Behavior of the Bend Elastic Constant near the Nematic–Smectic-*A*–Smectic-*C* Multicritical Point

Juyang Huang and John T. Ho
Department of Physics and Astronomy, State University of New York at Buffalo, Buffalo, New York 14260
(Received 12 February 1987)

The temperature dependence of the bend elastic constant near the nematic–smectic-*A*–smectic-*C* multicritical point has been measured directly by use of Fréedericksz deformation. The bend elastic constant in two different binary systems is found to increase monotonically in the nematic phase as the smectic-*C* phase is approached. The relation between the bend elastic constant obtained in this study and the smectic correlation lengths derived from x-ray scattering is not described by existing theories. This result also raises questions about the interpretation of previous light-scattering data.

PACS numbers: 64.70.Md, 61.30.Eb, 62.20.Dc

When a liquid-crystal material which has a nematic–smectic-*C* (NC) transition is mixed with another which undergoes both a nematic–smectic-*A* (NA) and a smectic-*A*–smectic-*C* (AC) transition, one obtains an interesting phase diagram containing a nematic–smectic-*A*–smectic-*C* (NAC) multicritical point. As they converge toward the NAC point, the second-order NA and AC phase boundaries and the first-order NC phase boundary are found to exhibit rather universal geometric features.[1] Moreover, the NC transition entropy diminishes toward zero as the NAC point is approached.[2] The many theoretical approaches that have been applied to describe various phenomena associated with the NAC phase diagram fall into two general categories. The first is based on a single infinite-dimensional density-wave order parameter proposed by de Gennes.[3] Using this approach, Chen and Lubensky[4] predicted that the NAC point is analogous to the Lifshitz point originally proposed for magnetic systems.[5] The second class of models involves two order parameters, one for the density wave and another for the tilt of the director relative to the smectic-layer normal.[6-9] These models result in different predictions about the algebraic form of the mass-density fluctuations and about the relation between the Frank elastic constants and the smectic correlation lengths above the NC transition both close to and away from the NAC point. Experimentally, x-ray scattering studies have confirmed the validity of the Chen-Lubensky model in describing the behavior of the smectic susceptibility in the entire NAC phase diagram.[10] Furthermore, very close to the NAC point, both the longitudinal ($\xi_\parallel$) and transverse ($\xi_\perp$) correlation lengths show unusual temperature dependences. As the temperature is decreased in the nematic phase, both quantities increase to a maximum and then decrease as the NC transition is approached, with $\xi_\perp$ increasing again as the density-wave fluctuations change from smectic-*A* type to smectic-*C* type.[10] Light scattering due to bend-mode director fluctuations also shows interesting behavior. Far away from the NAC point, the light-scattering result is consistent with the bend elastic constant K_3 being proportional to $\xi_\parallel\xi_\perp$ above the NC transition,[11] as predicted by the Chen-Lubensky model.[4] Close to the NAC point, however, the light-scattering intensity in the nematic phase as the smectic-*C* phase is approached decreases until it reaches a minimum, and then increases again in the vicinity of the NC transition temperature T_{NC}.[11] It has been suggested that, if the light-scattering intensity is *assumed* to be inversely proportional to K_3, the x-ray and light-scattering experiments are indicative of K_3 and $\xi_\parallel$ being proportional to each other near the NAC point,[12] in apparent agreement with the Chen-Lubensky model.[4] However, because the light-scattering data are subject to unknown corrections in the nonhydrodynamic regime, such a conjecture about the relation between K_3 and $\xi_\parallel$ can only be considered as tenuous until there is direct information about the temperature dependence of K_3. We report here the result of an independent measurement of the behavior of K_3 above the NC transition near the NAC point using Fréedericksz deformation.

Mixtures of heptyloxy-*p*′-pentylphenylthiobenzoate ($\bar{7}$S5) with either octyloxy-cyanobiphenyl (8OCB) or octyloxy-*p*′-pentylphenylthiobenzoate ($\bar{8}$S5) were used in our study. The two sets of mixtures were chosen because the former exhibits the empirically universal NAC phase diagram while the latter represents the earlier prototype that has been widely studied. For Fréedericksz deformation measurement, a magnetic field was applied normal to the director of a homeotropically aligned sample of thickness *d*. With the sample between crossed polarizers whose axes were oriented at 45° to the field direction, the intensity of transmitted light was monitored as a function of magnetic field. The critical field H_c for the Fréedericksz transition to take place gives K_3 through the relation[13]

$$H_c = (\pi/d)(K_3/\Delta\chi)^{1/2},$$

where $\Delta\chi$ is the diamagnetic anisotropy.[14] To correlate our results better with previous light-scattering observations, we also measured the temperature dependence of the light-scatterng intensity from bend-mode fluctuations in the specific mixtures reported here. This was achieved by our using homogeneously aligned samples and choosing the scattering wave vector **q** to be parallel to the director, with a typical magnitude of about 6×10^{-4} Å^{-1}.[15]

Figure 1 shows the temperature dependence of $K_3/\Delta\chi$ in a $\bar{7}S5_{1-x}8OCB_x$ mixture with 8OCB molar concentration of $x=0.0191$, which is close to the multicritical concentration of $x_{NAC}=0.0217$. It can be seen that $K_3/\Delta\chi$ increases monotonically in the nematic phase as the smectic-*C* phase is approached. With a sample of thickness 152 μm, the value of H_c increases from 0.47 kG at 11.15 °C above T_{NC} to 3.65 kG at 0.01 °C above T_{NC}. Since we do not expect any pronounced temperature dependence of $\Delta\chi$ near the NAC point (as confirmed by our independent measurement of the birefringence), the behavior of $K_3/\Delta\chi$ should essentially reflect that of K_3. Our observed temperature dependence of $K_3/\Delta\chi$ is qualitatively similar to that found near most NA transitions, but is vastly different from what is expected on the basis of light-scattering and x-ray diffraction data near the NAC point. For comparison, we have included in Fig. 1 the temperature dependence of the inverse light-scattering intensity I^{-1} from bend-mode director fluctuations that we have measured in the same mixture. The $K_3/\Delta\chi$ and I^{-1} data have been scaled to coincide at high temperatures. It can be seen that the two sets of data follow basically the same temperature dependence between 11 and 1.5 °C above T_{NC}. At lower temperatures, however, the value of I^{-1} falls below that of $K_3/\Delta\chi$, reaches a peak at 0.8 °C above T_{NC}, and then decreases upon further cooling. This behavior of I^{-1} has been seen previously in similar mixtures.[11,12] To contrast the temperature dependence of $K_3/\Delta\chi$ with that of $\xi_\parallel$, Fig. 1 also contains the data on $\xi_\parallel$ (measured at $q_\perp=0$) deduced from x-ray scattering in an almost identical mixture with $x=0.0197$,[10] again scaled to coincide with the $K_3/\Delta\chi$ data at high temperatures. The difference between $K_3/\Delta\chi$ and $\xi_\parallel$ data is clearly apparent. While $\xi_\parallel$ attains a peak value before reaching T_{NC} which is 12 times the high-temperature value, $K_3/\Delta\chi$ exhibits a fortyfold monotonic increase all the way to T_{NC}. It should be noted that our attempts to fit the $K_3/\Delta\chi$ data by a simple power-law temperature dependence were not successful.

To see whether our findings in the $\bar{7}S5$-8OCB mixture are unique to systems which are described by the empirically universal NAC phase diagram, we have also repeated our Fréedericksz-deformation and light-scattering measurements in $\bar{7}S5_{1-y}\bar{8}S5_y$ mixtures, which exhibit an NAC phase diagram with somewhat different topology.[1] Figure 2 shows the temperature dependence of $K_3/\Delta\chi$ and I^{-1} above the NC transition in a sample with a molar concentration in $\bar{8}S5$ of $y=0.569$, which is just below the multicritical concentration $y_{NAC}=0.58$. It can be seen that there exists the same dramatic difference between the behavior of $K_3/\Delta\chi$ and that of I^{-1} in this $\bar{7}S5$-$\bar{8}S5$ mixture as in the $\bar{7}S5$-8OCB mixture.

Our results lead to two intriguing but inescapable conclusions. The first, that K_3 is not proportional to I^{-1}, invalidates the key assumption previously used in the interpretation of light-scatterng data.[12] This is not exactly surprising, in view of the magnitude of the light-scattering wave vector **q** in our experiment and the values of $\xi_\parallel$ found by x-ray scatterng.[10] For the $\bar{7}S5$-8OCB mixture, $q\xi_\parallel$ exceeds 1 between 2.5 and 0.1 °C above T_{NC}. Under such a nonhydrodynamic condition, I^{-1} is expected to be less than what it would be if it

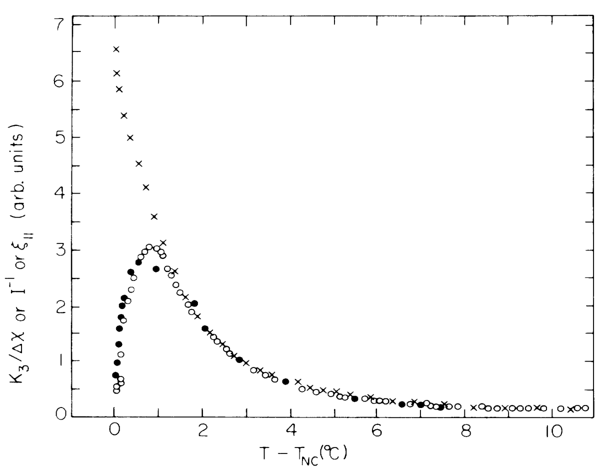

FIG. 1. Temperature dependence of $K_3/\Delta\chi$ (crosses) and inverse bend-mode light-scattering intensity I^{-1} (open circles) above T_{NC} in a $\bar{7}S5_{1-x}8OCB_x$ mixture with $x=0.0191$. The solid circles are data on $\xi_\parallel$ (measured at $q_\perp=0$) from Ref. 10 in a sample with $x=0.0197$.

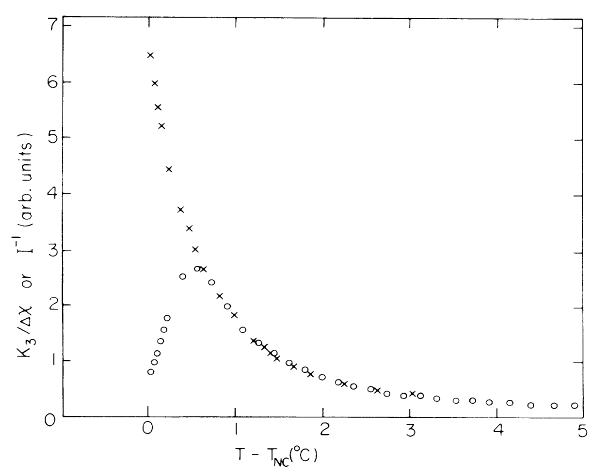

FIG. 2. Temperature dependence of $K_3/\Delta\chi$ (crosses) and I^{-1} (open circles) above T_{NC} in a $\bar{7}S5_{1-y}\bar{8}S5_y$ mixture with $y=0.569$.

were proportional to K_3, although there is no formalism for quantitative calculations. However, we do not have a simple explanation for the increase in light-scattering intensity in the immediate vicinity of T_{NC}.

The second consequence of our results is more fundamental. All existing theories on the NAC point predict simple relations between K_3 and the smectic correlation lengths above the NC transition. For example, K_3 is expected to be proportional to $\xi^{3/2}$ in the de Gennes model,[3] to $\xi_\parallel$ in the Chu-McMillan model,[6] and to $\xi_\parallel\xi_\perp$ (away from the NAC critical region) or $\xi_\parallel$ (within the NAC critical region) in the Chen-Lubensky model.[4] Clearly, none of these theories is able to account for the complicated relation between K_3 and $\xi_\parallel$ reported here. A reexamination of the theoretical models is needed in order to reconcile this discrepancy, especially the Chen-Lubensky model which has been fairly successful in describing other observed phenomena near the NAC point.

We would like to thank M. E. Neubert of Kent State University for our $\bar{7}$S5 and $\bar{8}$S5 samples. This work was supported by grants from the National Science Foundation and the U.S. Office of Naval Reserach.

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