

Temperature-jump method for characterization of structural fluctuations and irreversible relaxation processes in liquids and glasses

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Enthalpy relaxations of propylene glycol and glycerol were followed in the time domain at 160 and 182 K, respectively, in the glass-transition region with use of an adiabatic calorimeter. The relaxation processes were analyzed and fitted with a stretched-exponential function with nonexponentiality parameter β . Specification of the temperature jump prior to the relaxation measurement, $(\Delta T)_j$, was found to be indispensable for the characterization of the relaxation processes in the nonlinear-response regime and the value of β was studied as a function of $(\Delta T)_j$. The value of β depends on both the sign and magnitude of $(\Delta T)_j$, indicating a characteristic difference between the rates of creation and annihilation of structurally ordered regions in liquids. However, the values of β extrapolated from the positive and negative sides of $(\Delta T)_j$ to zero degree Kelvin agree with each other (0.62 ± 0.02 for propylene glycol and 0.65 ± 0.02 for glycerol, respectively), and are in excellent agreement with results obtained by heat-capacity spectroscopy. This is an experimental verification that the enthalpy-relaxational observation in time domain is equivalent to that in frequency domain only for $(\Delta T)_j = 0$ K.

Molecular liquids are characterized by disordered arrangements in both the positions and orientations of the constituent molecules. At any moment, however, there may exist short-range and, often, medium-range structurally ordered regions in the configuration of molecules¹; such regions to be named "structured clusters" appear and disappear in the time duration as so-called fluctuations of the liquid structure. The average size of these clusters and correspondingly the average relaxation time of the fluctuations, which are both generally considered to increase gradually with decreasing temperature, play an important role in determining the physicochemical properties, especially at low temperatures. The glass transition is then interpreted as a phenomenon of the average relaxation time to become longer than the experimental time scale, and the glass transition temperature T_g as the temperature below which the glassy state with frozen-in instantaneous liquid structure sets in.

Figure 1 shows schematically the configurational enthalpy versus temperature relation in the glass-transition region. The solid line represents the enthalpy curve under equilibrium; and the dashed line, the freezing-in configurational enthalpy under cooling at a moderate rate. Thus, when the temperature of the liquid was rapidly changed [corresponding to the solid line with arrow (2) or (2')] by $(\Delta T)_j$ in the transition region after having been held for a time long enough to reach equilibrium at T_i [$= T_a - (\Delta T)_j$] [as represented by a solid line with arrow (1)], the nonequilibrium liquid (namely, glass) displays enthalpy relaxation, reflecting the change in the clustered structure from nonequilibrium to equilibrium states at T_a [as indicated by a solid line with arrow (3) or (3')].² Because of this, a clarification of the relaxation phenomena is a prerequisite for understanding the structural fluctuations and other irreversible structural changes; e.g., details of the creation and/or annihila-

tion rates of the clusters and the size distribution and its temperature dependence.³

Such relaxation phenomena may be investigated either in frequency domain, for example, by means of heat-capacity spectroscopy or in time domain by tracking the enthalpy relaxation for a long time. In case the relaxation is of a Debye type, the two methods would be equivalent through a Fourier transformation. The point is, however, they should not be equivalent in an actual observation of structural relaxations in liquids and glasses. The reason is that frequency-scan method characteristically detects the cluster-size distribution

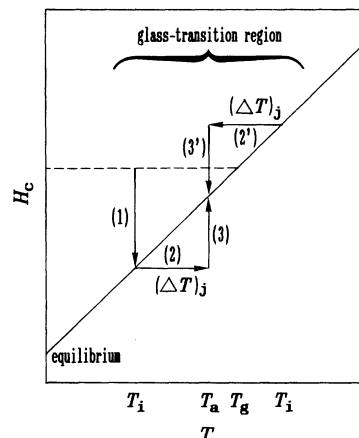


FIG. 1. Schematic diagram of configurational enthalpy vs temperature in the glass-transition region. Solid and dashed lines represent the configurational-enthalpy curve under equilibrium and the freezing-in configurational-enthalpy curve under cooling at a moderate rate, respectively. Solid lines with arrows (1)–(3) and (2')–(3') indicate the paths taken in temperature-jump experiments for the endothermic- and exothermic-relaxation processes, respectively.

essentially as a fluctuational property in the equilibrium state, while the time-scan method follows the irreversible (nonequilibrium to equilibrium) change in the very structure represented as the distribution of clusters and, therefore, the distribution of relaxation times. Such a viewpoint has been more or less lacking in studies of structural relaxation. As to the relaxational property of glycerol, Moynihan and co-workers⁴ compared the result obtained by differential scanning calorimetry (DSC) with that obtained by heat-capacity spectroscopy. But the outcome in DSC is too complicated to yield additional insight into both the distribution of relaxation times and its time evolution as a sum of nonequilibrium irreversible processes, since the temperature of sample continues to change at some considerable rate and since the configurational enthalpy relaxes with time as well.

In this work, the enthalpy relaxation of typical organic glasses, namely propylene glycol and glycerol, were tracked for a long time at the above T_a , and the results analyzed based on a stretched-exponential function (Kohlrausch-Williams-Watts equation)⁵ were compared with those of the enthalpy fluctuations studied in frequency domain by Birge and Nagel.⁶ The magnitude of the temperature jump $(\Delta T)_j$ prior to the relaxation measurement was taken as an independent variable characterizing the irreversible relaxation process.

All measurements were carried out under adiabatic conditions with a low-temperature calorimeter whose details will be described elsewhere.⁷ The calorimeter cell loaded with the sample is put under high vacuum ($\sim 10^{-4}$ Pa) and surrounded by two adiabatic shields within the cryostat. The temperature of shield is monitored as a deviation from that of the cell with a thermocouple and always so regulated as to keep the deviation essentially zero, resulting in the minimization of the heat leak into or out of the cell. Thermometry of the cell was carried out with high precision (10^{-5} K) by using a platinum resistance thermometer calibrated on the ITS-90 temperature scale.⁸ Heat capacity of the cell with or without the sample, C , can be obtained from the temperature increase ΔT caused by supplying a known quantity of electric energy ΔE under the adiabatic condition to be $C = \Delta E / \Delta T$.⁹ The inaccuracy of the heat-capacity measurement was found to be within 0.3%.⁷ When a rapid temperature change is desired, the calorimeter cell can be heated by allowing a large electric current to pass through the heater wire wound on it or be cooled by making mechanical contact with a liquid-helium tank by remote control of its position within the cryostat. If there exist some exothermic or endothermic effects due to the configurational-enthalpy relaxation in the glass-transition region, the temperature of the cell increases or decreases spontaneously under adiabatic conditions at rate dT/dt and the rate of relaxation can be evaluated by taking the heat capacity of the cell at that temperature to be $dH_c/dt = C dT/dt$.

An extra-pure reagent of propylene glycol, purchased from Wako Pure Chemical Industries, Ltd., was first distilled fractionally at reduced pressure, then dehydrated through coexistence with molecular sieves 3A (Wako Pure Chemical Industries, Ltd.) in vacuum for 12 h, and

purified by vacuum distillation two times. No impurity was observed gas-chromatographically for the purified sample. Glycerol (for fluorescence microscopy; assay > 99.5%, and most of the remaining is water), purchased from E. Merck was evacuated at 100°C for 10 h for dehydration and used as a sample as prepared. Each sample was loaded into a calorimeter cell under an atmosphere of helium gas. The masses of samples used were 18.0013 g (corresponding to 0.236 56 mol) for propylene glycol and 23.6775 g (0.257 08 mol) for glycerol, respectively.

Figure 2 shows the results of heat capacities (in the upper portion) and of spontaneous temperature-drift rates (in the lower portion) measured through repetition of the procedures of heating and temperature rating of propylene glycol in the glass-liquid transition region. Both dependences on temperature are characteristic of a glass transition as is well known.¹⁰ Long-time tracking of the enthalpy relaxations was executed under adiabatic conditions around the same $T_a \approx 160$ K as indicated by a broken line in the figure, after the calorimeter cell was brought there quickly from each initially equilibrated temperature T_i . The magnitude of temperature jump was evaluated to be $(\Delta T)_j = T_a - T_i$. Similar dependences of the heat capacity and temperature-drift rate were observed for glycerol at temperatures in the transition region, as shown in the upper and lower portions of Fig. 3, respectively. The enthalpy relaxations were tracked around 182 K in the case. Examples of spontaneous temperature-drift against time are given in the upper and lower portions in Fig. 4 of endothermic and exothermic enthalpy relaxations, respectively, in propylene glycol. Each of these dashed lines represents a constant "natural" drift due to the inevitable heat leak which exists in practice even under the adiabatic conditions prepared in the experiment.

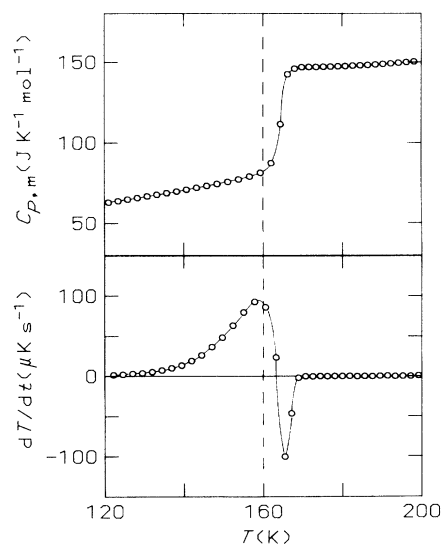


FIG. 2. Heat capacities (in the upper portion) and spontaneous temperature-drift rates (in the lower portion) observed in the course of intermittent heating in the glass-liquid transition region of propylene glycol.

The relaxation process is quite complicated because of two interlinked effects: the distribution of relaxation times and its irreversible change with time. The form of relaxation deviates strongly from an exponential function and has been often fitted with a stretched-exponential one so as to characterize its nonexponentiality as reduced to a value of single parameter β :

$$H_c(t) - H_c(\infty) = [H_c(0) - H_c(\infty)] \exp[-(t/\tau)^\beta].$$

While any nonunity value of β derived by the heat-capacity spectroscopy could be interpreted as essentially due to the existence of a certain distribution of relaxation times without change in the distribution at constant temperature, the β values obtained in time domain cannot be easily interpreted as indicative of any particular detail of the microscopic processes. However, the relaxation data is well fitted by the stretched-exponential function as shown below, and characterization of relaxation in terms of the β value as a function of $(\Delta T)_j$ would certainly be helpful, allowing comparison of the obtained β values, in the further development of theoretical descriptions of structural fluctuations and irreversible relaxation processes.

A series of temperature-drift data were directly used for the present fitting since the magnitude of the enthalpy relaxation ΔH_c is proportional to that of the temperature drift ΔT : $\Delta H_c = C \Delta T$, where C is heat capacity of the calorimeter cell loaded with sample and changes only slightly with temperature between $T(0)$ and $T(\infty)$:

$$T(t) - T(\infty) = [T(0) - T(\infty)] \exp[-(t/\tau)^\beta].$$

When the stretched-exponential function is transformed into the following form, the parameter β is given explicitly as a slope in the plot of the left-hand side versus $\log_{10}(t/s)$:

$$\begin{aligned} \log_{10}(\log_{10}\{[T(0) - T(\infty)]/[T(t) - T(\infty)]\}) \\ = \beta[\log_{10}(t/s) - \log_{10}(\tau/s)] + 0.3623. \end{aligned}$$

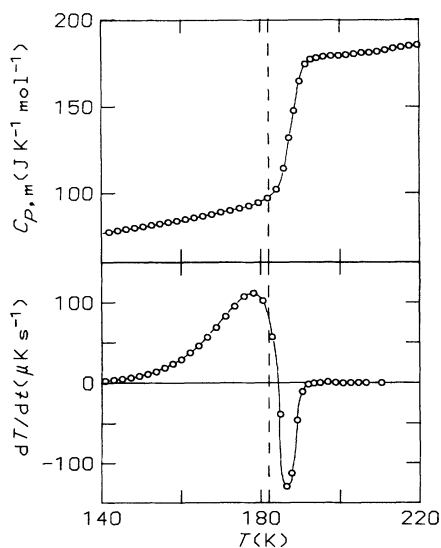


FIG. 3. Temperature dependences of heat capacities (in the upper portion) and spontaneous temperature-drift rates (in the lower portion) in the glass-transition region of glycerol.

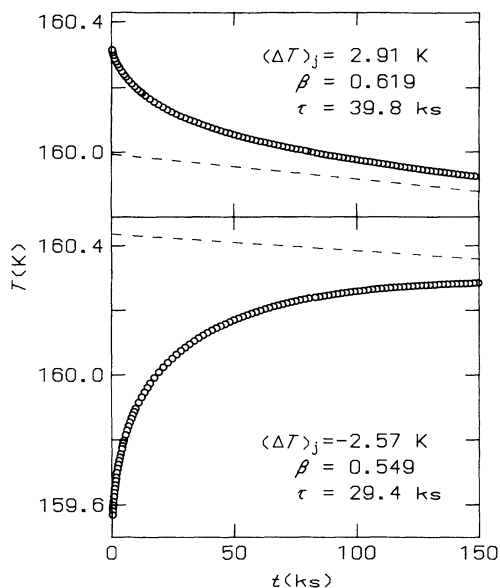


FIG. 4. Spontaneous exothermic temperature drift at 160 K after the temperature jump of 2.91 K (in the upper portion) and -2.57 K (in the lower portion) in propylene glycol. A dashed line represents a "natural" temperature drift due to the inevitable heat leak between the calorimeter cell and its surroundings.

Figures 5(a) and 5(b) show the plots of the endothermic and exothermic enthalpy-relaxation processes, respectively, in propylene glycol. Each set of data gives a straight line, implying a reasonable fit by this function. The

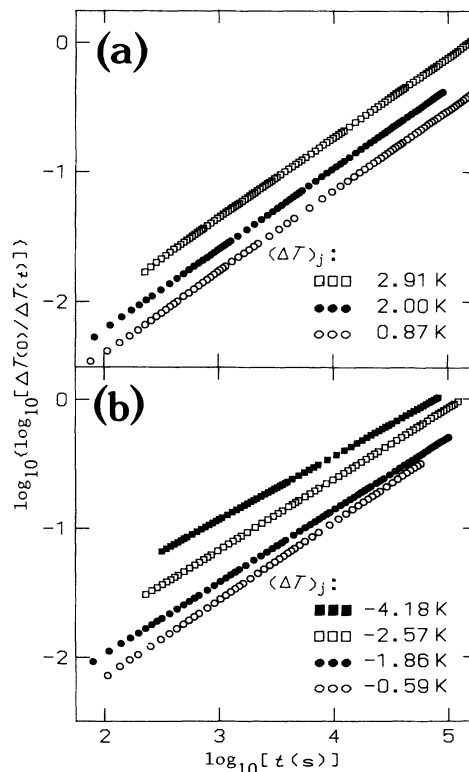


FIG. 5. Fitting of the endothermic (a) and exothermic (b) temperature-drift process in propylene glycol in terms of the stretched-exponential function.

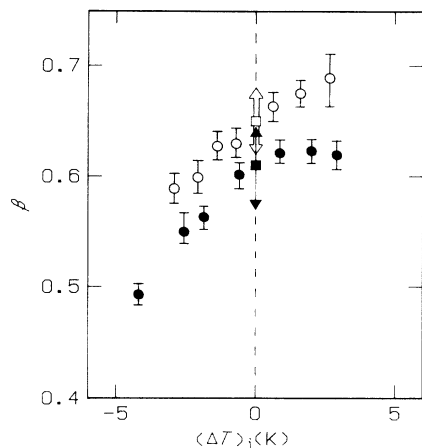


FIG. 6. Dependence of the nonexponentiality parameter β on the magnitude of temperature jump in propylene glycol (solid circles) and glycerol (open circles). Solid and open squares represent the β values of propylene glycol and glycerol, respectively, obtained by heat-capacity spectroscopy. (See Ref. 6.)

slopes are almost the same for various positive temperature jumps, while decidedly different for different negative jumps in magnitude.

The β values obtained are plotted as a function of the magnitude of temperature jump $(\Delta T)_j$ in Fig. 6, where solid circles stand for the results of propylene glycol and open circles for those of glycerol, respectively. The corresponding values obtained by heat-capacity spectroscopy were reported to be 0.61 ± 0.04 for propylene glycol and 0.65 ± 0.03 for glycerol, respectively,⁶ as represented by solid and open squares, respectively, at $(\Delta T)_j = 0$ K in the figure. Two remarkable features of the plots stand out.

(1) The β value depends on both the sign and magnitude of $(\Delta T)_j$, and its slope $d\beta/d(|(\Delta T)_j|)$ depends also on the sign of $(\Delta T)_j$. The difference between relaxation properties in the exothermic and endothermic processes has been pointed out in the calorimetric observation of glycerol and dilatometric one of glucose by Davies and Jones,² and that the β value in the endothermic process

was larger than that in the exothermic one has been reported in the calorimetry of 1-butene by Takeda and co-workers.¹¹ The present results are consistent with these earlier observations. These facts indicate that the exothermic and endothermic processes, namely, the time evolutions of the creation and annihilation rates of structurally ordered regions in liquids, are quite different in character.

(2) Meanwhile, the values extrapolated from positive and negative sides of $(\Delta T)_j$ to zero degree Kelvin agree with each other (0.62 ± 0.02 for propylene glycol and 0.65 ± 0.02 for glycerol respectively) and are in excellent agreement with the results obtained by heat-capacity spectroscopy.⁶ Thus the observations in time domain and in frequency domain were found to be equivalent only in the $(\Delta T)_j = 0$ K limit for such structural relaxations in liquids and glasses.

The above results clearly demonstrate the power of the temperature-jump method in characterizing structural fluctuations and the nonequilibrium irreversible processes, especially in the nonlinear-response regime, provided that the magnitude of temperature jump is well defined and can be treated strictly as an independent variable of the relaxation. When the stretched-exponential function is used for data processing, knowledge of the slope $d\beta/d(|(\Delta T)_j|)$ is key to deeper insights into irreversible and hierarchical structural changes. At present, it may be noted that these slopes are found to differ between exothermic and endothermic processes, even when both temperature jumps are quite close to zero degree Kelvin, and that they are negative and quite large in the exothermic process, leading to a remarkably nonexponential property in the relaxation of quenched glass with large negative $(\Delta T)_j$. The latter statement is in good agreement with our previous results on vapor-deposited amorphous butyronitrile, which gave quite small β values of $0.07-0.21$.¹²

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