

## Simple and coupled processes of reorientational relaxation in the isotropic phase of *p-n*-hexyl *p'*-cyanobiphenyl

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(Received 19 June 1996; revised manuscript received 29 August 1996)

Both polarized (*VV*) and depolarized (*VH*) light scattering experiments were performed in the isotropic phase of the nematogen *p-n*-hexyl *p'*-cyanobiphenyl (6CB), over a temperature range up to 67.5 °C, and the results were analyzed along a line of the Landau-de Gennes theory. The simple decaying process of the pseudonematic domains in the pretransitional region appears in the shape of the *VV* spectrum. The relaxation frequency of the cooperative reorientation decreased to zero as *T* decreased to *T*\* = 28.0 °C. The *VH* spectrum reflects the very complicated feature of the coupled relaxation path, in which the local viscous flow takes an important role. The coupling constant *C* between the shear flow and the cooperative reorientation was obtained: *C* rapidly decreased to zero as *T* decreased to *T*\*, while *C* was almost independent of *T* at *T* ≥ 40 °C. A qualitative description was given to this behavior of *C*. [S1063-651X(96)10812-6]

PACS number(s): 42.70.Df, 61.30.-v, 64.70.Md

### I. INTRODUCTION

Despite the increasing interest in pretransitional phenomena relating to the local orientation in the isotropic phase of nematogens, the underlying relaxation behavior still seems to be not clearly understood. Motion of the cooperative reorientation involves nearby molecules into a viscous flow, which in turn induces the orientation in the neighborhood, and the coupling between the rotation and the shear flow gives a complicated feature to the relaxation. Flow birefringence under static electric or magnetic field is useful to observe the coupling between the flow and the orientational order [1–3]. Experiments of the optical Kerr effect have also been made for the study of the pretransitional phenomena, though they do not yield information on the coupling effect [4–6]. Deeg *et al.* skillfully used an intensive pulse laser to introduce artificial orientation and observed the decaying process through the birefringence effect [6]. They found very fast relaxation processes ranging from ps to ~100 ps, which were associated with local reorientational dynamics within the pseudonematic domains. While these techniques treat the forced orientation over a macroscopic region, a dynamic light scattering experiment observes the thermal fluctuations in the molecular orientation and the local flow [3,7]. These two spontaneous modes of independent origins decay, interfering with each other, and the process affects the light scattering. The power spectrum of the polarized (*VV*) scattering has a fourth component at the center besides the Brillouin triplet, which yields the orientational relaxation time; and the coupling between the two fluctuation modes reveals itself as a central dip in the depolarized (*VH*) spectrum. The phenomenological theory proposed by de Gennes beautifully describes these light scattering spectra [8,9].

The present study is focused on this coupling constant, and its temperature dependence in particular. We made a careful experiment of light scattering in *p-n*-hexyl *p'*-cyanobiphenyl (6CB), varying the temperature.

### II. EXPERIMENTS AND RESULTS

To detect the narrow dip in the *VH* spectrum, the light scattering system needs an extraordinarily high resolution that

can only be attained by light beating spectroscopy. Figure 1 schematically illustrates the experimental setup used for the present study, which is in principle the same as the one developed for the hyper-resolution Brillouin scattering [10]. The light source is a Nd-YAG laser giving ~400 mW output at 532 nm in second harmonic generation. For fear of degrading the angular resolution, we used the output with ~1.0 mm beam width as the incident light without any focusing lens. This was, of course, done, however, at the expense of signal-to-noise ratio in the obtained spectrum. Further, very high laser intensity in the focused region would be undesirable since it might introduce a static and macroscopic anisotropy into the scattering volume through the optical Kerr effect. A glass plate splits off a small portion of the incident light, which is recombined with the incident beam in the scattering cell to work as a local oscillator of the optical heterodyne. The scattering angle is very accurately defined as the crossing angle of the two beams. Only the light scattered into the direction of the local beam will be detected by the photo diode which generates the photo-beat current. The spectrum analyzer gives power spectrum of the scattered light with sufficient resolution. In the present study, we got both the *VV* and the *VH* spectra and, for the latter, needed a

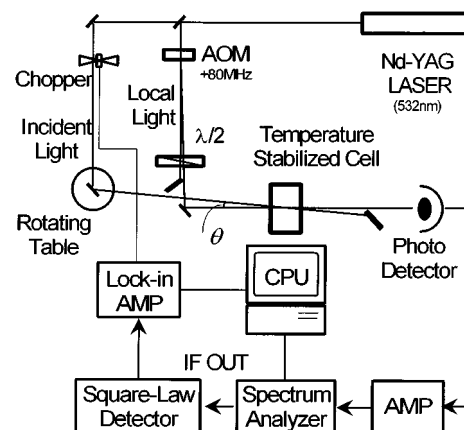


FIG. 1. Schematic block diagram of the experimental setup.

$\lambda/2$  plate to rotate the polarization plane of the local light by  $\pi/2$ . Thus we can readily select the  $VV$  or  $VH$  component.

The scattering cell was filled with liquid 6CB and controlled to within  $\pm 0.1^\circ\text{C}$ . The experiments were made at the scattering angles  $\theta=0.5, 1.0, \text{ and } 3.0^\circ$ , and over the temperature range from  $28.8$  to  $67.5^\circ\text{C}$ .

Figure 2 shows typical examples of the spectra obtained at  $29.2, 32.5, \text{ and } 35.0^\circ\text{C}$ . The scattering angle is  $1.0^\circ$ . The

upper (open circles) and the lower (closed circles) of each set represent the  $VV$  and the  $VH$  spectra, respectively. When the correlation length of the thermal fluctuation is much shorter than the light wavelength, these curves are theoretically predicted by the Landau–de Gennes model as [11]

$$S_{VV}(q, \omega) = \frac{2\Gamma}{\omega^2 + \Gamma^2}, \quad (1)$$

$$S_{VH}(q, \omega) = \frac{2\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{2\Gamma \left\{ \omega^2 + \left( \frac{\eta}{\rho} q^2 \right)^2 (1-C) \right\}}{\left\{ \omega^2 - \Gamma \left( \frac{\eta}{\rho} q^2 \right) \right\}^2 + \omega^2 \left\{ \Gamma + \left( \frac{\eta}{\rho} q^2 \right) (1-C) \right\}^2} \cos^2 \frac{\theta}{2}, \quad (2)$$

where  $q$  is the scattering wave number determined from  $\theta$  as  $q = 2k \sin(\theta/2)$ ,  $k$  being the optical wave number,  $\Gamma$  the orientational relaxation frequency,  $\eta/\rho$  the kinetic viscosity, and  $C$  a coupling constant discussed in Sec. IV. Note here that Eq. (1) is independent of  $q$ , hence of  $\theta$ ; and the first term of Eq. (2) is safely ignored in the present experiment made at  $\theta \leq 3.0^\circ$ .

The Lorentzian curve of Eq. (1) was successfully fitted to the observed  $VV$  curve:  $\Gamma$  was determined very accurately at each temperature. Then we fitted the second term of Eq. (2) to the experimental  $VH$  spectra with the values of  $\Gamma$  already known,  $\eta$  taken from the literature [12] and  $\rho = 1.0$  ( $\text{g}/\text{cm}^3$ ) as a good approximation in this temperature range. Hence, only  $C$  is the adjustable parameter in this curve fitting. The solid lines in the figure show the fitted spectra.

### III. ORIENTATIONAL RELAXATION

As has been well verified by many experiments [2–4] and also by theories [11], nematogenic molecules form microscopic regions of ordered orientation in the isotropic phase. Those pseudonematic domains are created spontaneously by thermal fluctuation and decay with a certain time constant. The rate of this reorientational relaxation depends on the domain size and decreases as the temperature decreases toward  $T_c$ , the transition point from isotropic to nematic phase. The Landau–de Gennes theory predicts [9]

$$\Gamma = \frac{a}{\nu} (T - T^*), \quad (3)$$

where  $\Gamma$  is the relaxation frequency,  $a$  a constant,  $\nu$  a kind of viscosity associated with a motion of collective orientation, and  $T^*$  the virtual transition temperature, which is slightly lower than  $T_c$ . The isotropic phase is absolutely unstable below  $T^*$ .

The relaxation frequency was experimentally obtained from the width of the  $VV$  curves and is shown in Fig. 3, in which the inset shows the lower-temperature region on an expanded scale. Assuming no dependence of  $\nu$  on temperature in a limited range near  $T^*$  as is the case in the shear

viscosity, we determined  $T^* = 28.0^\circ\text{C}$  from the linear extrapolation shown in the inset figure. Here,  $T_c(29.0^\circ\text{C}) - T^* = 1.0^\circ\text{C}$  is a quite reasonable difference. For a curve over a broader temperature range, one must take the temperature dependence of  $\nu$  into account. We assumed  $\nu$  in Eq. (3) to follow an Arrhenius-type dependence on  $T$ , i.e.,  $\nu \propto \exp(E_\nu/kT)$ , and fitted the equation to the experimental points up to  $67.5^\circ\text{C}$ . The result is shown by the solid line in Fig. 3. The activation energy  $E_\nu$  for  $\nu$  was obtained:  $E_\nu/k = 2890$  K.

It should be emphasized here that  $\Gamma$  is a relaxation frequency of a single domain process: a whole pseudonematic domain decays independently without any interaction with others. Appearances and decays of these domains cause anisotropic fluctuation in the dielectric response of the medium, which is expressed by a time- and space-dependent dielectric tensor. The three diagonal components of the tensor contribute to the  $VV$  spectrum of Eq. (1), and off-diagonal components to the  $VH$  spectrum given by the first term of Eq. (2), though it is completely absent in the low-angle scattering geometry.

In the mean field approximation, the domain size is given by [13]

$$\xi = \xi_0 \left( \frac{T^*}{T - T^*} \right)^{1/2}, \quad (4)$$

where  $\xi_0$  is one molecular length. Though the domains grow rapidly as  $T$  approaches  $T^*$ , the present experiment was made at temperatures  $T - T^* \geq 0.8^\circ\text{C}$  and the relevant size was smaller than 20 molecular lengths:  $\xi$  ( $\approx 35$ – $40$  nm) is much shorter than the optical wavelength and the  $VV$  spectrum is safely approximated to a Lorentzian form of Eq. (1). Microscopic domains of similar size distribute themselves almost uniformly over the scattering volume and the power spectrum reflects the behavior of each.

Besides the orientational fluctuation, there is an isotropic density fluctuation which is expressed by a time dependent scalar dielectric constant. The density-density correlation brings about the Brillouin triplet which is superimposed on the  $VV$  spectrum. Actually we found a narrow Rayleigh peak

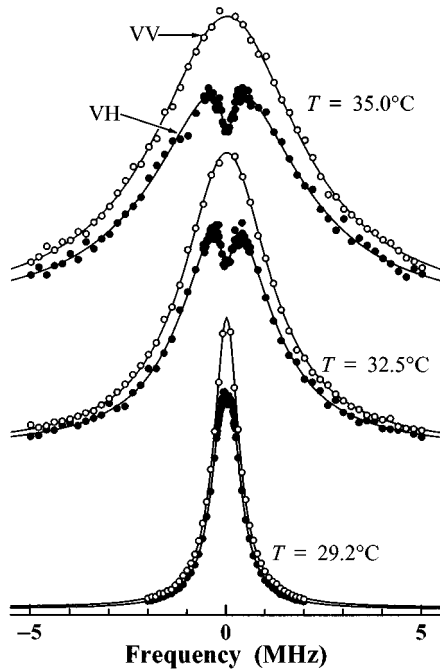


FIG. 2. Typical examples of VV and VH spectra obtained in the isotropic phase of 6CB. The solid lines represent the fitted curves of Eqs. (1) and (2). Depth of the dip in the VH spectrum roughly gives  $C$ , which decreases as  $T$  approaches  $T^*$ .

in a sweep at  $\omega \sim 0$  made with much increased resolution and two phonon peaks around the frequency determined by  $\theta$  and the phonon phase velocity.

#### IV. COUPLED RELAXATION

Here we must take another fluctuation mode into account besides that of the local orientation: i.e., the local and temporal shear flow. The coupling between these two degrees of freedom is inevitably present and presents another relaxation path of the local anisotropy, which is much more complicated than the simple process characterized only by  $\Gamma$ .

The shear flow causes a birefringence effect and affects the off-diagonal components of the fluctuating dielectric tensor. The coupling with the orientational fluctuation happens only in the off-diagonal places; and the components which give rise to the VV scattering are independent. The second term of Eq. (2), which is directly observable as the VH spectrum at low-angle scattering, illustrates the complicated feature of the coupled relaxation in the frequency domain. Since the shear flow has a long correlation length and involves more than two pseudonematic domains, interdomain interactions may occur and the VH spectrum is strongly dependent on  $q$  or  $\theta$ .

The two relaxation paths, the simple process and the coupled process, are neatly separated into the polarized and the depolarized scattering, which yield  $\Gamma$  and  $C$ , respectively. Here is no doubt the greatest advantage of the application of dynamic light scattering for the investigation of this pretransition phenomenon.

de Gennes introduced another viscosity  $\mu$  associated with the momentum transfer between collective rotation and translation. Then  $C$  is given by

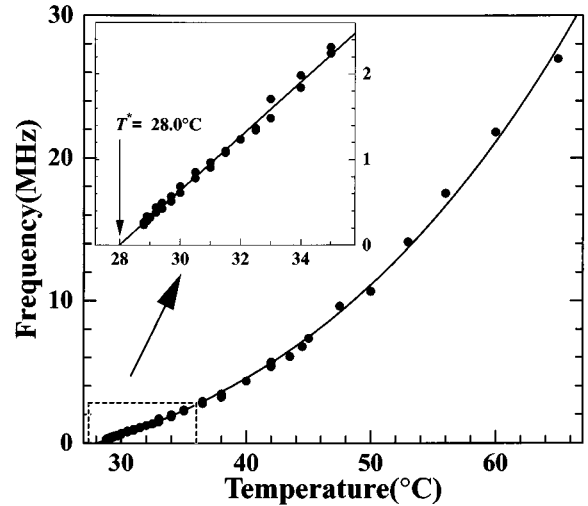


FIG. 3. Temperature dependence of  $\Gamma$  observed at three scattering angles. The inset shows the low-temperature region in an expanded scale.

$$C = \frac{2\mu^2}{\eta\nu}. \quad (5)$$

Of the three viscosities appearing in this equation,  $\nu$  has already been determined as  $\nu \propto \exp(2890/T)$ ,  $\eta$  is found in the literature [12] as  $\eta = 6.13 \times 10^{-5} \exp(4020/T)$ , and only  $\mu$  is unknown at present.

The observed values of  $C$  are shown in Fig. 4, which is a collection of all the data obtained at the three scattering angles. They are well on one universal curve. This figure tells us two important facts: First,  $C$  seems to be almost independent of  $T$  at  $T \geq 40.0^\circ\text{C}$ , and secondly  $C$  rapidly decreases to zero as  $T$  approaches  $T^*$ . The former suggests that  $\mu$  is not an independent value at least in the off-critical region and is probably associated with a combination of a rotation and a translation. We can conclude from Eq. (5) that the coupling viscosity  $\mu$  also follows the Arrhenius law as the other viscosities over a certain temperature range, whose activation energy is given by a simple average as

$$E_\mu = (E_\eta + E_\nu)/2 \quad (6)$$

where  $E_\mu$  and  $E_\eta$  are activation energies for  $\mu$  and  $\eta$ , respectively. With  $E_\eta/k = 4020$  K and  $E_\nu/k = 2890$  K, one gets  $E_\mu/k = 3450$  K and  $\mu \propto \exp(3450/T)$ .

At temperatures below  $40^\circ\text{C}$ , however,  $C$  has a strong dependence on  $T$  which can by no means be attributed to  $\eta$  or  $\nu$ . These two viscosities show no anomaly near  $T^*$ , or a very subtle one if any. We therefore assumed a critical exponent  $\gamma$  for  $\mu$ . Then

$$\mu \propto (T - T^*)^\gamma \exp\left(\frac{3450}{T}\right), \quad (7)$$

and

$$C = C_0(T - T^*)^{2\gamma}. \quad (8)$$

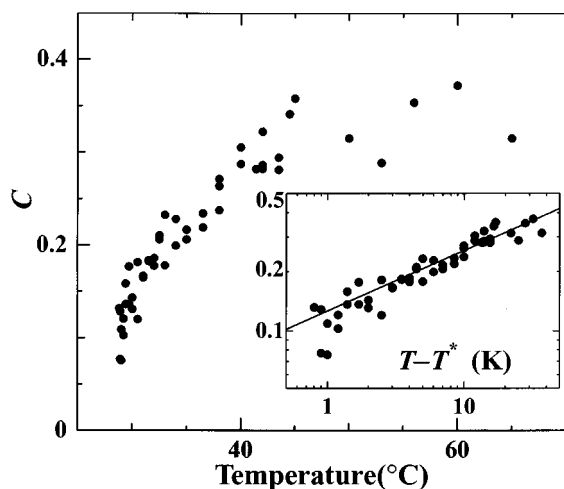


FIG. 4. Temperature dependence of the coupling constant between the orientational fluctuation and the local shear flow. The inset is the plot of  $C$  versus  $T-T^*$  on a logarithmic scale.

The inset in Fig. 4 shows a plot of  $C$  versus  $T-T^*$  on logarithmic scales, which gives  $\gamma=0.15$  in the fitting shown by the solid line in the inset.

The discussion made so far on the light scattering spectra and the temperature dependence of  $\Gamma$  and  $C$  could give a rather vague phenomenological understanding lacking a direct insight into the dynamics of the nematogenic molecules. What we know as a basis of the consideration is that they are rodlike molecules swaying and rotating under weak influence of the neighbors in the isotropic phase, and spontaneously make very vague domains of orientational order which appear and disappear temporally and spatially. Superimposed on this motion is the fluctuation of the fluid dynamical shear flow in all the directions. Consider a newborn domain which is roughly directed along the  $x$  axis in the horizontal plain, for example. Some of the molecules in it begin to stand up in the natural process toward isotropy. The rotational motion would cause a shear flow in the  $x$  direction or, at least, enhance the fluctuation in that direction. The shear flow is accompanied by a viscous force which works, however, to restore the initial orientation, i.e., to lay down the upright molecules. Of the three anisotropic shear viscosities of the nematic phase, the lowest one is that for the flow parallel to the director. This would hold also in the nematic domain and the viscous flow is most likely to occur along its anisotropic axis helping the ordering. Thus the motion of reorientation and the coupled shear flow are somewhat counteracting by nature, and the whole phenomenon bears a self-inconsistency. This is the essential meaning of the central dip in the  $VH$  spectrum. At higher temperatures where  $\eta$  is small and  $\Gamma$  is large, for instance, the whole reorientation process

is described by a simple superposition of a quick decay characterized by  $\Gamma$  and a slow exponential curve with negative sign representing the ordering effect of the coupled flow. In the approximation  $\eta q^2/\rho \ll \Gamma$ , the second term of Eq. (2) reduces to a form given by subtracting a narrow Lorentzian curve with the width  $\eta q^2/\rho$  from a large Lorentzian curve whose width is  $\Gamma$ .

The above illustration of the coupled relaxation would be valid, however, only for domains whose size is smaller than  $\xi \approx 5-6\xi_0$ , including about 100 molecules. In these small domains the order parameter and the domain shape could not be independent degrees of freedom: the reorientation process is inevitably accompanied by deformation of the domain shape. This would be the primary factor causing the coupling with the shear flow, and hence the large value of  $C$  at  $T \geq 40^\circ\text{C}$ . As the domain size increases with decreasing temperature, i.e.,  $\xi \geq 10\xi_0$  or one domain has  $\sim 10^3$  molecules, the two degrees of freedom lose the close connection with each other. The reorientation of a domain can take place without changing its whole shape, spherical, oval, or more complicated. The coupling with the shear flow naturally decreases as  $T$  decreases to  $T^*$ . In the absence of any appropriate ways to observe the fluctuation in the domain shape, this description of the temperature dependence of  $C$  cannot be extended beyond the limit of hypothesis. The coupling constant  $C$  seems to show a critical behavior near  $T^*$ . Unfortunately, however, we have no clear idea for its physical origin at present. Anyway, the result reported here would be evidence for the critical behavior of  $C$ , and we will continue further and more detailed experiments to clarify its physical mechanism.

At higher temperatures where  $\xi$  is smaller than  $2-3$  molecular lengths, the pretransitional anomaly disappears and  $\mu$  or  $C$  would lose its meaning. Deeg *et al.* experimentally observed this range,  $T-T^* \geq 35\text{ K}$  in 5CB [6].

In summary, we investigated both the simple and the coupled relaxation of reorientation as pretransitional phenomena in a liquid nematogen. We found that  $C$ , a measure of the coupling between the collective motion of reorientation and the shear flow, rapidly decreases as  $T$  decreases to  $T^*$  while it shows very weak dependence at  $T-T^* \geq 12\text{ K}$ . A qualitative description of this behavior was proposed under the assumption that the domain shape takes an important role in the coupling.

#### ACKNOWLEDGMENTS

We wish to thank Dr. Yamamoto of University of Tokyo, and Dr. Matsuoka of Nagoya University for a very useful discussion. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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