

# Critical increase of the bending fluctuations of molecules and the nematic-to-isotropic liquid phase transition

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A critical increase of bending fluctuations in the mobile molecular chains of a nematic, which induces a sudden transition to the isotropic state in a system of rigid molecular nuclei and a continuous transition in a system of impurity dye molecules, was observed.

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1. The nature of a phase transition between the nematic phase of a liquid crystal (NLC) and the isotropic liquid is not clear at the present time. The LC molecules, as a rule, have a rigid molecular nucleus and rather long flexible chains whose mobility can

play an important role in the LC stability. Recently, we reported<sup>1</sup> that the lengthening of flexible chains has a disordering effect on a system of rigid molecular nuclei in the tolane class of NLC. Information about the mobility of molecular chains can be obtained from a comparison of the orientation order parameters of the rigid molecular nuclei  $S_0$  of the LC matrix and  $S_{\text{dye}}$  of the impurity dye molecules.<sup>2</sup>

2. We investigated the behavior of the parameters  $S_0$  and  $S_{\text{dye}}$  of the NLC 4-n-pentyl-4'-cyanobiphenyl (5CB) doped with a dye (4-dimethylamino-4'-nitroazobenzene) in the 22–35°C temperature interval of the mesophase. According to x-ray structure data,<sup>3</sup> 5CB has a local quasi smectic structure in which a high mobility of the flexible chains and appreciable pretransition effects are expected. In addition, the order parameters  $S_{\text{dye}}$  of the individual segments of the flexible 5CB chain were measured<sup>4</sup> by the NMR method at  $t = 28^\circ\text{C}$ . A reproducible planar orientation of the molecules in the 10 to 40- $\mu\text{m}$ -thick LC layers was achieved by a directional polishing of the inner surfaces of the cell-sandwich made of plane-parallel NaCl plates. The accuracy of the temperature measurement and of the temperature stabilization was  $\pm 0.1^\circ\text{C}$ . A 0.1 mol% dye concentration did not alter the temperature  $T_{NI}$  of the NLC-to-isotropic phase ( $N-I$ ) transition of the pure 5CB. The order parameter  $S_0$  of the rigid molecular nuclei of the matrix was determined from the dichroism of the IR absorption band of the valence  $C\equiv N$  vibration of the 5CB ( $\lambda_{\text{max}} = 4.5 \mu\text{m}$ ) by using the previously described method.<sup>1</sup> The parameter  $S_{\text{dye}}$  was obtained from the dichroism of the electron absorption band of the dye ( $\lambda_{\text{max}} = 490 \text{ nm}$ ). At  $\Delta T = 4^\circ\text{C}$  our data  $S_0 = 0.50 \pm 0.01$  (Fig. 1) agree with the NMR measurements of <sup>4</sup>  $0.51 \pm 0.02$ . The difference between the  $S_0$  and  $S_{\text{dye}}$  values in 5CB is large and increases as the  $N-I$  transition is approached.

3. Ignoring the even-odd alternation, we represent the flexible alkyl chain in the form of an assembly of  $n$  segments having a length  $l = l_{C-C} \sin 56^\circ$ , oriented along the

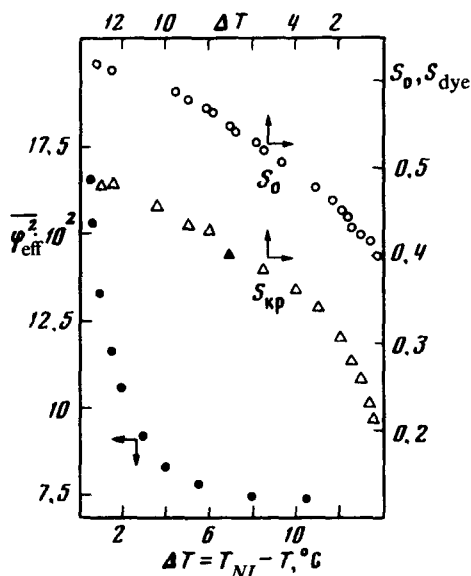


FIG. 1. Temperature behavior of the rigid nuclei 5CB impurity NLC: (O) —order parameter  $S_0$  of the rigid nuclei of the matrix molecules; ( $\Delta$ ) —order parameter  $S_{\text{dye}}$  of the impurity dye molecules; ( $\blacktriangle$ ) — $S_{\text{dye}}$ , which was determined from the NMR<sup>4</sup> data for  $S_k$  by using Eq. (2); ( $\bullet$ ) —effective fluctuation  $\overline{\phi^2}_{\text{eff}}$  of bending of the alkyl chain of 5CB molecules.

axis of the chain ( $n$  is the number of carbon atoms in the chain and  $l_{C-C}$  is the length of the  $C-C$  bond). The thermal fluctuation  $\overline{\phi^2}$  of the angle between the axes of adjacent chain segments increases with their distance from the rigid molecular nucleus, and this increase is linear in a first approximation:  $\overline{\phi^2}_{i-1,i} = \overline{\phi^2} + \alpha(i-1)$ ,  $i = 1, \dots, n$ . We denote  $S(\phi_i) = 1 - 3/2 \sin^2 \phi_{i-1,i} \approx 1 - 3/2 \overline{\phi^2}_{i-1,i}$  and, taking into account only the terms linear with respect to  $\phi^2$ , we obtain the order parameter of the  $k$ th segment of the flexible chain

$$S_k = S_0 \prod_{i=1}^k S(\phi_i) = S_0 - \sigma_1 k - \sigma_2 k^2, \quad (1)$$

where  $\sigma_1 = 3S_0(\overline{\phi^2} - \alpha/2)/2$ ,  $\sigma_2 = 3S_0\alpha/4$ . At  $\alpha = 0$  Eq. (1) gives the linear dependence of  $S(k)$  in accordance with the experiment<sup>4</sup> for a NLC with short flexible chains.

According to Ref. 2,

$$S_{\text{dye}} = \sum_{k=0}^N S_k l_k / \Lambda_m - \kappa (\Lambda_m - \Lambda_{\text{dye}}), \quad (2)$$

where  $l_k$  is the length of the  $k$ th segment of the matrix molecule and  $\Lambda_m, \Lambda_{\text{dye}}$  are the longitudinal dimensions of the matrix and dye molecules. In 5CB the length of the associate of the two molecules with overlapped nuclei and antiparallel orientation must be chosen as  $\Lambda_m$ .<sup>3</sup> For the LC's of the cyanobiphenyls and similar DMANAB dyes we obtain<sup>5</sup>  $\kappa = 6 \times 10^{-3} \text{ \AA}^{-1}$ . Using the molecular data and the NMR values of  $S_k$ <sup>4</sup> for  $t = 28^\circ \text{C}$ , we determine from Eq. (2)  $S_{\text{dye}} = 0.405$ , in good agreement with the experiment (Fig. 1). Substitution of (1) into (2) makes it possible to express the effect bending fluctuation of the 5CB chain in terms of the experimental values of the parameters  $S_0$  and  $S_{\text{dye}}$  in the form

$$\overline{\phi^2}_{\text{eff}} = \overline{\phi^2} + \frac{4}{3} \alpha = \Lambda_m [S_0 - S_{\text{dye}} - \kappa (\Lambda_m - \Lambda_{\text{dye}})] / 45 S_0 l. \quad (3)$$

The temperature dependence of  $\overline{\phi^2}_{\text{eff}}$ , calculated from (3), has a pronounced critical rise near  $T_{NI}$  (Fig. 1). In the temperature interval  $0.5^\circ \text{C} \ll \Delta T \ll 4^\circ$  the variation of  $\overline{\phi^2}_{\text{eff}}$  is described by the formula  $\overline{\phi^2}_{\text{eff}} = 0.02(1 - T/T_{NI})^{-0.33 \pm 0.01}$ . The critical increase of  $\overline{\phi^2}_{\text{eff}}$  leads to a continuous transition to the disordered state in the system of flexible molecular chains, since  $S(\phi_i), S_k, 1/n \sum_{k=1}^n S_k \rightarrow 0$  as  $T \rightarrow T_{NI}$ . At the same time, the system of rigid molecular nuclei of the LC undergoes a first-order phase transition at the point  $T_{NI}$  with a sudden jump in the parameter  $S_0$ . Taking into account the results of Ref. 1, we conclude that the orientation melting of the flexible chains induces the  $N-I$  phase transition in the system of rigid molecular nuclei of the NLC.

As follows from (3), continuous transition to the disordered state can occur at a temperature  $T^* < T_{NI}$  as a result of a rapid increase of  $\overline{\phi^2}_{\text{eff}}$  of the impurity sub-system

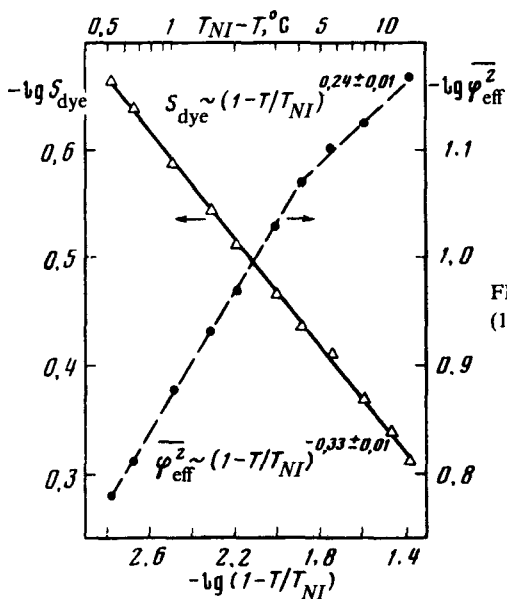


FIG. 2. Dependence of  $S_{\text{dye}}$  ( $\Delta$ ) and  $\overline{\phi^2}_{\text{eff}}$  ( $\bullet$ ) on  $(1 - T/T_{NI})$  on a log-log scale.

of the NLC; in addition, the value of  $(T_{NI} - T^*)$  increases with increasing  $\kappa(A_m - A_{\text{dye}})$ . As follows from Fig. 2, the behavior of  $S_{\text{dye}}$  in the temperature interval  $0.5^\circ\text{C} \leq \Delta T \leq 13^\circ\text{C}$  is described well by the expression  $S_{\text{dye}} = (1.0 \pm 0.05)(1 - T/T_{NI})^{0.24 \pm 0.01}$ . Thus, the  $N - I$  phase transition occurs as a result of the interaction of two order parameters:  $S_0$  and the average over the flexible chain  $\bar{S} = 1/n \sum_{k=1}^n S_k$ . Further experimental and theoretical studies are needed for a detailed understanding of this interaction.

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