Mode-Selective Dynamic Light Scattering Spectroscopy: Application to the Isotropic Phase of Liquid Crystals

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We have developed a new method of "mode-selective" dynamic light scattering spectroscopy. This method allows us to study dynamic modes usually hidden behind large fluctuations of a critical mode. Here we apply this method to measurements of three dynamic modes of the isotropic phase of liquid crystals near the isotropic-nematic transition. In conventional methods detecting thermally excited modes, the thermal diffusion and sound modes are usually overwhelmed by the orientational relaxation mode since the intensity of the last mode diverges toward the isotropic-nematic critical point. Thanks to the phase-coherent detection ability of our method, we have successfully observed the thermal diffusion and sound modes without the interference of incoherent critical orientational fluctuations.

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Dynamic light scattering (DLS) has been one of the most powerful means for investigating the dynamic properties of fluids [1]. For simple liquids, there are two dynamic modes that can be observed by DLS: the propagating sound and the thermal diffusion mode. In a frequency domain, the former yields the Brillouin doublet, whose frequency shift is proportional to the sound velocity, while the latter produces the Rayleigh line, whose linewidth is proportional to the thermal diffusivity D_T.

In contrast to simple liquids, Rayleigh scattering of complex fluids usually stems from more than one kind of diffusive or relaxational modes, reflecting the additional degrees of freedom. Rayleigh scattering of a thermotropic liquid crystal (LC) in the isotropic phase, for example, comes from both thermal diffusion and orientational relaxation modes. In conventional DLS methods, such coexistence of several fluctuation modes often lead to the overlap of Rayleigh lines in a similar frequency range. Moreover, near the isotropic-nematic (IN) transition temperature T_{IN}, the spectra of the thermal diffusion mode are often overwhelmed by those of orientational modes since the amplitude of the latter mode diverges due to the pseudocritical behavior of the orientational fluctuation mode [2–4]. Thus, it is extremely difficult to study the thermal diffusion mode or the sound mode near T_{IN} with conventional DLS methods.

It was revealed by combining the calorimetric measurements of the heat capacity at constant pressure C_P and the thermal conductivity Λ that the thermal diffusivity $D_T(=\Lambda/\rho C_P)$ (ρ being the mass density) has the critical singularity near T_{IN} in both isotropic and nematic phases [5]. On the other hand, there have been few DLS studies of the thermal diffusion mode of LC because of the difficulty mentioned above. The only exception is, to our knowledge, the work done by Urbach *et al.* [6]; they used a forced Rayleigh scattering method (FRS) to create a laser-induced temperature grating [7–9] instead of thermal fluctuations. However, the critical anomaly of D_T was not studied there.

Recently we developed phase-coherent light scattering (COLS) spectroscopy on the basis of a new principle of DLS [10–12]. In our method, we optically excite coherent dynamic modes in a sample as in FRS, instead of using thermally induced random fluctuations. Thus, our method for Rayleigh scattering (phase-coherent Rayleigh scattering, CORS) can *selectively* excite the thermal diffusion mode as largely as possible by increasing the amplitude of the optically generated temperature grating. Moreover, COLS has another advantage over conventional methods including FRS: we can detect only the scattering from the light-induced *coherent mode* while completely rejecting that from thermally induced *incoherent* fluctuations, with *phase-sensitive* optical superheterodyne detection [10,12]. This enables us to observe the thermal diffusion mode even under the influence of large incoherent fluctuations of the orientational relaxation mode without their interference.

Here we briefly explain the basic principle and the experimental configuration of our method (see [10–12] for the details). We generate a coherent moving interference pattern in a transparent sample by intersecting two cw lasers (L_1 and L_2), whose frequencies are slightly different with each other. Since the frequency difference ω is much smaller than the optical frequencies, the wave numbers of the two beams have almost the same value k; thus, the wave vector difference is expressed as $q = |\mathbf{q}| = 2k\sin(\theta/2)$, where θ is the beam-crossing angle. Because of the interference of the two beams, the light intensity in the crossing region is modulated by $\delta I(\mathbf{r}, t) = \Re[2E_1E_2e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}]$, where $E_i(i = 1, 2)$ is the electric field strength of the pump beam L_i. This modulation term means that the scanning interference pattern with the phase velocity of ω/q is created in the sample.

Anisotropic molecules tend to align along the polarization direction of light. This leads to coherent orienta-

tional motions of LC molecules in the moving interference pattern [11]. The probe beam is scattered by this collective coherent motion. By detecting it, including its phase, we can measure complex spectra of the orientational relaxation mode, $Q_{zz}(\mathbf{q}, \omega) = \frac{2\Delta\epsilon E_1 E_2/\nu}{-i\omega+\Gamma_Q}$, where $\Delta\epsilon$ is the dielectric anisotropy of a fully oriented state, ν is the viscosity for rotational motion of molecules, and Γ_Q is the orientational relaxation frequency. In the above, we assume that the polarization directions of the two beams are vertical (along z axis). There should be no q dependence of the half width at the half maximum (HWHM) of the spectra, Γ_Q. The mean-field theory predicts [2] that in the isotropic phase Γ_Q decreases in proportion to the temperature difference $(T - T^*)$, (T^* is the critical temperature of LC) while approaching T^*. This was experimentally confirmed by Stinson and Litster [3].

If the sample absorbs the light energy, on the other hand, the moving interference pattern also induces the coherent temperature modulation [11], $\delta T(\mathbf{q}, \omega) = A_T/[-i\omega + \Gamma_T(q)]$. The amplitude A_T is in proportion to the light absorption coefficient α as $A_T = \frac{\epsilon_0 nc\alpha E_1 E_2}{\rho C_P}$, where n is the refractive index of a liquid, ϵ_0 is the dielectric constant of vacuum, and c is the light speed. The resulting density pattern scatters the probe beam, from which we can measure the complex spectra of the thermal diffusion mode. HWHM of the spectra is expressed as $\Gamma_T(q) = D_T q^2$. Thus, the spectra obtained by our CORS method are physically equivalent to those of conventional DLS methods [11]. The amplitude of the spectra is, however, proportional to the laser power modulation δI and also the light absorption constant α for the thermal diffusion mode; thus, we can control the amplitude of CORS spectra in contrast to the conventional methods. More important, we can measure only the signal coherent to the light modulation, including its phase.

Finally, if the phase velocity of the optical grating coincides with the phonon velocity, acoustic phonon can resonantly be excited via the electrostriction effects [10,11]. The Brillouin shift frequency satisfies the dispersion relation $\omega_B = vq$, where v denotes the phonon velocity.

We have newly built a system which combines both CORS [12] and phase-coherent Brillouin scattering (COBS) [10] methods on a common optical base (see Fig. 1). For CORS measurements we used one continuous wave, frequency doubled Nd:YAG laser (DPSS Model 532-400, Coherent Inc.; 400 mW). A vertically polarized beam radiated from the laser source is first divided into three beams, two of which work as the pump beams, L_1 and L_2, and generate the laser-field grating in the beam-crossing region of a sample. We use frequency-tunable acousto-optic modulators to sweep the frequency of the laser-induced grating. The third beam passes through the $\lambda/2$ plate; thus, its polarization direction is rotated by 90°. This beam with the horizontal

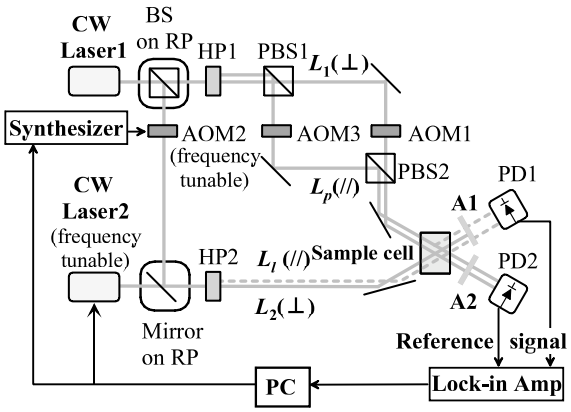

FIG. 1. A block diagram of our experimental system. BS stands for a beam splitter, PBS for a polarizing beam splitter, AOM for an acousto-optic modulator, PD for a photodetector, A for an analyzer, RP for a resettable plate, and HP for a half-wave plate. // indicates light with horizontal polarization, while $\perp$ indicates light with vertical polarization.

polarization works as the probe beam L_p, which enters into the sample and then is scattered by the optically generated coherent grating. The scattered light is then mixed with the weak local light L_l with the horizontal polarization and the resulting beat signal of the fixed frequency ($f = 2$ mHz) is measured by a silicon PIN photodetector (S2858, Hamamatsu Photonics). The lock-in detection of the photocurrent with a reference signal of $\cos(2\pi ft)$ gives us the real and imaginary parts, respectively, as the in-phase and out-of-phase components of the signal. We used a two-phase lock-in amplifier (model 200, Palo Alto Research), and a lock-in extender (model PAR 100, Palo Alto Research) for the detection of the signal coherent to the reference sinusoidal signal of $f = 2$ mHz.

For COBS measurements, on the other hand, we need a much wider frequency range than for CORS ones. The frequency shift with acousto-optic modulators is not enough. Thus, we used another frequency-tunable cw laser source (Model 142-532-200, Lightwave Electronics) with the output power of 200 mW in order to tune the frequency difference over a wider frequency range ($\sim$ 10 GHz) [10]. To switch the configuration between the CORS and COBS setups without any readjustments, we use two resettable plates for the beam splitter following the laser 1 and the mirror following the acousto-optic modulator 2 (see Fig. 1). We remove them for COBS measurements, while we set them for CORS ones. In this way we can make DLS measurements for the same sample, retaining both a high frequency-resolution (less than 100 Hz) and a wide frequency range (more than 10 GHz).

The liquid crystal samples we used were two kinds of cyanobiphenyls (CB), 5 CB and 7 CB, purchased from Merck. They were used without further purification but filtered through pore size of 0.1 μm. Then a filtered

sample was filled in an optical cell with the optical path length of 10 mm. Temperature of the cell was stabilized within ± 0.05 K by holding it between the metal jackets, through which temperature-regulated water circulates. All the spectra were obtained in the transparent isotropic phase of LC above T_{IN}.

Typical complex light scattering spectra of 5 CB above T_{IN} from the orientational relaxation, thermal diffusion, and sound modes are shown, respectively, in Fig. 2(a)–2(c) . Pure 5 CB in the isotropic state, which is almost optically transparent, has very weak light absorption. Thus, for pure 5 CB, we can excite the orientational motion of anisotropic molecules coherently by the laser-field grating, while we cannot excite the coherent temperature modulation. Figure 2(a) shows the complex spectra of the orientational relaxation mode observed at a temperature above $T_{IN} = 34.2\,^{\circ}\mathrm{C}$. This is the first observation of complex light scattering spectra of the orientational relaxation mode. For measurements of the thermal diffusion mode, we added a little amount of blue dye (about 2 ppm by weight of phenol blue, purchased from Wako chemical) to pure 5 CB [13] in order to enhance the light absorbability. The laser power was appropriately reduced with a neutral density filter to prevent photo bleaching of dye molecules and also to avoid the coherent excitation of orientational motion of molecules. In this way, we can detect only the coherent thermal diffusion mode [14]. It can indeed be confirmed in Fig. 2(b) that there is no effect due to the scattering from the orientational relaxation mode. We note that near T_{IN} the sample becomes slightly turbid due to large orientational fluctuations. Even under such conditions, we can measure the complex light scattering spectra of the thermal diffusion mode free from the interference from large incoherent signals. This is because we *selectively* detect only the signal scattered by the optically-induced *coherent* mode. This feature is realized by the phase-sensitive (lock-in) superheterodyne detection of the scattered light. Finally, Fig. 2(c) shows complex Brillouin spectra from propagating longitudinal acoustic modes. The sound velocity is determined by the dispersion relation to be 1.62×10^3 m/s, which agrees well with previous reports [15]. Note that there is no overlap with the Rayleigh component in our COBS measurements due to its mode-selective nature. In conventional methods, Brillouin peaks appear as shoulders of the strong Rayleigh line for LC samples [4,15]. In this way, we can measure the complex spectra of each mode *selectively and independently.*

By mode-selective COLS measurements, we studied dynamics of the orientational relaxation and the thermal diffusion of 7 CB in its isotropic phase. First, we measured complex spectra of the orientational relaxation mode as functions of T and the scattering angle θ. As illustrated in Fig. 3, Γ_Q is in proportion to $(T - T^*)$ but does not exhibit any wave number dependence, as it should be [2]. No deviations from the mean-field behavior are detected in our measurements. From the extrapolation

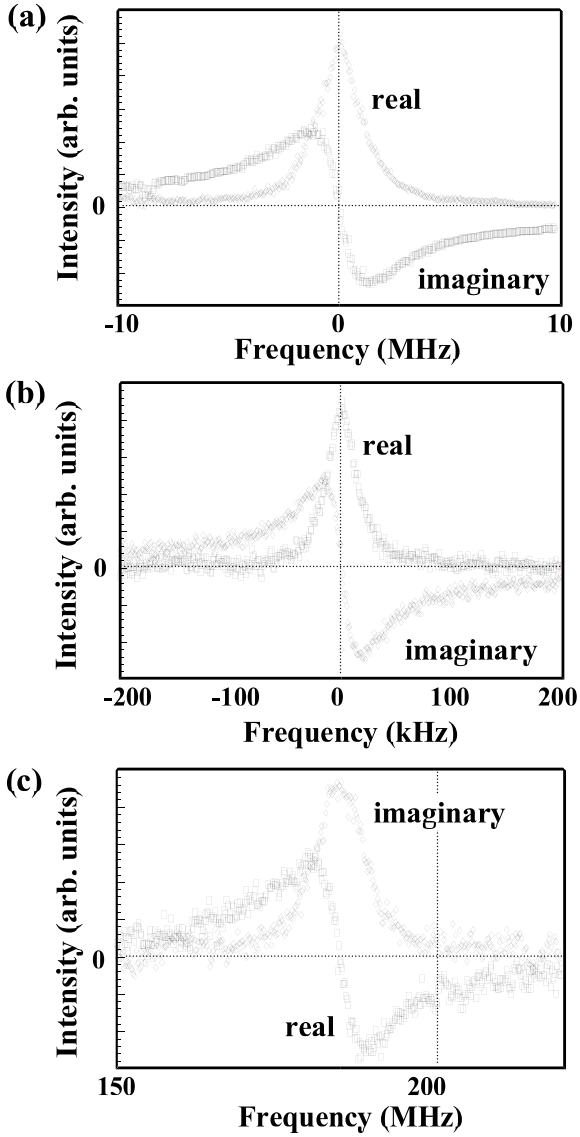

FIG. 2 (color online). Typical complex light scattering spectra of 5 CB in the isotropic phase. (a) Complex spectra of the orientational relaxation mode at $T = 36.1\,^{\circ}\mathrm{C}$ at $\theta = 6^{\circ}$. HWHM is measured as 1.15 MHz. (b) Complex spectra of the thermal diffusion mode at $T = 34.6\,^{\circ}\mathrm{C}$ at $\theta = 5.5^{\circ}$. HWHM is measured as 15.7 kHz. (c) Complex Brillouin spectra of the longitudinal acoustic mode (Stokes component) at $T = 35.1\,^{\circ}\mathrm{C}$ at $\theta = 3.44^{\circ}$. Brillouin frequency and HWHM of the spectra are measured as 182.4 MHz and 8.1 MHz, respectively. Frequency-resolution bandwidth was set to be 1 MHz in both (a) and (c) and to be 2 kHz in (b). See [11] on the phase relation among these modes.

of the fitting line, T^* is determined to be about 1 K below T_{IN}. These results are consistent with previous ones [3,16,17].

We also performed measurements of the thermal diffusion mode. We can obtain the information on the specific heat C_P and that on the thermal diffusivity D_T, respectively, from the amplitude [note $A_T = \frac{\epsilon_0 n c \alpha E_1 E_2}{\rho C_P}$

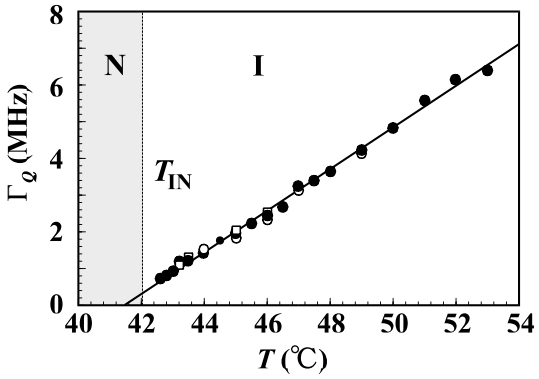

FIG. 3. Temperature dependence of the orientational relaxation frequency Γ_Q of 7 CB in the isotropic (I) phase. Filled circles, empty squares, and empty circles represent the data obtained at the scattering angle of 4°, 2.4°, and 1.4°, respectively. There is no q dependence of Γ_Q, as expected.

and $D_T = \Lambda/\rho C_P$] and HWHM of the complex spectra. θ was fixed to 5° for these measurements. Both amplitude and HWHM gradually decrease with a decrease in T near T_{IN}. D_T was estimated by dividing the value of Γ_T by the square of $q/2\pi = 1.03 \times 10^4$ cm^{-1} as $D_T \sim 8.0 \times 10^{-4}$ cm^2/s (see Fig. 4). This coincides well with that obtained previously by calorimetric measurements [5]. The temperature dependence of D_T should reflect the critical divergence of the specific heat C_P near T_{IN}, which is due to the critical phenomena of the weakly first-order phase transition, since there is no anomaly in Λ. Using the C_P data measured by Iannacchione and Finotello [18], we performed the least square fittings to both HWHM and amplitude. The results are shown in Fig. 4 as a solid line for D_T and a dashed line for A_T. D_T data are well fitted by the solid curve, while A_T data slightly deviate from the dashed curve near T_{IN}. This deviation might be caused by an effective decrease of the scattered light intensity due to multiple scattering effects near T_{IN} where the sample becomes more turbid while approaching T_{IN}. We note that this is probably the first direct light scattering measurement of the thermal diffusivity for LC in the isotropic phase near T_{IN}.

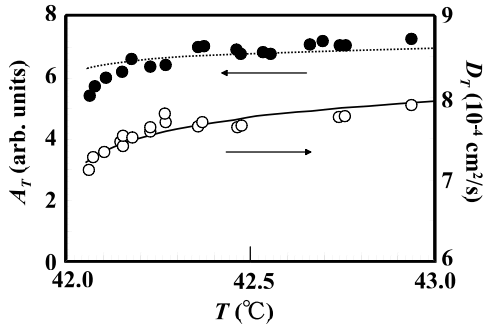

FIG. 4. Temperature dependence of the spectral amplitude (filled circles) and thermal diffusivity (empty circles) of 7 CB. While approaching T_{IN}, both amplitude and half width decrease, reflecting the critical-like divergence of the specific heat C_P. The solid and dashed curves are theoretical predictions (see the text).

In summary, we have succeeded in performing mode-selective Rayleigh-Brillouin scattering measurements of the thermal diffusion, orientational relaxation, and propagating sound modes for LC in its isotropic phase, thanks to the phase-sensitive superheterodyne detection of the scattered light coherent to the optical dynamic interference pattern. Coherent signal detection is a key to complete rejection of the interference due to large-amplitude incoherent thermal fluctuations. Our method opens up the possibilities of making direct light scattering measurements of dynamics of various modes usually hidden behind critical fluctuations near a critical point.

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