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Calorimetric characterization and computer simulation, based on a thermal activation model, of irreversible structural relaxation processes in liquid dibutylphthalate

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Abstract. The irreversible enthalpy relaxation processes in liquid dibutylphthalate were tracked under constant-temperature conditions by the temperature jump method with an adiabatic calorimeter, and the relaxation functions were characterized in terms of the stretched exponential function with a nonexponentiality parameter, β . Remarkable nonlinearity, δ , of the relaxation functions with the magnitude of temperature jump, $\Delta_j T$, was found, and reasonably interpreted to be due to the fragility, m , of the liquid from the comparison with the result of computer simulation based on a thermal activation model for the microscopic rearrangement of molecules. The validity of the Tool–Narayanaswamy model is also discussed on the basis of the simulation result.

1. Introduction

Molecular liquids are characterized by disordered arrangements with respect to both positional and orientational degrees of freedom of the molecules. However, the intermolecular interactions are so effective that some short-range structural order, called a structured cluster, may exist among the molecules and the molecules cannot change their arrangement without surmounting a potential barrier, $\Delta\varepsilon_a$. The cluster size increases with decreasing temperature, since the enthalpic contribution to the Gibbs energy of the system favours the clustering of molecules. When liquid is cooled rapidly without crystallization, the molecules are frozen in a certain arrangement as the thermal energy, kT , becomes insufficient for surmounting the potential barrier along the rearrangement. The freezing in phenomenon is called a glass transition [1–3], and the transition point, T_g , has been often defined as the temperature at which the average relaxation time, τ , for the rearrangements becomes 10^3 s. Since the crossing occurs between the relaxation time and the calorimetric time scale of 10^2 – 10^6 s in the glass transition temperature range, the relaxation phenomena of clustered structures are observed as those of thermodynamic quantities such as enthalpy and volume. Thus the close investigation of the relaxations of thermodynamic quantities promises to yield information about the fluctuations and irreversible relaxations in the structures of liquids and glasses.

Three characteristics have been mentioned concerning the relaxations; the non-Arrhenius property of the average relaxation times, the nonexponentiality of the relaxation function,

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and the nonlinearity of the function. The degree of non-Arrhenius property has been defined, according to a 'strong-fragile' concept by Angell [4], by fragility, m ;

$$m \equiv \left. \frac{d \log \tau(T)}{d(T_g/T)} \right|_{T=T_g} \quad (1)$$

Provided that the potential barrier for any molecular rearrangement is independent of temperature, the relaxation times should obey the Arrhenius equation;

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta \varepsilon_a}{RT}\right) \quad (2)$$

where τ_0 is interpreted to be related to the frequency of trial for the activation unit to surmount the barrier, and has been discussed to be in the range of $10^{-13} - 10^{-16}$ s [5, 6]. The apparent non-Arrhenius properties described above are then interpreted as due to increase in the potential barrier along with the decrease in temperature [5]. Thus it is quite reasonable that the non-Arrhenius property is mainly due to the change in the potential barrier could be evaluated by use of the fragility.

The nonexponentiality has been often discussed by using a parameter, β , in the stretched exponential function, namely KWW equation [7-9];

$$Y(t) = Y(0) \exp\left\{-\left(\frac{t}{\tau}\right)^\beta\right\} \quad (3)$$

where Y denotes any physical quantity which relaxes along with time after a sudden jump in force, X , at $t=0$. Since liquid has some microscopically heterogeneous structure due to the presence of clusters, there should exist a distribution in the energetic circumstances of molecules and thus in the response functions for the elementary rearrangement units: the macroscopically observed relaxation function is therefore written in the form

$$Y(t) = \sum_{\nu} g_{\nu} \phi_{\nu}(t) \Delta X \quad (4)$$

where g_{ν} and $\phi_{\nu}(t)$ are the weighting factor and the response function, respectively, for mode ν . The relaxation function, $Y(t)$, has been determined by both the frequency domain and time domain methods. The former method yields a resonance spectrum for the rates of molecular rearrangements essentially under equilibrium, and thus gives a distribution in the relaxation times, $g_{\nu}(\tau)$. The β parameter obtained by the frequency domain method represents essentially information about a distribution in the structured clusters in the equilibrium state. By the latter, time domain method, on the other hand, since the process proceeding corresponds with the change from the nonequilibrium to equilibrium states with respect to the configurations of molecules, the β parameter obtained is interpreted as involving information about the irreversibility of the processes proceeding in addition to the distribution in the structured clusters.

The nonlinearity is a property pertaining to the dependence of the relaxation function on the jump, ΔX , in force, and thus the time domain method is preferable for examining the property of nonlinearity. If the relaxation process is of a linear response, the parameters, τ and β , in equation (3) for the relaxation should be kept constant, while the magnitude of $Y(0)$ is proportional to ΔX . The nonlinearity of the process is thus characterized by the ΔX dependence of τ or β [10]. The Tool-Narayanaswamy model (TN model), applied to the analyses of DSC curves by Moynihan *et al* [7, 11, 12], introduces the nonlinearity parameter, x , through the expression for $\tau(T, T_f^{\text{TN}})$;

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

where A is a constant, ΔH^* is the apparent activation energy closely connected with the fragility, m , stated above, R is a gas constant, and T_f^{TN} is the fictive temperature supposed to represent the structure of the liquid [7,11,12]. x and the β in equation (3) have been approximated to be constant in the narrow range of temperature. We have, on the other hand, defined a nonlinearity parameter, δ , by the dependence of β on $\Delta X = \Delta_j T$ in the temperature jump experiments [10];

$$\delta \equiv \frac{d(\beta/\beta_0)}{d(\Delta_j T/T_a)} \quad (6)$$

here, T_a is the temperature at which the relaxation process is tracked, $\Delta_j T$ is defined by $(T_a - T_i)$ where T_i denotes the temperature at which the liquid has been kept constant for a long enough time, and β_0 is the β value at $\Delta_j T = 0$ K. τ is assumed to be a constant depending on $\Delta_j T$ and T_a .

We have previously tracked the irreversible relaxation processes in 1,2-propanediol (propylene glycol, PG, $m = 46$), glycerol (GL, $m = 51$), and 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (PMS, $m = 87$), indicated on the basis of the result that the β_0 parameter obtained by the time domain method is equal to that by the frequency domain method [13] and that the nonlinearity originates primarily due to the fragility of the liquid [10, 13], and showed that the simulation of relaxation based on a simple thermal activation model gives a qualitatively consistent result with the experiment on GL [10]. In the present study, first the irreversible enthalpy relaxation processes in dibutylphthalate (DBP) with a different value of fragility, $m = 73$, from the above three compounds are tracked under constant-temperature conditions by the temperature jump method, to confirm in combination with the previous data that a quantitative correlation really holds between the nonlinearity and the fragility. Second, the relaxation processes of the system with the structure-dependent activation energies expected in DBP are simulated based on the thermal activation model to examine the agreement, in the quantitative sense, between the characteristic relaxation functions obtained by the experiment and simulation and also to look into the distributions of the activation energies halfway through the relaxation by simulation. Thirdly, the TN model, often used in the analyses of irreversible relaxations, is discussed on the basis of the present thermal activation model to have some points clarified with respect to its physical picture.

2. Experimental details

Dibutylphthalate (DBP, $\text{C}_6\text{H}_4(\text{COOC}_4\text{H}_9)_2$, [84-74-2]), purchased from Wako Pure Chemical Industries, Ltd, was purified by a fractional distillation at reduced pressure. The purified sample was loaded into a calorimeter cell under an atmosphere of helium gas. Heat capacities of DBP were measured by an intermittent heating method with an adiabatic calorimeter [14]: The equilibrium temperature, $T_{e,f}$, of the cell was determined in the former temperature rating period for 9 min, a specified quantity of electrical energy, ΔE , was supplied into the cell to increase the temperature by 2 K, and the equilibrium temperature, $T_{e,l}$, of the cell was again determined in the latter rating period for 9 min. The gross heat capacity, C , of the cell is evaluated to be $\Delta E/\Delta T$ where $\Delta T = T_{e,l} - T_{e,f}$, and the latter temperature rating served as the former rating in the next set of heat capacity measurements. When spontaneous heat evolution or absorption due to a glass transition of the sample appears in the transition temperature region, one observes the corresponding spontaneous temperature rise or fall. The relaxation rate of the configurational enthalpy of

the sample, dH_c/dt , is given by the minus of the temperature drift rate, $-dT/dt$, multiplied by the gross heat capacity, C , of the cell; $dH_c/dt = -C(dT/dt)$.

The enthalpy relaxation processes under constant-temperature conditions were studied by the same temperature jump method as described in detail previously [10,13]: first the calorimeter cell loaded with the sample was kept for a long enough time at T_i , then the temperature of the cell was changed suddenly by $\Delta_j T (= T_a - T_i)$ from T_i to T_a , and finally the enthalpy which the sample should evolve or absorb was tracked at the constant temperature of T_a for a long time. The magnitude of the jump, $\Delta_j T$, was controlled by varying the T_i while keeping the T_a as constant as possible.

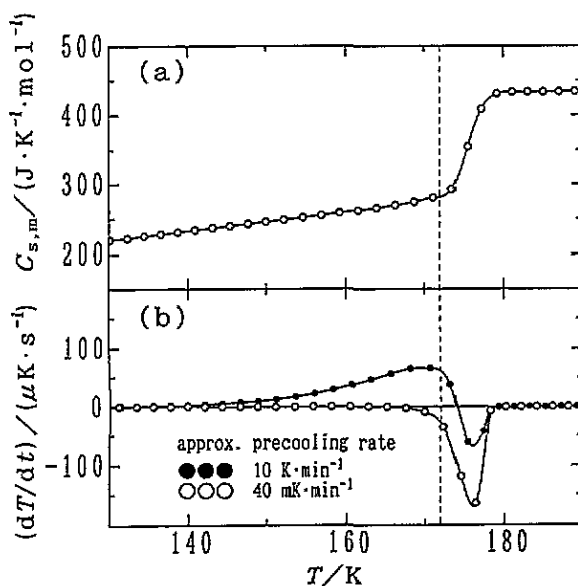


Figure 1. Molar heat capacities (a) and spontaneous temperature drift rates (b) in liquid and glass of dibutylphthalate, DBP, in the glass transition region.

3. Results

3.1. Tracking of the enthalpy relaxation under constant temperature

Figures 1(a) and 1(b) show the heat capacities obtained and the spontaneous temperature drift rates observed, respectively, around 170 K. When precooled rapidly at $10 \text{ K} \cdot \text{min}^{-1}$, the sample exhibited, in the following intermittent heating process for measurements, first an exothermic effect starting at around 140 K and showing its peak at around 170 K, and then an endothermic effect starting at around 174 K and showing its peak at around 175 K. When precooled slowly at $40 \text{ mK} \cdot \text{min}^{-1}$, on the other hand, the sample exhibited only the endothermic effect starting at around 165 K and showing its peak at around 175 K. The endothermic effects of both the samples disappeared at around 178 K. A large heat capacity jump was observed in association with the systematic, spontaneous heat evolution and following heat absorption effects, as shown in figure 1(a). Such appearances indicate the existence of a glass transition in the region [1, 2]. The glass transition temperature, at which the average relaxation time became 10^3 s , was determined to be $(174 \pm 1) \text{ K}$ from the temperature dependence of the drift rate according to an empirical law [14, 15]. The

relaxation time is also expected empirically to become $\sim 10^5$ s at the temperature at which the rapidly precooled sample exhibits the maximum of the exothermic temperature drift rate [14, 15], namely at around 170 K. Therefore the long tracking of the enthalpy relaxation was carried out at 172 K at which the average relaxation time was expected to become $\sim 10^4$ s; the time scale is just in the middle of the calorimetric time scale of 10^2 – 10^6 s

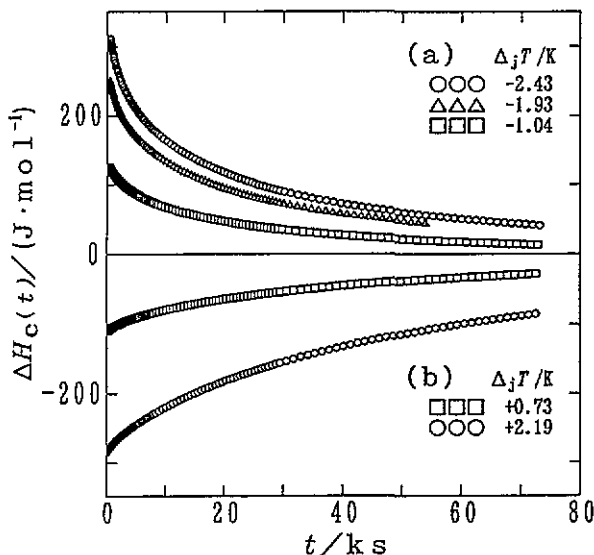


Figure 2. Spontaneous exothermic (a) and endothermic (b) configurational-enthalpy drifts at constant temperature 172 K in DBP. $\Delta H_c(t) = H_c(t) - H_c(\infty)$.

Figures 2(a) and 2(b) show the data of exothermic and endothermic, respectively, enthalpy relaxation processes obtained at constant temperature. The data were characterized in terms of the stretched exponential function;

$$\Delta H_c(t) = \Delta H_c(0) \exp \left\{ - \left(\frac{t}{\tau} \right)^\beta \right\}. \quad (7)$$

This equation can be transformed to

$$\log \left[\log \left\{ \frac{\Delta H_c(0)}{\Delta H_c(t)} \right\} \right] = \beta (\log t - \log \tau) - 0.3623. \quad (8)$$

The nonexponentiality parameter, β , is then given by the slope of the left-hand side against $\log t$ curve. Figures 3(a) and 3(b) show the double logarithmic plots of $\Delta H_c(0)/\Delta H_c(t)$ using the same sets of data given in figures 2(a) and 2(b), respectively. Each set of data being on a straight line, the enthalpy relaxation processes are indicated to be well expressed by the stretched exponential function. The β values derived from the slopes of the lines are plotted as a function of $\Delta_j T$ in figure 4. They depend strongly on $\Delta_j T$, indicating that the nonlinearity is remarkable in the structural relaxation processes in DBP. The value of β_0 at $\Delta_j T = 0$ K was determined by extrapolating the $\Delta_j T$ dependence of β from both the positive and negative, in $\Delta_j T$, sides to $\Delta_j T = 0$ K to be 0.67 ± 0.02 . Figure 5 shows the derived δ value as a function of m , together with the results for other liquid glasses studied so far: PG ($m = 46$), GL ($m = 51$), and PMS ($m = 87$) [10, 13]. A diamond represents the δ and m values for the 'strongest' liquid that is expected to show a linearity in the response to temperature jump, $\Delta_j T$. Dotted lines are guides for eyes. It is confirmed that a

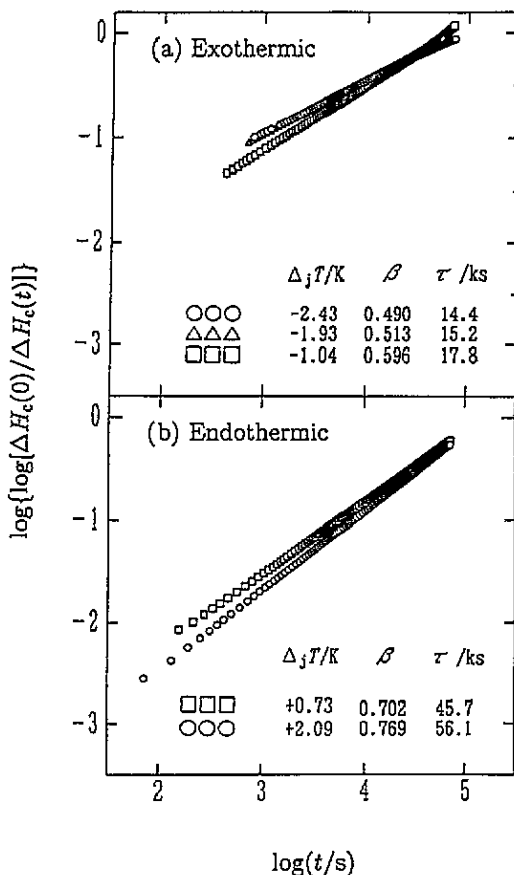


Figure 3. Double logarithmic plots of the exothermic (a) and endothermic (b) configurational-enthalpy drifts expressed in terms of a stretched exponential function, equation (3), with parameters β and τ .

reasonable linear relation holds between δ and m for each of the positive and negative $\Delta_j T$, and that the $d\delta/dm$ is larger in $\Delta_j T < 0$ than in $\Delta_j T > 0$. In view of the situation that the structured clusters are developed on average in the relaxation processes of $\Delta_j T < 0$ while destroyed in those of $\Delta_j T > 0$, the nonlinearity is concluded to appear more remarkably in the process of cluster creation than in the process of cluster annihilation.

3.2. Relaxation in a model system with DBP resembling temperature dependence of activation energies

The thermal activation model for the relaxation processes is adapted in this section to the system with the activation parameters expected in DBP: the enthalpy relaxation in the time domain is considered to correspond to an irreversible equilibration process in the configurational arrangements of molecules through classical thermal activation processes. The potential curve for each activation process is thus represented by a curve of double-well form with two parameters [10]: $\Delta\varepsilon$ is the difference between the potential energies in the two stable configurations relevant to the process, and $\Delta\varepsilon_a$ the activation energy along the process. The population probabilities, p_1 and p_2 , in the microscopic states 1

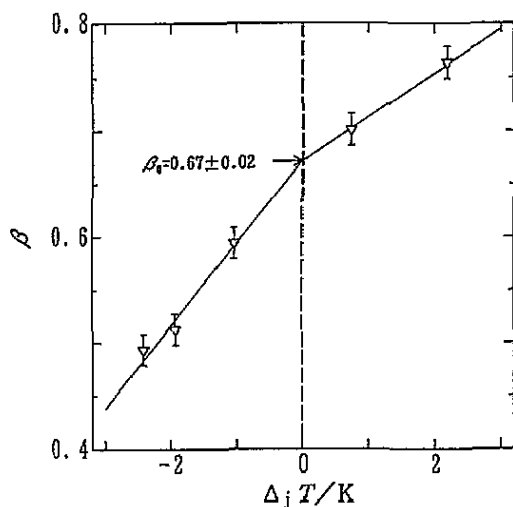


Figure 4. Dependences of the nonexponentiality parameter, β , on $\Delta_j T$ in DBP. A solid line represents two straight lines fitted to the data of β values so as to meet at $\Delta_j T = 0$ K. The β value, β_0 , at $\Delta_j T = 0$ K is determined from the lines to be 0.67 ± 0.02 .

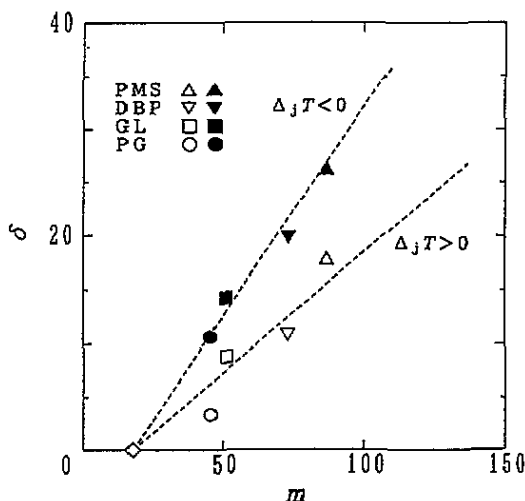


Figure 5. Correlation between the nonlinearity parameter, δ , of the relaxation process and the fragility, m : circles, PG; squares, GL; inverted triangles, DBP; triangles, PMS. Open and filled symbols represent the results for positive and negative $\Delta_j T$, respectively. An open diamond represents the values expected for the 'strongest' liquid. The nonlinearity increases with increasing fragility, and the slope depends on the sign of temperature jump, $\Delta_j T$.

and 2 at equilibrium are given according to Boltzmann's distribution function [10]. In the model, (1) the number of activation units is assumed to be constant, (2) the development of a clustered structure with decreasing temperature is taken into consideration through increasing the activation energy, $\Delta \varepsilon_a$, with increase in the probability of a lower-energy microscopic state 1, p_1 , for each activation unit, and (3) the relaxation rate of the deviation in the probabilities from the equilibrium values is expressed by the Arrhenius equation,

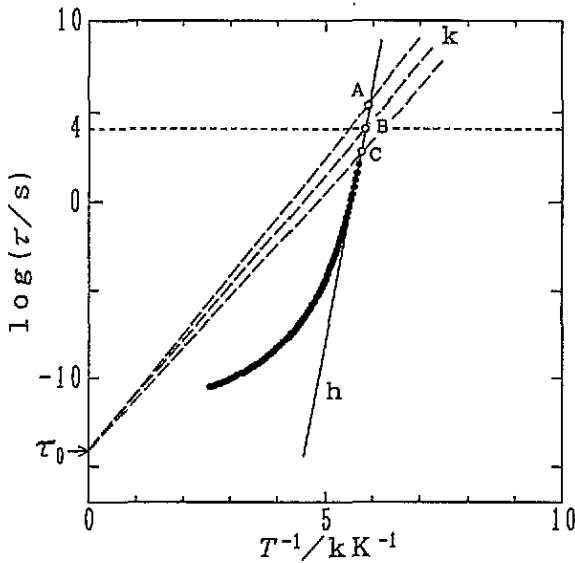


Figure 6. Schematic diagram of the logarithmic average relaxation times against the inverse temperature. Filled circles represent experimental data taken from [16], and show a non-Arrhenius behaviour. A tangential line, h , at the point B is related to the fragility, m , of the liquid. The slopes of dashed lines, k , represent the activation energies at the respective points, A, B and C, when the pre-exponential factor, τ_0 , in the Arrhenius equation is assumed to be constant, and are indicated to increase with decreasing temperature.

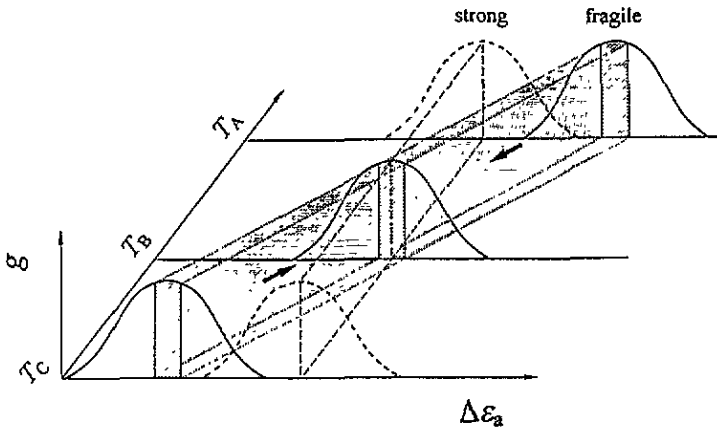


Figure 7. Gaussian distributions of activation energies with the same σ at three different temperatures, T_A , T_B and T_C . Dashed lines at T_A and T_C represent the distributions in the case of the 'strong' liquid without change in the activation energies. Solid lines, on the other hand, represent those in the case of the 'fragile' liquid, and the shaded part at T_A or T_C is, on statistical average, supposed to relax to the shaded part at T_B with changing activation energies along the arrow.

equation (2), with constant $\tau_0 = 10^{-14}$ s. The last two considerations have been previously discussed to be reasonable based on the experimental results [5].

Figure 6 illustrates the temperature dependence of the activation energies for a rearrangement unit based on an Arrhenius plot of the average relaxation times obtained

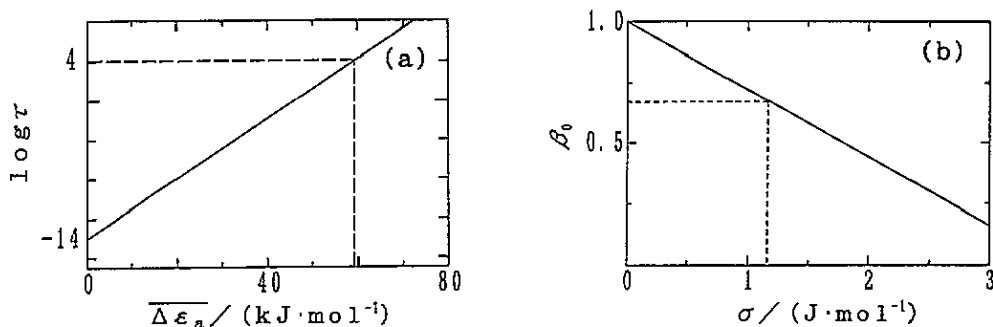


Figure 8. The relations between the average relaxation time and average activation energy ($\overline{\Delta\epsilon_a}$) (a) at $T_a = 172$ K, and between the nonexponentiality parameter, β_0 , at $\Delta_j T = 0$ K and root mean square deviation, σ , of activation energies of a Gaussian distribution (b): in the present simulation, $\overline{\Delta\epsilon_a}$ is taken to be 59.3 kJmol^{-1} so that the relaxation time should become 10^4 s at $T_a = 172$ K, and σ to be 1.2 kJmol^{-1} so that β_0 should be 0.67.

by dielectric measurements [16]. The isostructural relaxation times for structure systems given by points A, B, or C are expressed by the respective Arrhenius equations, and indicated with the respective dashed lines, k;

$$\tau = \tau_0 \exp\left(\frac{\Delta\epsilon_a i}{RT}\right) \quad (9)$$

where i represents A, B, or C and $\Delta\epsilon_{aA} > \Delta\epsilon_{aB} > \Delta\epsilon_{aC}$. Thus, assuming that T_B corresponds to the tracking temperature, T_a , of enthalpy relaxation and T_A and T_C to the initial temperatures in the sudden temperature jumps, the activation energies become gradually small and large, respectively, as the structural relaxation process proceeds, namely as the 'fictive' temperature representing the structure approaches the equilibrium temperature T_B . Approximating the temperature dependence of relaxation times at equilibrium around the tracking temperature, T_B , by a tangent, line h, at T_B , the activation energy, $\Delta\epsilon_a$, is related to the fragility, m ;

$$\Delta\epsilon_a(T_f) = 2.303 R T_f m \left(\frac{T_a}{T_f} - 1\right) + \frac{T_f}{T_a} \Delta\epsilon_a(T_a) \quad (10)$$

where T_f is given by

$$T_f = \frac{\Delta\epsilon}{R} \ln\left(\frac{p_1}{p_2}\right). \quad (11)$$

The distribution in the activation energies due to the heterogeneity in the microscopic structure of the liquid at equilibrium was expressed by the Gaussian distribution:

$$g(\Delta\epsilon_a) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{\{\Delta(\Delta\epsilon_a)\}^2}{2\sigma^2}\right] \quad (12)$$

where σ^2 is the mean square deviation of activation energies, $\overline{\{\Delta(\Delta\epsilon_a)\}^2}$.

Figure 7 shows the distributions against $\Delta\epsilon_a$ having the same σ under equilibrium at the three temperatures, T_A , T_B and T_C . In cases where the relaxation times behave according to the Arrhenius equation as shown by the lines k in figure 6, namely in the case of a 'strong' liquid, the corresponding distribution in the activation energies remains unchanged with change in temperature as is depicted with dashed lines in figure 7. In the case of a 'fragile' liquid, on the other hand, the activation energies change with the fictive temperature. The

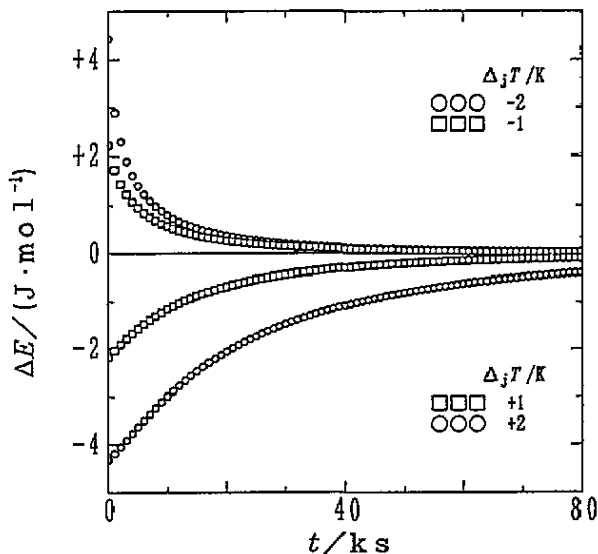


Figure 9. Internal energy relaxation processes, at 172 K, found by computer simulation.

shaded part as one division in $\Delta\varepsilon_a$ at T_A or T_C is assumed to relax toward the corresponding shaded part at $T_B = T_a$.

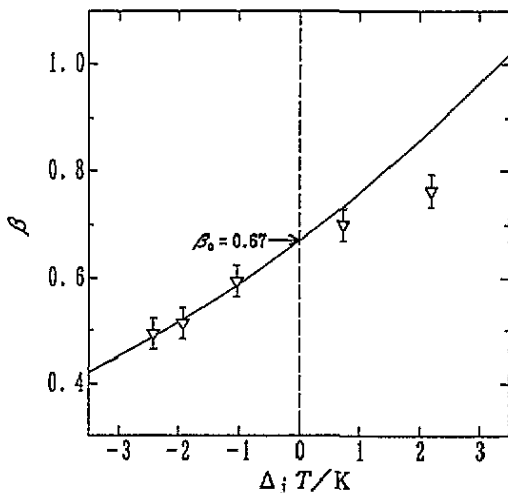


Figure 10. The temperature jump dependence of the nonexponentiality parameter, β , for the system corresponding to DBP: inverted triangles represent the results obtained experimentally and a solid line that obtained by the computer simulation.

Figure 8 illustrates how the particular Gaussian distribution was taken for application to the DBP resembling system: the average activation energy, $\overline{\Delta\varepsilon_a}$, was determined to be 59.3 kJ mol^{-1} so as to bring the average relaxation time to 10^4 s at $T_a = 172 \text{ K}$, as shown in figure 8(a). The different σ values yielded different nonexponentiality parameter, β_0 , values at $\Delta_j T = 0 \text{ K}$; the σ dependence of β_0 is shown in figure 8(b). The σ value was thus determined to be 1.2 kJ mol^{-1} to give $\beta_0 = 0.67$ derived experimentally in the last

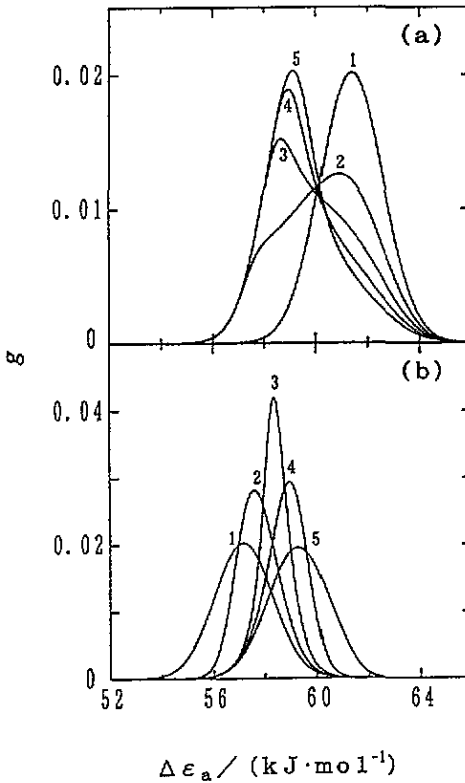


Figure 11. Time evolution of the distribution of activation energies during the structural relaxations simulated by a model computation. Endothermic process after the temperature jump from 170 K to 172 K (a): 1, 0 ks; 2, 20 ks; 3, 40 ks; 4, 60 ks; 5, 80 ks. Exothermic process after the temperature jump from 174 K to 172 K (b): 1, 0 ks; 2, 0.8 ks; 3, 2 ks; 4, 8ks; 5, 80 ks along the arrow.

section 3.1.

Figure 9 shows the results of simulation for the internal energy relaxation of the system with different $\Delta_j T$ in the case of $m = 73$ corresponding to the value of DBP [16]. $\Delta \varepsilon$ was taken for each activation unit to be constant at 10% of $\Delta \varepsilon_a$ at T_a . The β values obtained by fitting the KWW equation, equation (3), to the relaxation data depend definitely on the $\Delta_j T$, indicating a remarkable nonlinearity of the irreversible structural relaxations in the fragile model system. The $\Delta_j T$ dependence of β is shown with a solid line in figure 10, together with the experimental results (represented by inverted triangles) for DBP. The agreement between the β values by simulation and by experiment is excellent quantitatively on the negative side of $\Delta_j T$. This indicates that the present model reproduces well the structural relaxations in the exothermic, namely cluster developing, processes in which the relaxation times become gradually longer on the whole with the progress of relaxations. On the positive side of $\Delta_j T$, on the other hand, the deviation of the β values by the simulation from the experimental results is large, indicating that the real endothermic processes are different from those pictured from the model or involve another factor which is ineffective in the exothermic processes with negative $\Delta_j T$.

The characteristic difference between the processes with $\Delta_j T > 0$ and $\Delta_j T < 0$ should appear in the distribution of microscopic structures, and therefore of activation energies,

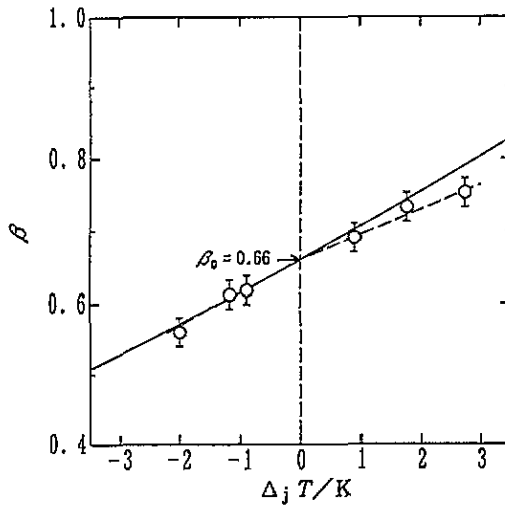


Figure 12. The temperature jump dependence of the nonexponentiality parameter, β , for the system corresponding to GL: circles represent the results obtained experimentally, a solid line that obtained by the computer simulation with the corrected β_0 value of 0.66, and dashed lines the straight lines assumed as tentatively approximating the $\Delta_j T$ dependences of the experimental values to derive the δ values.

halfway through the course of relaxation. Figures 11(a) and 11(b) show the distributions of activation energies at five different times for the relaxation processes simulated above with $\Delta_j T = 2$ K and -2 K, respectively. Components which first have relatively low activation energies relax rather fast while those which have relatively large ones do so rather sluggishly. Thus, in the former case (a), the distribution of activation energies first becomes wide as accompanied with a deviation from the initial Gaussian distribution, and then recovers the Gaussian distribution supposed as the final state. In the latter case (b), on the other hand, it first becomes narrow, keeping the shape of Gaussian distribution, and then recovers the final Gaussian distribution. The characteristic difference in the evolution of the distribution would have given rise to the different $\Delta_j T$ dependence of β between the two cases with $\Delta_j T > 0$ and $\Delta_j T < 0$, and the large deviation from the Gaussian distribution halfway through the relaxation simulated for the case with $\Delta_j T > 0$ might be related to the systematic discrepancy between the β values obtained by the experiment and by the simulation. Experimental determination of the distributions halfway through the relaxation is desired.

4. Discussion

The agreement between the nonexponentiality parameters, β , obtained by the temperature jump experiment and its computer simulation is excellent on the negative side of $\Delta_j T$. A small systematic difference between the two sets of β values has been found in the case of GL in [12]. If the β_0 value of 0.66 was taken instead of 0.67, however, the agreement becomes excellent on the negative side of $\Delta_j T$ as shown in figure 12: the new value, 0.66, is closer to the β_0 obtained by the frequency domain method, 0.65 ± 0.04 [16], than the previous one, 0.67. These agreements would give evidence that the irreversible relaxation of liquid structure is pictured essentially by an assembly of classical processes of microscopic thermal activation units with their activation energies depending on the microscopic structure

of molecules, namely the fictive temperature assigned to each small region.

There is a difference found between the quantities to relax, $\Delta H_c(0)$ in figure 2 and $\Delta E(0)$ in figure 9, as was pointed out in the case of GL before [10]; the difference amounts to more than an order of magnitude. The primary reason for the difference is that $\Delta H_c(0)$ is given as the quantity per mole of molecules while $\Delta E(0)$ as that per mole of activation units. The difference indicates that one molecule carries 10 microscopic activation units in the order of magnitude. It follows from this that most molecules would not be in the ordered state with respect to their positions or orientations even within the structured clusters in liquid and glass.

The enthalpy relaxation processes have been often analysed by using the TN model. From the above results and consideration, however, the model would have some essential problems. The model supposes first that the β value in equation (3) is a constant inherent to each substance at least within a small temperature region, second that the relaxation time, $\tau(T, T_f^{\text{TN}})$, is expressed by equation (5) with a fictive temperature, T_f^{TN} , characterizing the whole liquid structure at each moment, and third that the nonlinearity of the relaxation functions is characterized by a constant value, x in equation (5). Considering the situation at the limit of $\Delta_j T = 0$ K, namely of $T_a = T_f^{\text{TN}}$, the distribution of relaxation times, and thus of activation energies in the above simulation, at equilibrium determines the β value in equation (3). Therefore the first is equivalent to the supposition that the shape of the distribution is independent of the progress of the irreversible relaxation as it is at equilibrium. This supposition is discrepant from the results of the above computer simulation (see figure 11(b)) which explains well the results of the temperature jump experiment at least with $\Delta_j T < 0$. The primary problem concerning the second supposition would be, of course, that it is very difficult to form any physical picture for the expression, equation (5), of the relaxation time; otherwise, the equation is no more than an expression for fitting experimental data just like the KWW equation adapted to the nonequilibrium irreversible relaxations in the present experiment. The origins of the problem would be that both the ΔH^* and A in equation (5) do not represent quantities relevant to any real molecular motions, but only the apparant parameters. The additional problem is concerned with the fact that the distribution of activation energies, according to the above simulation, changes severely during the relaxation so that the whole liquid structure cannot be represented by the fictive temperature; that is, the structure represented by T_f^{TN} halfway through the relaxation is quite different from that at $T = T_f^{\text{TN}}$ at equilibrium. As concerned with the third supposition, it has been stated that some difficulty is encountered in reproducing the DSC curves in terms of the expressions, equations (3) and (5) [12]. After all, considering that the liquid has a microscopically or mesoscopically heterogeneous structure [9, 17], the TN model would contain some inadequacy in forming a real physical picture for the structural relaxation in a liquid.

5. Conclusion

Good correlation was indicated by the present experiment and computer simulation to hold between the nonlinearity, δ , of the relaxation function with the magnitude of temperature jump and the fragility, m , of the liquid. This leads to the reasonable conclusion that the nonlinearity is determined primarily by the fragility corresponding to the temperature dependence of relaxation times under equilibrium.

In view of the strong temperature dependence of the average relaxation times under equilibrium, a glass transition is generally expected to be due to freezing in of classical thermal activation for the rearrangement of molecules. The present, excellent agreement

between the β values obtained by the experiment and the computer simulation based on the thermal activation model is interpreted as verifying the validity of the expectation. This would be very significant in forming a real picture for the liquid structure and its relaxation phenomenon in the future.

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References

- [1] Suga H and Seki S 1974 *J. Non-Cryst. Solids* **16** 171
- [2] Suga H and Seki S 1980 *Faraday Discussions* **69** 221
- [3] Elliott S R 1983 *Physics of Amorphous Materials* (New York: Longman)
- [4] Angell C A 1985 *J. Non-Cryst. Solids* **73** 1; 1991 *J. Non-Cryst. Solids* **131-133** 13
- [5] Fujimori H and Oguni M 1995 *Solid State Commun.* **94** 157
- [6] Mazurin O V and Potselueva L N 1978 *Fiz. Khim. Stekla* **4** 570
Mazurin O V, Startsev Yu K and Potselueva L N 1979 *Fiz. Khim. Stekla* **5** 82
Mazurin O V, Startsev Yu K and Stoljar S V 1982 *J. Non-Cryst. Solids* **52** 105
- [7] Scherer G W 1990 *J. Non-Cryst. Solids* **123** 75
- [8] Williams G and Watts D C 1970 *Trans. Faraday Soc.* **66** 80
- [9] Lindsey C P and Patterson G D 1980 *J. Chem. Phys.* **73** 3348
- [10] Fujimori H, Fujita H and Oguni M 1995 *Bull. Chem. Soc. Japan* **68** 447
- [11] Hodge I M 1994 *J. Non-Cryst. Solids* **169** 211; 1995 *Science* **267** 1945
- [12] Moynihan C T, Crichton S N and Optlka S M 1991 *J. Non-Cryst. Solids* **131-133** 420
- [13] Fujimori H and Oguni M 1994 *J. Non-Cryst. Solids* **172-174** 601
- [14] Fujimori H and Oguni M 1993 *J. Phys. Chem. Solids* **54** 271
- [15] Oguni M, Matsuo T, Suga H and Seki S 1977 *Bull. Chem. Soc. Japan* **50** 825
- [16] Dixon P K, Wu L, Nagel S R, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108
Birge N O and Nagel S R 1985 *Phys. Rev. Lett.* **54** 2674
Birge N O 1986 *Phys. Rev. B* **34** 1631
- [17] Moynihan C T and Schroeder J 1993 *J. Non-Cryst. Solids* **160** 52