Observation of shear-orientation coupling near isotropic-to-nematic phase transition

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Abstract. In addition to the Brillouin scattering component by thermal phonons carrying molecular translation, the fluctuation of molecular rotation appears in the light scattering spectrum due to a quasi-elastic component in case that a molecule has anisotropy in its shape. Two degrees of freedom, the translation and the rotation, interact with each other in some soft condensed matters consisting of rod-like molecules. A typical example of the coupling is seen in liquid crystals, even in the isotropic phase. Under the strong shear-orientation coupling, the shear wave phonon, which does not normally propagate in fluids, appears in the spectrum of the depolarized (VH) scattering. The spectrum has the shape of a Lorentzian curve with another Lorentzian peak subtracted, and the depth of the inner dip to the outer spectral height directly gives the coupling constant. We measured the coupling constants in the 4-cyano-4'-pentylbiphenyl (5CB) and the 4-cyano-4'-hexylbiphenyl (6! CB) with our optical beating method used for the Brillouin scattering. The obtained values of the coupling constant showed clear dependence on temperature and its behavior was interpreted as critical decreasing towards the virtual transition point of the isotropic-nematic phase transition.

1. Introduction
It is widely recognized that a shear mode phonon does not propagate in fluids, which does not possess the shear elasticity. A shear deformation in fluids is dominated by the Navier-Stokes equation, which describes the shear flow with the wave number $k$ as $\rho \ddot{v} = -\eta k^2 v$, and the temporal behavior of the shear deformation shows the exponential decay of $v \sim v_0 \exp(-\eta k^2 t)$.

In some complex fluids, the various degrees of molecular motion interfere to each other. A partial energy of the shear flow induced by the thermal fluctuation dissipates to the heat, however, the rest might be converted to that of the other internal degrees. Under the strong coupling of the shear deformation and the degree, the energy repeatedly transfers between them. Since the energy transfer is the relaxing process and takes a finite time, it looks like a periodical exchange between the different degrees.

Note here, the shear deformation is an order parameter described by the second order tensor and the degree to be coupled with the shear mode should be in the same order. The most promising candidate of such a parameter is the local anisotropy in the medium[1, 2]. The coupling process in the isotropic phase of liquid crystals was firstly pointed out by de Gennes[3] from the viewpoint of the dynamics of the local anisotropy, which is the orientational order of the anisotropic molecules generally represented by $Q_{ij}$.

In this study, we observe the thermal fluctuation of the non-diagonal component of the dielectric tensor, which carries the information on the shear deformation in liquid crystal coupling.
to the local orientational order of molecules. Very accurate light scattering measurements were carried out and we successfully observed the peaky shape of the power spectrum of the depolarized component, which indicates the spatial propagation of the periodical shear flow with the real angular frequency. The power spectrum of the non-depolarized component is also observed, which is quantitatively compared with the depolarized spectrum.

2. Experiment

2.1. Samples
Molecules of 5CB and 6CB are the suitable samples for the light scattering experiment of the present purpose, since they are tough against light exposure and their physical properties have been thoroughly investigated. The samples were purchased from Merck and used without further purification. The scattering cell was kept in a water jacket to control the sample temperature within ±0.1 K. We conducted the experiments cooling down the sample temperature gradually from the isotropic phase towards the transition temperature $T_{IN}$ to the nematic phase.

2.2. Optical Beating System
The optical beating technique has been successfully employed in the light scattering spectroscopy for the ripplon[4] and the Rayleigh-Brillouin experiments[5, 6]. The system could be also applied for the accurate measurement of the depolarized light scattering spectroscopy in liquid crystals in the vicinity of $T_{IN}$[7]. In the present study, we made effective improvements in the experimental setup and increased the sensitivity as well as the available frequency range[8]. Here, the brief account of our system is described. The light source is a cw-mode Nd-YAG laser emitting 2 W power at 532 nm. The output beam is divided with a beam sampler into two paths. The intensive one is used for the incident light, and the weak one for the reference light generating the optical beat with the scattered light. The reference beam crosses the incident light in the sample cell and is mixed with a scattered light to work as a local oscillator of the heterodyne method. The beat current supplied by a photo detector is analyzed with a spectrum analyzer. The output of the internal frequency (IF) signal from the spectrum analyzer is detected by a lock-in amplifier to gain the detection sensitivity. An acousto-optic modulator is used to shift up the frequency of the local oscillator light by 110 MHz, since the serious electric noise appearing around zero frequency is avoided. The frequency resolution of our system is determined by the bandwidth of the spectrum analyzer and is better than 10 kHz. The depolarized and polarized components are observed with the VH and VV configurations. We can readily select each of them by rotating a half-wavelength plate put into the reference path.

2.3. Propagation of shear deformation in liquid
Here, we consider three transportation coefficients, $\eta$, $\nu$ and $\mu$, which represent the viscosities with respect to the motions of shear, rotation and their coupling, respectively. Dynamics of fluid under the coupling to the orientational order is described by the expanded Euler’s equation $\sigma_v = \eta \dot{\sigma}_v + 2\mu \dot{Q}$, and the equation of motion $\rho \ddot{v} = \partial \sigma_v$, where we assume the non-compressibility of fluid. On the other hand, the orientational order is dominated by the following equation of $\dot{Q} = \nu \dot{Q} + \mu \dot{\sigma}_v$, where the force of restriction is given for the isotropic phase to $\sigma_Q = -AQ$. Replacing $A$ by $\nu \Gamma$, we obtain the power spectrum of the fluctuating shear flow as,

$$S_v(\omega) = \text{Re} \frac{1}{i\omega + \frac{\omega^2}{\rho k^2} \left( 1 - \frac{\omega^2 C}{\omega^2 + 1} \right)}.$$  \hspace{1cm} (1)

where $C$ is the coupling constant given by $C = 2\mu^2/\eta \nu$. The power spectrum of thermally excited shear flow without the coupling is given as the simple Lorentzian function, showing the excited shear flow exponentially decays with the time constant of $(\eta k^2/\rho)^{-1}$. Under the
condition of $C > 0$, the power spectrum is modified and the shear viscosity becomes complex. The shear deformation then apparently behaves like a wave.

In the actual light scattering experiment, we observe the non-diagonal component of the dielectric tensor, which directly leads to the power spectrum of the fluctuating orientational order of

$$S_Q(k, \omega) = \frac{2\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{2\Gamma \{\omega^2 + \frac{nk^2}{\rho}(1 - C)\}}{(\omega^2 - \frac{nk^2}{\rho} \Gamma)^2 + \omega^2 \{\Gamma + \frac{nk^2}{\rho}(1 - C)\}} \cos^2 \frac{\theta}{2},$$

(2)

We set the scattering angle $\theta$ enough small ($\theta \ll 3^\circ$), and then the first term of eq. (2) can be ignored. The VV spectrum showing the single Lorentzian curve with the relaxation frequency $\Gamma$ is also observed, which provides us with a precise value of $\Gamma$ at each temperature. As a result, obtained VH spectrum can be fitted with eq. (2) with only two unknown parameters of $\eta/\rho$ and $C$. Additionally, temperature dependence of $\Gamma$ determines the virtual transition temperature $T^*$, which is used in analysis of the critical behavior. The Landau-de Gennes theory predicts $\Gamma = a(T - T^*)/\nu$, where $a$ is a constant concerned with the molecular shape[3]. The isotropic phase is expected to be absolutely unstable below $T^*$, which is approximately 1 K below the actual transition point $T_{IN}$.

3. Results and Discussions

Figure 1(a) shows typical spectra of VV and VH scattering components observed for 6CB in the isotropic phase. The decay of the shear phonon clearly appears as the width of the central dip in the low-frequency region of the spectrum. The shape of the skirt in the high frequency region, on the other hand, shows the orientational relaxation, and the VV and VH spectra coincide. For the accurate comparison of both curves, the intensity of the VH spectrum is multiplied by 4/3, which is analytically determined as the fraction from the geometrical analysis of the light scattering configuration[9]. The temperature dependence of VH spectra is shown in

![Figure 1](image1.png)

**Figure 1.** (a)Typical spectra of depolarized(○) and polarized(●) components. (b) VH spectra observed at various temperatures: 305.2 K(△), 313.6 K(●), and 328.2 K(○).

Fig. 1(b). The orientational relaxation frequency rapidly decreases with temperature, and the contribution of the coupled shear flow becomes indistinctive towards $T^*$. The great advantage of our measurement system is high frequency resolution, which results in the precise determination of the coupling constant.

Figure 2 shows the detailed temperature dependences of $\Gamma$ and $C$. The virtual phase transition temperature $T^*$ of 5CB and 6CB were determined as 306.8 K and 301.2 K, respectively, from
Figure 2. Temperature dependence of the coupling constant $C$ and the relaxation frequency $\Gamma$. The open circles, closed circles, open triangle, and closed triangle denote $C_{6CB}$, $C_{5CB}$, $\Gamma_{6CB}$, and $\Gamma_{5CB}$, respectively.

the linear temperature dependence of $\Gamma$ in the vicinity of the phase transition point, in which the temperature dependence of $\nu$ can be ignored. The decreasing of $C$ with temperature is supposed to be a critical behavior towards $T^\ast$. The characteristic power-law is observed in the logarithmic plot, shown in the inset of Fig. 2, indicating all the points are in good agreement with a straight line. The critical exponents of $C$ on temperature were determined to be 0.310 and 0.316 for 5CB and 6CB, respectively.

The measurements of $C$ have been conducted for some liquids including anisaldehyde[1], triphenyl phosphate[10], ethyl benzoate[11], and so on[12, 13]. All the results, however, showed that $C$ has little dependence on temperature. Therefore, the value of the critical exponent may be characterized with respect to the isotropic-to-nematic phase transition. We expect that the result is independent on the molecular species of the liquid crystal, though other similar experiments and a theoretical prediction on the critical exponent of $C$ are absent at present.

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