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Abstract. The broadband light scattering spectra of propylene glycol were studied by using a Sandercook-type $3+3$-pass tandem Fabry–Pérot interferometer and a triple-grating spectrometer. The depolarized spectrum in the liquid phase at 363 K clearly shows an α peak and a boson peak, and the former peak becomes lower remarkably on cooling. The line shape of the spectra was analysed by the superposition of α relaxation of Davidson–Cole type, a fast relaxation of Debye type and a boson peak. Although the fast relaxation time is temperature independent, its intensity tends to zero at 140 K. Another fast relaxation process was also observed by the Brillouin components of the polarized spectra. Its relaxation time is between the α-relaxation time and the fast relaxation time and obeys an Arrhenius law.

1. Introduction

Among the dynamical properties of complex liquids, supercooled liquids show some of the most interesting phenomena related to the cooperative phenomena of liquid–glass transitions. Various kinds of experiment have been performed in relation to the mode coupling theory (MCT) [1], because it predicts characteristic features, i.e. the α relaxation with the stretched exponential response function, and the fast β relaxation, which occurs at much higher frequencies than the Johari–Goldstein β process [2]. For most fragile liquids, the observed dynamical properties are well reproduced by MCT.

When the liquid becomes less fragile, the deviation from MCT increases because the vibrational contribution is pronounced. In fact an intense broad peak has been observed in many glass-forming materials in the low-frequency region of light and neutron inelastic scattering spectra. This peak is called a boson peak and its origin has been considered to be localized vibration, but the exact explanation is still unclear. Although the boson peak was calculated as a peak of microscopic origin by MCT [3, 4], the perfect reproduction of this peak is difficult in spectra for a large range of frequency. As another way to analyse broadband spectra, phenomenological fitting was reported by the superposition of α relaxation, two fast relaxations and the boson peak for o-terphenyl, a typical fragile liquid [5]. However, for intermediate and strong liquids the best method of analysis has not yet been determined.

In the present work, broadband light scattering spectra were investigated in a liquid–glass transition of propylene glycol, which belongs to the class of intermediate glass-forming materials according to the classification by Angell [6].

2. Experimental details

Broadband light scattering spectra were measured by the use of two kinds of spectrometer. The lower range between 1 and 300 GHz was measured by a Sandercook-type $3 + 3$-pass tandem Fabry–Pérot interferometer. The range higher than 100 GHz was measured by a triple-grating spectrometer of additive dispersion (Jobin Yvon TR64000). An Ar ion laser was used as an exciting source. The wavelengths were 4880 and 5145 Å for the low and high frequency ranges, respectively. The propylene glycol sample with 99.5% purity was purchased from Wako Pure Chemical Industries, Ltd. It was distilled and deyhdrated with Molecular Sieves 3A (Wako Pure Chemical Industries, Ltd) prior to use.

3. Results and discussion

3.1. Broadband dynamic susceptibility

In depolarized light scattering, the intensity of the Stokes component $I_{VH}(\omega)$ is related to the imaginary part of the dynamical susceptibility $\chi''(\omega)$:

$$I_{VH}(\omega) = I_0\{n(\omega) + 1\}\chi''(\omega) \tag{1}$$

where $n(\omega) = \{\exp(\hbar\omega/kT) - 1\}^{-1}$ and I_0 are the Bose factor and a constant related to the experimental conditions, respectively.

Figure 1 shows the temperature variation of the broadband dynamical susceptibility spectra. As the analysis by MCT was unable to reproduce well the present spectra [7], a phenomenological fitting is discussed below. The line shape of the susceptibility was analysed by the superposition of α relaxation, a fast relaxation and the boson peak as shown:

$$\chi''(\omega) = \chi''_\alpha(\omega) + \chi''_{fast}(\omega) + \chi''_{bp}(\omega) \tag{2}$$

where for the α relaxation the Davidson–Cole formula [8] was used, which is closely related to a stretched exponential function [9],

$$\chi_\alpha(\omega) = \chi_\alpha(\infty) + \{\chi_\alpha(0) - \chi_\alpha(\infty)\}\{1 + i\omega\tau_\alpha\}^{-\beta} \qquad (0 < \beta < 1). \tag{3}$$

The temperature dependence of the α-relaxation time τ_α obeys the Vogel–Fulcher–Tammann law [10, 11]

$$\tau_\alpha = \tau_0 \exp\{A(T - T_0)^{-1}\} \tag{4}$$

where A and τ_0 are constants, and T_0 is the Vogel–Fulcher–Tammann temperature, which is an idealized glass transition temperature and not far from the Kauzmann temperature [12]. In the fitting, the parameters were determined from the dielectric data.

The fast relaxation was given by the Debye form

$$\chi_{fast}(\omega) = \Delta\chi_{fast}\{1 + i\omega\tau_{fast}\}^{-1} \tag{5}$$

where τ_{fast} is a fast relaxation time, and $\Delta\chi_{fast}$ is a constant.

In order to describe the boson peak a formula originating from the disorder-induced model was used. The physical meaning of this is questionable because the photoelastic constant usually shows no remarkable anomaly, while it can reproduce the line shape of the boson peak accurately [13].

$$\chi_{bp}(\omega) = C\omega^2\{\omega^2 + \omega_{bp}^2\}^{-2} \tag{6}$$

where C is a constant, and ω_{bp} is the peak frequency of the boson peak. The values of the two parameters were determined from the spectra at 90 K where the contribution of the α
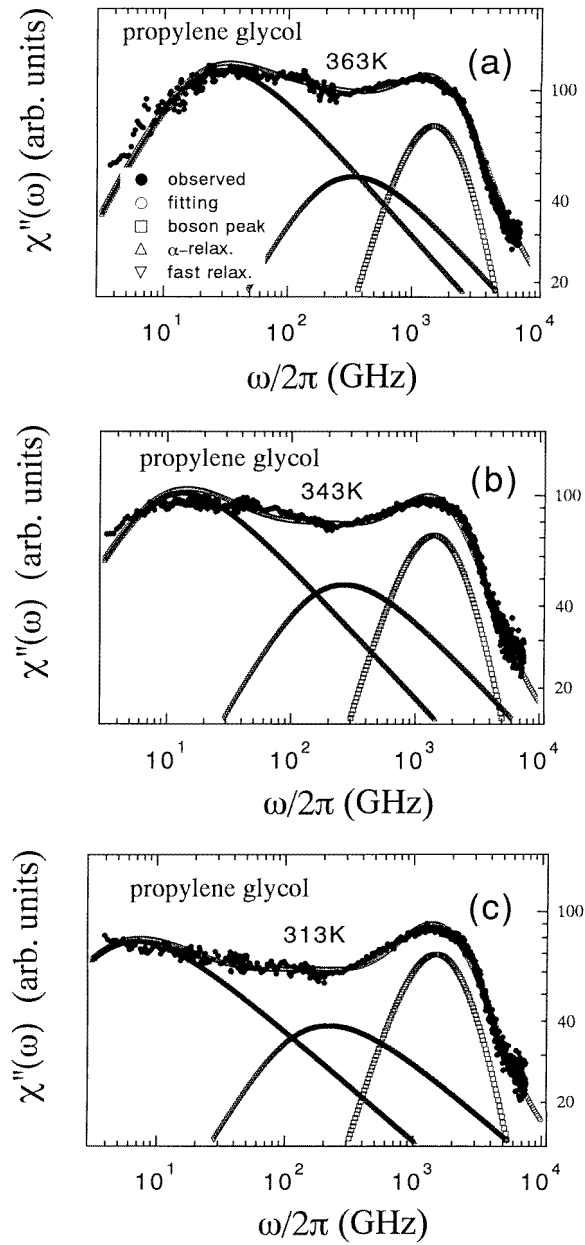
Figure 1. Broadband dynamical susceptibility spectra of propylene glycol measured by Raman and Brillouin scattering experiments. (a) 363 K, (b) 343 K, (c) 313 K, (d) 293 K, (e) 265 K, (f) 240 K.

and fast relaxations is negligible. The spectra were fitted by (2) and are shown in figure 1 with three components.

At 363 K the α-relaxation peak appears at about 12 GHz, and with decreasing temperature its maximum shifts remarkably to lower frequency according to the Vogel–Fulcher–Tammann law. In contrast, the peak frequency of the fast-relaxation and the boson
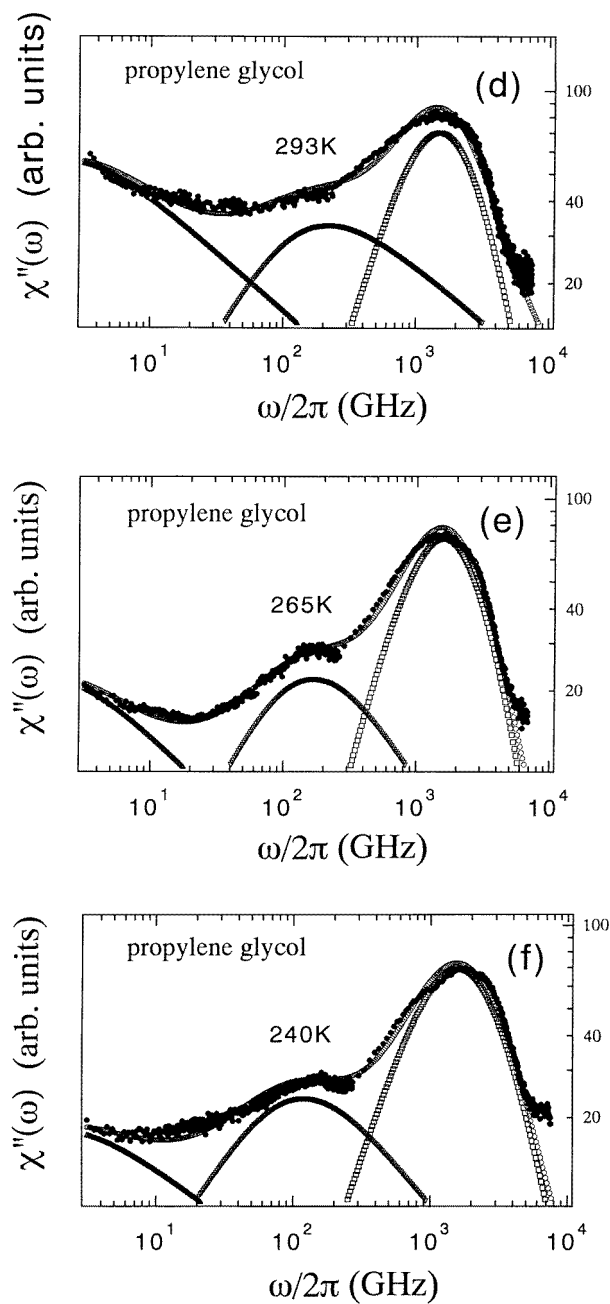
Figure 1. (Continued)

peaks hardly change with temperature. The intensity of the fast-relaxation peak decreases gradually towards 140 K as shown in figure 2. Thus it appears that

$$\Delta\chi_{fast} = a(T - 140 \text{ K}) \tag{7}$$
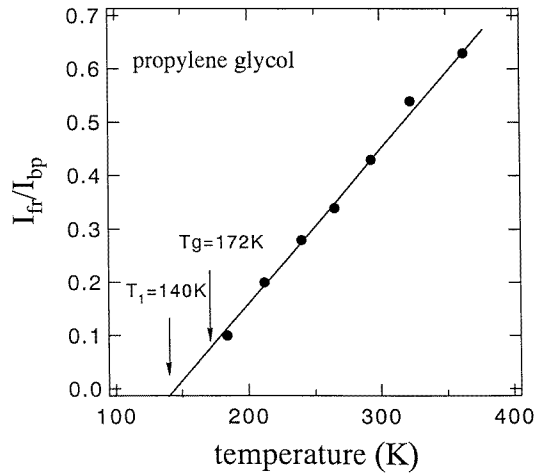
where a is a constant.

Figure 2. Temperature dependence of the fast relaxation intensity determined from the fitting of depolarized light scattering spectra.

This temperature is in the range of $T_0 = 117$ K [14] or 122 K [15] obtained from dielectric measurements. On the other hand, when the free volume is calculated by the total thermal expansion above T_0, it obeys

$$V_{free}(T) = b(T - T_0) \tag{8}$$

where b is a constant [16]. Since both temperature dependences are similar, this suggests that the fast-relaxation intensity is correlated to the free volume. In fact, the actual temperature dependence is not exactly linear as in (7). Recently the temperature dependence of the free volume was accurately determined by positron-annihilation experiments [17]. However, no data have been reported yet in propylene glycol. Very recently this problem was also discussed analytically on the basis of the coupling model between fast-relaxation and boson peak vibrations [18].

On the other hand, the Vogel–Fulcher–Tammann law for the α relaxation may be derived from (8) and the Doolittle law [20] given by

$$\tau_\alpha = \tau_0 \exp(A/V_{free}). \tag{9}$$

From the comparison of (7), (8) and (9) it is concluded that the fast relaxation is connected with the α relaxation through the free volume above T_0.

3.2. Temperature dependence of relaxation processes

As characteristic features of a supercooled liquid the two-step relaxation processes are predicted by the mode coupling theory and by some molecular dynamics simulations. A number of experimental data were reported recently in relation to this fact [21]. However most studies were confined to a limited frequency range. Therefore the broadband range is of advantage to define the various relaxation processes systematically.

The temperature dependences of the boson peak and two fast relaxations are shown in figure 3 together with the α relaxation determined by dielectric and photothermal measurements [22]. The boson peak hardly depends on temperature. The fast relaxation determined from the depolarized spectra also is temperature independent. A similar result
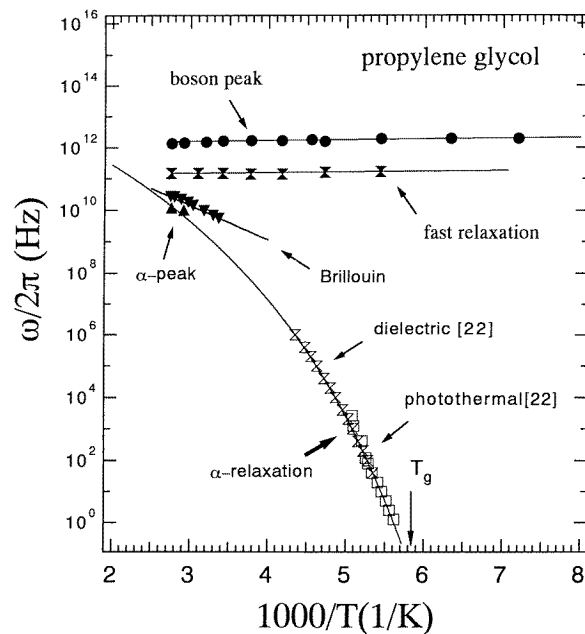
Figure 3. Temperature dependence of the relaxation times obtained from Raman and Brillouin scattering, dielectric and photothermal measurements.

is reported for o-terphenyl [5], and suggests that this process is the fast β-process predicted by MCT. Another fast process was obtained from the Brillouin components of the polarized spectra. In a previous report of the Brillouin scattering from propylene glycol, the relaxation time was determined only at the temperature at which the half width of the Brillouin component becomes a maximum, and its origin was interpreted as the high-frequency part of the α relaxation [19]. However, in the present work the temperature dependence of the relaxation time was accurately determined by fitting the polarized spectra and it shows no marked temperature dependence, similar to that of the α relaxation. In the supercooled liquid this process become faster than the α relaxation as determined by dielectric and photothermal measurements [22]. This process does not bifurcate from the α relaxation at T_c, so it cannot be the Johari–Goldstein β process [2]. Its temperature dependence obeys the Arrhenius law and the activation energy, about 6 kcal mol^{-1}, may be related to the rotation of the alkyl group. However, in the present analysis of the Brillouin spectra, the relaxation is determined under the assumption of a single Debye relaxation time [23]. Therefore the possibility still remains for a coupling of acoustic phonons to both slow and fast relaxations as discussed in [24]. Therefore, to clarify this difference, extended analysis is now in progress.

4. Conclusions

We have studied the temperature dependence of dynamical properties of an intermediate glass over a broadband range of frequency from 1 GHz to 10 THz using a combination of Brillouin and Raman scattering measurements. Our purpose was particularly to clarify the temperature behaviour of a fast relaxation, which is still unclear. The depolarized spectra

observed were analysed simply by the superposition of the α relaxation, a fast relaxation and a boson peak, because the introduction of the coupling among these modes increases the ambiguity in fitting the gently undulating spectra. It is found that the fast relaxation time is approximately temperature independent, similar to the peak frequency of a boson peak. The intensity of the fast relaxation decreases in connection with free volume, and seems to transfer into that of the boson peak. This fact suggests that the fast relaxation and the boson peak have a common origin on an intermediate correlation length.

Another fast relaxation process was found from the viscoelastic analysis of LA Brillouin components in the polarized spectra. Its relaxation time is temperature dependent, and lower than the fast relaxation time determined from the depolarized spectra. The value of its activation energy suggests that its origin is the rotational motion, but further accurate study is required to clarify its contribution to a glass transition.

In this paper we discussed the temperature behaviour of the α relaxation, two kinds of fast relaxation and the boson peak. Although these four motions seem to merge into a microscopic motion near the melting temperature, they exist as macroscopic, mesoscopic and microscopic motions at low temperatures, and play some roles in a glass transition.

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