

## Light-Scattering Study of the Structure of Blue Phase III

E. P. Koistinen and P. H. Keyes

*Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48202*

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We measure the structure factors of both the isotropic liquid and the as yet poorly understood blue phase III (BPIII) in the vicinity of the transition between these two phases. The data taken in the isotropic phase are consistent with conventional short-range correlations decaying exponentially with distance, whereas the BPIII data indicate a new and different type of short-range order.

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Chirality can have a profound effect on liquid crystalline structures and phase transitions. Nowhere is this more evident than in the cholesteric liquid crystals where high chirality induces new structures—the blue phases—and also produces strong fluctuation effects. The blue phases known as BPI and BPII, found at intermediate chiralities, are unusual cubic structures in which the orientational (but not the positional) ordering is periodic in three dimensions [1]. At higher chiralities the BPI and BPII lattices become unstable because of fluctuation effects [2], as is evidenced by the measurements of the temperature dependences of the Debye-Waller factors [3], and these structures “melt” into the third blue phase (BPIII).

The determination of the structure of BPIII (also known as the “fog phase” and the “blue fog”) is one of the outstanding unsolved problems in liquid crystal physics and is the subject of this Letter. Although various exotic structures with long-range order have been proposed for BPIII, most observations suggest that it is amorphous. What remains to be determined is how the isotropic “melted liquid crystal” that constitutes BPIII differs from the usual isotropic liquid phase found at temperatures just above the BPIII range.

For amorphous materials the only meaningful measure of structure is the structure factor, the Fourier transform of the correlation function of the short-range order. In this Letter we report on a light-scattering experiment that measures the structure factors of both BPIII and the isotropic phase in a relatively low chirality system in which the transition between these two liquids is decidedly first order. There is already a well developed Landau–de Gennes mean-field theory for the temperature and wave-vector dependence of the structure factor of the isotropic phase [4]. This theory is tested here more thoroughly than ever before and is found to be in good agreement with all of the data taken in the isotropic phase right up to the transition to BPIII. The structure factor in BPIII, however, is found to be different from that of the isotropic phase, the more so the farther below the isotropic-BPIII transition one goes.

We must first point out that the structure factor to be discussed here is more complex than that of an ordinary liquid whose order parameter, the density, is merely a

scalar. For orientational ordering the order parameter is a rank-two tensor which, using a macroscopic description, can be taken to be the anisotropic part of the dielectric tensor,

$$\delta \varepsilon_{\alpha\beta} = \varepsilon_{\alpha\beta} - \frac{1}{3} \varepsilon_{\gamma\gamma} \delta_{\alpha\beta}. \quad (1)$$

The thermal average of this quantity is zero in an isotropic liquid, so the left-hand side of the above equation has been labeled with a “ $\delta$ ” to emphasize that it is only the fluctuations about zero value that constitute the “structure” in the isotropic phase and, as far as we know, in BPIII.

Since  $\delta \varepsilon_{\alpha\beta}$  is both symmetric and traceless, it has just five independent components and can be expanded as

$$\delta \varepsilon_{\alpha\beta} = \sum_{m=-2}^2 \varepsilon_m M_{\alpha\beta}^{(m)}, \quad (2)$$

where the  $\varepsilon_m$ 's are the magnitudes of the five components of the order parameter and the  $M^{(m)}$ 's are a set of basis matrices

$$\begin{aligned} M^{(0)} &= \frac{1}{\sqrt{6}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \\ M^{(\pm 1)} &= \frac{1}{2} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & \pm i \\ 1 & \pm i & 0 \end{pmatrix}, \\ M^{(\pm 2)} &= \frac{1}{2} \begin{pmatrix} 1 & \pm i & 0 \\ \pm i & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (3)$$

that are isomorphic to the five  $Y_{2m}$  spherical harmonics [4].

The structure factor, proportional to the intensity of light scattered at wave vector  $q$ , is given by

$$S(q) \propto \langle |i_\alpha \delta \tilde{\varepsilon}_{\alpha\beta}(\mathbf{q}) f_\beta|^2 \rangle, \quad (4)$$

where  $i_\alpha$  and  $f_\beta$  are, respectively, the polarization vectors of the incident and scattered light and  $\delta \tilde{\varepsilon}_{\alpha\beta}(\mathbf{q})$  is the Fourier transform of  $\delta \varepsilon_{\alpha\beta}(\mathbf{r})$ . It is clear from Eqs. (2) and (4) that the structure factor can have contributions from all five components of the order parameter fluctuations, but through judicious choice of experimental geometry this number can be reduced. In our experiment we effectively see only the fluctuations of  $\tilde{\varepsilon}_2(q)$ , which, as

we shall see, is also the most important component of the order parameter in that it has the highest effective critical temperature and the largest fluctuations in all of the blue phases as well as in the isotropic phase.

To reduce the number of contributing components we first let both  $i_\alpha$  and  $f_\beta$  be left circularly polarized states, and, then, with the scattering angle indicated by  $\theta$ , the scattered intensity will be given by

$$I(q) \propto [1 + \sin(\theta/2)]^4 \langle |\tilde{\varepsilon}_2(q)|^2 \rangle + [1 - \sin(\theta/2)]^4 \langle |\tilde{\varepsilon}_{-2}(q)|^2 \rangle + \frac{2}{3} \cos^4(\theta/2) \langle |\tilde{\varepsilon}_0(q)|^2 \rangle, \quad (5)$$

which involves only three components of the order parameter. If, in addition, attention is confined to the backscattering region ( $\theta \approx 180^\circ$ ), only the first term in Eq. (5) will be expected to contribute significantly. In fact, even for angles as far away from backscattering as  $\theta = 70^\circ$ , the smallest angle used in our experiment, the prefactors of the second and third terms are, respectively, less than 0.5% and 5% of that of the first term. In addition, the magnitude of  $\langle |\tilde{\varepsilon}_2(q)|^2 \rangle$  for a left-handed system is expected to be larger than that of either  $\langle |\tilde{\varepsilon}_{-2}(q)|^2 \rangle$  or  $\langle |\tilde{\varepsilon}_0(q)|^2 \rangle$ , so we believe that our experiment measures essentially only the  $m = 2$  component, the most important component of the structure.

The strength of fluctuations in the isotropic phase may be evaluated by applying the equipartition theorem to the quadratic part of the free energy which looks like

$$F = F_0 + \frac{1}{3} A \delta \varepsilon_{\alpha\beta} \delta \varepsilon_{\beta\alpha} + \frac{1}{2} L \delta \varepsilon_{\alpha\beta,\gamma} \delta \varepsilon_{\alpha\beta,\gamma} - L q_0 e_{\alpha\beta\gamma} \delta \varepsilon_{\alpha\mu} \delta \varepsilon_{\beta\mu,\gamma}. \quad (6)$$

Here, as usual, the coefficient  $A$  is assumed to be linear in temperature,  $q_0$  is the cholesteric wave vector, and we have, for simplicity, employed the one elastic constant approximation. The average squares of the order parameter components are then easily evaluated to be

$$\langle |\varepsilon_m|^2 \rangle \propto \frac{k_B T}{A + L(q^2 - m q q_0)}. \quad (7)$$

Thus, as mentioned above, the greatest scattered intensity will be for  $q \approx q_0$  and  $m = 2$ , for which one has

$$\langle |\varepsilon_2|^2 \rangle \propto \frac{k_B T}{A - L q_0^2 + L(q - q_0)^2} = \frac{k_B T}{A' + L(q - q_0)^2}. \quad (8)$$

In the last part of this equation we define  $A'$  through  $A' = A - L q_0^2$  and  $T^*$  through  $A' = A_0(T - T^*)$ . The half-width of the Lorentzian of Eq. (8) is the correlation length  $\xi$  for the  $m = 2$  mode, i.e.,  $\xi^2 = L/A' = \xi_0^2 t^{-1}$ , where the reduced temperature  $t$  is defined as  $t = (T - T^*)/T^*$  and the bare correlation length  $\xi_0$  is given by  $\xi_0^2 = L/A_0 T^*$ .

For our study we chose the liquid crystal cholesteryl oyl carbonate (COC) because it has a very wide BPIII range while at the same time having a selective reflection that is not too far into the ultraviolet. To bring the

selective reflection into the visible range, and hence  $q_0$  into the experimentally accessible region, we added 12% by weight of cholesteryl chloride, whose chirality is the opposite handedness, to the COC. For this mixture and with the 442 nm He-Cd laser used for the incident beam, the value of  $q_0$  should in theory correspond to a scattering angle of  $\theta = 140^\circ$ , bringing the peak of the structure factor just inside our maximum accessible angle of  $150^\circ$ .

A further reason for using COC is that its dielectric anisotropy is relatively small and multiple scattering problems are, thereby, minimized. If we had instead used a chiral nematic compound having a larger dielectric anisotropy, such as CE2, for instance, the present experiment would probably not have been possible to perform because of the enormous turbidity of the sample in the BPIII region.

To summarize the experimental arrangement, we use a linear polarizer and a quarter wave plate to produce a left circularly polarized incident beam and a similar combination of polarizer and wave plate in front of the photomultiplier detector in order to receive left circularly polarized scattered light. Starting at  $37^\circ\text{C}$ , we move downward in steps of  $0.05^\circ\text{C}$  and at each temperature record the scattered intensity for scattering angles for  $70^\circ$  to  $150^\circ$  at intervals of  $5^\circ$ .

Figure 1 shows the inverse of the intensity measured at the  $140^\circ$  scattering angle, where the scattering is strongest. All of the other angles show the same general features: The inverse intensity is a linear function of the temperature in the isotropic phase (up to at least  $37^\circ\text{C}$ ), nonlinear in the BPIII region, and discontinuous at the isotropic-BPIII phase transition. Extrapolating the linear isotropic data gives an effective  $T^*$  for each scattering angle and this  $T^*(\theta)$  is displayed in the inset of Fig. 1. A quadratic fit to these data does indeed peak at the angle corresponding to the wave vector  $q_0$  deduced from the measurement of the cholesteric selective

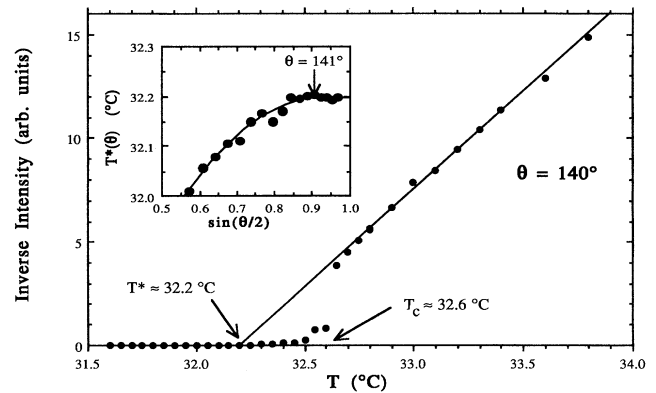


FIG. 1. The inverse of the scattered intensity taken at  $\theta = 140^\circ$ , the angle of maximum scattering. The intercept gives the temperature  $T^*$  for this angle. Inset:  $T^*$  obtained for all of the scattering angles used in the experiment.

reflection ( $\lambda_0 = 4800 \text{ \AA}$ ) and, furthermore, using Eq. (8) and the definitions following it, the quadratic fit provides a determination for the bare correlation length  $\xi_0$  of  $15 \text{ \AA}$ .

To continue the analysis of the data further to obtain the  $\langle |\tilde{\epsilon}_2(q)|^2 \rangle$  contribution to the structure factor requires a normalization of the measured intensities. A correction for the angular variation given by the trigonometric prefactor of  $[1 + \sin(\theta/2)]^4$  in Eq. (5) must be made and then the change in scattering volume with angle must also be taken into account. We accomplish both of these tasks simultaneously by normalizing the intensity at each angle so that the derived value of  $\langle |\tilde{\epsilon}_2(q)|^2 \rangle$  will be independent of  $q$  at temperatures very far above the transition, as required by Eq. (8). This empirical method of normalizing the data is close to but not exactly the same as the theoretical combination of the trigonometric correction factors discussed above, probably because the actual change in the scattering volume with angle does not follow the theoretical  $1/\sin(\theta)$  dependence precisely.

At temperatures close to the phase transition to BPIII the  $q$  variation of the normalized intensities becomes apparent and should, according to Eq. (8), be given by a Lorentzian centered on  $q_0$  and whose half-width is the correlation length  $\xi$ . In order to see if this predicted behavior is indeed followed, it is convenient to plot the inverse normalized intensity versus  $(q/q_0 - 1)^2$ , as we have done in Fig. 2. The straight line behavior for data in the isotropic phase as well as the constancy of slopes verifies the predictions of the mean-field theory and the harmonic approximation. Although we have not shown all the high temperature data, the predicted behavior persists at higher temperatures and allows us to calculate a correlation length with confidence up to at least  $34 \text{ }^\circ\text{C}$ .

From  $34$  down to  $32.6 \text{ }^\circ\text{C}$ , the transient temperature, the correlation length we thus find increases from  $180$  up to  $370 \text{ \AA}$ . These values are much larger than one finds in a nematic liquid crystal, where for a typical thermotropic material one finds  $\xi \approx 100 \text{ \AA}$  at  $T_c$ . The main reason for this difference is that in the case of the cholesteric material one approaches  $T^*$  more closely ( $0.4 \text{ }^\circ\text{C}$  rather than  $1 \text{ }^\circ\text{C}$ ). However, it is important to note that the correlation length is still significantly smaller than the cholesteric pitch.

At a temperature of  $32.60 \text{ }^\circ\text{C}$ , just below the phase transition, the linear behavior that had been followed in the isotropic phase quite suddenly and discontinuously ceases to hold and the structure factor in the BPIII region is therefore not describable as a simple Lorentzian. The data at  $32.55 \text{ }^\circ\text{C}$  more or less repeat those of  $32.60 \text{ }^\circ\text{C}$ , which we take to be evidence of a two phase region of the order of  $0.05 \text{ }^\circ\text{C}$ , further indication of the first order character of the transition. As the temperature is lowered the deviation from Lorentzian shape progresses more and more.

There is at present no theory for the BPIII phase and, therefore, no predictions against which to check our experimental results. In the absence of any such

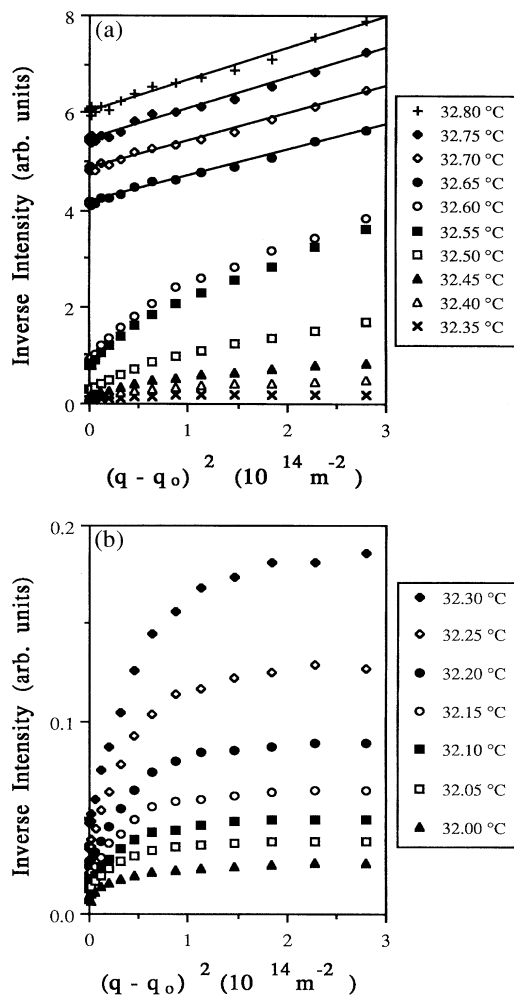


FIG. 2. (a) The inverse of the scattered temperature vs  $(q/q_0 - 1)^2$  for various temperatures both above and below the phase transition. (b) The inverse of the scattered temperature vs  $(q/q_0 - 1)^2$  for various temperatures well within the BPIII region. Note the change in the vertical scale compared to that of (a).

specific guidance, we tried fitting the data by various expressions including a sum of two Lorentzians and a single Lorentzian raised to a power, but no expression we tried gave a satisfactory fit over the entire range of temperatures and angles. These data, we believe, will serve as a test of the viability of any future theoretical model for BPIII, which should be able to predict the form of this structure factor.

We close by briefly discussing the implications of these results for the various proposed models of the BPIII structure. Consider first the possibility that BPIII is not amorphous but actually has some long-range order that has so far escaped detection. Such would be the case, for example, if the *octupolar* orientational ordering of

the molecules is retained even though the quadrupolar ordering has vanished [3]; this situation would occur if the "bond-orientation order" of BPI is preserved at the melting to the BPIII structure [5,6]. Since we have provided no means of aligning the sample, our light-scattering data would then have to be representative of the scattering from a powder specimen. We consider such a possibility to be unlikely owing to the smoothness of the data collected in the BPIII region, their reproducibility, and the lack of thermal hysteresis. By way of contrast, when BPII is cooled just below 32 °C into the BPI region, the data points collected display much more scatter, are irreproducible, and depend upon the thermal history of the sample, as one might expect since the cubic crystallites anneal with time. Because the light-scattering behavior in BPII is much more like that of the isotropic phase, we believe that BPII is an amorphous phase as well.

If that is indeed the case, the BPIII and the isotropic phase, respectively, are presumably analogous to the ordinary liquid and vapor phases, both having the same type of short-range order and differing only quantitatively in the degree of this order. One would then expect the transition between these two phases to be first order, as we have found here, and to end at an ordinary critical point as some parameter, such as the chirality, is increased. There are already indications that the BPIII-isotropic latent heat becomes smaller as the chirality increases [7]. Measurements that we have recently performed on

samples more chiral than the one studied here are also consistent with this critical point scenario; we find that the change from Lorentzian to non-Lorentzian line shape is much less discontinuous than what we have reported here. These results will be reported in the future in a longer publication.

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