COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on ''Photon transmission technique for studying multiple phase transitions in a liquid crystal''

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Contrary to the recently published results by Özbek *et al.* [Phys. Rev. E **59**, 6798 (1999)], we argue that the transmitted light intensity through an unoriented sample is by no means a good measure of the order parameters of the different phase transitions of a liquid crystal.

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The turbidity of liquid crystals (LC's) in their ordered mesophases as well as their sudden change to a clear water-like substance in the isotropic phase are some of their most striking features. Since the early days of the physics of LC's it was recognized that elastic (Rayleigh) and quasielastic scattering of light could bestow important information on the microscopic origin of these remarkable characteristics. It is well established nowadays that the milestone experiments of Chatelain [1] on Rayleigh scattering by nematic LC cells can be very well accounted for by orientational fluctuations within the continuum theory. This interpretation, put forward by de Gennes and the Orsay Liquid Crystal Group [2], not only explains the intensity but also the angular dependence and the quasielastic frequency spectrum of the scattered light. In oriented samples, the angular dependence of the scattered Rayleigh intensity for different polarizations offers, in principle, a method for the determination of the Frank elastic constants [3]. Very recently, Özbek *et al.* [4] have measured transmission of light in a sample of 4-butoxyphenyl-4′-declyoxybenzoate (BOPDOB) and identified four phase transitions by recording the intensity (I) as a function of temperature (time), assuming that I is proportional to the corresponding order parameters of the different transitions. Thence, critical exponents were obtained and compared with theoretical predictions. In our humble opinion, the assumption that the transmitted intensity is proportional to the order parameter of the transition is incorrect and bears a contradicting picture with the standard interpretation of light scattering experiments. In this manner, we regard the agreement between the experimental critical exponents in Ref. [4] and theoretical predictions as fortuitous. It is the purpose of this comment to clarify this point.

To this end, let us consider for the sake of clarity the example of the nematic (N) to isotropic (I) phase transition and analyze this specific case, albeit similar conclusions could be obtained from other LC phase transitions down to the smectic mesophases. It is interesting to realize that the cross section $(d\sigma/d\Omega)$ for elastic light scattering in the nematic state *is remarkably independent of temperature* (T) even very close to the transition to the isotropic phase, in spite of the fact that $(d\sigma/d\Omega)$ is related to highly temperature dependent physical parameters such as the dielectric anisotropy $(\Delta\epsilon)$ and the elastic constants (K's). This very interesting result has been observed in the original experiments of Chatelain [1] and was later confirmed by Haller and Lister [5]; it finds a natural explanation within the continuum theory of LC's and the scattering by orientational fluctuations. It is a textbook result that the elastic scattering cross section behaves as [6–8]

$$\frac{d\sigma}{d\Omega} \sim \frac{(\Delta\epsilon)^2}{K}. \tag{1}$$

Both $\Delta\epsilon$ and K decrease rather abruptly when T approaches the $N-I$ phase transition temperature T_c. Notwithstanding, $\Delta\epsilon \propto S(T)$, while $K \propto S(T)^2$, where $S(T)$ is the order parameter of the nematic phase. Accordingly, $(d\sigma/d\Omega)$ does not show a temperature dependence and, therefore, *cannot be used as a measure of the order parameter* $S(T)$. The transmitted intensity through a LC cell of thickness d is proportional to $\exp[-(\alpha+\beta)d]$, where α is the absorption coefficient and $\beta \propto d\sigma/d\Omega$ is the scattering loss per unit length [9]. The main assumption here is that the scattering losses arise from *single scattering* events; if multiple scattering processes were included, the interpretation of the experimental data in terms of microscopic quantities becomes typically intractable. In the nematic phase, β can be several orders of mag-

nitude larger than α and completely dominates the scattering losses. The opposite, however, may hold in the isotropic phase (see Ref. [9], p. 58) and detailed measurements are required to isolate the two different contributions. Being $d\sigma/d\Omega$ temperature independent in the nematic phase, it produces a fairly insensitive transmitted light intensity up to T_c where the scattering efficiency by orientational fluctuations in the I phase is greatly reduced (typically by $\sim 10^3-10^6$) as compared to the nematic phase. Above T_c, and even if $\alpha=0$, there will remain a sizable scattering cross section by orientational fluctuations due to the presence of birefringent swarms. This *pretransitional* scattering mechanism has been studied in detail by Lister and Stinson [10] and also by Decoster *et al.* [11]. Wu and Lim [12] have developed a cell for measuring the absorption and scattering losses through transmission of a laser beam in an unoriented nematic. The cell thickness can be continuously varied in the design of Ref. [12], thereby allowing for a separation of the effects of α and β in the transmitted intensity. The typical sudden changes in the light scattering efficiency of LC's observed at the clearing point are neither directly related to the order parameter of the transition nor a real proof that the phase transition is of first order. In fact, it has been demonstrated that the temperature dependence of $S(T)$ can be very well approximated in most nematics by an analytic function of the form [13]

$$S(T)=\left[1-\frac{0.98TV^2}{T_cV_c^2}\right], \tag{2}$$

where V and V_c are the molar volumes at T and T_c, respectively. Several LC's show, accordingly, a small (in some cases negligible) jump of the order of $\sim 20\%$ or less in $S(T)$ at T_c. This is the case, for example, of the commercial LC E7 (Merck) [14], which is also the same LC studied in Ref. [12]. The sudden change in the scattering efficiency by approximately three orders of magnitude in β at the clearing point of E7 [12] which is governed by pretransitional fluctuations (or residual absorption) and by a fairly temperature-independent function above and below T_c, respectively, is by no means a good measure of $S(T)$. A relatively good estimate of the order parameter can be obtained by optical means in high-resolution measurements of the optical birefringence in ordered samples. An example of these sort of experiments are the results of Lim and Ho [15] who analyzed the nematic-smectic-A (S_A) and the smectic-A-smectic-C (S_C) phase transitions; they found that the temperature dependence of the birefringence does not follow the predictions of the mean-field theories in the N-S_A transition and that the S_A-S_C transition has a critical exponent which is considerably larger than that expected from a heliumlike system. The underlying assumption in the analysis of these data is that the birefringence is proportional to the order parameter and also depends on its fluctuations above T_c. This assumption, however, must also be taken with care, for local field corrections can badly affect the conclusions [16]. The relation between the microscopic molecular polarizabilities and the macroscopic optical properties, known as *local field problem*, is always the most serious limitation to quantitatively obtain the order parameter of a transition from optical data. It is well known, in this sense, that agreement between optical data and other techniques not affected by local fields (such as NMR spectroscopy) can only be obtained if the appropriate corrections are applied [17].

Similar conclusions could be drawn from other LC-phase transitions. The S_A-S_C is a textbooklike example of phase transition where the mean-field approach can be successfully applied [18]; it has been studied by light scattering in Ref. [19]. The elastic scattering cross section is in this case proportional to [20]

$$\frac{d\sigma}{d\Omega}\sim\frac{1}{a+b\langle\phi\rangle^2+cq^2}, \tag{3}$$

where a, b, and c are constants coming from the expansion of the Landau free energy and its gradients [20], q is the scattering wave vector, and $\langle\phi\rangle$ is the order parameter (the tilt angle of the director relative to the normal to the smectic planes). The calculation of β for the scattering losses in transmission requires the integration of Eq. (3) for all q's $\neq 0$. In any case, the relation between β (or the transmitted intensity) and the order parameter of the transition is rather more complex than a simple proportionality.

Last but not least, it is well known [21] that the scattering of light in LC cells strongly depends on the cell geometry and, in particular, on the cell thickness. In this sense, any meaningful experimental result should include these details. In particular, the solid angle spanned by the collecting optics and the cell thickness are crucial parameters to find a relation between β and $(d\sigma/d\Omega)$ and to estimate whether single or multiple scattering processes may be involved.

In closing, we believe that the intensity jumps observed in the transmission of light through an unoriented LC cell at the different phase transitions are very interesting but they are by no means a good measure of the order parameters and that any data analysis based of this assumption should render incorrect conclusions. We therefore strongly disagree with the data analysis and main conclusions of Özbek *et al.* in Ref. [4]. We believe that a good theoretical explanation of these data should be very interesting and probably related to the sort of approach put forward very recently by Lubensky and co-workers [22], where multiple scattering is explicitly treated.

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