrium value, $a_g(\infty)=a_l$, following the equation proposed by Tool[8]:

$$a_g(t)=a_l-\int_0^{\xi}[a_l-a_g(0)]\varphi(\xi-\xi')\frac{\mathrm{d}T}{\mathrm{d}\xi'}\mathrm{d}\xi' \qquad (19)$$

In this case the value of T_f appearing in equation (16) is constant during the relaxation process corresponding to the intersection point B of *Figure 1*. The second choice involves the time evolution of T_f according to equation (6), where the glassy thermal expansion coefficient is considered to be constant under the relaxation process.

In the present study, the first procedure has been followed, meaning that structural relaxation interferes with the recovery of any other property affecting its evolution up to the equilibrium state. To apply equation (19), the determination of parameters a_l, $a_g(0)$, as well as the pre-exponential factor and activation energy for structural relaxation time is required. By evaluating the time evolution of T_x, the relaxation time of any property (such as dielectric properties) could be obtained, given that the pre-exponential factor and activation energy for such a process have been defined independently[13].

COMPARISON WITH EXPERIMENT

The proposed model has been tested by fitting the experimental data for isothermal dielectric measurements on PvAc, carried out in a wide frequency range by Schlosser and Schonhals[12]. These authors executed experiments in the temperature range from (T_g+50) to (T_g-15) K, using frequency and time domain measurements. Above T_g the complex permittivity

$$\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$$

was measured in the frequency range 1-10^5 Hz, using bridge methods described in refs 14 and 15. Near and below T_g, the relaxation behaviour was measured by the density of the depolarization current, $j(t)$, for a field E_0 which was switched off at time $t=0$:

$$j(t)/E_0\varepsilon_a=\varepsilon'(t) \qquad t>0$$

where the relaxation function $\varepsilon'(t)$ is the time derivative of the time-dependent dielectric permittivity, $\varepsilon(t)$, and ε_a is the permittivity of the free space.

In order to discuss the dielectric properties in the time domain, the measurements obtained in the frequency range were evaluated by fitting the imaginary part of the model function of Havriliak and Negami[16]. This combination leads to the $t\varepsilon'(t)$ function *versus* time[17], shown schematically in *Figure 2*, where three characteristic times, t_1, t_2 and t_m, are defined. These are the position parameters due to the maximum (t_m) and half height of the function $t\varepsilon'(t)$ at short (t_1) and long (t_2) times.

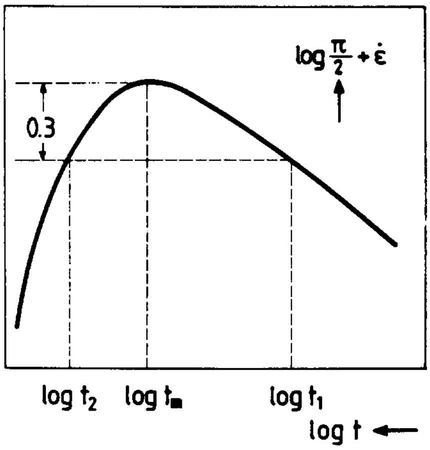

Figure 2 Definition of the characteristic times t_m, t_1 and t_2

Table 1 Parameters for the Vogel–Fulcher equation, from ref. 12

	$\log A$	T_2 (K)	D/R (K)
t_1	−12.5	269.3	563.1
t_m	−11.45	270.8	554.8
t_2	−10.75	271.5	549.0

Table 2 Parameter values for the models tested

	$\log A$	T_2 (K)	D/R (K)	a_1[a]	a_g[a] (10^{-4} K^{-1})	b
Model calculation	−11.33	270.8	554	6	3	0.5
Hodge equation	−11.33	272	602	–	–	0.5

[a] Values taken from ref. 18

Below T_g the relaxation process depends strongly on the thermal prehistory. For examining this effect, a well defined thermal treatment was executed, where three different annealing times, t_e (elapsed from the beginning of cooling) of 300, 1600 and 8530 s, were studied.

The plots of *Figure 3* illustrate the variation of the characteristic times t_1, t_2 and t_m in respect of temperature, where experimental values are represented by solid lines. The parameter values of the Vogel–Fulcher equation fitted in the equilibrium state, according to ref. 12, are listed in *Table 1*, which also includes the results of the proposed description for relaxation time. The corresponding calculations, given in equation (18) in conjunction with equations (1), (16) and (19), are described in detail in appendix B of ref. 5.

The second set of experimental data, with the mean relaxation time measured for three different annealing times of 300, 1600 and 8530 s, is illustrated by the plots of *Figure 4*. The graphical representation of theoretical values is also included in this figure, where an excellent fitting is observed.

It is worth mentioning here that the isovolume fictive temperature model makes a unique determination of parameters a_g, a_l and activation energy, appearing in relaxation time equations. In this way, assuming reasonable values for these parameters included in *Table 2*, and solving numerically the related expressions, all features included in *Figures 3* and *4* are adequately

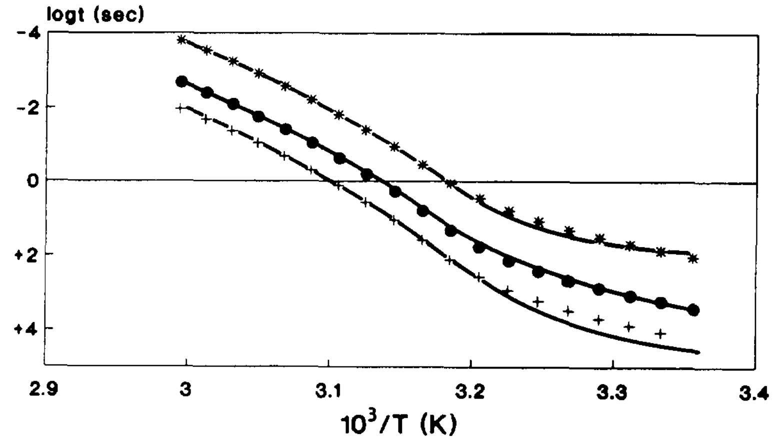

Figure 3 Plots of the characteristic times *versus* $10^3/T$ for elapsed time $t_e = 300$ s. Solid lines represent the experimental data of ref. 12. Model calculations: *, time t_1; ●, time t_m; +, time t_2

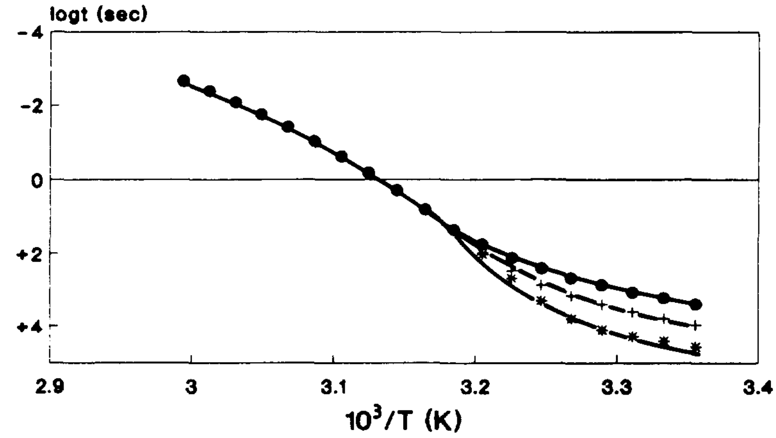

Figure 4 Plots of the characteristic time, t_m, *versus* $10^3/T$ for various elapsed times. Solid lines represent the experimental data of ref. 12. Model calculations: *, $t_e = 300$ s; ●, $t_e = 1600$ s; +, $t_e = 8530$ s

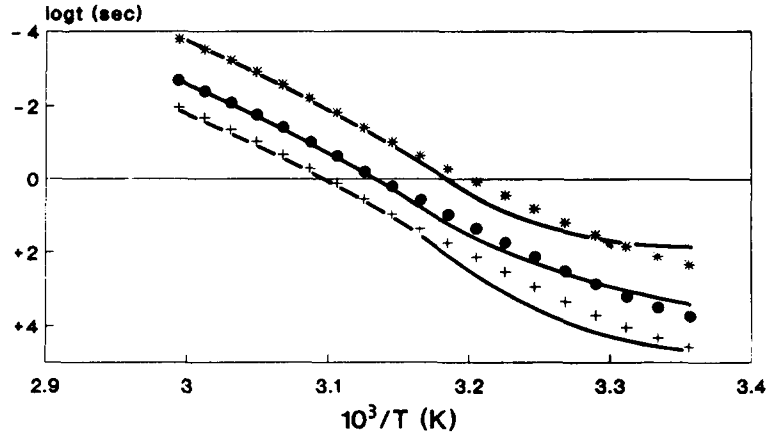

Figure 5 Plots of the characteristic times *versus* $10^3/T$ for elapsed time $t_e = 300$ s. Solid lines represent the experimental data of ref. 12. Hodge approximation: *, time t_1; ●, time t_m; +, time t_2

reproduced for every thermal history and temperature range.

However, the ability of this approach to obtain satisfactory agreement with experimental results could be better established if it is compared with other phenomenological models. Equation (3), introduced by Hodge in conjunction with equations (1), (6) and (7), was applied to the same experimental data, as presented in *Figures 5* and *6*. The inadequacy of this approximation in describing in detail the variation of relaxation times

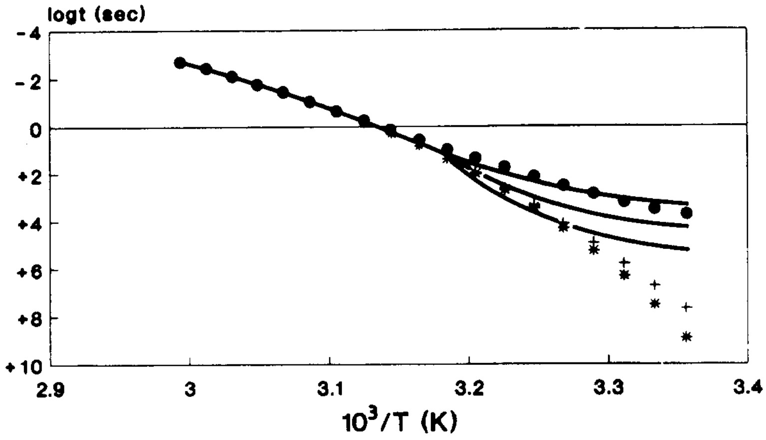

Figure 6 Plots of the characteristic time t_m *versus* $10^3/T$ for various elapsed times. Solid lines represent the experimental data of ref. 12. Hodge approximation: *, time t_1; ●, time t_m; +, time t_2

below T_g is confirmed, especially in *Figure 6*. Therefore, the parameter values required for optimal fitting should be changed from one set of experiments to the next.

CONCLUSIONS

Based on the Adam–Gibbs procedure for describing the relaxation process of glass-forming liquids, a Vogel–Fulcher type equation has been obtained, determined by a new structural parameter called the isovolume fictive temperature, T_x. This parameter expresses a temperature in the equilibrium state, where the total volume of the recovering system is equal to the volume of the disturbed system. In this way, part of the configurational entropy due to volume changes between the two states should be avoided. For describing the time evolution of T_x, the time dependence of the thermal expansion coefficient of the glassy state has been taken into account, following an equation proposed by Tool[8].

The resulting expression for the relaxation time has been applied satisfactorily to the experimental data of dielectric relaxation during physical ageing of PvAc. For testing the reliability of the proposed model, comparison with Hodge's phenomenological approach has been made. It has been found that, according to our approach, a unique determination of parameters describing the structural relaxation is sufficient for interpreting all experimental results of dielectric relaxation.

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