# Renormalization of the susceptibility in the isotropic phase of a liquid crystal due to an interaction of the orientational and translational order parameters

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The nature of the deviations from the mean-field approximation for the orientational susceptibility of the isotropic phase of a liquid crystal is related to the existence and proximity of a smectic phase. The observed effects can be described at a quantitative level by a theory incorporating the interaction of two order parameters: orientational (nematic) and translational (smectic).

**1.** A series of experimental studies[1–3] showed that the behavior of the orientational susceptibility in the approach to the transition from the isotropic phase of a liquid crystal to an ordered mesophase (nematic and smectic) differs from the predictions of the Landau–de Gennes theory[4]: In all cases the susceptibility increases more rapidly than $\chi \sim (T - T^*)^{-1}$ (the Curie-Weiss law), where $T^*$ is the temperature of the divergence of the critical fluctuations of the orientation. In principle, these deviations can be explained by allowing for the fluctuational contributions which stem from the nonvanishing cubic invariant in the Landau–de Gennes expansion.[5] For liquid crystals which also have a smectic mesophase, however, the smectic fluctuations which grow near the transition may be more influential. Theoretical models have been proposed[6,7] which incorporate the interaction of an orientational order parameter (nematic) and a one-dimensional translational order parameter (smectic). The result has been a renormalization of the temperature dependence of the susceptibility (the parameter $T^*$ begins to depend on the distance to the transition point). The renormalization should be more extensive, the closer the smectic phase lies to the isotropic phase. The conclusions which have been reached in the few experimental studies[1–3,5,6] of this subject have been contradictory. The apparent reasons are the inadequate experimental accuracy, the narrow temperature interval in which the measurements have been carried out, and the difficulties which confront a comparison of results for liquid crystals belonging to different homologous series.

**2.** For a study of the effect of the proximity of the smectic phase on the orientational susceptibility in the isotropic phase it is convenient to use a mixture of two liquid crystals, so that the width of the nematic zone can be adjusted continuously by adjusting the concentration. The orientational susceptibility in the isotropic phase of a liquid crystal is proportional to the intensity of scattered light.[4] We have carried out some detailed, precise measurements of the temperature dependence of the relative intensity of the scattered light in a mixture of 4-*n*-hexyloxyphenyl-4′-*n*′-hexyloxynitrobenzoate ($\bar{6}O\bar{6}NO_2$) and 4-*n*-hexyloxyphenyl-4-*n*′-decyloxybenzoate ($\bar{6}O\,\overline{10}$), and also in a homologous series of liquid crystals, 4-*n*-hexyloxyphenyl-4-*n*′-*m*-oxybenzoate ($\bar{6}O\bar{m}$), where $m$ is the order of the homolog. The measurements were carried out in

  

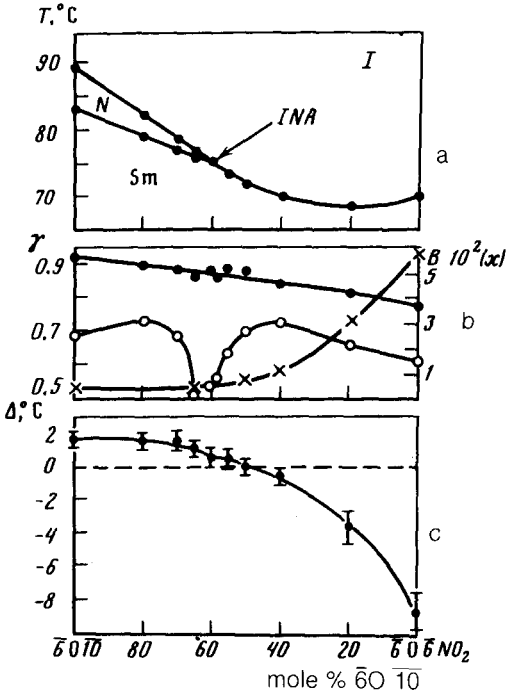


FIG.1. Results of a study of the $\bar{6}O\bar{6}NO_2$/$\bar{6}O\ \bar{1}\bar{0}$ mixture. a—Phase diagram; b—effective curvature $\gamma$ [●—far from the transition; ○—near the transition] and "degree of primogeniture" of the transition; $B = [(T - T^*)/T^*]^\gamma$; c—evolution of the parameter $\Delta$ over a wide neighborhood of the triple point *INA*.

$\bar{6}O\bar{8}$, $\bar{6}O\ \bar{1}\bar{0}$, $\bar{6}O\ \bar{1}\bar{2}$, and their mixtures. Furthermore, we carried out measurements in two samples of a homologous series of cyanobiphenyls: 8CB and 9CB. Figure 1a shows the phase diagram of the $\bar{6}O\ \bar{1}\bar{0}/\bar{6}O\bar{6}NO_2$ mixture; Fig. 2a shows phase diagrams of the $\bar{6}O\ \bar{1}\bar{0}/\bar{6}O\bar{8}$ and $\bar{6}O\ \bar{1}\bar{0}/\bar{6}O\ \bar{1}\bar{2}$ mixtures.[1)]

For the measurements we use an automatic photometer controlled by a DVK-1M microcomputer.[8] The cells are made of a material equivalent to Pyrex, with an inside diameter $\sim 10$ mm. The experimental curves are reproducible within $\sim 1\%$. To evaluate the multiple scattering, we also study some of the samples in cells with an inside diameter $\sim 3$ mm. It turned out that the multiple-scattering contribution does not exceed the experimental error. The cells are filled with the material through a membrane filter (with a pore diameter of 0.22 $\mu$m); then the air is pumped out of the cells, and the cells are hermetically sealed with caps of a material equivalent to Teflon in a nitrogen atmoshere. The temperature of the samples is measured with a platinum thermometer. The error in the temperature regulation does not exceed 0.2 mK. The beam from a helium-neon laser ($\lambda_0 = 6328$ Å, $P = 15$ mW) is attenuated to $\sim 0.3$ mW to avoid any local heating of the sample. The laser beam is polarized vertically, and the scattering angle is 90°. We measure both the polarized and depolarized components of the scattered light.

3. The results are analyzed in accordance with the formula

$$T/I = At^\gamma \qquad (1)$$

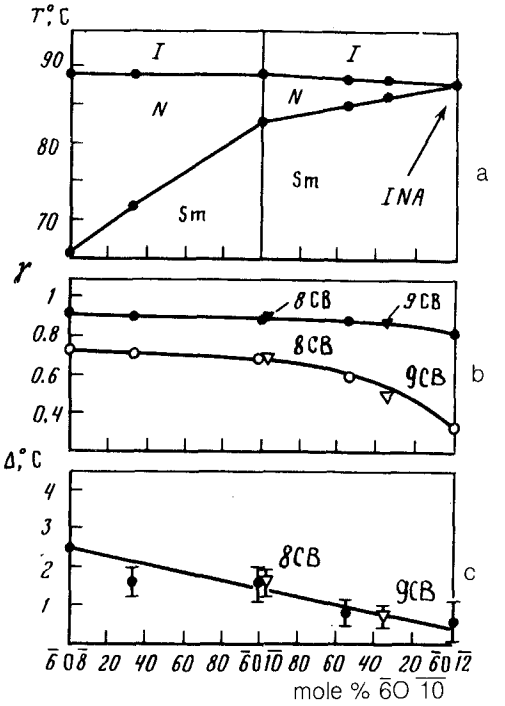


FIG. 2. Results of a study of the mixtures $\bar{6}O\,\bar{1}0/\bar{6}O\bar{8}$ and $\bar{6}O\,\bar{1}0/\bar{6}O\,\bar{1}2$. a—Combined phase diagrams; b—effective curvature $\gamma$ (●,▲—far from the transition; ○,△—near the transition) and the parameter $\Delta$ as the triple point *INA* is approached.

where $I = I(90°)/I(0°)$ is the relative intensity of the scattered light, and $t = T - T^*/T^*$ is the reduced temperature. The effective index $\gamma$ is a measure of the curvature of the temperature dependence (in the mean-field approximation it would be $\gamma = 1$). Since $\gamma$ is a function of $t$, we approximate the data over two $t$ scales: a) far from the transition, at $0.01 < t < 0.1$; b) near the transition, at $t < 0.01$. The results for all of the samples are shown in Figs. 1b and 2b. The data on 8CB and 9CB are presented with the corresponding nematic zones. Comparison of Figs. 1a and 1b and of Figs. 2a and 2b shows that while $\gamma$ exhibits only a weak dependence on the width of the nematic zone far from the transition, with an average value $\gamma \simeq 0.87$, near the transition $\gamma$ varies in accordance with the width of the nematic zone and has a sharp minimum near the triple points INA. The quantity $B$ in Fig. 1b is a measure of the "degree of primogeniture" of the transition. We see that this quantity, after remaining constant at the transition from the isotropic phase to the nematic mesophase, increases sharply at the transition from the isotropic phase to the smectic-$A$ mesophase. We believe that these experimental results clearly prove the existence of an interaction between fluctuations of the orientation (fluctuations of the nematic order) and smectic fluctuations (fluctuations of a one-dimensional density wave), when the nematic zones are sufficiently narrow.

We approximated our data with a model which directly incorporates the interaction of orientational and translational order parameters.[6,7] In the first approximation we have

$$\frac{T}{aI} = \frac{T - T_{IN}^*}{T_{IN}^*} - \frac{B_{NS}^2 T_{IN}^{*3/2}}{(T - T_{IN}^* + \Delta)^{3/2}} \quad (2)$$

where $T_{IN}^*$ and $T_{IS}^*$ are the divergence temperatures of the nematic and smectic fluctuations, respectively, in the absence of an interaction between them; $\Delta = T_{IN}^* - T_{IS}^*$ and $B_{NS}$ is the interaction constant. The constant $B_{NS}$ determines the magnitude of the deviation of $I^{-1}$ from a linear law, while $\Delta$ determines the curvature near the transition. As $\Delta$ decreases the scattering intensity (or the susceptibility) increases progressively more steeply near the transition. This formula gives a good description of the experimental data over the entire temperature range. Figures 1c and 2c show the values of the parameter $\Delta$ for these samples. The value of the parameter $\Delta$ is typically extremely small near the triple point *INA*, and it goes negative for the case of a transition into the smectic mesophase. This result is evidence that the relation $T_{IS}^* > T_{IN}^*$ holds for this transition: The translational order tends to become established before the orientational order.

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[1)]Interestingly, the triple point *INA* corresponds precisely to pure $\overline{6}O\,\overline{12}$. This unusual fact was established by precise calorimetric measurements carried out by V. P. Voronov.

[1]T. W. Stinson and J. D. Litster, Phys. Rev. Lett. **25**, 503 (1970).
[2]E. F. Grambergen, L. Longa, and W. H. de Jeu, Phys. Reports **135**, 195 (1986).
[3]H. J. Coles and C. Strazielle, J. Phys. (Paris) **40**, 895 (1979).
[4]P. G. de Gennes, The Physics of Liquid Crystals, Oxford University Press, 1974.
[5]L. V. Adzhemyan, L. Ts. Adzhemyan, Yu. A. Val'kov, L. A. Zubkov, I. V. Mel'nik, and V. P. Romanov, Zh. Eksp. Teor. Fiz. **87**, 1244 (1984) [Sov. Phys. JETP **60**, 712 (1984)].
[6]A. Gohin, C. Destrade, H. Gasparoux, and J. Prost, J. Phys. (Paris) **44**, 427 (1983).
[7]M. A. Anisimov, E. E. Gorodetskiĭ, and V. É. Podnek, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 412 (1983) [JETP Lett. **37**, 489 (1983)].
[8]V. I. Labko, V. V. Nikitin, G. L. Nikolaenko, G. I. Olefirenko, and I. K. Yudin, Tezisy VIII Vesesoyuznoĭ konferentsii Planirovanie i avtomatizatsiya éksperimenta v nauchnykh issledovaniyakh (Proceedings of the Eighth All-Union Conference on Planning and Automating Experiments in Scientific Research), Leningrad, 1986.

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