

A non-linear structural relaxation model for the refractive index of glass during annealing

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A two internal thermodynamic ordering parameter non-linear model is used to explain the structural relaxation of glass. These two internal thermodynamic ordering parameters are also used to characterize the frozen-in structural state of glass. For an isobaric isothermal annealing process, the internal state of the glass can be characterized by the two internal ordering parameters such as fictive temperature, T_f , and configurational part of activation energy, H_s . Therefore, these two internal thermodynamic ordering parameters are used in a non-linear structural relaxation model of glass for explaining the volume relaxation and predicting the refractive index of glass during annealing, and they are also extended to characterize the thermal history of the frozen-in structure of the glassy state.

1. Introduction

The structural relaxation of a glass is the primary factor in determining its rheological properties in any forming or annealing process. In a glass-making process, viscosity plays a key role in the range of melting and refining temperatures. On the other hand, the structural relaxation phenomenon dominates the process of stabilization of the glass in the working range and annealing range. For example, in the manufacture of a very high quality optical glass it is important not only that there should be no mechanical stresses or birefringence, but also that the properties of glass should be uniform throughout the body of the glass. This is controlled by the structure or volume relaxation phenomenon during the annealing process. Therefore, there is a need to understand further the structural relaxation of glass.

That the structural relaxation phenomenon of glass exhibits a non-linear rheological behaviour has been shown by Tool [1, 2] and Ritland [3] among others. Recently, Gardon and Narayanaswamy [4], Ohlberg and Woo [5], and Crochet *et al.* [6] have used Tool's fictive temperature, T_f , in a thermal stress study during the annealing process. However, both thermodynamically and kinetically it proves that there is a deficiency by only using an

internal thermodynamic ordering parameter such as fictive temperature, T_f , for interpreting the kinetic phenomenon of the structural relaxation and characterization of the internal state of the non-equilibrium frozen-in structure of the glass. Prigogine and Defay [7], Davies and Jones [8, 9], Staverman [10, 11], and Goldstein [12], have shown that if the Prigogine-Defay relation is in an inequality, i.e. $\Delta\beta/\Delta\alpha > TV\Delta\alpha/\Delta C_p$, more than one internal thermodynamic ordering parameter is required to characterize the frozen-in structural state of the glassy state, where $\Delta\beta$, $\Delta\alpha$, and ΔC_p denote the differences in compressibility, thermal expansion, and specific heat as measured in slow and fast experiments at the glass transformation temperature. Actually the inequality of the Prigogine-Defay relation has been found in most glass systems. Therefore, more than one internal thermodynamic ordering parameter is needed for characterizing the internal state of the frozen-in structure of the glass and explaining the structural relaxation of the glass. The author has used a two internal thermodynamic ordering parameter non-linear model [13] to explain the structural relaxation of the glassy state. It is important to know whether or not the two internal thermodynamic ordering parameters concept can interpret both

thermodynamically and kinetically the physical picture of glassy state logically. In the following, a discussion is given regarding internal thermodynamic ordering parameters and the relationship between the thermodynamics and the kinetics in the frozen-in structural state of the glass. Since the concept is thermodynamic in nature, the model should be suitable for all glass systems either of inorganic or organic composition.

2. Thermodynamic and kinetic aspects of glass

Glass has been recognized as being in a thermodynamic non-equilibrium state. The physical and the chemical properties depend not only on thermodynamic variables such as pressure and temperature, but also depend on the thermal and mechanical history of the glass. Therefore Duhem's theorem [7], which states that only two independent thermodynamic variables are needed for completely characterizing a state of an equilibrium system, cannot apply to a glass system. According to de Donder [7] the frozen-in structural state or the physical properties of glass can be explained by a set of internal thermodynamic ordering parameters, $\{\xi_i\}$, i.e., $\tilde{P} = f(T, P, \{\xi_i\})$. The set of ordering parameters, $\{\xi_i\}$, have been frozen-in at some particular value depending on the thermal and mechanical history of the glass.

Simon [14] claims that the vitreous state is distinguished from the liquid state by the fact that the internal equilibrium state is not established. Following Simon [14], Prigogine and Defay [7, 8] also concluded that a relaxation process of the glass during stabilization below the normal T_g is a structural change towards a configuration in which only reduced rotational motions are possible, which therefore has an influence upon the enthalpy. This agrees with Simon's explanation that the contribution of configurational structure changes itself to the value of the enthalpy. The concept of the configurational changes influencing the enthalpy during the process of stabilization of glass is equivalent to the concept of two internal thermodynamic ordering parameters which is proposed by the author in his non-linear model [13] of the structural relaxation of the glassy state.

In the model, a larger structural dependent part of the activation energy is used at a lower annealing temperature. It is concluded that there

is a relationship between thermodynamics and kinetics. Thermodynamically, once the rotational motion is reduced, then the configurational energy state is frozen-in at a particular internal state of the glass structure. During the relaxation process, the kinetic phenomenon is also governed by the internal state of the glass (i.e., H_s/RT_f). Therefore, for glass having the Arrhenius behaviour in viscosity, the same activation energy is used for explaining the viscous flow and structural relaxation of glass. The internal thermodynamic ordering parameters not only characterize the non-equilibrium frozen-in state of glass but also play a major role in a kinetic process.

From the above one knows that the internal thermodynamic ordering parameters in the glassy state are important both in thermodynamics and kinetics. Therefore, it is necessary to explore how many internal thermodynamic ordering parameters, and what kinds of ordering parameters, can both characterize the internal state in thermodynamics, and therefore can explain the structural relaxation phenomenon in kinetics of the glassy state. Staverman [10, 11] has shown that for a glass system having a set of n ordering parameters $\{Z_i\}$, $i = 1 \dots n$, the relationship of Prigogine-Defay can be written as

$$(V/T)\Delta\beta\Delta C_p - V^2(\Delta\alpha)^2 = \quad (1)$$

$$\sum_j \sum_k \frac{S_j^2 S_k^2}{G_{jj} G_{kk}} (V_j/S_j - V_k/S_k)^2$$

Where V_j , V_k , S_j , S_k are the volume and entropy changes resulting from changes of Z_j and Z_k ; and where $G_{jj} = \partial^2 G/\partial Z_j^2$, $G_{kk} = -\partial^2 G/\partial A_k^2$, G being Gibbs free energy.

From the conditions of thermodynamic stability [7] both G_{jj} and G_{kk} must be negative. Therefore, the Prigogine-Defay relationship is always positive except in the special case of $V_j/S_j = V_k/S_k$, or where all V_i and S_i are equal to zero for all $i = 1$ to n . Dimarzio's condition [15] for equality of the Prigogine-Defay relationship, i.e. $\Delta C_p \Delta\beta = TV(\Delta\alpha)^2$, is a special case in Staverman's equation, in which V_i and S_i are all equal to zero. This condition is unlikely to be true for the glass systems as pointed out by Goldstein [12]. Davies and Jones [8, 9] found large values for the ratio $\Delta\beta\Delta C_p/TV(\Delta\alpha)^2$ ranging from 2.4 to 16. They concluded that for glasses, the one-parameter model is not adequate. We also can see this from the approach equilibrium curves of

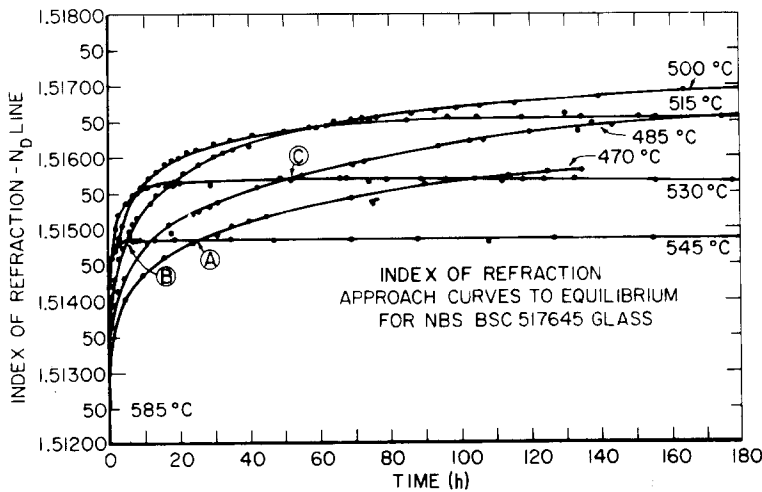


Figure 1 Index of refraction approach curves from 585°C to equilibrium.

Spinner and Napolitano's data [16] as shown in Fig. 1. All data are measured at room temperature and atmospheric pressure. However, the indices of refraction of glass are different due to different annealing histories. If one used Tool's fictive temperature [1, 2] alone to characterize the structural state of glass, then one would not be able to distinguish the thermal histories of glasses which have the same fictive temperature (or the same indices of refraction) but which have different thermal histories as shown in the different curves of Fig. 1. Therefore, from Spinner and Napolitano's approach equilibrium curves, it is also shown that it is not possible to use only one parameter to characterize fully the internal state of the frozen-in structure of glass.

As mentioned before, we know theoretically and experimentally that more than one parameter is needed to characterize the frozen-in structure of glass. For the next step it is important for us to know what the minimal ordering parameters for a particular thermal and mechanical history are, and what kinds of parameters are suitable for characterizing the internal state and structural relaxation of glass. For practical inorganic or organic glass making, without considering the chemical reaction [17] and phase separation or other phenomena which will affect the frozen-in structure during the stabilization process of glass, the internal state of glass can be identified by the structural part of the activation energy, H_s (or $\xi = H_s/H$), fictive temperature, T_f , and fictive pressure, P_f . Therefore we can write the physical properties of glass as $\tilde{P} = f(T, P|\xi, T_f, P_f)$. However, in an inorganic glass making process, normally we keep pressure in the order of atmospheric pressure, i.e., there is no

substantial pressure jump during the glass making process. The fictive pressure is the same as actual pressure and there is no fictive pressure affecting the internal state of the frozen-in structure of glass. Therefore, in this case only two ordering parameters are needed to completely characterize the structural state of glass and its structural relaxation process, as the author used in his non-linear model [13].

3. Applications and results

We have mentioned that to identify the internal thermodynamic ordering parameters it is important to understand the structure of glass. But for the glass industry it is most important to know how to use the internal ordering parameters and the concept of frozen-in structure of glass to improve glass making. We will discuss elsewhere [17, 18] how melting, refining and forming processes are affected by internal ordering parameters, and how the physical properties are also affected by them in these processes. In the following we will use the concept of two internal thermodynamic ordering parameters in a non-linear structural relaxation model for an annealing study and for predicting the refractive index of glass during annealing.

Gardon and Narayanaswamy [4] have modified the model of Lee *et al.* [19] by adding a structural relaxation function for the calculation of the internal stress of glass in the annealing process. However, the structural relaxation model which is used by Gardon and Narayanaswamy [4], and Narayanaswamy [20] is basically different from the present model. In Narayanaswamy's model he explains that any non-equilibrium state of glass is

a mixture of several equilibrium states as shown in his Equation 7. On the contrary, in the new model, the non-equilibrium internal state of the frozen-in structure of glass is characterized by the internal thermodynamic ordering parameters such as fictive temperature, T_f , and the structural part of the activation energy, H_s , during the stabilization process of glass. The author's internal ordering parameter concept is devoted to building a relationship between thermodynamics and kinetics. It is similar to the concept of frozen-in configurational structure of Simon, *et al.* Therefore, the ordering parameters consistently serve to characterize the internal state of glass in thermodynamics and to explain the structural relaxation of glass in kinetics.

We will see that the model is different from Narayanaswamy's in explaining structural relaxation data of borosilicate crown glass which was taken by Spinner and Napolitano [16]. Narayanaswamy [20] uses the same structural dependent part of the activation energy, $H_s = 74 \text{ kcal mol}^{-1}$, and temperature dependent part of the activation energy, $H_T = 84 \text{ kcal mol}^{-1}$, for all different temperature curves. His model does not use the total activation energy in the structural relaxation process as the same as the activation energy in the viscous flow process. The activation energy of viscous flow is $140 \text{ kcal mol}^{-1}$ [21] which

appears much smaller than Narayanaswamy used in his model, (i.e., $H = H_T + H_s = 158 \text{ kcal mol}^{-1}$). Narayanaswamy claims the two parameters in his model are the two different fictive temperatures, T_{f1} and T_{f2} used in a two-single relaxation. However, when a different distribution function is used for different glass systems, he might have difficulty in logically explaining the significance of the physical meanings of the ordering parameters. But the author's internal thermodynamic ordering parameter concept always consistently and logically explains the glass structure thermodynamically and kinetically for the different structural relaxation functions. As one will see later, a β -function instead of a two-single relaxation function is used to explain the structural relaxation of BSC glass. The author has distinguished the basic difference between the two models in the above. However, Gardon and Narayanaswamy [14] were successful in using their model for their applications.

Non-linear behaviour of the structural relaxation of glassy state appears both in organic and inorganic glass. Goldbach and Rehage [22–25] used a method of step-wise changes in temperature and pressure for measuring the isothermal-isobaric volume retardation of atactic polystyrene. They discovered when the temperature steps exceeded about 1.8°C or the pressure jumps exceeded

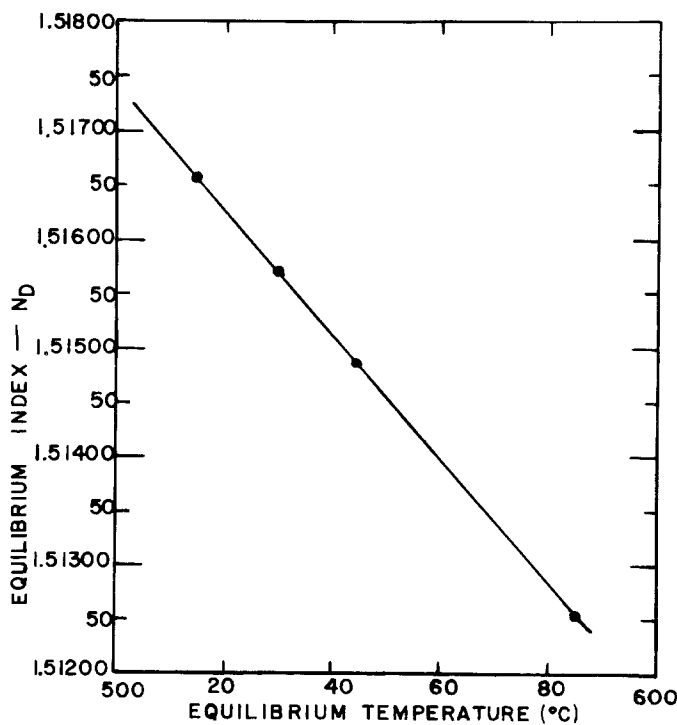


Figure 2 Equilibrium temperature–equilibrium refractive index curve.

40 atm., a non-linear behaviour appears in the structural relaxation process. Therefore, the intrinsic non-linearity and memory effects appear both in organic and inorganic glasses.

In the following we apply the model to the BSC glass, the data is taken from Spinner and Napolitano [16] and shown in Fig. 1. A β -function is used for BSC glass instead of two-single relaxation functions which are used by Narayanaswamy [19]. We can write the structural relaxation function as

$$\frac{N(T, t) - N_\infty}{N_0 - N_\infty} = \psi(T|T_f, \xi) = \exp \left[- \left(\sum_i \frac{t_i - t_{i-1}}{\tau(T, t)} \right)^\beta \right] \quad (2)$$

$$\begin{aligned} \tau(T, t) &= \tau_0 \exp \left(\frac{H_T}{RT} + \frac{H_S}{RT_f} \right) \\ &= \tau_0 \exp \left[\frac{(1-\xi)H}{RT} + \frac{\xi H}{RT_f} \right] \quad (3) \end{aligned}$$

Where N_0 and N_∞ are the initial and equilibrium refractive indices, $N(T, t)$ is the refractive index of the frozen-in structure of the glass, τ_0 and β are the constants, and ξ is the ratio of the structural part of the activation energy, H_s , to the total activation energy, H , as mentioned before. The fictive temperature, T_f , can be calculated by using Tool's definition: the fictive temperature, T_f , is the actual temperature of an equilibrium state that corresponds to the given non-equilibrium state

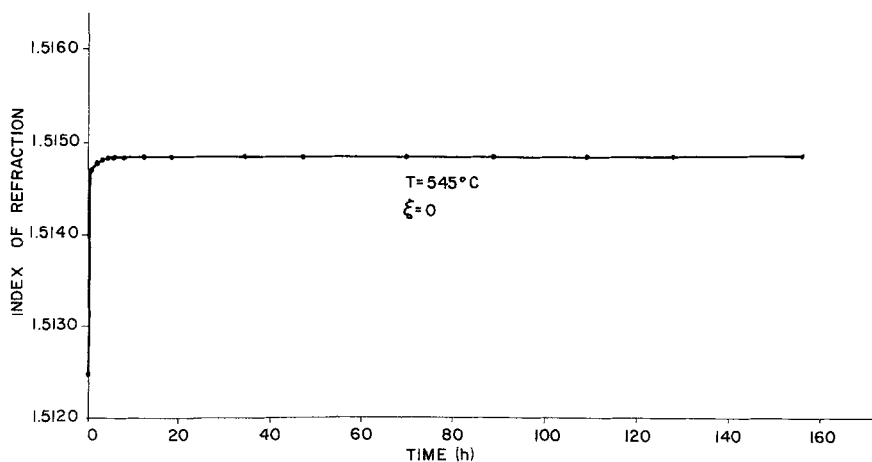


Figure 3 Theoretical prediction (smooth curve) and experimental data of approach curve to equilibrium temperature 545° C.

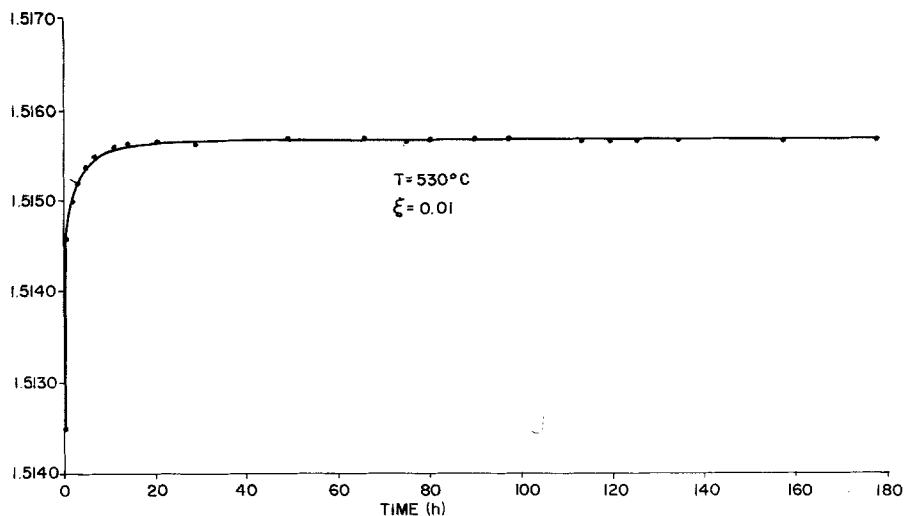


Figure 4 Theoretical prediction (smooth curve) and experimental data of approach curve to equilibrium temperature 530° C.

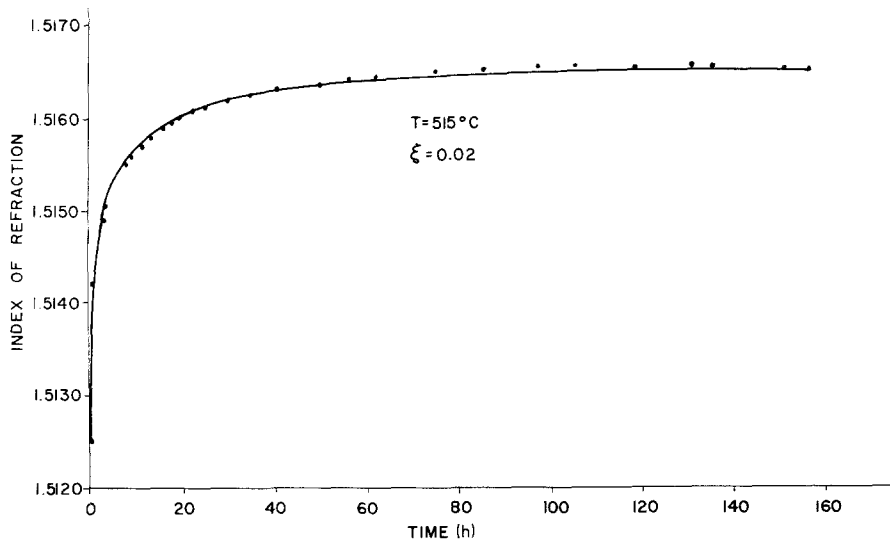


Figure 5 Theoretical prediction (smooth curve) and experimental data of approach curve to equilibrium temperature 515° C.

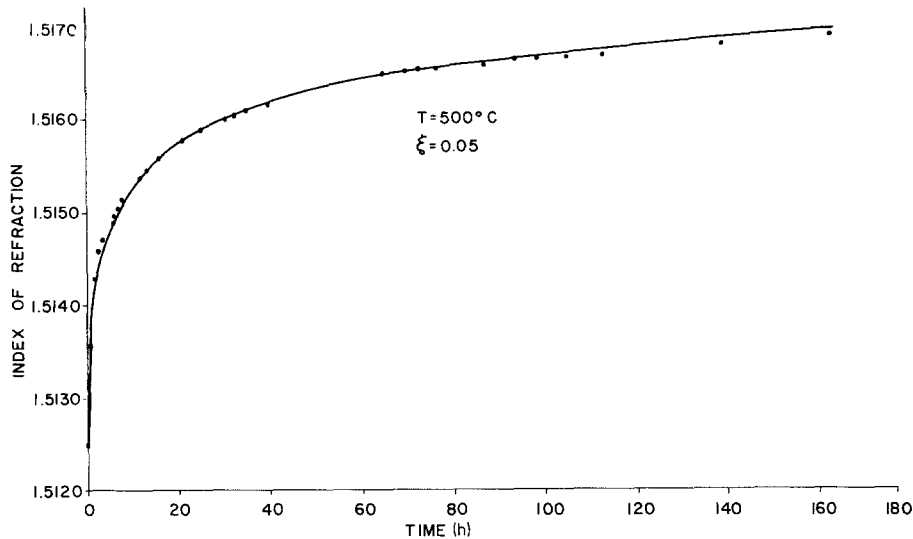


Figure 6 Theoretical prediction (smooth curve) and experimental data of approach curve to equilibrium temperature 500° C.

having the same values of physical properties. We rewrite Equation 2 as

$$N(T, t) = N_{\infty} + (N_0 - N_{\infty}) \exp \left[- \left(\sum_i \frac{t_i - t_{i-1}}{\tau(T, t)} \right)^{\beta} \right] \quad (4)$$

Following the previous method [13] for calculating the refractive index and its corresponding fictive temperature, T_f , at each time in the sequence, $0 < t_1 < t_2 < t_3 \dots < t_i < t_{i+1} \dots$; initially, we let the fictive temperature equal the initial temperature, i.e., $T_f = T_0$. From Equations 4 and 3 we calculate $N(T, t)$ at t_1 , then by using

the relationship of refractive index and temperature at the equilibrium state as shown in Fig. 2, one can calculate T_f at time t_1 . This T_f at time t_1 is used to calculate $N(T, t_2)$ and from that T_f at time t_2 is obtained. By continuing these calculations, the fictive temperatures, T_f , at the times in the sequence $0 < t_1 < t_2 < t_3 < \dots < t_i < t_{i+1} < \dots$ are obtained. These in turn are used for calculating the refractive index by using Equations 4 and 3. The best fit to the equilibrium approach curves as shown in Fig. 1, are plotted in Figs. 3 to 8. The constants are $\tau_0 = 9.4 \times 10^{-37}$ h, $\beta = 0.4$. The activation energy for the structural relaxation, H , is the same as the activation energy for viscous

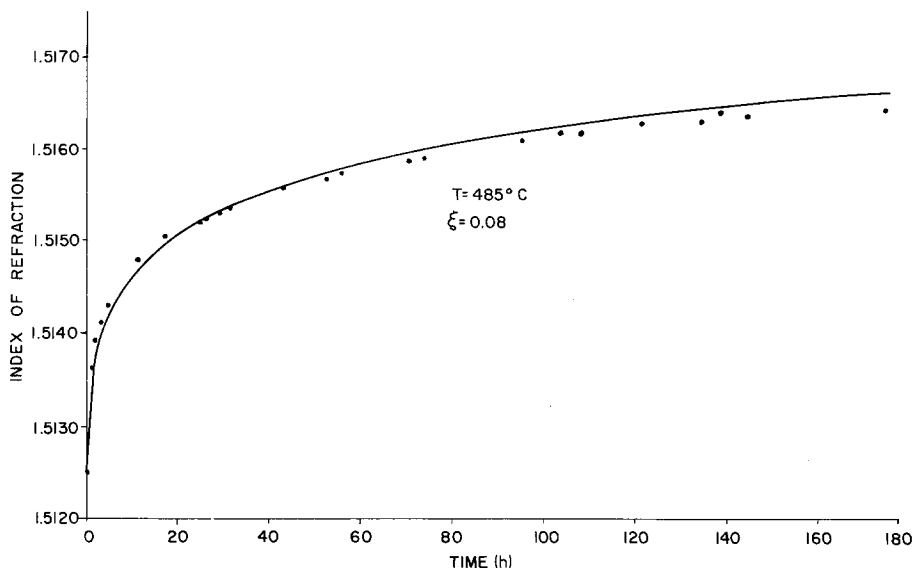


Figure 7 Theoretical prediction (smooth curve) and experimental data of approach curve to equilibrium temperature 485°C.

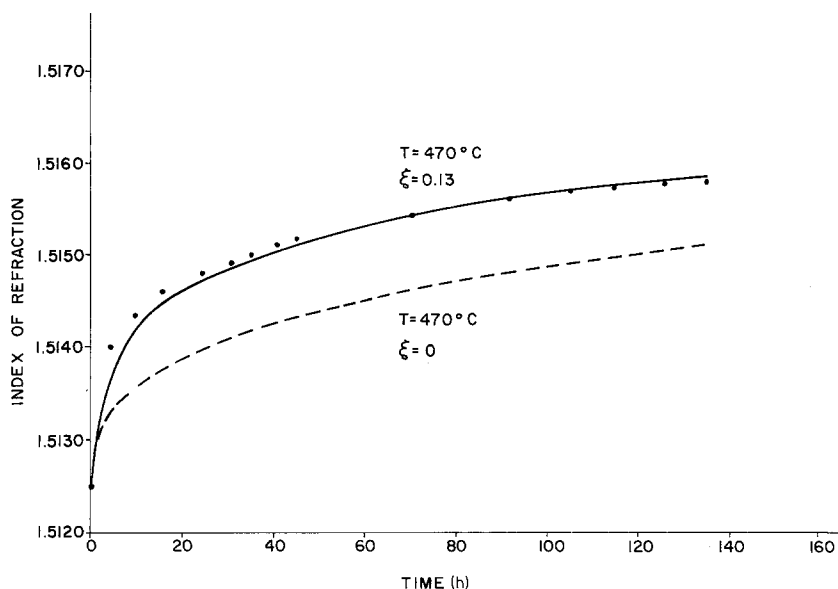


Figure 8 Theoretical prediction (smooth curve) and experimental data of approach curve to equilibrium temperature 470°C.

flow, i.e., $H = 140 \text{ kcal mol}^{-1}$. The second thermodynamic ordering parameter, $\xi = H_s/H$, as function of temperature is plotted in Fig. 9; it decreases as temperature increases.

The comparison of the results obtained by using two different ordering parameters for the curve at a temperature of 470°C gives $\xi = 0.13$ as the best fit for the curve, and $\xi = 0$ is the value used in the highest temperature curve at 545°C also shown in Fig. 8. Therefore, the result is consistent with the conclusion mentioned in the previous paper [13].

The present model agrees more closely than the earlier model with experimental relaxation data. It also has the advantage that it does so regardless of the structural relaxation function [13]. These two ordering parameters can be used to characterize the internal state and the physical properties of the frozen-in structure of the glassy state. Therefore one would expect that the ordering parameters, T_f and ξ , will help to predict other physical properties, such as volume, non-equilibrium viscosity [26], thermal expansion, heat capacity, dielectric constant etc. since the glassy state has

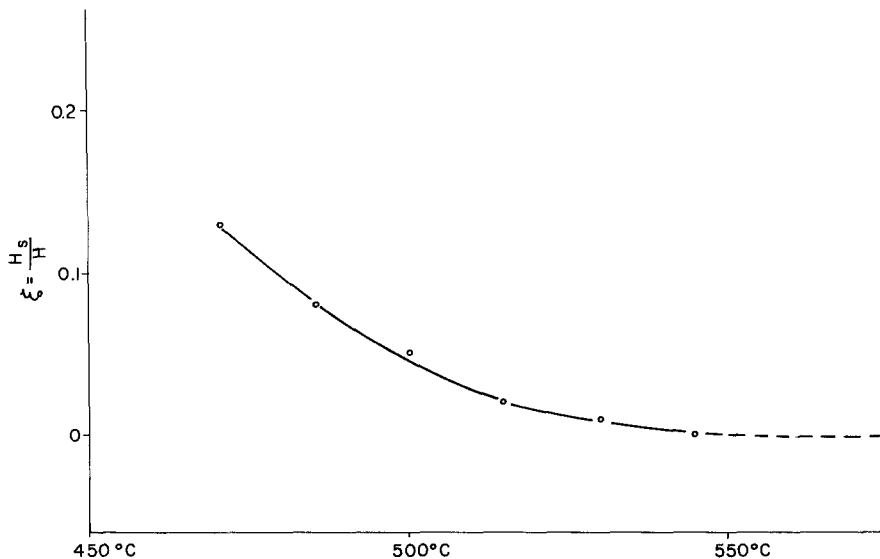


Figure 9 The second ordering parameter, ξ , versus annealing temperatures.

been frozen-in at a particular temperature and configurational energy state.

4. Conclusion

Since the glassy state is distinguished from the super-cooled liquid-like state by the fact that the internal equilibrium state is not established, the distribution relaxation function, which exists both in the super-cooled liquid-like state and the glassy state, cannot alone explain the physical properties of the frozen-in structure of the glassy state.

The two internal thermodynamic ordering parameters, i.e., the fictive temperature, T_f and the structural dependent part of the activation energy H_s , are used in a model for explaining the structural relaxation of the glassy state. These two ordering parameters are also used to characterize the internal state of the frozen-in structure of glass. The structural dependent part of the activation energy, H_s , has been frozen-in in a particular state, according to the proposal of Simon and of Prigogine and Defay that the configurational energy is frozen-in due to the reduction of the molecular rotational motion in the process of stabilization of glass.

The study of the structural relaxation of the glassy state concludes:

(1) a distribution relaxation time spectrum exists in the structural relaxation process and is due to the phenomenon of the co-operative molecular motion;

(2) the total activation energy of the structural relaxation of glass is the same as the activation energy in the viscous flow;

(3) two internal thermodynamic ordering parameters are needed to explain the structural relaxation of glass;

(4) the structural dependent part of the activation energy, H_s , increases as temperature decreases due to the reduction of the molecular rotational motion in the process of structural relaxation of glass. Therefore, the non-linear model of the structural relaxation of the glassy state will allow one to predict the volume relaxation and programme the refractive index of optical glass by annealing.

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