The effect of structural relaxation on the Rayleigh–Brillouin spectra of liquids consisting of chain molecules

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The temperature dependence of the Rayleigh–Brillouin spectrum in the n-tetracosane melt has recently been interpreted in terms of an onset of a mesomorphic transition in the liquid state. The present paper reports the results of temperature dependent Rayleigh–Brillouin measurements on di(2-ethyl hexyl) sebacate (DOS), which is chemically similar to n-tetracosane. DOS has a lower melting point and thus a broader liquid range. It displays a temperature dependent behaviour similar to that of n-tetracosane. It is shown that the Rayleigh–Brillouin data of both systems can be described by the generalized hydrodynamic theory previously proposed by Lin and Wang. The temperature dependence of the Rayleigh–Brillouin spectra can be attributed to the relaxation of the longitudinal stress modulus. There is no need to postulate a phase transition.

(Keywords: chain molecules; hypersonic dispersion; Landau–Placzek ratio; structural relaxation)

INTRODUCTION

Rayleigh–Brillouin scattering of chain molecules arises from fluctuations in the centre of mass position and the orientation of chain segments. The fluctuations in the centre of mass position result in local fluctuations of the particle number density. The density fluctuations give rise to an isotropic spectrum, consisting of a central Rayleigh component due to entropy fluctuations and a pair of symmetrically shifted Brillouin sidebands due to the longitudinal acoustic waves associated with pressure fluctuations. The fluctuations in the orientation of chain segments also contribute to the spectral intensity of polarized (VV) scattering. Recent studies of molecular liquids which can be supercooled have shown that, via a translation–rotation coupling, the orientation fluctuations can cause the shear viscosity to relax, thereby making the bulk viscosity (or the bulk modulus) play a dominant role in determining the VV Rayleigh–Brillouin spectra of molecular liquids above T_g[1-3]. Consistent studies of the effect of the rotation–translation coupling can be carried out by simultaneous measurements of the VV and VH (depolarized) spectra[2,4].

The longitudinal sound velocity V_s can be determined by measurement of the Brillouin frequency shift f_B (in Hz) via

$$V_s = f_B/q \tag{1}$$

where $q = (4\pi n/\lambda_0)\sin\theta/2$ is the amplitude of the scattering vector. Here n is the refractive index of the medium, λ_0 is the wavelength of the incident light *in vacuo* and θ is the scattering angle.

Of particular interest for this article is the observation that for n-tetracosane in the liquid state the sound velocity V_s does not depend linearly on temperature but displays a gradual increase in the slope near 110°C. It was suggested by Krüger *et al.*[5-7] that this nonlinear behaviour was associated with a mesomorphic phase transition. This interpretation was questioned, however, by Patterson *et al.*[8] where both the longitudinal Rayleigh–Brillouin spectrum and the depolarized Rayleigh spectrum were studied as a function of temperature up to 240°C.

In order to clarify the nature of this non-linear behaviour in n-tetracosane we have carried out polarized Rayleigh–Brillouin measurements on di(2-ethyl hexyl) sebacate $C_{26}H_{50}O_4$[DOS], which is chemically similar to n-tetracosane ($C_{24}H_{50}$). Above 51°C, the melting temperature of n-tetracosane, DOS shows a temperature dependence of both the sound velocity V_s and the Brillouin linewidth Γ_B almost identical to that of n-tetracosane. However, due to its much lower melting temperature ($T_m = -48$°C), a temperature range in the liquid state greater than that of n-tetracosane can be covered in the light scattering measurement.

For comparison, we have also repeated the measurements of the Rayleigh–Brillouin spectra of two n-tetracosane samples (Riedel de Haën, Wiley Organics) from 51°C to 238°C. It is shown in this paper that the frequency shifts f_B, the linewidths Γ_B of the Brillouin doublet, as well as the Landau–Placzek ratios LPR of both n-tetracosane and DOS can be described by the generalized hydrodynamic theory of Lin and Wang[9] without postulating the onset of a mesomorphic transition.

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EXPERIMENTAL

The polarized Rayleigh–Brillouin spectra were taken with an optical system similar to that reported previously[10]. The excitation light at 400 mW was an etalon selected single frequency line at 514.5 nm from a Spectra-Physics-165 Argon Ion Laser. The scattered light collected at $\theta = 90°$ was spectrally analysed with a Burleigh DAS-10 stabilized Fabry–Perot interferometer operating in triple-pass. The finesse of the complete optical system was about 50. In order to provide a sufficient separation of the Brillouin lines over the entire temperature range studied, plate separations were set to give free spectral ranges of 22.2 GHz for the DOS and 13.2 GHz for n-tetracosane.

To obtain dust free samples so that accurate intensity data could be obtained, all samples used in this study were purified first by centrifugation in the melt at about 65°C–70°C for five hours at 9000 rpm and then filtered directly into a clean rectangular optical cell. The purity of the samples was manifested by the low Landau–Placzek ratio (*LPR*), which was at high temperatures approximately 0.28 and thus very close to the high temperature limit $LPR_{T\to\infty} = \gamma - 1$ $(\gamma = C_p/C_v)$ to be expected from theory.

The spectral data were collected over two Fabry–Perot orders with a multichannel analyser, which contains at least 400 points. The instrumental function was determined by using a standardized emulsion doped quartz cube. The instrumental spectrum was numerically convoluted with three Lorentzians (one central peak and two shifted sidebands) to fit the observed spectrum. This calculate-and-compare procedure allows the correct determination of the frequency shift f_B and the linewidth Γ_B of the Brillouin peak.

For the evaluation of V_s according to equation (1) the temperature dependence of n is required. It was measured in an Abbé refractometer in the range 20°C–170°C, n-values outside this range were obtained by linear extrapolation.

RESULTS AND DISCUSSION

The temperature dependence of f_B and Γ_B for DOS is shown in *Figure 1*. f_B is seen to increase continuously with decreasing temperature. At temperatures above 380 K an almost linear temperature dependence is observed. However, a continous change of slope is found between 235 K and 380 K. This change is accompanied by gradual changes in Γ_B. As T is lowered, the Γ_B value increases, reaches a maximum at about 273 K and then decreases again at still lower temperatures. This temperature dependence behaviour of f_B and Γ_B for the DOS resembles that usually found in both viscoelastic polymeric and non-polymeric liquids[11–14]. The effects have been shown to be due to structural relaxations[9,14,15].

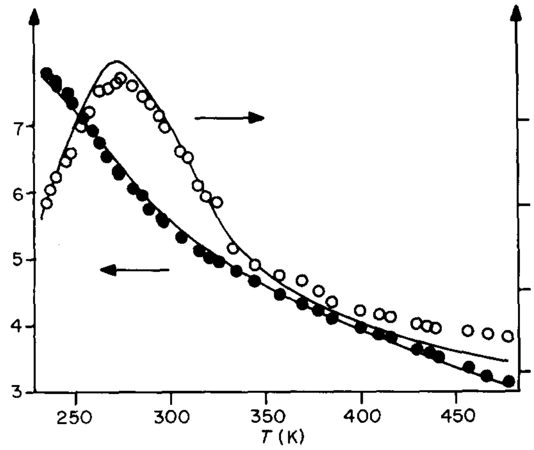

Figure 1 Temperature dependence of f_B (●) and Γ_B (○) for DOS. The solid lines were calculated from theory[9] using the values of *Table 1*

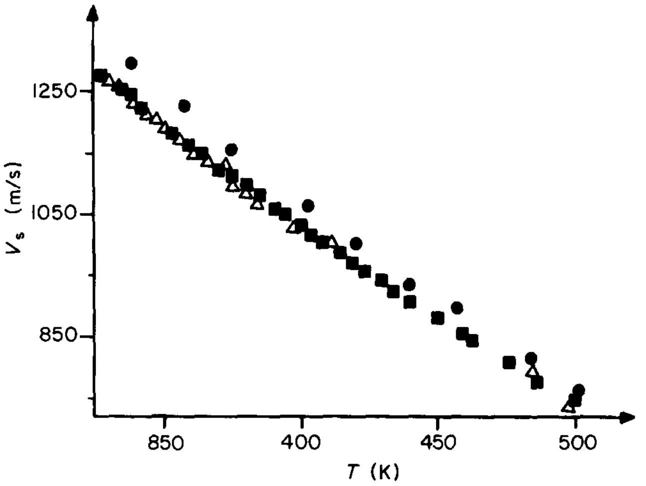

Figure 2 Comparison of the temperature dependence of the hypersonic velocity V_s of n-tetracosane obtained in various laboratories (■) this paper, (●) Patterson *et al.*[8], (△) Krüger[5]

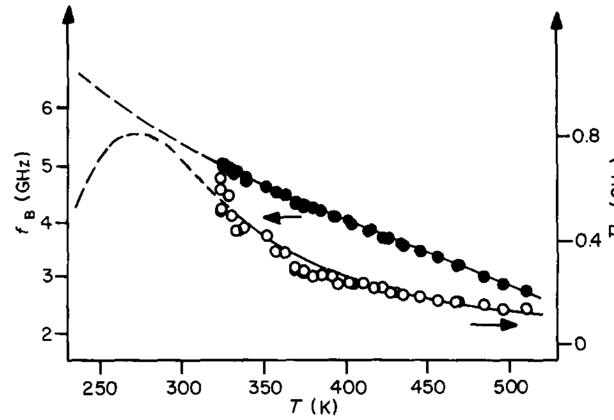

Figure 3 Temperature dependence of f_B (●) and Γ_B (○) for n-tetracosane. The solid lines were calculated from theory[9] using the values of *Table 1*

Figure 2 shows a comparison of data of the longitudinal sound velocity V_s of the n-tetracosane melt obtained in various laboratories. The presently determined V_s values are lower than the results of Patterson *et al.*[8], but are in good agreement with those reported by Krüger[5].

Figure 3 shows f_B and Γ_B of n-tetracosane as a function of temperature obtained in our laboratory (our Γ_B values lie between those reported in refs. 5 and 8). Above the melting point f_B and Γ_B decrease continuously with rising temperature. It is found that the curves $f_B(T)$ and $\Gamma_B(T)$ for n-tetracosane and DOS practically coincide. Owing to the onset of crystallization, however, a maximum in the linewidth for n-tetracosane corresponding to the one of DOS at lower temperatures cannot be observed.

The chemical similarity that exists in these two samples thus suggests that in both cases the same mechanism is responsible for the temperature dependence of f_B and Γ_B.

In order to ascertain whether the results obtained for these two systems could be described as arising from structural relaxations, we used the theory developed by Lin and Wang[9] to interpret the data. Ref. 9 gives a generalized hydrodynamic theory based upon the assumption that the density fluctuations are coupled to fluctuations of the longitudinal momentum and energy densities. The Zwanzig–Mori linear response theoretical technique was used to compute the Rayleigh–Brillouin spectral density at finite q. In the small q limit, it has been shown that this theory reduces to that which can be obtained from the linear viscoelastic constitutive equation for the stress–strain relation[16].

Even in this limit, the general result for the Rayleigh–Brillouin spectral density is rather complex. However, since Brillouin scattering spectra are not very sensitive to relaxation time distributions, Lin and Wang have computed the Rayleigh–Brillouin spectrum by assuming that the longitudinal modulus relaxes with one single relaxation time τ_s. In this simplification, the Rayleigh–Brillouin spectrum depends on this relaxation time τ_s, the ratio of the specific heats $\gamma(=C_p/C_v)$, the unrelaxed adiabatic sound frequency ω_s, the unrelaxed longitudinal (or bulk) modulus $\alpha_2=(R-1)\omega_s^2$ (R = relaxation strength), and the thermal diffusivity D_T. The theory predicts a four peak structure, consisting of an unshifted Rayleigh peak, a symmetrically shifted Brillouin doublet, and an unshifted peak known as the Mountain peak, whose width is determined by τ_s, ω_s and α_2.

This theory shows that f_B and Γ_B are significantly affected by the relaxation of the bulk (or longitudinal) modulus. Relaxation of the bulk modulus can occur either through intramolecular energy transfer processes or through structural relaxation processes. For liquids of chain molecules, the structural relaxation process dominates the dynamic behaviour of the bulk modulus.

Although the expression for the spectral power density is rather complex (even assuming a single structural relaxation time), perturbation solutions for f_B and Γ_B appropriate for viscoelastic liquids are easily obtained. These are given by[9]

$$f_B=\pm\omega_s\left\{1+\frac{1}{2}\left(\frac{\alpha_2}{\omega_s^2}\right)\frac{\omega_s^2\tau_s^2}{1+\omega_s^2\tau_s^2}\right\} \tag{2}$$

$$\Gamma_B=\frac{\alpha_2\tau_s}{1+\omega_s^2\tau_s^2}+(1-1/\gamma)D_Tq^2 \tag{3}$$

where Γ_B is the full linewidth at half height.

Using a least squares fitting routine, equations (2) and (3) were used to describe the measured f_B and Γ_B data at all temperatures. In this analysis the adiabatic sound frequency was assumed to depend on the temperature as $\omega_s=\omega_s^\circ(1-aT)$, a being a constant; the mean stress relaxation time τ_s was assumed to follow an Arrhenius equation $\tau_s=\tau_s^\circ\exp(E_a/RT)$; γ was kept constant. In all experiments the relaxation frequency due to the thermal diffusivity was found to be on the order of 10^7 Hz.

The solid lines in *Figures 1* and *3* are the results of this analysis. The fitting parameters used to compute these lines are listed in *Table 1*. In the case of n-tetracosane, holding α_2 constant already yields a good description of the observed variations in f_B and Γ_B. Allowing for a slight temperature dependence of α_2 improves the fit. To show the similarity of the two systems, we have calculated τ_s at 325 K for both (see *Table 1*).

To give a consistency check regarding the various parameters used in the fits, we have computed an apparent Landau–Placzek ratio *LPR* from the experimental as well as from the theoretical spectra, where the parameters of *Table 1* were used. The procedure to obtain the intensity integrals I_C and I_B needed for $LPR=(I_C/2I_B)$ is illustrated in *Figure 4*. Part of one order of an experimental Rayleigh–Brillouin spectrum is seen consisting of the Rayleigh line R, one Brillouin line B and a broad Mountain peak, which causes the corrected intensity to be non-zero between the peaks R and B. The abscissa interval R_{max}–B_{min} between the maximum of the Rayleigh line and the minimum between Brillouin lines of neighbouring orders covers one half order of the spectrum. The measured intensity in this range is corrected for the background and then integrated to yield $(I_{tot}/2)$. Subsequently the outer half of the Brillouin peak is integrated in the limits B_{max},B_{min} to give $(I_B/2)$, since this half is least affected by the Mountain peak intensity. Finally, the integrated intensity $I_C=I_R+I_M$ of the two central peaks, i.e. the sum of the Rayleigh (R) and the Mountain peak (M), is obtained as $I_C=I_{tot}-2I_B$.

The theoretical spectra were calculated using equation 56 of ref. 9 and were then treated also as described above (not reproduced here).

The results are shown in *Figure 5*. In the high temperature range, the *LPR* depend only slightly on the temperature, the values being close to the ones expected for nonrelaxing simple liquids, i.e. $LPR\approx\gamma-1$. At lower temperatures, however, the *LPR* increase strongly. This is caused by the presence of the Mountain component I_M. While, in simple liquids ($I_C=I_R$), I_C and I_B grow with temperature proportional to one another, in the relaxing liquids n-tetracosane and DOS the central component

Table 1 Set of theoretical parameters used to calculate the theoretical curves in *Figures 3, 4* and *5*

	DOS	n-Tetracosane
$\omega_s^{325}/2\pi$ (GHz)	4.945	4.897
a (K^{-1})	1.41×10^{-3}	1.34×10^{-3}
α_2^{325} (GHz^2)	13.204	8.9
τ_s^{325} (seconds)	4.9×10^{-11}	6.7×10^{-11}
E_a (kcal mol^{-1})	3.84	3.03
γ	1.28	1.2
D_Tq^2 (MHz)	40	40

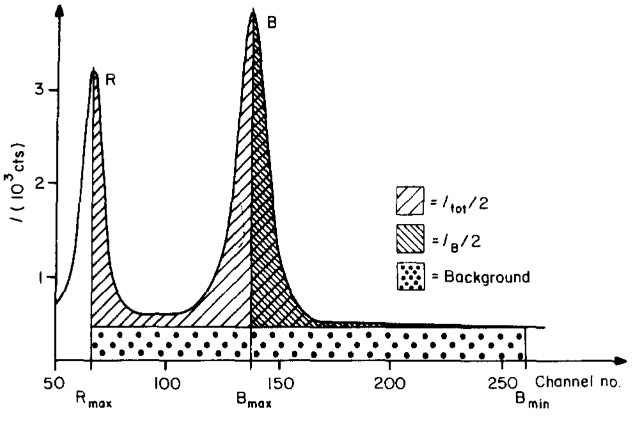

Figure 4 Rayleigh–Brillouin spectrum of DOS at 127°C to demonstrate the evaluation method for the apparent *LPR* (see text)

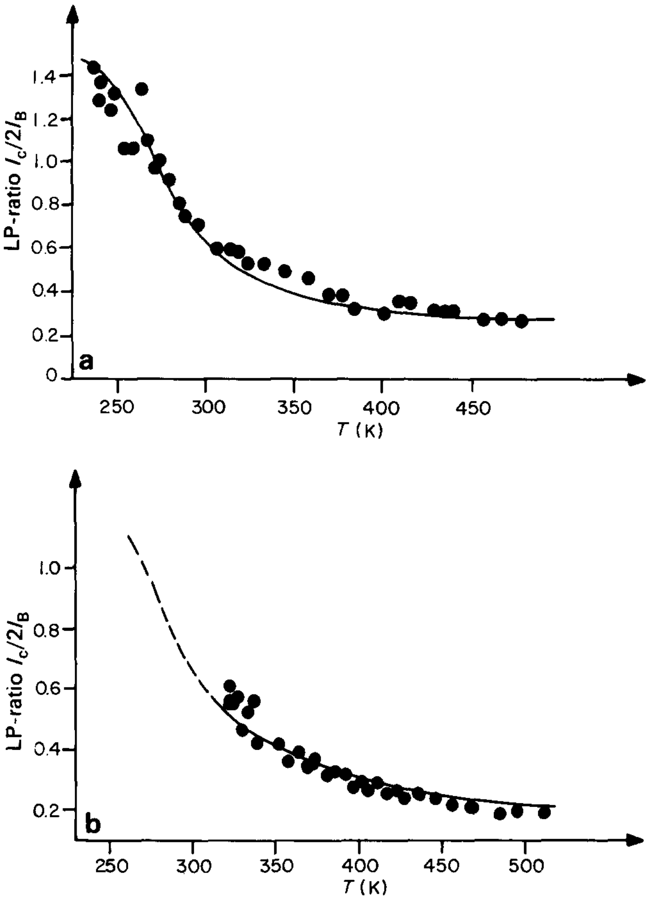

Figure 5 Apparent Landau–Placzek ratio (*LPR*) for (a) DOS and (b) n-tetracosane as a function of temperature. Points were determined from experimental spectra, the solid line was obtained from the theoretical spectra

$I_C = I_R + I_M$ was experimentally found to be constant in the entire temperature range covered. The strong increase of the *LPR* is the direct consequence.

The *LPR* obtained from the experimental and from the theoretical spectra agree well, which proves that the set of parameters in *Table 1*, which was obtained only from the experimental parameters f_B and Γ_B, is indeed a good set to describe the entire spectra.

In conclusion, this success of the relaxation theory in describing the experimental data of f_B,Γ_B, and *LPR* in a broad temperature interval, and the similarity of the Brillouin data of n-tetracosane and DOS suggest that n-tetracosane does not display a mesomorphic transition in the melt. The non-linear temperature dependence in f_B and the Brillouin linewidth maximum can be attributed to a structural relaxation mechanism. Additional results supporting this conclusion were also obtained from a depolarized Rayleigh scattering study which will be a topic of a future publication.

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REFERENCES

1 Wang, C. H., Ma, R.-J. and Lin, Q.-L. *J. Chem. Phys.* 1984, **80**, 617
2 Wang, C. H. and Zhang, J. *J. Chem. Phys.* 1985, **82**, 4332
3 Wang, C. H., Fytas, G. and Fischer, E. W. *J. Chem. Phys.* (in press)
4 O'Steen, B. L., Wang, C. H. and Fytas, G. *J. Chem. Phys.* 1984, **80**, 3774
5 Krüger, J. K. *Solid State Commun.* 1979, **30**, 43
6 Krüger, J. K., Peetz, L., Wildner, W. and Pietralla, M. *Polymer* 1980, **21**, 620
7 Krüger, J. K., Peetz, L., Pietralla, M. and Unruh, H. G. *Colloid Polym. Sci.* 1981, **259**, 215
8 Patterson, G. D., Carroll, P. J. and Pearson, D. S. *J. Chem. Soc., Faraday Trans. II* 1983, **79**, 677
9 Lin, Y. H. and Wang, C. H. *J. Chem. Phys.* 1979, **70**, 681
10 Huang, Y. Y. and Wang, C. H. *J. Chem. Phys.* 1974, **61**, 1868
11 See for example: Wang, C. H., Lin, Y. H. and Jones, D. R. *Molec. Phys.* 1979, **37**, 287
12 See for example: Higathigaki, Y. and Wang, C. H. *J. Chem. Phys.* 1981, **74**, 3175
13 Patterson, G. D. *J. Polym. Sci.* 1977, **15**, 455
14 Patterson, G. D. 'CRC Critical Reviews in Solid State and Mat. Sci.', 1980, 373
15 Lin, Y. H. and Wang, C. H. *J. Chem. Phys.* 1978, **69**, 1546
16 Wang, C. H., Fytas, G. and Zhang, J. *J. Chem. Phys.* 1985, **82**, 3405