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Correlation Range of Fluctuations of Short-Range Order in the Isotropic Phase of a Liquid Crystal*

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We have measured the correlation range for fluctuations of the orientational order parameter in the isotropic phase of the liquid crystal *p*-methoxy benzylidene, *p*-*n* butyl aniline (MBBA). The correlation range was found to diverge as $(T - T_c^*)^{-1/2}$, in agreement with the predictions of de Gennes. This result is in contradiction with the behavior reported by Chu, Bak, and Lin.

The nematic-isotropic phase transition has been the subject of considerable recent research.[1-4] Although a first-order phase transition, it displays such a striking variety of pretransitional phenomena that it might be said to be "almost" second order. In the isotropic phase the light-scattering power[1] (Rayleigh ratio), the magnetic[1] and flow[2] induced birefringence, and the relaxation time[3] for the fluctuations in short-range order all increase rapidly as the phase transition is approached. These observations are all satisfactorily accounted for[4] by a phenomenological (Landau type) model proposed by de Gennes.[5] There remains one prediction of this model which has yet to be confirmed—the temperature dependence of the correlation length for short-range order in the isotropic phase. In this Letter we report experimental measurements of this correlation length which agree with the predictions of the de Gennes model.

An appropriate order parameter for a nematic liquid crystal is a symmetric traceless second-rank tensor proportional to the anisotropy in the dielectric-constant tensor.[5] One may write this as $Q_{\alpha\beta} = (3/2\Delta\epsilon)(\epsilon_{\alpha\beta} - \bar{\epsilon}\delta_{\alpha\beta})$, where $\Delta\epsilon$ is the maximum anisotropy for a perfectly ordered liquid crystal. In the de Gennes model the free energy is assumed to be an analytic function of temperature and order parameter. In the vicinity of the phase transition the free-energy density has the form ($\partial_\alpha \equiv \partial/\partial x_\alpha$)

$$\varphi = \varphi_0 + \tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha} - \tfrac{1}{3}BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \tfrac{1}{4}C(Q_{\alpha\beta}Q_{\beta\alpha})^2 + \tfrac{1}{2}L_1\partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma} + \tfrac{1}{2}L_2\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} + \cdots. \quad (1)$$

de Gennes chooses $A = a(T - T_c^*)^\gamma$ and all other coefficients only weakly temperature dependent. In the mean-field approximation $\gamma = 1$; this is experimentally verified.[1]

This free-energy expression may be used to calculate the mean square fluctuations in $Q_{\alpha\beta}$ in the isotropic phase, and hence the intensity of the light scattered by these fluctuations, by applying the equipartition theorem to the Fourier transform of Eq. (1). One finds[4,5] that when the incident and scattered light are both polarized perpendicular to the scattering plane (polarized scattering), the intensity of scattered light is proportional to

$$\langle \delta\epsilon_{VV}{}^2(\vec{q}) \rangle = \tfrac{4}{3}(2kT\Delta\epsilon^2/9AV)(1 - \xi_1{}^2q^2 - \tfrac{1}{6}\xi_2{}^2q^2). \tag{2a}$$

When the incident light is polarized normal to, and the scattered light parallel to, the scattering plane (depolarized scattering), the intensity is proportional to

$$\langle \delta\epsilon_{VH}{}^2(\vec{q}) \rangle = (2kT\Delta\epsilon^2/9AV)[1 - \xi_1{}^2q^2 - \tfrac{1}{2}\xi_2{}^2q^2\cos^2(\theta/2)]. \tag{2b}$$

In these expressions V is the scattering (illuminated) volume, while $\xi_1 = (L_1/A)^{1/2}$ and $\xi_2 = (L_2/A)^{1/2}$ are two correlation lengths which define the size and ellipticity of the spatial region over which fluctuations in $Q_{\alpha\beta}$ are coherent. (The expressions are not exact; they omit terms of order ξ^4q^4 and higher.) The magnitude of the scattering wave vector $\vec{q}$ is $q = (4\pi/\lambda)n\sin(\theta/2)$, where θ is the scattering angle. Therefore, in principle, the correlation lengths can be determined from measurements of the angular dependence of the intensity of the scattered light. Previous attempts by the present authors[1] indicate that ξ_1 and ξ_2 are quite small, probably less than 100 Å. Thus $\xi q < 0.1$ and the omission of ξ^4q^4 terms from Eqs. (2a) and (2b) is justified.

The measurement of correlation lengths smaller than 100 Å with visible light requires careful attention to the experimental apparatus and method. To measure this small angular dependence, we have used the apparatus shown in Fig. 1. When the chopper wheel (*CH*) is in a position so the right-hand aperture is open, the laser[6] beam is transmitted directly through the scattering cell (*SC*). When the chopper aperture is open on the left side of the wheel, the direct beam is blocked, and the beam reflected by the beam splitter (*BS*) is transmitted by mirrors M_1, M_2, and M_3 along the same path in the cell but in the reverse direction. Photocells P_1 and P_2 sense which direction the beam is traveling through the sample and operate an electronic switch to channel pulses from the photomultiplier tube (PMT) into the appropriate counter. The chopper operates at a frequency of about 240 Hz and thus enables one to measure the ratio of the intensities of light scattered by an angle θ and its supplement. An absolute calibration is obtained by making a measurement at $\theta = 90°$.

Certain precautions are necessary when using this technique. Mechanical stability of the optical alignment is essential in order that the positions of the two beams in the scattering cell remain stable. This we assured by massive optical mountings and supporting the entire apparatus on a $1\frac{1}{2}$-ton granite table. It is also vital that the optics be designed and aligned so that the scattering volume observed by the PMT does not shift with scattering angle. This is especially important in a liquid crystal where the turbidity (which determines the relative intensities of the incident beams in the scattering volume) has the same

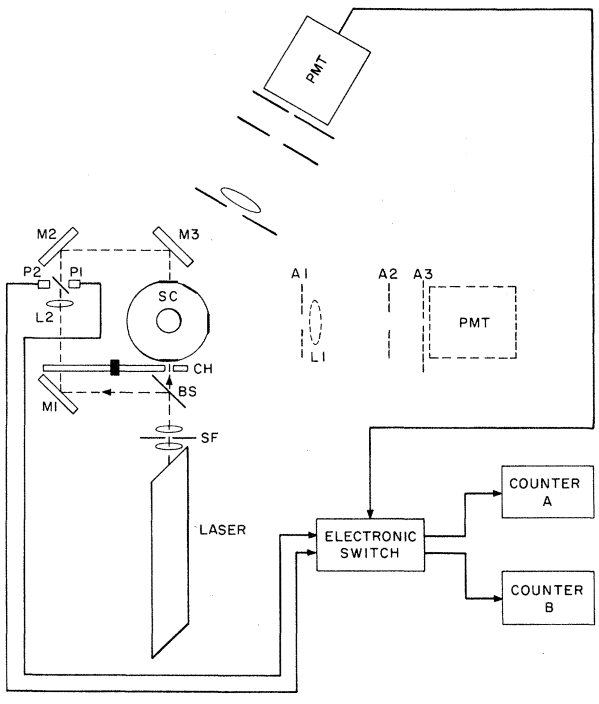

FIG. 1. Diagram of the apparatus used to measure very small anisotropies in the intensity of scattered light.

temperature dependence as the angular intensity anisotropy we seek to measure. Finally, the most difficult requirement to meet is the exclusion of all stray light, for the presence of stray light only a few tenths of a percent of the intensity scattered by the sample region being studied can cause anisotropies as large as that being measured. This problem becomes even more serious as the temperature is raised farther above the phase transition because both the intensity scattered by the sample and the effect being studied become smaller. By very careful cell design we were able to eliminate stray light originating outside the sample cell and from reflections within the cell. As we shall discuss presently, we experienced difficulty with light scattered by particulate impurities in the sample.

The liquid crystal sample used was commercially available p-methoxy benzylidene, p-n butyl aniline (MBBA).[7] The scattering cell was first flushed with a large amount of solvent filtered through a 0.22-μm membrane filter, then dried, and the MBBA added, also through a 0.22-μm filter. This was the finest filter we could practically use because of the high viscosity of MBBA.

Our measurements of the temperature-dependent anisotropy in the depolarized light intensity enable us to deduce ξ_1 as a function of temperature. [Examination of Eq. (2b) for the anisotropy between an angle and its supplement shows that the ξ_2 term cancels out.] We find that

$$\xi_1 = (6.8 \pm 1.0)(T/T_c^* - 1)^{-1/2}\ \text{Å},$$

which has the temperature dependence predicted by de Gennes's model and also the magnitude one would estimate from other considerations.[1,5] The experimental points are shown as solid circles in Fig. 2, along with a least-squares fit using the prediction of Eq. (2b). Data are shown for two samples with differing phase-transition temperatures. We see that the effect of impurities is principally to lower T_c^*, all other parameters in the free energy, Eq. (1), being essentially constant for small enough amounts of impurity. This is also confirmed by our earlier measurements on MBBA[1]; we have found T_c^* to be 1.0°C below the first-order phase transition even in samples with T_c^* as low as 35°C.

Our measurements of the anisotropy in the polarized component of the scattered light revealed quite different behavior. Immediately above the phase transition the apparent value of ξ decreased but then it leveled off at about 50 Å and actually

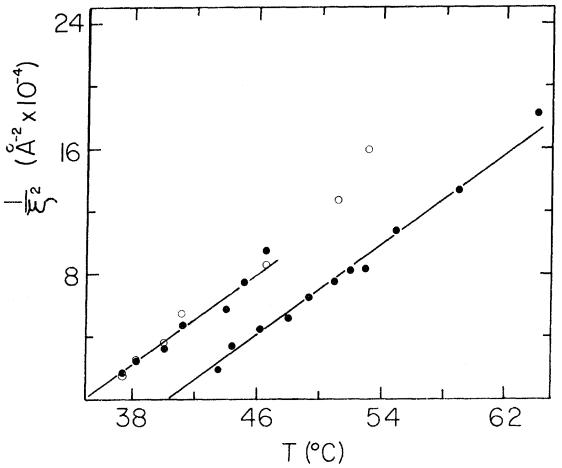

FIG. 2. Reciprocal of the square of the correlation length ξ_1 as a function of temperature in the isotropic phase of MBBA. Data are shown for two samples (see text). Open circles denote corrected data for polarized component. Closed circles denote depolarized component.

increased slightly at the highest temperatures we measured. (This is similar to the behavior noted by Chu, Bak, and Lin,[8] who found, however, a leveling off in both polarized and depolarized values for ξ at a considerably higher value of $\xi \simeq 120$ Å.) We do not believe these results to be a characteristic of the liquid crystal; it is physically unreasonable that the correlation range should remain essentially constant over a temperature range where other quantities such as magnetic birefringence or the intensity of scattered light are changing rapidly. On the face of these results L_2 would have to be strongly temperature dependent, which contradicts the observed temperature dependence[9] of the elastic constants in the ordered phase.[10]

Therefore, we believe that the explanation for the temperature dependence of the anisotropy in the polarized light (shown as an effective ξ in Fig. 3) lies in the presence of small amounts of particulate impurities in the sample. We might expect these impurities to scatter only polarized light with a temperature-independent cross section. This would suffice to explain completely the temperature dependence of the effective correlation length for polarized scattering.

There are two ways to test this hypothesis. First, one expects the depolarization ratio to differ from $\frac{4}{3}$. If a constant is added to Eq. (2a), the depolarization ratio may be written as $\frac{4}{3}[1 + p(T - T_c^*)]$. The parameter p is a measure of

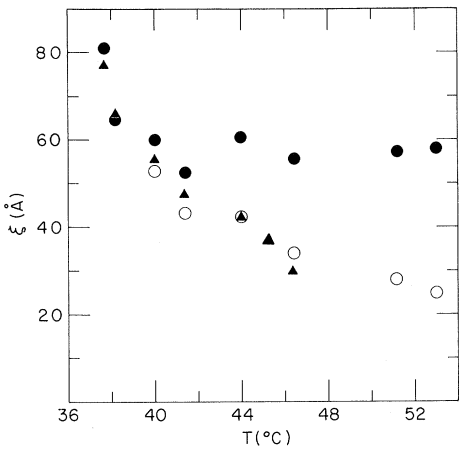

FIG. 3. Functions of temperature in the isotropic phase of MBBA: triangles, correlation length ξ_1; closed circles, effective correlation length for polarized light scattering; open circles (see text), corrected correlation length for polarized light.

the intensity of the light scattered by the impurity particles. From its angular dependence one can estimate their effective diameter. By careful measurements of the depolarization ratio we find $p \simeq 4\times10^{-3}$ °C^{-1} at $\theta = 30°$ and $p \simeq 3\times10^{-3}$ °C^{-1} at $\theta = 90°$. These values are consistent with particles of diameter 1150 Å,[11] which is an effective mean size for the distribution of particles that were able to pass through the 2200-Å filter. It is striking that these particles scatter less than 1% as much light as do the order-parameter fluctuations close to the phase transition, and yet they account quantitatively for the effective correlation length we observe with polarized scattering. If the index of refraction of these impurity particles differed from that of MBBA by 5%, the effects we observe could be accounted for by a volume fraction of 1 part in 10^6 of impurity.

A second test for the presence of particle impurities lies in the spectrum of the light they scatter. Using a digital autocorrelator, we were able to detect a spectral component caused by the Brownian motion of the particles. The correlation time observed was 20 ± 4 msec at a scattering angle of 30°. This corresponds[12] to particles of diameter 1050 ± 150 Å diffusing in MBBA at 350°K with a viscosity of 7 cP.[2]

Knowing the effective size of the impurity particles in the liquid crystal and the relative intensity of light they scatter, we are able to correct for their presence in the polarized-light-scattering results. The corrected results are shown in Fig. 3 as open circles. From Eq. (2a) we expect the effective correlation length for polarized scattering to be $\xi_p^2 = \xi_1^2 + \frac{1}{6}\xi_2^2$. Within our experimental errors it appears to be identical to the length for depolarized scattering $\xi_d^2 = \xi_1^2$. We are able to place un upper bound of 1.6×10^{-12} cm^2 °C on L_2/a as compared with our measured value of $(1.45\pm0.4)\times10^{-12}$ cm^2 °C for L_1/a. This may be compared with the value $L_1/a = 3.7\times10^{-12}$ cm^2 °C found by Yang[13] for a cholesteric liquid crystal and reinforces de Gennes's hypothesis that there is little thermodynamic difference between cholesteric and nematic liquid crystals. Imura and Okano also report[14] that a value $L_1/a \simeq 10^{-12}$ cm °C accounts for the anomalous specific heat observed in the isotropic phase of *p*-azoxyanisole.

In conclusion, we feel that de Gennes's phenomenological model accounts satisfactorily for all properties of the isotropic phase of nematic liquid crystals that can be observed by direct optical measurements of the order parameter. We believe that the correlation range values for MBBA reported in Ref. 8 are in error; we do not presume to explain the cause of the error, but it could be due to any of the experimental problems we have discussed.

We appreciate helpful discussions with Professor David S. Cannell and the late Dr. Joseph H. Lunacek whose technique for measuring the correlation range for critical density fluctuations[15] was the inspiration for the apparatus described here.

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Fluctuation Diamagnetism in a "Zero-Dimensional" Superconductor*

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The diamagnetic transition of ensembles of single-crystal aluminum particles with radii less than the superconducting coherence length ξ_0 has been measured over a wide range of temperature, field, and average radius. The particles are sufficiently small that the Ginzburg critical region is experimentally accessible. Fluctuation effects are observed inside and outside this critical region. The data agree with recent exact theoretical calculations based on the Ginzburg-Landau functional.

The effect of thermodynamic fluctuations on a zero-dimensional superconductor, i.e., one with all of its dimensions less than the superconducting coherence length, has been the object of recent theoretical interest[1-7] because the Ginzburg critical region,[8] within which the mean field theory cannot be expected to be valid, was expected[2] to become accessible to experiment in sufficiently small particles. This case permits a detailed investigation for the first time of the true critical region in a superconductor to determine whether the analytical form of the Ginzburg-Landau (GL) free energy breaks down completely there, or whether this free energy can be used as an energy functional in a canonical average over all accessible values of the order parameter. Fortunately, there also exists an exact fluctuation theory[1,3-7] based on the GL functional which is expected to be valid both outside and inside this critical region. Since spatial variations of the order parameter are energetically too costly to be thermally activated, only spatially uniform fluctuations need be considered, and the quartic term in the free-energy functional can be included exactly in fluctuation calculations. In systems of higher dimensionality this quartic term is either approximated or neglected. Thus most fluctuation calculations tend to fail as the critical region is approached. The feature of the zero-dimensional superconductor that greatly facilitates measurements is the suppression of the magnitude of the mean-field diamagnetism below T_c as particle size decreases. Hence, fluctuation effects, though small in absolute magnitude, can be readily observed at and below T_c as well as above.

We report here the results of an extensive set of measurements that we have made both inside and outside the critical region on the superconducting diamagnetic transition of ensembles of small electrically isolated nearly perfect single-crystal Al particles. The average radius of these mostly spherical particles varied from over 4000 Å to less than 125 Å and readily satisfied the zero-dimensional criterion. The measurements were carried out in magnetic fields varying from less than 0.01 Oe to more than 1500 Oe and over a temperature range extending from less than $0.5T_c$ to more than $3T_c$. This large variation in experimental parameters allowed clear identification of the various features of the transitions and permitted close comparisons to be made with theoretical calculations.

Shmidt[1] and others[3-6] have calculated the susceptibility of zero-dimensional particles in the temperature region around T_c by assuming the validity of the GL free-energy functional and evaluating the integral

$$\langle|\psi|^2\rangle = \int \psi^2 \exp(-F_{GL}/k_B T)\, d\psi^2,$$

where

$$F_{GL} = \int (\alpha|\psi|^2 + \tfrac{1}{2}\beta|\psi|^4 + \hbar^2|\nabla\psi|^2/2m)\, d^3r$$