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The liquid–glass transition in n-propanol: the pressure dependence of the Brillouin spectra

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Abstract. The liquid–glass transition in n-propanol has been investigated in detail by measuring the pressure dependence of the Brillouin scattering spectra. Using a home-made Brillouin microscope equipped with a diamond anvil cell, backward-geometry spectra were measured as a function of pressure from 1 atm to 8.3 GPa. As the pressure increased, the Brillouin shift changed its slope from 5 GPa, at which the liquid–glass transition is induced. The experimental data were analysed using a spectral function based on the theory of viscoelasticity and the Vinet equation of state. This yielded the pressure dependences of the limiting zero- and infinite-frequency sound velocities, the relaxation time, and the density.

1. Introduction

As a glass-forming liquid is supercooled, its viscosity and relaxation time τ increase until the temperature reaches the glass temperature T_g (Angell 1988). These phenomena indicate structural relaxation, and therefore sound velocity dispersion is observed. The structural relaxation of viscoelastic liquids is a very interesting subject (Angell 1995). However, the fundamental mechanism of the glass transition is still not fully understood. In particular, a few experiments have been performed to determine the pressure dependence of the dynamics of viscoelastic systems. It is very important to determine the pressure dependence of the structural and dynamical properties of liquids (Oliver *et al* 1991). This can be expected to give some information different from the results of temperature dependence studies.

Brillouin scattering (BS) is a useful technique for studying the dynamics of various viscoelastic liquids. In particular, the use of a tandem Fabry–Perot (FP) interferometer enables one to measure BS spectra over a very wide frequency range. Therefore, a tandem FP is useful in studying structural relaxation processes in viscoelastic liquids. Also, Brillouin microscopy (Takagi and Kurihara 1992) makes it easy to apply a diamond anvil cell (DAC) (Ahart *et al* 1996). We used it to investigate the structural relaxation of liquids as a function of pressure.

The sample used is pure n-propanol, which is a monohydric alcohol (Yatsu *et al* 1994). n-propanol is known to be a glass-forming alcohol, even under slow-cooling conditions. According to the Angell definition of ‘fragility’, it is intermediate between a fragile liquid and a strong liquid.

In the analysis (Oliver *et al* 1991) of Brillouin scattering data as a function of pressure, the velocity and linewidth data are fitted self-consistently using the Vinet equation of state (Macdonald 1969, Vinet *et al* 1987) and the spectral function derived from the viscoelastic

theory (Montrose *et al* 1968, Tao *et al* 1992) in the single-relaxation-time approximation. We obtained the pressure dependences of the limiting zero- and infinite-frequency sound velocities, the relaxation time, and the density. In this work, we discuss the structural and relaxation properties of n-propanol.

2. Experimental procedure and results

The measurements were performed using a Brillouin scattering microscopy (Takagi and Kurihara 1992) with the back-scattering geometry. A longitudinal single-mode Ar-ion laser was used as a light source. The laser was operated at a wavelength of 514.5 nm with an average power of about 100 mW. Brillouin spectra were obtained using a Sandercock 3–3-pass tandem FP. However, a multipass method different from that of the Sandercock system was utilized using two corner cubes. The sample was n-propanol of reagent grade with a purity of 99.5 %. The pressure on the sample was generated using a conventional DAC, and calibrated by measuring the ruby fluorescence. The pressure was also corrected using the Brillouin shifts of the n-propanol measured.

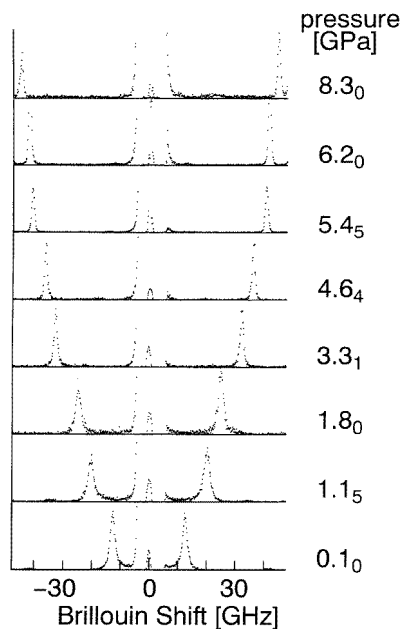


Figure 1. The pressure dependence of the Brillouin spectra below 50 GHz. The central peaks show the Rayleigh line cut by the shutter.

The pressure dependence of the Brillouin spectra below 50 GHz up to the maximum pressure of 8.3 GPa is shown in figure 1. We assigned 1000 channels for each spectrum, which was scanned for 10 s. When the pressure increased, the Brillouin peak intensity for the longitudinal acoustic mode decreased only slightly, so the peak remained sharp. This is one advantage of measuring the pressure dependence as opposed to the temperature dependence. The Brillouin spectra for the transverse acoustic mode cannot be observed, due to the fact that backward-scattering geometry is used. Figure 2 shows the pressure dependence of the peak shifts $\Delta\nu$ and the peak full widths (2Γ). The true Brillouin half-widths Γ were estimated by extracting the half-widths of the central line from the observed

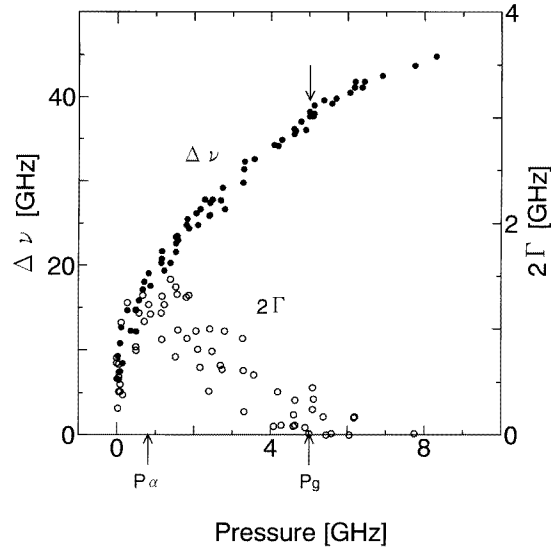


Figure 2. The pressure dependence of the Brillouin shift $\Delta\nu$ and width 2Γ (FWHM). P_g and P_α represent the pressure at which the glass transition occurs and the pressure at which Γ is a maximum.

half-widths (Oliver *et al* 1992). The central component of the Brillouin spectra is broadening beyond the limit of the experimental accuracy. Therefore, the Rayleigh central linewidth was taken as the overall instrumental linewidth. The scatter of the estimated widths is large due to the low accuracy of the pressure measurement, which is at worst ± 0.2 GPa. With increasing pressure, the Brillouin shift continued to increase up to 8.3 GPa and showed a slight change of curvature at about 5 GPa (P_g), at which point the glass transition occurred. The linewidth reached a maximum value at a low pressure of about 0.8 GPa (P_α) and then decreased gradually.

3. Data analysis and discussion

In light scattering spectroscopy, the spectrum $I(\omega)$ is generally given by

$$I(\omega) = (n(\omega) + 1) \text{Im} \chi(\omega). \quad (1)$$

Here, ω is the angular frequency, $n(\omega)$ is the Bose factor and $\text{Im} \chi(\omega)$ is the imaginary part of the dynamic susceptibility, which is determined using models. The expression for χ used in viscoelastic theory (Montrose *et al* 1968, Tao *et al* 1992), can be simplified to

$$\chi(\omega) = \chi(0) \frac{\omega_0^2}{\omega_0^2 - \omega^2 + i\omega\gamma^*(\omega)} \quad (2)$$

with $\omega_0^2 = V_0^2 q^2$ and

$$\gamma^*(\omega) = (\eta_0 q^2 / \rho) + (V_\infty^2 - V_0^2) q^2 \phi(\omega). \quad (3)$$

Here, η_0 is the frequency-independent longitudinal viscosity, n is the refractive index, and $q = (4\pi n / \lambda_i) \sin(\theta/2)$ is the momentum transfer determined with the following scattering parameters: scattering angle θ and incident wavelength λ_i (the sound velocity V can be estimated from the Brillouin peak shift ω using $q = \omega/V$). Then, V_0 and V_∞ are the

velocities in the low-frequency and high-frequency limits, respectively. In the single-relaxation-time approximation, $\phi(\omega)$ is given by the following Debye equation:

$$\phi(\omega) = \frac{\tau}{1 - i\omega\tau} \quad (4)$$

where τ is the relaxation time. It is found that $\chi(\omega)$ in equation (2) is equivalent to a damped harmonic oscillator (DHO) (Takagi 1979) if $\gamma^*(\omega)$ is frequency independent.

In order to obtain the velocities V_0 and V_∞ and the relaxation time τ from the pressure dependence of the Brillouin spectra, we did not try to fit the experimental spectra directly to the spectral function in equation (2) (Takagi et al 1995), because the observed spectral profile contains a large contribution from the instrument function (Oliver et al 1992), and the density ρ of n-propanol is strongly dependent on pressure. Instead, using the fitting method proposed by Oliver et al (1991), we estimated the parameters V_0 , V_∞ , and τ using the following equations derived from the spectral function and the Vinet equation of state (EOS) (Vinet et al 1987). Using the spectral function, the Brillouin shift $\omega(P)$ and the Brillouin linewidth $\Gamma(P)$ of the longitudinal acoustic mode can be represented in the form

$$\omega^2(P) = \frac{\gamma_R(P)K(P)q^2}{\rho(P)} + \frac{M(P)q^2}{\rho(P)} \frac{\omega^2(P)\tau^2(P)}{1 + \omega^2(P)\tau^2(P)} \quad (5)$$

$$\Gamma(P) = \frac{M(P)q^2}{4\pi\rho(P)\omega(P)} \frac{\omega(P)\tau(P)}{1 + \omega^2(P)\tau^2(P)}. \quad (6)$$

Here, K is the static isothermal bulk modulus, M is the relaxation component of the modulus, and γ_R is the specific-heat ratio, C_p/C_v . K and M , respectively, can be related to the velocities in equations (2), (3), and (4) as follows:

$$\gamma_R(P)K(P)/\rho(P) = V_0^2 \quad (7)$$

and

$$M(P)/\rho(P) = V_\infty^2 - V_0^2. \quad (8)$$

Here, we neglected η_0 , since it has a small value.

It is fundamentally necessary to know the pressure dependence of $\rho(P)$ and $K(P)$ from the Vinet EOS before using equations (5) and (6). The Vinet EOS relates the pressure P and the relaxed isothermal bulk modulus K to $X = (\rho_0/\rho)^{1/3}$ as follows:

$$P(X) = 3K(0) \left\{ \frac{1-X}{X} \right\} e^{\eta(1-X)} \quad (9)$$

where

$$\eta \equiv \frac{3}{2} \left\{ \left. \frac{\partial K}{\partial P} \right|_{P=0} - 1 \right\}. \quad (10)$$

Then,

$$K(X) = \frac{K(0)}{X^2} [2 + (\eta - 1)X - \eta X^2] e^{\eta(1-X)}. \quad (11)$$

In practice, the fitting procedure was carried out as follows. The pressure P and the bulk modulus K are functions of X together with $K(0)$ and an adjustable parameter η in equation (11).

(1) $K(0)$ was obtained from $\omega(0)$, the value of the Brillouin shift at atmospheric pressure (atm). Here, $\rho(0) = 799.5 \text{ kg m}^{-3}$ and $n = 1.39$ were used in the calculation. The pressure dependence of n is neglected, hereafter.

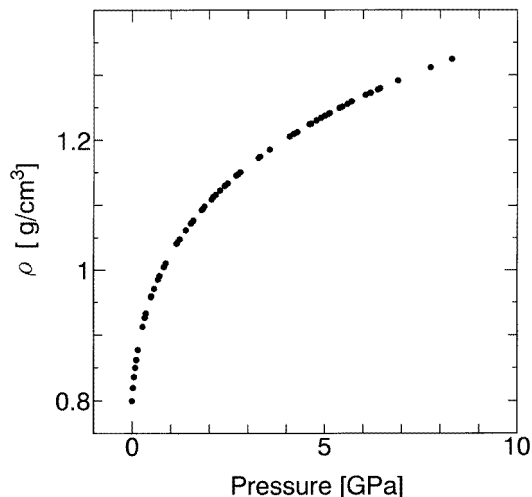


Figure 3. The pressure dependence of the density ρ .

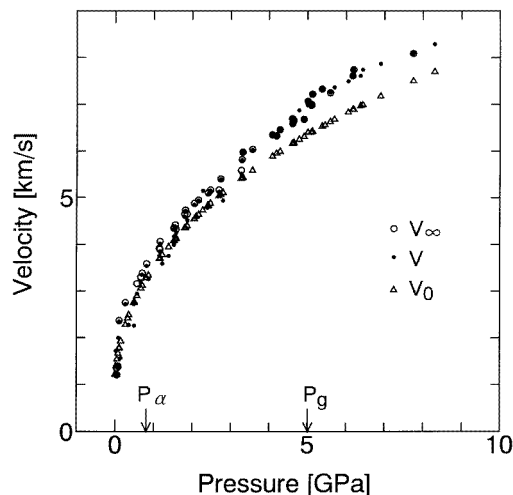


Figure 4. The pressure dependence of the velocity V_∞ in the high-frequency limit, the observed velocity V , and the velocity V_0 in the low-frequency limit.

(2) The values of K/ρ and M/ρ were estimated using equations (5) and (6) for the condition $\omega\tau = 1$ and a pressure of $P_\alpha = 0.8$ GPa, at which the linewidth reached a maximum. Here, we used $\omega(P_\alpha) = 114$ GHz ($\Delta\nu = 18.2$ GHz) and $\Gamma(\text{HWHM}) = 0.6$ GHz.

(3) The value of η was determined using equation (11) to fit the value of K/ρ at P_α obtained in step (2), and the value of $K(0)$ at 1 atm obtained in the first step; hence $\eta = 17$.

(4) $K(P)$ and $\rho(P)$ were estimated using equations (9) and (11). To our knowledge, there are no data available that can be compared with these results. The pressure dependence of ρ obtained is shown in figure 3.

(5) $M(P)$ and τ were obtained using equations (5) and (6).

(6) The whole process was repeated until self-consistent values were obtained.

The pressure dependences of the velocities V_0 , V_∞ , and V are shown in figure 4. None of the curves obtained are linear with respect to pressure. The curves are sensitive to the value of P_α estimated at the maximum linewidth from the broad peak of the scattered linewidth in figure 2. Therefore, the curves are valid within the error of the measured value of the pressure. The velocity V_0 in the low-frequency limit is equal to the observed V up to about P_α , and diverges from V with increasing P . The observed velocity V reaches V_∞ at P_g and is equal to it above P_g , where the n-propanol is a glass. It appears that the relaxation of n-propanol occurs over a wide range of pressure. These results cannot be compared directly with those for the temperature dependence. Therefore, we expressed the results as a function of ρ_0/ρ rather than P in figure 5. This is very similar to the result obtained as a function of temperature (Pinnow *et al* 1967). It is assumed that ρ_0/ρ is a parameter related to temperature. From figures 4 and 5, it is found that the relaxation process starts at a low pressure of less than 1 GPa, and velocity dispersion is observed over a wide range of pressure.

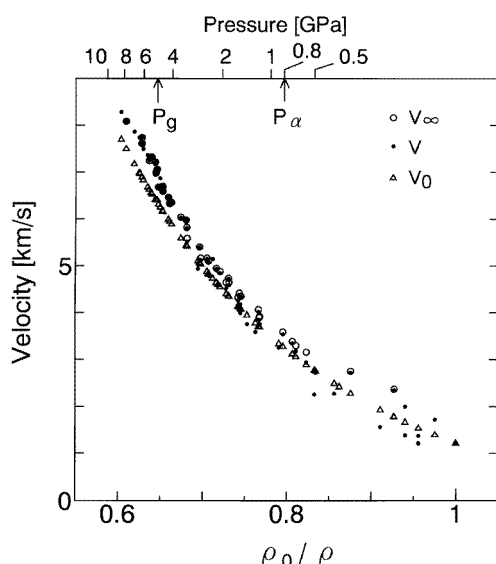


Figure 5. The velocities V_∞ , V , and V_0 as functions of $\rho_0\rho$.

Next, the relaxation time τ is estimated using two methods, i.e. directly from equations (5) and (6), and using the following expression (Torell 1985) derived from equations (5) and (6):

$$\tau(P) = \frac{1}{4\pi\Gamma} \frac{V^2 - V_0^2}{V^2}. \quad (12)$$

The values of τ obtained are shown in figure 6. At P_α , the value of τ is 8.0×10^{-12} s, which is obtained using the condition $\omega\tau = 1$ from $\omega(P_\alpha)$. At present, we do not know of a suitable model for the pressure dependence of the relaxation time. It is assumed that the models corresponding to the Arrhenius and Vogel–Tammann–Fulcher laws for the temperature dependence of τ can also be applied for the pressure dependence. However, due to the large scatter and weak pressure dependence of τ , it is uncertain whether the Arrhenius law or the Vogel–Tammann–Fulcher law is applicable.

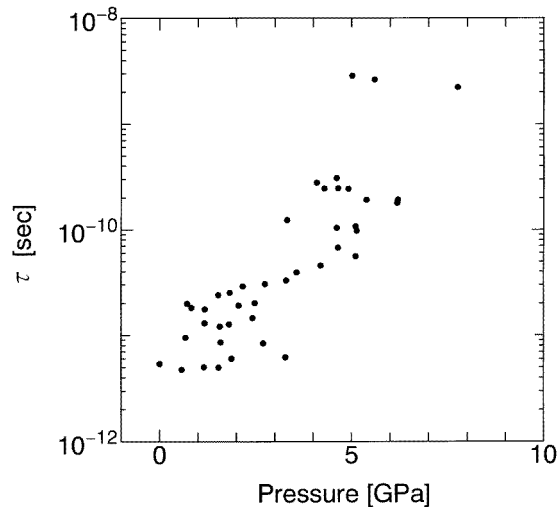


Figure 6. The pressure dependence of the relaxation time τ .

4. Conclusion

In order to investigate the relaxation of the liquid–glass transition induced by pressure in n-propanol, the pressure dependence of the Brillouin spectra was measured. A self-consistent analysis of the Brillouin spectra was performed using expressions for the spectral function based on the viscoelastic theory with the single-relaxation-time approximation and the ‘universal’ Vinet equation of state. As a result, the pressure dependences of the velocities V_0 and V_∞ , in the low-frequency and high-frequency limits, respectively, and the relaxation time τ were estimated. It was found that the relaxation of n-propanol occurs over a wide range of pressure, from below 1 GPa to P_g , and that ρ_0/ρ can be considered as a parameter corresponding to temperature.

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