

Orientalional melting of low chains of molecules and nature of the nematic-smectic *A* phase transition

E. M. Aver'yanov, P. V. Adomenas, V. A. Zhuikov, and V. Ya. Zyryanov
L. V. Kirenskiĭ Institute of Physics, Siberian Branch, Academy of Sciences of the USSR

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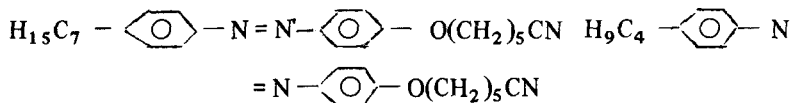
An orientational melting of the end fragments of flexible molecular chains has been observed in a transition from the nematic phase to the smectic *A* phase of a liquid crystal. This melting has a strong effect on the interaction of the order parameters of these phases and on the localization of the tricritical point on the nematic-(smectic *A*) transition line.

1. Several distinctive features of the nematic-smectic (*N-A*) phase transition have yet to be explained.^{1,2} The region in which the *N* phase exists, $\Delta = 1 - T_{NA}/T_{NT}$, for example, which corresponds to the tricritical point on the line of *N-A* phase transitions, depends on the nature of the systems under study, varying from values³ $\Delta_T \simeq 0.1$, in close agreement with the prediction of the microscopic theory of Ref. 4, to anomalously small values⁵⁻⁷ $\Delta_T \simeq 10^{-2} - 10^{-3}$. The implication is that the parameter Δ is not a universal parameter for describing the nature of *N-A* phase transitions and that there are some additional restrictions, which depend on the particular molecular structure, on the nature of the interaction of the order parameters of the *N* and *A* phases. The elementary reasons for these restrictions are not clear at this point. On the other hand, we also lack an explanation for the fact that as Δ is increased from 0.025 to 0.13, the forward correlation length ξ_{\parallel}^0 increases from 4 to 40 Å in bilayer smectics,⁸ leading to the suppression of the fluctuational anomalies in the heat capacity, the nematic order parameter, and the volume near the *N-A* phase transition.²

In the present letter we use new experimental data to show that these features of the *N-A* phase transition can be explained by the strong mutual coupling (seen here for the first time) between the rigidity and the orientational order of flexible chains of molecules with the order parameters of the *N* and *A* phases.

2. A change in Δ_T indicates that the coupling between the smectic order and the nematic order⁴ or the interaction constants of the corresponding order parameters² depend on the particular molecular structure, which determines the nature of the smectic mesomorphism. Since the condensation of a smectic density wave is caused by the strong interaction of the molecules through flexible end chains, it is important to determine how the flexible chains influence the nature of the interaction of the order parameters of the *N* and *A* phases, i.e., to experimentally study the change in the orientational order of the end fragments of flexible chains in these phases.

In the present experiments we use the liquid-crystal mixture (50:50 by weight)



with the following phase-transition temperature (in degrees Celsius): crystal $62^\circ A$ $74.3^\circ N$ $79.2^\circ I$. The parameter of the orientational order of the end fragments of the chains is $S_k = \langle 3\cos^2\theta - 1 \rangle / 2$ (θ is the angle between the special axis of the fragment and the director of the liquid crystal, and $\langle \dots \rangle$ means a statistical average over all the molecules of the sample) and is determined from the dichroism of the IR band of the $C\equiv N$ valence vibration ($\nu_{\max} = 2245 \text{ cm}^{-1}$) by the method of Ref. 9. The parameter S_0 for rigid molecular frameworks is found from the dichroism of the doublet band $\nu_{\max} = 1585$ and 1600 cm^{-1}) of vibrations of the benzene ring, polarized along the $N \dots 0$ direction. The nematic order parameter $S \sim (n_{\parallel}^2 - n_{\perp}^2)$ is found from the refractive indices $n_{\parallel, \perp}$ of the mixture at $\lambda = 589$ and 735 nm and is normalized to the value of S_0 at $\Delta T = T_{NI} - T = 14^\circ$ in the A phase. The methods used for the spectral measurements, the refractometry, and the determination of the components L_{\perp} of the Lorentz tensor from the dichroism of the $C\equiv N$ vibration band in the N phase (we assume $L_{\perp} = 0.395$ in the A phase) are all described in Ref. 9. The measurements of S_0 and S_k are carried out in fluorite sandwich cells with planar and homeotropic orientations of the molecules in the N and A phases. The thickness of the liquid-crystal layer is 5 or $30 \mu\text{m}$. The error in the temperature regulation of the samples is $\pm 0.1^\circ\text{C}$. The results of the measurements are shown in Fig. 1.

3. The values of S and S_0 agree well with each other, except near T_{NI} , where $S < S_0$; this difference increases with decreasing ΔT . The reason for this increase is the

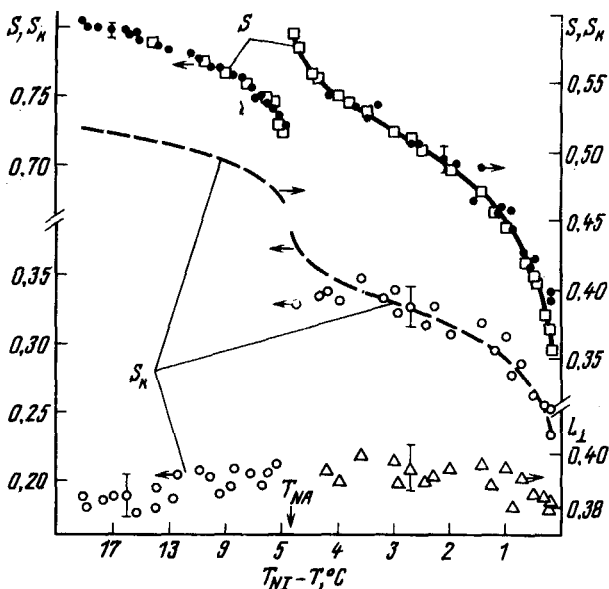


FIG. 1. Temperature dependence of the nematic order parameter S (\square), the parameters of the orientational order of the rigid frameworks, S_0 (\bullet), and of the end fragments of the flexible chains of molecules, S_k (\circ), and the component L_{\perp} (Δ) of the Lorentz tensor in the N and A phases of a liquid-crystal mixture. Solid line—Interpolation of data on S and S_0 ; dashed line—dependence $S_k(S)$ calculated from (1) for $\lambda_{\perp} \chi = 0.642$.

decrease in the flexible-chain component of the birefringence of the liquid crystal, due to a decrease in the rigidity of the chains in the region before the transitions.^{10,11} As $T \rightarrow T_{NA}$, we observe the predicted² anomalous pretransition increase in S due to fluctuations of the smectic order; this increase indicates that the N - A phase transition in the mixture is near the tricritical point. At the N - A transition, an increase in S by ~ 0.14 occurs in an interval $\Delta T \simeq 0.2^\circ$, giving us an upper estimate of the width of the possible two-phase region. In the N phase, the $C \equiv N$ end fragments of the flexible chains are far less ordered than the rigid frameworks of the molecules. As S increases, the parameter S_k also increases, but this increase slows near T_{NA} , and at the N - A phase transition the value of S_k decreases sharply, to values below $S_k(T_{NI})$. As the temperature of the A phase is lowered, we observe a decrease in S_k , while S increases noticeably. The N - A phase transition is thus accompanied by an orientational melting of the end fragments of flexible chains, and the contributions of the orientational and translational ordering of the liquid-crystal molecules to the change in S_k are opposite in sign.

It follows from the general symmetry properties of the N and A phases¹ that S_k depends on the nematic (S) and smectic (Ψ) order parameters:

$$S_k = \chi (\lambda_1 S - \lambda_2 |\Psi|^2 + \dots), \quad (1)$$

where χ is the susceptibility of the liquid crystal to a change in the order parameter S_k in the "field" h , whose role is played by the expression in parentheses, $|\Psi|$ is the amplitude of the density wave of the smectic layers, and $\lambda_{1,2}$ are constants.

The function in (1) gives a good description of the change in $S_k(S)$ in the N phase. Near the N - A phase transition, as $T \rightarrow T_{NA}$, we find a difference between the predicted and observed behavior $S_k(S)$, indicating an orientational melting of the chains due to fluctuations of the smectic order. The values of $S_k(S)$ calculated from (1) for the A phase are far higher than the experimental values. Comparison of the calculated and experimental values of S_k with $\Delta T = 19^\circ$ and with the estimate² $|\Psi|^2 \simeq 0.1$ yield $\lambda_2/\lambda_1 \simeq 5$; i.e., the ordering of the chains is far more sensitive to the particular features of the smectic order than those of the nematic order. It is thus not by chance that the nature of the ordering of the end fragments of the chains is qualitatively different from that for the rigid frameworks during phase transitions between smectic phases.¹²

4. The orientational melting of the end fragments of the chains stabilizes the layered smectic structure, preventing a diffusion of molecules from layer to layer and weakening the fluctuations in the phase of the smectic density wave. The coupling between the order parameters S and Ψ weakens, and the constant of their interaction, λ_0 , in the corresponding free-energy term^{1,2} $\lambda_0 S |\Psi|^2$ is renormalized in the direction of a decrease in $\lambda = \lambda_0 - \lambda_1 \lambda_2 \chi$. The result is a decrease in Δ_T . An extensive melting of the end fragments at the N - A phase transition should be expected for molecules with two flexible chains of different lengths or for molecules with a common chain and a highly polar framework; such molecules tend to form clusters and bilayer smectic structures. Included in these two classes of systems are some liquid crystals studied previously, 10S 5 (Ref. 5), OOGTsS (Ref. 6), 9CB (Ref. 7), with anomalously small values of Δ_T . On the other hand, for molecules with two chains of identical length, the

melting of the end fragments at the N - A phase transition is considerably less apparent (these results will be discussed in a separate paper). This situation corresponds to an increase in λ and Δ_T . Similar systems were studied in Ref. 3. The melting of chains at the N - A phase transition can thus explain the dependence of Δ_T on the molecular structure.

Taking the S dependence of the rigidity of the chains into account,¹⁰ we add terms $\sim S^m$ with $m \geq 3$ (Ref. 11) to (1). The role played by these terms becomes more important as Δ and S increase. At large values of Δ and S , the rigidity of the chains increases, the amplitude $|\Psi|$ decreases,⁴ and the orientational melting of the chains is insignificant. The direct correlation length ξ_{\parallel}^0 along the direction parallel to the director should correspond approximately to the interlayered distance d (for bilayer smectics of the n OCB type,⁷ we have $d \simeq 30$ – 40 Å).

As Δ and S decrease, the rigidity of the chains falls off rapidly, $|\Psi|$ increases,⁴ $S_k(T < T_{NA}) < S_k(T_{NI})$ (Fig. 1), and ξ_{\parallel}^0 decreases to the correlation scales of intramolecular fragments, ~ 5 Å, as in the isotropic phase. These features in the change in $\xi_{\parallel}^0(\Delta)$ are observed experimentally.⁸

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