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Merging of α and slow β relaxation in supercooled liquids

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Dielectric relaxation spectroscopy (1 Hz – 20 GHz) has been performed on supercooled glass-formers from the temperature of glass transition (T_g) up to that of melting. Precise measurements particularly in the frequencies of MHz order have revealed that the temperature dependences of secondary β relaxation times in well above T_g deviate from the Arrhenius relation below T_g: the β process does not merge with the α process around the dynamical crossover temperature in contradiction to previously speculated extrapolations.

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I. INTRODUCTION

In recent years, much of the focus on glassy dynamics has been shifting to a considerably higher temperature than T_g [1]. The topical temperature is located around $1.2T_g$, where the dynamics of supercooled liquids has been found to change fairly (dynamical crossover). So far, the following phenomena have been observed around the dynamical crossover temperature:

(i) Rössler scaling reveals that the Stokes-Einstein relation becomes invalid when cooled [2,3]. This indicates a change of diffusion mechanism there.

(ii) Stickel analysis [4] clarifies that temperature dependence of viscosity changes. Therefore, in order to fit the primary α relaxation time τ_α using the Vogel-Fulcher-Tamman (VFT) relation,

$$\tau_\alpha = \tau_0 \exp\left(\frac{C}{T-T_0}\right), \tag{1}$$

the coefficients (τ_0, C, T_0) have to vary around the temperature (called T_B on this topic). This suggests that the mechanism of slow structural relaxation makes some alternation there.

(iii) The Johari-Goldstein-type β process (secondary process in the context of dielectric relaxation) [5–12] is speculated to merge into the α relaxation there, because extrapolation of the Arrhenius-type temperature dependence below T_g of the β relaxation times [3,4,13–17] intersects that of the α process at the temperature (called T_{ex} on this topic).

Theoretically, the characteristic dynamical crossover temperature is thought to be comparable to T_C where the schematic mode coupling theory (MCT) predicts a dynamical phase transition [18]. Indeed, the above first two phenomena [(i), (ii)] can be regarded as indicators of the dynamical transition at T_C. However, the schematic MCT is irrelevant to the third one (iii), the bifurcation of α,β modes; even the existence of the Johari-Goldstein-type β process cannot be derived. There is no general consensus about the cause of β relaxation though this process is widely considered to be intrinsically important for supercooled liquids [15,19].

Furthermore, from experimental aspects, while the dynamical crossover phenomena [(i), (ii)] have been confirmed from either Rössler or Stickel plot definitely, the bifurcation of (iii) is inferred from the extrapolation. Actually, however, it remains an open problem as to whether the Arrhenius behavior of the β process persists in higher temperatures near the dynamical crossover temperature: the α,β merging speculated so far is not conclusive.

Incidentally, recent theoretical study with a free-energy landscape model predicts that the β-relaxation times in a higher temperature region deviate from the Arrhenius relation defined below T_g and do not merge with the α process at the temperature of extrapolation, T_{ex} [20].

This paper thus aims to investigate the secondary β mode in high temperatures well above T_g by carrying precisely out the broadband measurements of dielectric relaxation. Our main result is the following: *as will be clearly seen from Figs. 1 and 2, there exist both α and β relaxation even above T_{ex}.*

II. EXPERIMENT

In order to trace the α,β mode in wide temperature range from T_g to above the melting temperature T_m, we set up a broadband dielectric relaxation measurement system that the following three apparatuses can work simultaneously: the Solartron1260 impedance analyzer with parallel-plate electrodes (1 Hz – 32 MHz), the HP4191A reflectance analyzer with coaxially cylindrical electrodes (1 MHz – 1 GHz), and the HP54750A with the HP54754A Time Domain Reflectometry (TDR) system with flat-end-cable-type electrodes (10 MHz – 20 GHz). The three sets of electrodes were installed in the same sample bath for their identical temperature control.

As a typical glass-forming sample with a large strength of the β relaxation, we employed sorbitol $[\mathrm{CH_2OH-(CHOH)_4-CH_2OH}, T_m = 383\ \mathrm{K}, T_g = 264\ \mathrm{K}]$ purchased

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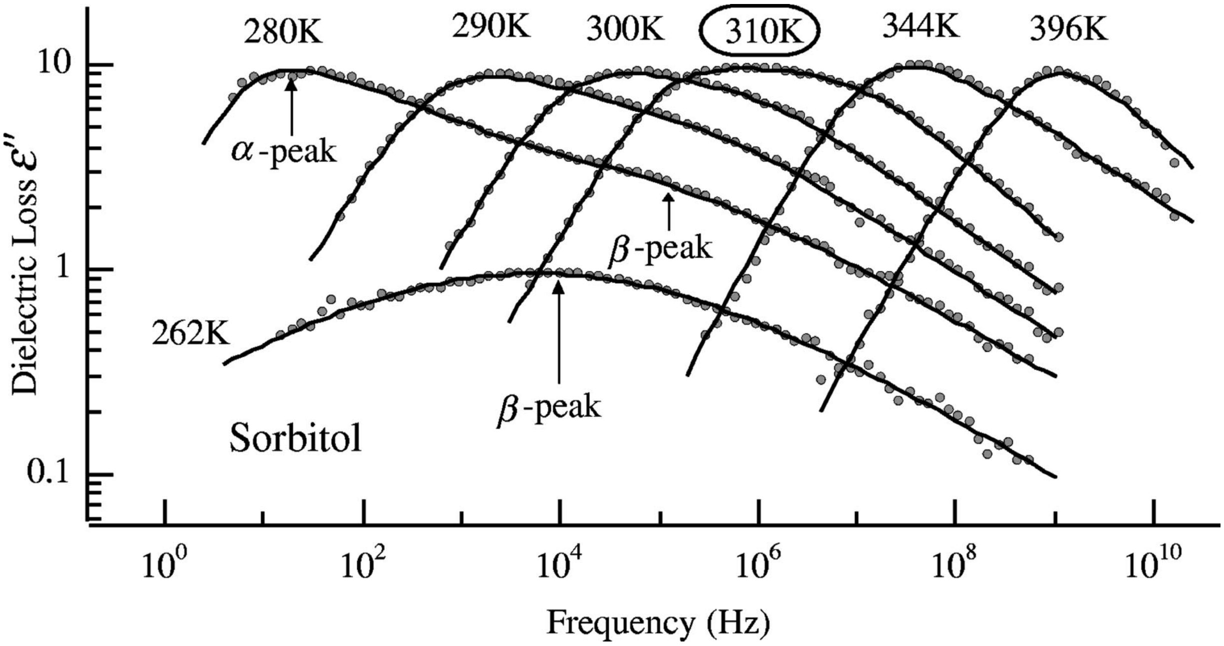

FIG. 1. Dielectric loss spectra of sorbitol at various temperatures. Circles represent the experimental data and the solid curves are the best fitting results by Eq. (2).

from Nacalai Tesque Co. In preparation, we heated the sample at 400 K for 20 min in vacuum for complete melting and purification. The obtained simple-liquid-state sample loaded in the sample bath was quickly quenched into deeply supercooled liquid near T_g at the cooling rate of 56.7 K/min. We then started measurements isothermally at specified temperatures under an accuracy to within 0.1 K. Reproducibility of the results were independent of the heating rate between measurement temperatures, 2.5 – 7.5 min/K. These series of procedures were performed in dry-nitrogen atmosphere to prevent the samples from absorbing moisture.

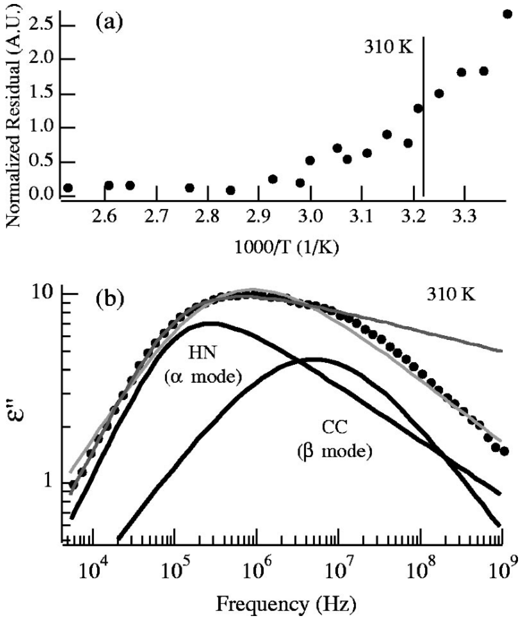

FIG. 2. (a) The temperature dependence of residual by one-relaxation (HN) fitting. The vertical axis is normalized by the number of data points which are analyzed. (b) A loss spectrum at a temperature (310 K) near T_{ex} (circles). It is found that any attempts of one-relaxation analysis are invalid (gray lines). Two-relaxation fittings with the use of Eq. (2) are also shown by black lines. As seen from Fig. 1, two-relaxation analysis works much better.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the dielectric loss spectra of sorbitol at various temperatures, exhibiting an obvious β mode in lower temperatures and its overlap with the α mode as temperature increases. It should be noticed that the two modes can be discriminated even around T_{ex} (see 310 K, for example, which is above T_{ex} as will be shown in Fig. 3). That is, *only observing dielectric spectra tells us that the β relaxation*

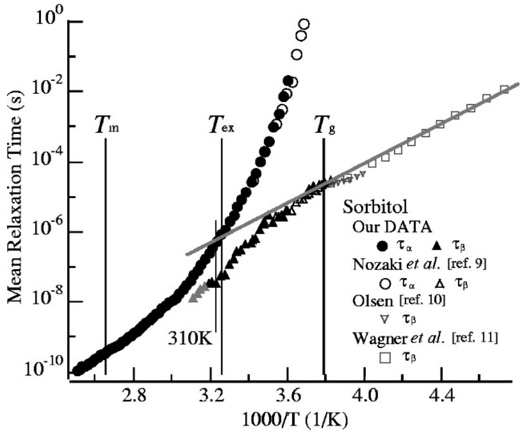

FIG. 3. Temperature dependence of the α,β-relaxation times of sorbitol, which exhibits good consistency with low temperature data reported so far [9–11]. The error bar for each datum can be drawn within the correspondent marker.

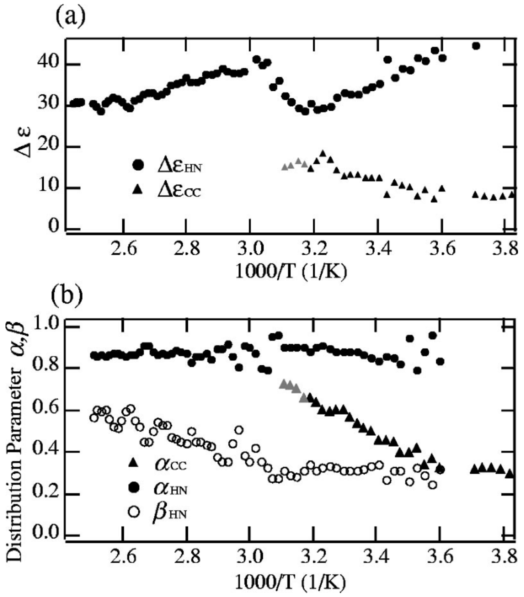

FIG. 4. Temperature dependences, for sorbitol of (a) dielectric increments $\Delta\epsilon_{\mathrm{HN}}, \Delta\epsilon_{\mathrm{CC}}$ and (b) broadness parameters $\alpha_{\mathrm{HN}}, \alpha_{\mathrm{CC}}$ and skewness parameter β_{HN}.

does not merge into the α mode around T_{ex}.

In the line-shape analysis of these spectra by the method of least squares, we used the Havriliak-Negami (HN) function for fitting the α process and the Cole-Cole (CC) function for the β one, relying on the additive ansatz [21]. At low temperatures where the α peak and the β peak are well resolved, the β relaxations were perfectly fitted by the CC function, but could not be fitted by the Fourier transform of the Kohlrausch-Williams-Watts (KWW) or Cole-Davidson function. Therefore, in order for comparison between α and β relaxations, we used not the KWW but the HN function for the α process.

The relaxation functions we used include broadness and skewness of the relaxation-time distributions:

$$\varepsilon^{*}=\varepsilon_{\infty}+\frac{\Delta\varepsilon_{\mathrm{HN}}}{[1+(i\omega\tau_{\mathrm{HN}})^{\alpha_{\mathrm{HN}}}]^{\beta_{\mathrm{HN}}}}+\frac{\Delta\varepsilon_{\mathrm{CC}}}{1+(i\omega\tau_{\mathrm{CC}})^{\alpha_{\mathrm{CC}}}}. \quad (2)$$

Here $\Delta\varepsilon_{\mathrm{HN}}$ and $\Delta\varepsilon_{\mathrm{CC}}$ are the dielectric increments, τ_{HN} and τ_{CC} are the functional relaxation times, α_{HN} and α_{CC} are the parameters of distribution broadness of the relaxation times, β_{HN} is a parameter reflecting the skewness of relaxation-time distribution, ε_{∞} is the high-frequency limit of ε^{*}, and ω is the angular frequency. We would like to note here that relaxation times τ_{α} and τ_{β} do not refer to the functional relaxation times τ_{HN} and τ_{CC}, but to the mean relaxation times $\langle\tau_{\mathrm{HN}}\rangle$ and $\langle\tau_{\mathrm{CC}}\rangle$. Accordingly, *the mean relaxation times do not depend on the choice of fitting functions*, which we have confirmed from comparing among HN+CC, Cole-Davidson [$\alpha_{\mathrm{HN}}=1$ in Eq. (2)] +CC, and KWW+CC.

Let us then consider the temperature region to apply the two-relaxation fitting with use of Eq. (2). To this end, we show in Fig. 2(a) the temperature dependence of residual when only one HN-function fitting is performed. Figure 2(a) shows the rapid increase of residual around $1000/T=3$. A good example above $1000/T=3$ is seen in Fig. 2(b), the spectrum at 310 K. As found from the spectrum, any attempts by one-relaxation fitting are invalid as shown by gray lines. Two-relaxation fitting, on the other hand, achieves unique and certain results independently of the initial values of adjustable parameters as it is represented by black lines in Fig. 2(b). This indicates that there certainly exist both α and β relaxations in the temperature region of $1000/T>3$. We would like to thus stress again the following: *Fig. 2(b) reveals that the β relaxation does not merge into an α process around T_{ex} in contradiction to previous extrapolations.*

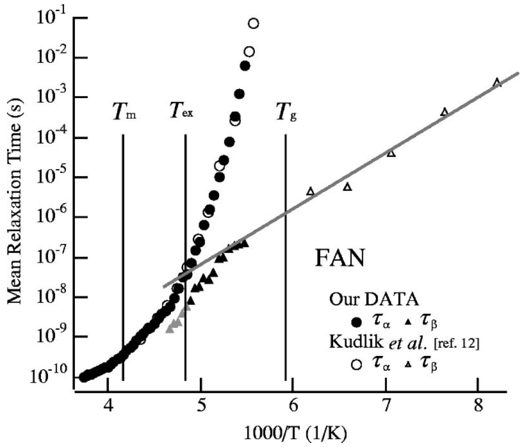

FIG. 5. Temperature dependence of the α,β-relaxation times of *m*-fluoroaniline. The temperature behavior is similar to that of sorbitol displayed in Fig. 3. The error bar for each datum can be drawn within the correspondent marker.

The above discussion forms the basis of two-relaxation fitting which we performed in the temperature region of $1000/T\geqslant3.1$. Figures 3 and 4 show the fitting results. Above $1000/T=3.2$, unique results were obtained irrespectively of initial parameters. In $3.1<1000/T<3.2$, represented by gray markers in Fig. 3, we found 3–4 minima of residual due to the close relaxation time of α and β process. Nevertheless, there is a unique set of fitting parameters that are relevant even in the temperature region. The other sets are definitely irrelevant because relaxation times or strengths make large jumps, by a decade for instance, in comparison with values at the nearest temperature.

We then investigate the temperature dependences of the α,β-relaxations times in more detail in Fig. 3. Our data are smoothly connected to the results reported so far [9–11]. Remarkably, for the β process, the Arrhenius relation below T_{g} does not persist to T_{ex}. The β relaxation times start to decrease with larger activation energy just before T_{ex}. Above T_{ex}, the β process seems to approach smoothly the α process around T_{m} [22], though it should be noted that the results in $3.1<1000/T<3.2$ are marginal.

Indeed, Fig. 4(a) shows that the $\Delta\epsilon$ of the α process has a dip in the marginal region ($3.1<1000/T<3.2$), which could be ascribed to lower certainty of fittings. In Fig. 4(b), the broadness parameters α_{CC} reveals the increasing distribution of the β relaxation time as temperature decreases. Also α_{HN} and β_{HN} are consistent with the familiar tendency about the

α process in supercooled liquids: skewness is large, but broadness is negligible (i.e., $\alpha_{\mathrm{HN}} \approx 1$).

We have further checked another material of entirely different-molecular structure: *m*-fluoroaniline (FAN) ($NH_2-C_6H_4-F, T_m = 238$ K, $T_g = 169$ K). Figure 5 shows the temperature dependences of α, β relaxations times, which have good continuity with previous ones as before [12]. The temperature region of two-relaxation fitting was determined from the residual of one-relaxation analysis in the same way as that of sorbitol [remember Fig. 2(a)], and gray markers denote the same for sorbitol. Figure 5, the result of FAN, also suggests that the β relaxation remains around T_{ex}.

IV. CONCLUDING REMARKS

We have performed broadband dielectric spectroscopy (1 Hz–20 GHz) on supercooled sorbitol and *m*-fluoroaniline with focusing on the behavior of the β mode in well above the T_g region. Precise spectra particular in the MHz region have clarified, as shown in Fig. 2(b), the certain existence of both the α and β mode even around T_{ex} where the $\alpha-\beta$ merging has been extrapolated. Further analysis has also revealed that the β relaxation times rapidly decrease around the T_{ex} with larger activation energy than that below T_g. This behavior of secondary relaxation, common to two materials of different molecular structures, is expected to be universal for supercooled liquids, though wider materials should be checked carefully in the future.

Thus, we have gained important clues for elucidating molecular mechanism of β relaxation: The temperature dependence of β relaxation changes around $T_{\mathrm{ex}} \approx T_{\mathrm{B}}$ [23] as wellas the α process, and the α and β relaxations merge together well above T_{ex} (possibly around T_m). The synchronized change of the α, β relaxations is to be explained by some theoretical model, though there has been few studies on such a high-temperature behavior of the β relaxation.

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