Bull. Chem. Soc. Jpn., 68, 447—455(1995)

## *Headline Articles*

# Nonlinearity of the Enthalpic Response Function to a Temperature Jump and Its Interpretation Based on Fragility in Liquid Glasses

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(Received September 30, 1994)

Irreversible enthalpy-relaxation processes were tracked under a constant temperature condition by the temperature jump method for liquid 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane with an adiabatic calorimeter, and simulated based on a double-well potential model with a computer. The processes were observed to show remarkable nonexponentialities and were characterized in terms of a stretched exponential function. The nonexponentiality parameter ($\beta$) depended strongly on the magnitude of the temperature jump, indicating the nonlinearity of the relaxation processes. The results of the nonlinearity parameter ($\delta$) combined with those of 1,2-propanediol and glycerol indicated that the nonlinearity originated primarily due to the fragility of the liquid, namely the non-Arrhenius property of the relaxation times. The degree of the nonlinearity was smaller in the endothermic processes than in the exothermic ones. The difference is discussed based on the results of a computer simulation.

A liquid is characterized as the state of the aggregation of molecules being in a disordered arrangement with respect to both their positional and orientational degrees of freedom. There, however, exists a short-range structural order among molecules concerning both degrees. This has been verified by many structural and thermodynamic studies,[1,2] and the formation of crystal embryos at low temperatures is recognized as being the appearance of one kind of such order. The aggregate region of molecules with the short-range order, to be named a structured cluster, is considered to increase in size with decreasing temperature. The so-called structural fluctuation is a process in which the clusters appear and disappear during the course of a time lapse in a liquid ubiquitously. However, the molecular mechanisms and their properties have hardly been clarified so far concerning the creation and annihilation of clusters.

The relaxation time for a rearrangement of molecules gradually becomes long as the temperature decreases, and crosses the experimental time scale of $10^2$—$10^6$ s at some low temperature ($T_g$). When cooled rapidly without crystallization, the liquid thus undergoes a glass transition, generally due to a simultaneous freezing-in of both configurational degrees of freedom of the molecules. In the transition region, the relaxation phenomena of thermodynamic quantities, such as the enthalpy and volume, are observed as originating from a crossing of the relaxation times with the experimental time scale.[3,4] Any quantitative evaluation of the enthalpy relaxation process should therefore involve an understanding of the molecular rearrangement processes proceeding in the liquid.

The enthalpy relaxation processes can be investigated by either a frequency domain or a time domain method.[4] In the former method, measurements are carried out for the liquid at equilibrium while detecting any structural fluctuations as functions of the temperature and frequency. In the latter case using the temperature jump method, on the other hand, measurements are carried out while tracking any irreversible enthalpy relaxation from nonequilibrium to equilibrium states as a function of time.[5,6] Figure 1 shows the experimental procedure using a schematic diagram of the configurational enthalpy against the temperature relation in the glass transition region. The solid line drawn from the upper right to the lower left represents the configurational enthalpy curve under equilibrium, and $T_a$ denotes the temperature at which the enthalpy relaxation is tracked. The temperature of the liquid is rapidly changed to $T_a$ from $T_i$, at which point the liquid has been kept constant for a sufficiently long time to reach the equilibrium state. The temperature jump ($\Delta_j T$) is defined by $\Delta_j T \equiv T_a - T_i$, and can be changed by varying the starting temperature ($T_i$).

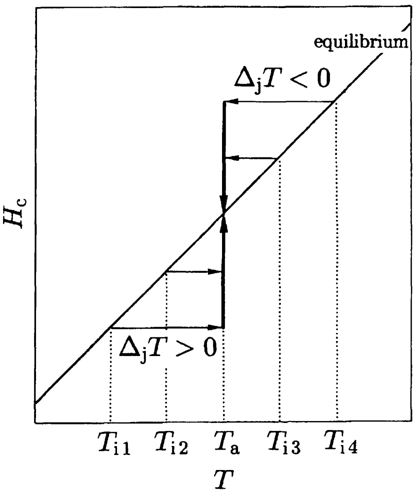

Fig. 1. Schematic diagram of configurational enthalpy against temperature relation in the liquid-glass transition region and experimental procedures taken for tracking the irreversible enthalpy-relaxation processes. Temperature is jumped from $T_i$ to $T_a$, and magnitude of the jump is defined by $\Delta_j T \equiv T_a - T_i$.

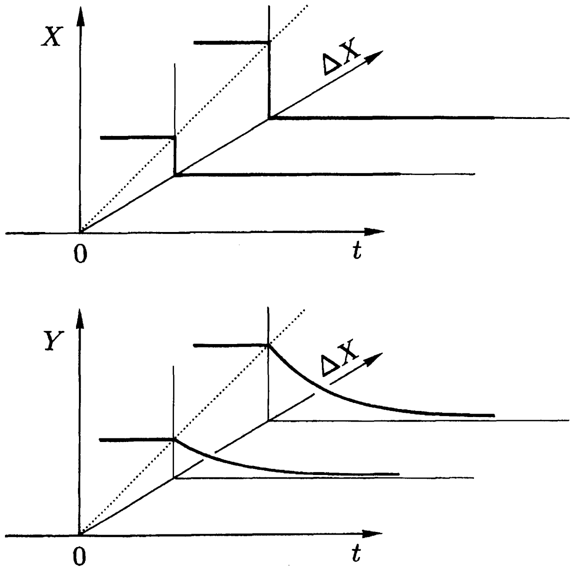

Fig. 2. Schematic diagram of the relation between external intensive parameter ($X$) and the response function ($Y$) of internal extensive parameter as a function of time. $\Delta X$ denotes the magnitude of jump in $X$ at $t=0$.

The enthalpy relaxation properties are considered to be determined by the magnitude of the jump and the response function. Figure 2 shows a schematic diagram illustrating the situation of the irreversible relaxation process by the time domain method, where $X$ denotes an external intensive parameter and $Y$ some extensive thermodynamic quantity. The relaxation process of $Y$ is tracked for a long time after a sudden jump in $X(t)$ at $t=0$ from $X(t)=X$ at $t<0$ to $X(t)=0$ at $t \geq 0$. In the linear irreversible process, the relaxation function ($Y(t)$) for $t \geq 0$ is written in the form

$$Y(t) = \sum_{\nu} \phi_{\nu}(t) \cdot X, \tag{1}$$

where $\phi_{\nu}(t)$ is the response function for the $\nu$ mode; the sum would be required due to the presence of a distribution in the structured clusters. In the present temperature-jump experiment, the jump in $X$ at $t=0$ corresponds to $\Delta_j T$ and $Y(t)$ to $\Delta H_c(t)$. The relaxation function ($Y(t)$) can be macroscopically found only as a function of time, and has been simply expressed by the following stretched exponential function (KWW equation):[7]

$$Y(t) = Y(0) \cdot \exp\left\{ -\left(\frac{t}{\tau}\right)^{\beta} \right\}, \tag{2}$$

where $\tau$ and $\beta$ are constants characterizing the relaxation time and the nonexponentiality, respectively, of the function. Thus, if the relaxation process is linear against $X$, the derived $\tau$ and $\beta$ should be independent of $X$ while $Y(0)$ is proportional to $X$. If the process is nonlinear, on the other hand, $\tau$ and $\beta$ would be dependent on $X$ while $Y(0)$ would remain more or less proportional to $X$. The nonlinearity of the relaxation process could be characterized by the $X$ dependence of $\beta$, since $\tau$ changes severely along with a small shift in the temperature at which the relaxation is tracked.

Birge and Nagel[8] have investigated the enthalpy relaxation processes of typical glasses, 1,2-propanediol (propylene glycol, PG) and glycerol (GL), by the frequency domain method; we have carried out studies of these processes by the time domain method. The former result, as a function of the frequency at each temperature, gives essentially information about the distribution of the relaxation times, and is usually transformed numerically by a Fourier transformation technique into a stretched exponential function (Eq. 2) as an expression in the time domain. The obtained $\beta$ values, 0.61±0.04 for PG and 0.65±0.04 for GL, respectively, were rather independent of the temperature, implying that the distribution of the relaxation times would not change very much with the temperature.[8] The $\beta$ values obtained using the latter method depended strongly on the temperature jump ($\Delta_j T$); the $\beta_0$ values as the $\beta$ values at $\Delta_j T=0$ K were in complete agreement with those in the frequency domain.[5,6] This indicates not merely that both methods are equivalent to each other at the limit $\Delta_j T=0$ K in the time domain, but also that the nonlinearity of the relaxation processes can be investigated uniquely by the time domain method. The origin of the observed nonlinearity, however, still remains open to a question to be clarified and a quantitative clarification is expected to enhance our understanding on the molecular rearrangement processes and on the creation and annihilation processes of clusters in a liquid.

Angell[9] classified liquids according to a "strong-fragile" concept based on the non-Arrhenius behavior of the relaxation times ($\tau$); the fragility ($m$) is defined[10] by

$$m \equiv \left. \frac{\mathrm{d} \log \tau(T)}{\mathrm{d}(T_\mathrm{g}/T)} \right|_{T=T_\mathrm{g}}. \tag{3}$$

Here, it is attractive to inquire about any quantitative correlation, if any, between the fragility ($m$) and the following nonlinearity parameter ($\delta$):

$$\delta \equiv \frac{\mathrm{d}(\beta/\beta_0)}{\mathrm{d}(\Delta_\mathrm{j} T/T_\mathrm{a})}. \tag{4}$$

The reason is that both $\delta$ and $m$ would be properties reflecting any change in the liquid structure with temperature.

In the present study, first the enthalpy relaxation processes in 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (PMS) were tracked under a constant temperature condition by the time domain method using an adiabatic calorimeter. With its fragility known to be 87,[13] PMS is one of the most fragile liquids hitherto known,[14] and is more fragile than typical liquid glasses, PG ($m$=46) and GL ($m$=51). Thus, this result combined with those concerning the latter two glasses should experimentally clarify the relationship between the fragility and the nonlinearity of the relaxation function. Second, the relationship was also examined through a computer simulation of irreversible relaxation processes by the temperature jump method in the time domain. Further, the implication based on a comparison of the result with the experimental result concerning the nonlinearity is discussed concerning the difference between microscopic structural-relaxation processes with $\Delta_\mathrm{j} T > 0$ and $\Delta_\mathrm{j} T < 0$.

## Experimental

PMS (>97%), purchased from PCR Inc., was distilled fractionally at reduced pressure. Calorimetry was carried out with the previously described adiabatic calorimeter.[12] The sample was loaded into a calorimeter cell under an atmosphere of helium gas. The mass of the sample used was weighed to be 16.123 g (corresponding to 56.271 mmol). The purity was found to be 99.78% by a calorimetric fractional-melting experiment.[11]

Figure 3 (a) and (b) shows the heat capacities and the rates of spontaneous temperature drifts, respectively, observed during heat capacity measurements by the intermittent heating method in the liquid phase.[11] The temperature dependence of the drift rates, which changes with precooling treatments of the sample, and the associated jump in heat capacity indicate the presence of a glass transition definitely. The glass transition temperature was determined based on the temperature dependence of the drift rates to be 167 K as the temperature at which the average relaxation time would be around $10^3$ s. The enthalpy relaxation processes were tracked by the temperature jump method under a constant temperature condition, as described previously.[6] The temperature at which the enthalpy relaxation processes should be tracked ($T_\mathrm{a}$) was chosen to be 165 K at which the average relaxation time was expected to be on the order of magnitude of $10^4$ s. The time scale was taken to be just in the middle of our experimental time scale of tracking, $10^2$—$10^6$ s.

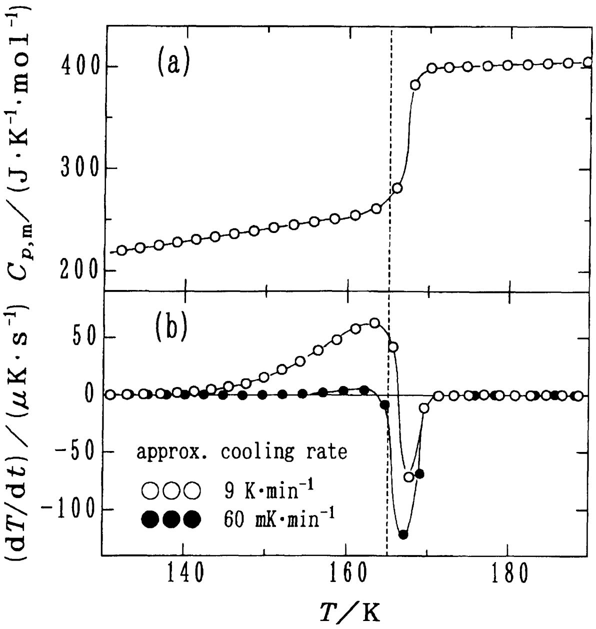

Fig. 3. Molar heat capacities (a) and spontaneous temperature drift rates (b) in liquid and glass of 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (PMS) in the glass transition region.

## Calorimetric Results

Figure 4(a) and (b) shows the obtained data of exothermic and endothermic enthalpy relaxation processes, respectively. The data were characterized by fitting the following stretched exponential function:[7]

$$\Delta H_\mathrm{c}(t) = \Delta H_\mathrm{c}(0) \cdot \exp\left\{ -\left(\frac{t}{\tau}\right)^\beta \right\}. \tag{5}$$

When Eq. 5 is transformed into

$$\log\left[\log\left\{\frac{\Delta H_\mathrm{c}(0)}{\Delta H_\mathrm{c}(t)}\right\}\right] = \beta(\log t - \log\tau) - 0.3623, \tag{6}$$

the nonexponentiality parameter ($\beta$) can be given as the slope of the left-hand side vs. log $t$. Figure 5(a) and (b) shows double logarithmic plots of the same data as Fig. 4(a) and (b), respectively. Each set of data are well on a straight line, indicating that the relaxation function is to a good approximation expressed by a stretched exponential function. Figure 6 shows the decay functions, i.e. the relaxation functions normalized by the respective fitting parameters ($\Delta H_\mathrm{c}(0)$ and $\tau$), where the solid lines represent the results of numerical calculation in Fig. 6(a) and the fitting curves for each set of data in Fig. 6(b), respectively. It can be seen how drastically the decay function changes with $\Delta_\mathrm{j} T$.

The $\Delta_\mathrm{j} T$ dependence of the obtained $\beta$ is shown graphically in Fig. 7 together with the results of PG

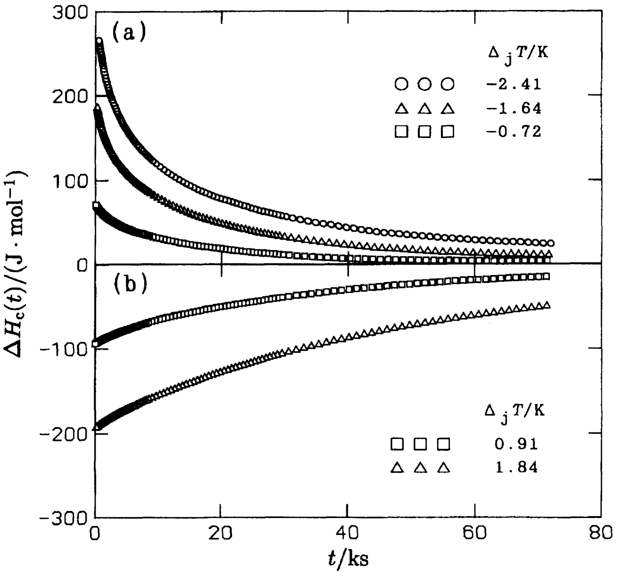

Fig. 4. Spontaneous exothermic (a) and endothermic (b) configurational-enthalpy drift at constant temperature 165 K in PMS. $\Delta H_\mathrm{c}(t) = H_\mathrm{c}(t) - H_\mathrm{c}(\infty)$.

and GL.[6] The $\beta$ value, which clearly depends on the magnitude of $\Delta_\mathrm{j} T$, becomes large as the $\Delta_\mathrm{j} T$ increases. This trend is just the same as those obtained in PG and GL, indicating that the nonlinearity is remarkable in the irreversible structural relaxation in liquid glasses, and that the exothermic and endothermic processes are very different in character. The $\beta_0$ of PMS was determined to be 0.76±0.03 as the $\beta$ value extrapolated from the positive and negative sides in $\Delta_\mathrm{j} T$ to zero Kelvin by straight lines. If extrapolation by a straight line holds reasonably well on the positive side of $\Delta_\mathrm{j} T$, the $\beta$ of PMS would cross 1 at $\Delta_\mathrm{j} T \approx 3$ K. Such a situation might be considered to be strange, since $\beta$ is recognized to be in the range $0 < \beta \leq 1$ and to have its maximum when there is no distribution in the relaxation time. However, this consideration only concerns the outcome in the frequency domain as based on the distribution of relaxation times being present. In the present case of the time domain, the hierarchical evolution of the distribution of the relaxation times should also be taken into consideration, and the situation may be admitted where $\beta$ becomes numerically larger than 1 (see Fig. 6(a)).

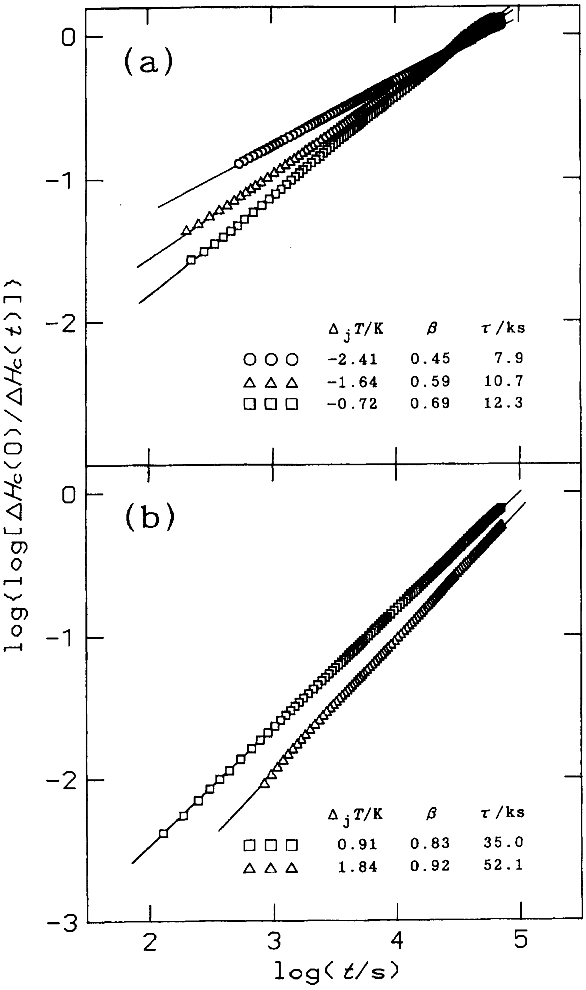

Fig. 5. Fittings of the exothermic (a) and endothermic (b) configurational-enthalpy drifts at 165 K in PMS in terms of the stretched exponential function. The apparent relaxation time $\tau$ is recognized to become systematically long as the $\Delta_\mathrm{j} T$ is increased from negative to positive values.

Böhmer et al.[15] have asserted that "the fragility $m$ is in the parallel relation to the *minus* of nonexponentiality parameter $\beta_0$". Although such a relation might hold as quite a rough trend, $m$ represents the temperature dependence of the average relaxation time at around $T_\mathrm{g}$ on an Arrhenius plot, while $\beta_0$ is interpreted to express the distribution of the relaxation times under equilibrium at some constant temperature. Therefore, there is no logical necessity for a relation to exist between the two. In fact, the $\beta_0$ values become large in the order of PG ($\beta_0 = 0.62$), GL ($\beta_0 = 0.67$), and PMS ($\beta_0 = 0.76$), and the $m$ values become large in the same order of PG ($m = 46$), GL ($m = 51$), and PMS ($m = 87$). The experimental result is completely opposite to the predicted relation. Figure 8 shows a replot of the relation between $\beta$ and $\Delta_\mathrm{j} T$ after normalizations by $\beta_0$ and $T_\mathrm{a}$, respectively. The nonlinearity of the irreversible processes can be characterized by the slope of each solid line. Figure 9 shows a plot of the nonlinearity parameter ($\delta$) against the fragility ($m$) in order to explore any correlation between the two. The diamond represents the result expected in the "strongest" liquid. The dotted lines are guides for the eye. The nonlinearity is concluded without doubt to increase with increasing fragility. The dependence, however, definitely differs between in the exothermic ($\Delta_\mathrm{j} T < 0$) and endothermic ($\Delta_\mathrm{j} T > 0$) processes: $\mathrm{d}\delta/\mathrm{d}m$ is larger in the former, cluster creation on the average, process than in the latter, cluster annihilation, process. In view of the facts that the fragility generally increases in a system as the tem-

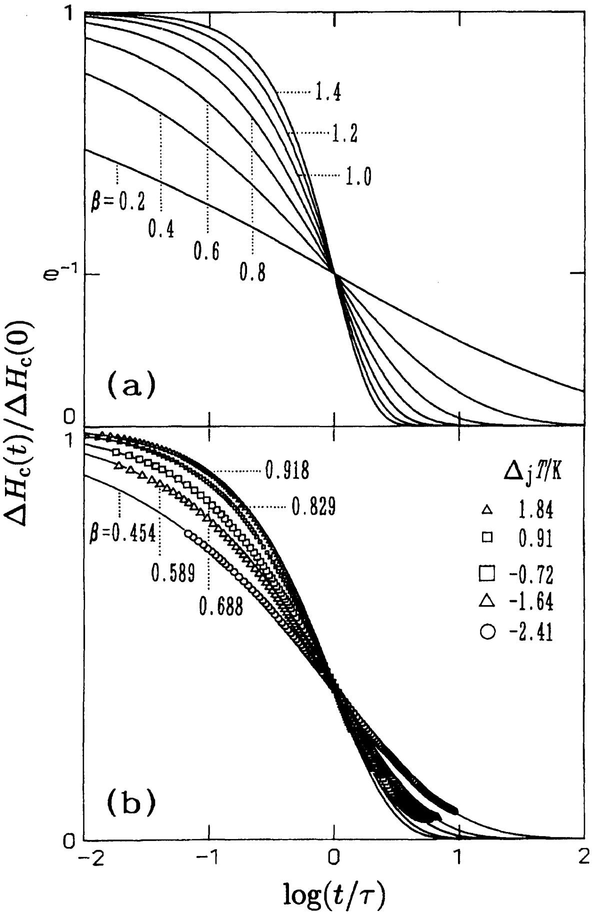

Fig. 6. Decay function of the stretched exponential type with different $\beta$ values: (a), numerical calculation; (b), experimental relaxation data obtained in PMS. Solid lines in (b) represent the results of fittings.

perature decreases and that the liquid structure being in the endothermic process corresponds to that at lower temperature than in the exothermic one at the same enthalpy-tracking temperature ($T_a$), this result is quite opposite to a simple extension of the idea based on the very $\delta$–$m$ relation.

## Computer Simulation of Irreversible Relaxation Processes

No picture has hitherto been proposed for the molecular rearrangement process in an irreversible structural change. Only the relaxation times have been obtained for various properties as a function of the temperature, as indicated by the solid line in Fig. 10; the glass transition takes place at around the temperature at which the relaxation time becomes ca. $10^3$ s. The most important point thus clarified so far is that the rearrangement process is based on thermal activation. Thus, any such microscopic configurational processes can be energetically depicted by a double-well potential curve, as shown in Fig. 11, where $\varepsilon$ and $r$ denote the potential energy and the configurational coordinate, respectively. The quantity to be detected macroscopically as the relaxation effect is given by the change in the sum of internal energies over all the rearrangement units in the liquid system, where the energy concerning each unit would be evaluated as the occupation fraction (in the higher-in-energy configuration) multiplied by the energy difference between the two minima.

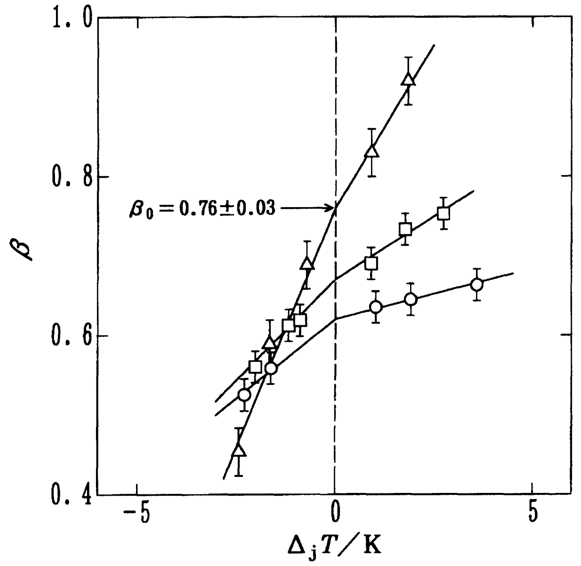

Fig. 7. Dependencies of the nonexponentiality parameter ($\beta$) on $\Delta_j T$: ○, 1,2-Propanediol (propylene glycol, PG); □, Glycerol (GL); △, PMS.

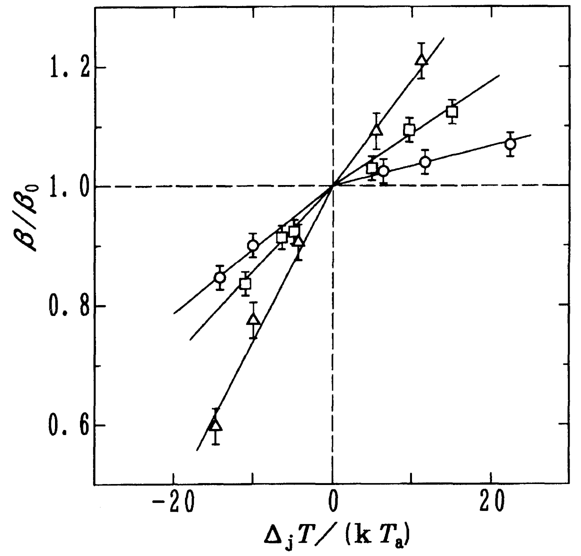

Fig. 8. Dependencies of the nonexponentiality parameter ($\beta$) normalized by $\beta_0$ on $\Delta_j T/T_a$: ○, PG; □, GL; △, PMS.

The average relaxation times ($\tau$) have been observed to show the temperature dependence expressed by a non-Arrhenius, VTF equation,[16] as represented by the solid line in Fig. 10; however, they have also been indicated to show the following Arrhenius behavior under each constant configurational structure,[13,17,18] as

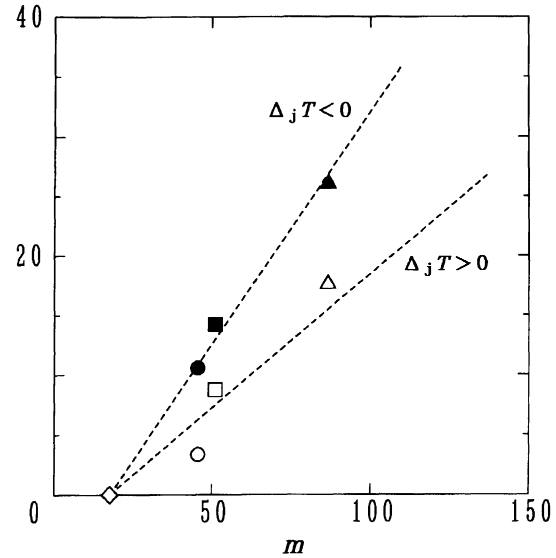

Fig. 9. Relationship between the nonlinearity parameter ($\delta$) of relaxation process and the fragility parameter ($m$): ○ and ●, PG; □ and ■, GL; △ and ▲, PMS. Open and filled marks represent the results for positive and negative $\Delta_j T$, respectively. An open diamond represents the values expected for the "strongest" liquid. The nonlinearity definitely increases with increasing fragility, but the relationship depends on the sign of temperature jump ($\Delta_j T$).

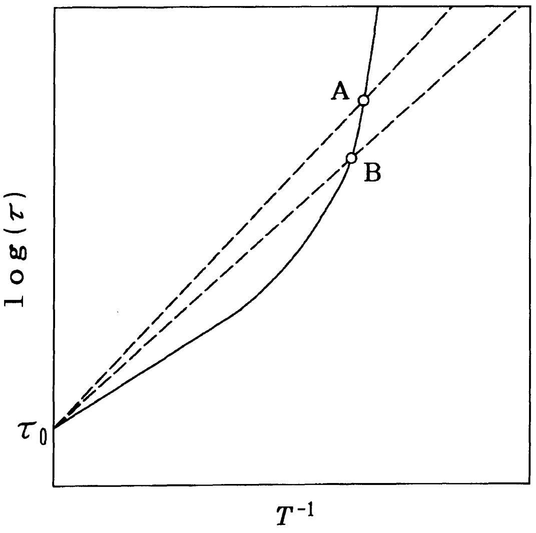

Fig. 10. Schematic diagram of the logarithmic average relaxation times against the inverse temperature. A solid line represents the non-Arrhenius dependence of relaxation times for liquid under equilibrium. The slopes of dashed lines are proportional to represent the activation energies at the respective points A and B when the preexponential factor in the Arrhenius equation is assumed to be constant.

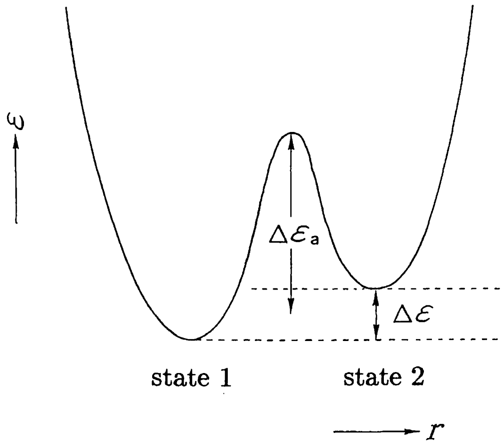

Fig. 11. Double-well potential curve representing any microscopic configurational change: $\varepsilon$, potential energy; $r$, configurational coordinate; $\Delta\varepsilon_a$, potential barrier; $\Delta\varepsilon$, energy difference between the two potential minima corresponding to states 1 and 2.

represented by the dashed lines while keeping the preexponential factor ($\tau_0$) constant:

$$\tau = \tau_0 \cdot \exp\left(\frac{\Delta\varepsilon_a}{RT}\right). \tag{7}$$

The latter indicates that the relaxation time for any microscopic activation process can be expressed essentially by the Arrhenius equation and that both appearances of the non-Arrhenius behavior and the large fragility originate from the temperature dependence of the average activation energy, which increases with decreasing temperature.

In real liquids, however, neither the details of the activation units expressed by the curve in Fig. 11 nor the number of units are known at all. Thus, in the present simulation, the simplest model using a double-well potential was adopted so as to extract the relation, if any, between the fragility of the relaxation times and any nonlinearity due to the irreversibility of the relaxation processes, and to verify the reasoning given above for the experimental result: 1) The number of activation units was assumed to be constant, and 2) the development of a clustered structure with decreasing temperature was taken into consideration through increasing the activation energy ($\Delta\varepsilon_a$) along with the increase in the probability of a lower-in-energy microscopic state 1, $p_1$, for each activation unit, as described in the following.

Probabilities $p_1$ and $p_2$ are given according to the Boltzmann's distribution function,

$$p_1 = \frac{1}{1+\exp\{-\Delta\varepsilon/(RT)\}} \tag{8}$$

and

$$p_2 = \frac{\exp\{-\Delta\varepsilon/(RT)\}}{1+\exp\{-\Delta\varepsilon/(RT)\}}, \tag{9}$$

respectively. The "fictive" temperature ($T_f$)[19] representing the structure of the system was defined using

$$\frac{p_2}{p_1} = \exp\left(-\frac{\Delta\varepsilon}{RT_f}\right) \tag{10}$$

or

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

When the temperature is suddenly jumped from $T_\mathrm{i}$ to $T_\mathrm{a}$, the ratio $p_2/p_1$ changes with time from the equilibrium value at $T_\mathrm{i}$ to that at $T_\mathrm{a}$, and, correspondingly, $T_\mathrm{f}$ changes from $T_\mathrm{i}$ to $T_\mathrm{a}$ with time. Since $\Delta\varepsilon_\mathrm{a}$ depends on $T_\mathrm{f}$, the relaxation time ($\tau$) even at constant $T_\mathrm{a}$ depends on the $T_\mathrm{f}$ as well:

$$\tau = \tau_0\cdot\exp\left\{\frac{\Delta\varepsilon_\mathrm{a}(T_\mathrm{f})}{RT_\mathrm{a}}\right\}, \tag{12}$$

where $\tau_0$ is assumed to be constant at $10^{-14}$ s in the present simulation.

The dependence of $\Delta\varepsilon_\mathrm{a}$ on $T_\mathrm{f}$ around $T_\mathrm{a}$ can be expressed by using the fragility ($m$) and $\Delta\varepsilon_\mathrm{a}(T_\mathrm{a})$. The activation energy and the relaxation time for any rearrangement process under equilibrium at $T_\mathrm{f}$ and $T_\mathrm{a}$ are equated as follows as the transformation of Eq. 7:

$$\Delta\varepsilon_\mathrm{a}(T_\mathrm{f}) = 2.303RT_\mathrm{f}\{\log\tau(T_\mathrm{f}) - \log\tau_0\} \tag{13}$$

and

$$\Delta\varepsilon_\mathrm{a}(T_\mathrm{a}) = 2.303RT_\mathrm{a}\{\log\tau(T_\mathrm{a}) - \log\tau_0\}, \tag{14}$$

respectively. Meanwhile, since the fragility ($m$) at $T_\mathrm{a}$ is given by

$$m = \left.\frac{\mathrm{d}\log\tau(T)}{\mathrm{d}(T_\mathrm{a}/T)}\right|_{T=T_\mathrm{a}}, \tag{15}$$

the relaxation time at $T_\mathrm{f}$ can be expressed as the difference from that at $T_\mathrm{a}$:

$$\log\tau(T_\mathrm{f}) - \log\tau(T_\mathrm{a}) = m\left(\frac{T_\mathrm{a}}{T_\mathrm{f}} - 1\right). \tag{16}$$

Combining Eqs. 13, 14, and 16 thus results in the following expression for the $\Delta\varepsilon_\mathrm{a}(T_\mathrm{f})$:

$$\Delta\varepsilon_\mathrm{a}(T_\mathrm{f}) = 2.303RT_\mathrm{f}m\left(\frac{T_\mathrm{a}}{T_\mathrm{f}} - 1\right) + \frac{T_\mathrm{f}}{T_\mathrm{a}}\Delta\varepsilon_\mathrm{a}(T_\mathrm{a}). \tag{17}$$

The distribution of the activation energies was tentatively expressed by the following Gaussian distribution:

$$g(\Delta\varepsilon_\mathrm{a}) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{\{\Delta(\Delta\varepsilon_\mathrm{a})\}^2}{2\sigma^2}\right], \tag{18}$$

where $\sigma^2$ is the mean square deviation of activation energies; $\overline{\{\Delta(\Delta\varepsilon_\mathrm{a})\}^2}$. $\overline{\Delta\varepsilon_\mathrm{a}}$ was so fixed at 62.7 kJ mol$^{-1}$ as to give the enthalpy-tracking temperature for GL, 182 K,[6] at $\overline{\tau}=10^4$ s. The probability density ($g$) corresponds to a weighting factor ($\omega_k$) in the decay function,

$$\frac{Y(t)}{Y(0)} = \sum_k \omega_k\phi_k(t). \tag{19}$$

Figure 12 shows Gaussian distributions against $\Delta\varepsilon_\mathrm{a}$ having the same $\sigma$ at two different temperatures of $T_\mathrm{i}$ and $T_\mathrm{a}$. The shaded part as one division in $\Delta\varepsilon_\mathrm{a}$ at $T_\mathrm{i}$ was assumed here to relax toward the corresponding shaded part in the distribution at $T_\mathrm{a}$. On the way of the relaxation, only the relaxation time changed along with the progress of relaxation, namely with a change in the fictive temperature; however, the probability density ($g$) of the part was kept constant throughout the relaxation at the value given by the presupposed distribution.

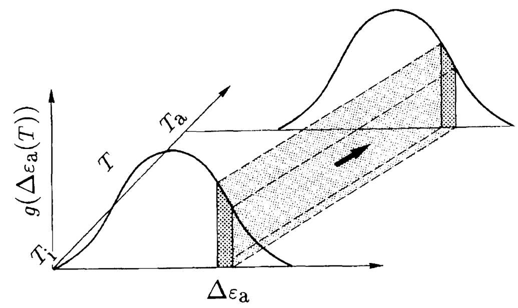

Fig. 12. Gaussian distributions of activation energies with same $\sigma$ at two different temperatures, $T_\mathrm{i}$ and $T_\mathrm{a}$. A thick bar with arrow indicates the direction of relaxation with time.

Figure 13 shows the results of a simulation of the internal energy relaxations of the system with different $\Delta_\mathrm{j}T$ in the case of $m$=51, where $\sigma$ was taken to be 1.24 kJ mol$^{-1}$ so as to yield $\beta_0$=0.67 for GL. $\Delta\varepsilon$ was taken for each activation unit to be constant at 10 percent of $\Delta\varepsilon_\mathrm{a}$ at $T_\mathrm{a}$. The $\Delta_\mathrm{j}T$ dependencies of the $\beta$ values for systems with different $m$ are shown in Fig. 14. Here, $m=18$ corresponds to the case where the relaxation times show an Arrhenius behavior against the inverse temperature. The $\beta$ value definitely depends on $\Delta_\mathrm{j}T$ at $m>18$; that is, the relaxation function definitely shows a nonlinearity to the $\Delta_\mathrm{j}T$. The degree of nonlinearity becomes remarkable with an increase in $m$. The tendency, being in agreement with the experimental result, supports the interpretation that the fragility, namely the non-Arrhenius property of the relaxation times, is responsible for the nonlinearity of the irreversible structural relaxation processes.

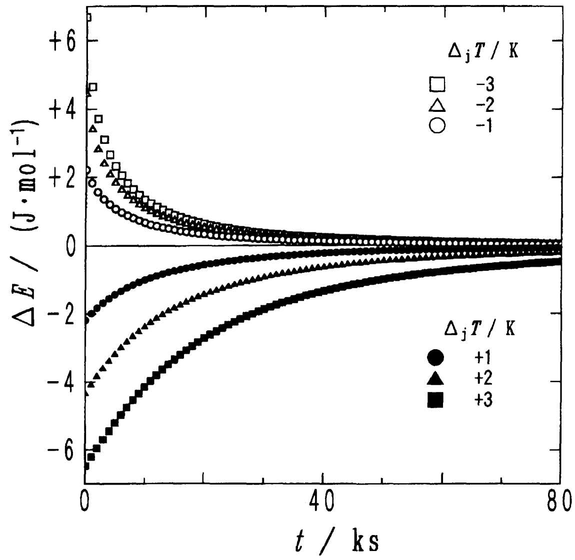

Fig. 13. Internal energy relaxation processes at 182 K of the system with fragility $m$=51 and Gaussian distribution of activation energies with $\overline{\Delta\varepsilon_\mathrm{a}}$=62.7 kJ mol$^{-1}$ and $\sigma$=1.24 kJ mol$^{-1}$.

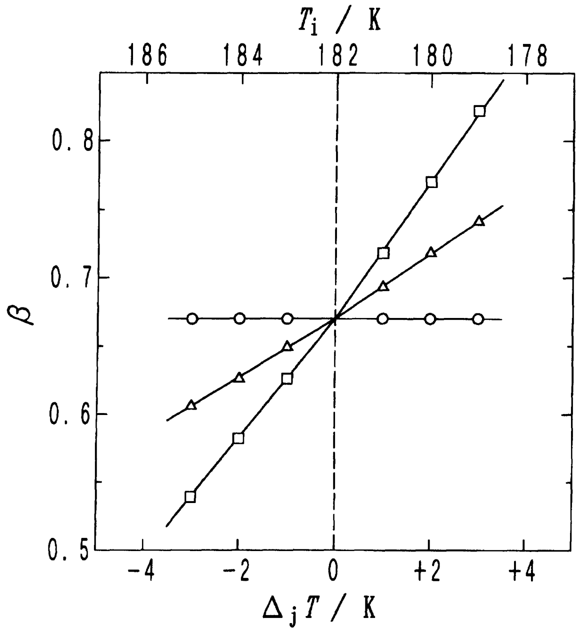

Fig. 14. Temperature jump dependence of the nonexponentiality parameter $\beta$ of the stretched exponential function fitted to the simulated relaxation processes: ○, $m=18$; △, $m=35$; □, $m=51$.

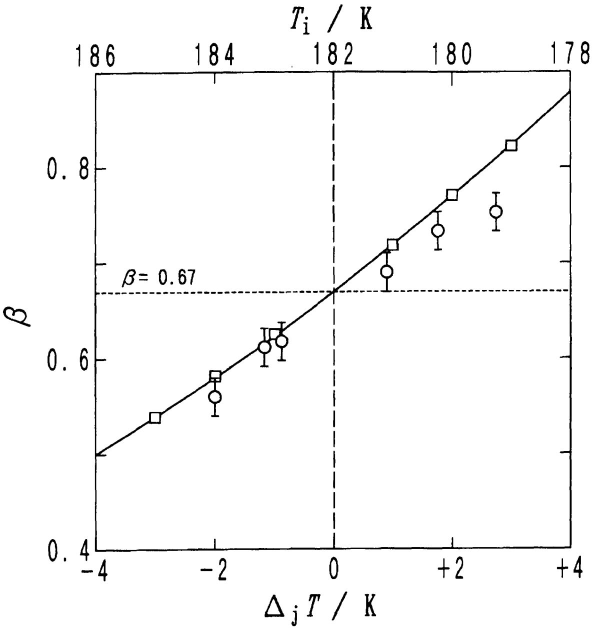

Fig. 15. Temperature jump dependence of the nonexponentiality parameter $\beta$ for the system corresponding to GL: Circles, experimentally derived; squares and a solid line, computer-simulated as shown in Fig. 13.

## Discussion

A good correlation between the fragility and the nonlinearity of the processes was obtained above in both the calorimetric experiment and the computer simulation. The results are interpreted to mean (in essence) that the relaxation times distributing become long on the whole in exothermic processes, due to an increase in the cluster sizes with time, while they become short in endothermic ones, due to a decrease in the cluster sizes oppositely.

The agreements between the nonlinearities obtained in the experiment and the simulation are, however, different, depending on whether the processes are exothermic ($\Delta_j T<0$) or endothermic ($\Delta_j T>0$). Figure 15 shows the $\beta$—$\Delta_j T$ relations for the systems with $m=51$ as an example corresponding to GL, where the circles represent the results of the experiment and the squares and the solid line those obtained in the simulation, respectively. The nonlinearities corresponding to the slopes are in rather good agreement between the two in the exothermic processes, but are considerably different from each other in the endothermic ones. The simulation assumes effectively that the decay of the relaxation time for each unit is more or less proportional to that of the internal energy as an observable. The above result indicates that such a picture of the above-mentioned simulation may describe the real time-evolution in the distribution of relaxation times on the whole of the detailed microscopic processes rather in the former case than in the latter. Further, the experimentally observed nonlinearity in a detailed examination became rather large in the former; on the other hand, it became considerably small in the latter, compared with those derived from the computer simulation. These facts would reflect just the difference between the processes of the creation and annihilation of clusters in liquids, and are essential points which must be clarified in the future.

It is noticed that $\Delta H_c(0)$ (see Fig. 6 in Ref. 6) and $\Delta E(0)$ (see Fig. 13) for GL differ by a factor of ca. 20. Even if the contribution to $\Delta H_c(0)$ from the molecular-vibrational degrees of freedom due to relaxations in the configurations of molecules is taken into consideration, the $\Delta H_c(0)$ would still be larger by an order of magnitude than $\Delta E(0)$. The primary reason, as a matter of course, is that $\Delta H_c(0)$ is given as a quantity per mole of molecules, while $\Delta E(0)$ is given as that per mole of activation units. This means that one molecule would result in 10 activation processes or so for the observed relaxation phenomenon. It might follow from the result that the molecular arrangements in the clusters would not be rigid differently from that in a completely ordered crystal lattice, but would be rather disordered like in the meso phases. This is also a point which must be clarified in correlation with the above-mentioned problem of nonlinearities in irreversible relaxations.

## Conclusion

In the present study, the irreversible enthalpy relaxation functions of liquid glasses were confirmed in the time domain to show a remarkable nonlinearity to a temperature jump. The nonlinearity was clarified by a calorimetric experiment and a computer simulation to originate essentially from the fragility of the liquid, namely the non-Arrhenius property of the relaxation times.

The degree of nonlinearity obtained experimentally depended on the sense of the relaxation, namely whether the processes are exothermic or endothermic: It was indicated that the relaxation time for microscopic rearrangement of molecules decays rather in harmony with the observed configurational enthalpy in the exothermic process, and that, on the other hand, it decays rather separately from the enthalpy in the endothermic process. A real microscopic picture for the relaxation processes should be made in the future in correlation with the mechanism of the creation and annihilation of clusters; however, for the picture it is worth noting that an idea was suggested here of separating the relaxation of the characteristic time for the molecular rearrangement from that of the molecular rearrangement, itself, contributing to the enthalpy relaxation to be observed.

This work was supported partly by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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