

Electron-diffraction study of a one-layer free-standing hexatic liquid-crystal film

Chia-Fu Chou* and John T. Ho

Department of Physics, State University of New York at Buffalo, Buffalo, New York 14260

S. W. Hui

Department of Biophysics, Roswell Park Cancer Institute, Buffalo, New York 14263

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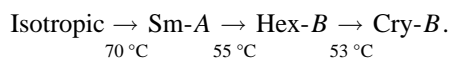
We report the successful formation of stable one-layer free-standing films of *n*-pentyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate on which structural measurements have been made using electron diffraction. We show that the scaling relation among the $6n$ -fold bond-orientational order parameters in the single-domain hexatic-*B* phase in a one-layer film is identical to that reported earlier in a two-layer film. This implies that a two-layer film indeed approaches the two-dimensional limit. [S1063-651X(97)05807-8]

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The technique of free-standing liquid-crystal films was developed by Young *et al.* in 1978 [1]. It paved the way for the use of this unique physical system to study the evolution of phase transitions from the thick-film to the thin-film limit, as well as for the investigation of substrate-free two-dimensional (2D) behavior and the effect of free surfaces. Films in the smectic-*A* (Sm-*A*) or smectic-*C* phase can be made by drawing a spreader that is wet with the liquid-crystal material across an aperture on a sample holder. After some practice, it is fairly easy to form films with thickness varying from a few molecular layers to hundreds of layers. However, it has been the conventional experience that one-layer films are not sufficiently stable to make measurements with.

Even though the thinnest free-standing liquid-crystal films that have hitherto been studied extensively contain two layers rather than one, it is generally believed that the two-layer film already possesses 2D properties [2]. It has been argued that a two-layer film, by being centrosymmetric and showing a single heat-capacity anomaly, exhibits 2D thermodynamic behavior [3,4]. However, no explicit experimental evidence has been available to directly support this argument. In this paper, we report the structural measurement of a one-layer film of *n*-pentyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC) using electron diffraction and the analysis of the bond-orientational order parameters C_{6n} in its single-domain hexatic-*B* (Hex-*B*) phase. Our objective is to compare the scaling parameter λ relating the C_{6n} 's in a one-layer film with that from a two-layer 54COOBC film.

The liquid-crystal 54COOBC undergoes the bulk phase transitions from the isotropic to the crystal-*B* (Cry-*B*) phase [5],

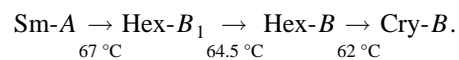


This compound is somewhat unique, not only in displaying the Sm-*A*–Hex-*B*–Cry-*B* phase sequence, but also in show-

ing an unusual layer-by-layer thinning behavior above its bulk Sm-*A*–isotropic transition temperature [6] at which free-standing films are not supposed to be stable due to the lack of layer structure in the isotropic phase. In the course of our study of thin 54COOBC films, we were able to make stable films for which the reflected light intensity R , according to the relation $R \propto N^2$ for $N \leq 15$, where N is the number of layers [7], indicated that the film thickness was equivalent to a single molecular layer. This therefore represents the report of the existence of stable one-layer free-standing films with thickness of the order of 25 Å suitable for physical measurements [8].

By spreading films in its Sm-*A* phase across circular apertures of different sizes, we have found that one-layer films are most likely to be stabilized with an aperture diameter of 1 mm or less. The one-layer film reported here was formed across a 0.7-mm aperture. The He-Ne laser beam was focused down to 0.3 mm at the sample for reflectivity measurement.

Upon cooling from the Sm-*A* phase, the electron-diffraction patterns observed in a one-layer 54COOBC film are illustrated in Fig. 1. The general features of these diffraction patterns are qualitatively the same as those of a two-layer film reported previously [9]. Our data suggest the temperature sequence



Above 67 °C, the film was in the Sm-*A* phase. Its diffraction pattern was typified by Fig. 1(a), which shows a diffuse ring of constant intensity, signifying the liquid nature of this phase. When the film was cooled down to about 67 °C, a diffraction pattern labeled as Hex- B_1 was observed, as shown in Fig. 1(b). This transition was characterized by the enhancement of the in-plane positional order, as indicated by a sharpening of the diffraction ring, without exhibiting any sixfold intensity modulation around the ring as expected from a single-domain Hex-*B* sample. A discussion of the possible nature of the Hex- B_1 phase will be given later. At around 64.5 °C, the Hex-*B* diffraction pattern appeared, consisting of six identical arcs that are indicative of a sample

*Present address: Department of Physics, Princeton University, Princeton, NJ 08544.

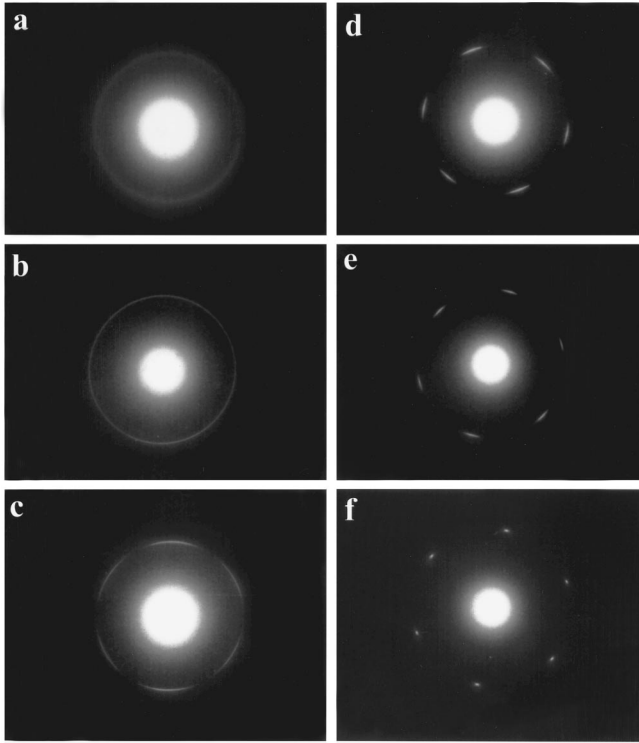


FIG. 1. Electron-diffraction patterns from a one-layer 54COOBC film: (a) Sm-A phase at 68.4 °C, (b) Hex- B_1 phase at 66.5 °C, (c) Hex- B phase at 63.7 °C, (d) Hex- B phase at 63.3 °C, (e) Hex- B phase at 62.7 °C, and (f) Cry- B phase at 61.2 °C. The radius of the diffraction circle is 1.4 \AA^{-1} .

with long-range bond-orientational order. The evolution of the Hex- B pattern with decreasing temperature, as shown in Figs. 1(c)–1(e), suggests a monotonic increase in the degree of hexatic order. The sample underwent an apparently continuous transition at about 62 °C to the hexagonal Cry- B phase, featuring a set of six sharp diffraction spots, as shown in Fig. 1(f).

To obtain the higher-harmonic $6n$ -fold bond-orientational order parameters $C_{6n} = \text{Re}\langle \exp[i6n\theta(\mathbf{r})] \rangle$, where θ is the angle between the local physical bond connecting neighboring molecules and some reference axis, the diffraction intensity $I(\chi)$ of the hexatic arcs as a function of the angle χ was fitted with the expression

$$I(\chi) = I_0 \left\{ \frac{1}{2} + \sum_{n=1}^{\infty} C_{6n} \cos[6n(\chi - 30^\circ)] \right\} + I_{\text{BG}}, \quad (1)$$

where I_{BG} is a fitting parameter representing the background intensity. The values of the C_{6n} 's so determined in the single-domain Hex- B phase are displayed in Fig. 2.

Aharony *et al.* [10] showed that the order parameters C_{6n} , at least in the critical region, should follow the scaling relation

$$C_{6n} = C_6^{\sigma(n)}, \quad (2)$$

where the exponents $\sigma(n)$ are related to the crossover exponents from the XY to other universality classes. In three dimensions, they can be expressed as

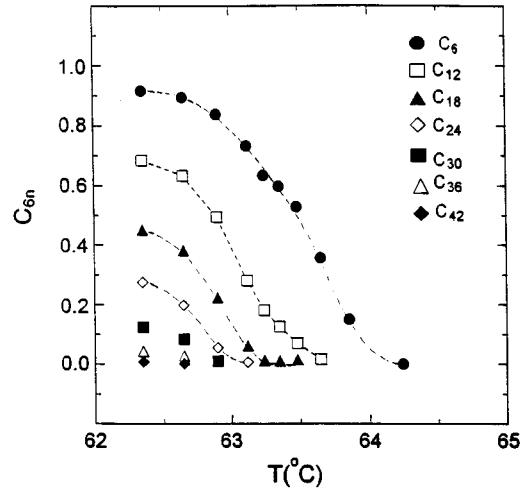


FIG. 2. Temperature dependence of the bond-orientational order parameters C_{6n} from a one-layer 54COOBC film. The dashed lines are a guide to the eye.

$$\sigma(n) = n + \lambda n(n-1), \quad (3)$$

with $\lambda \cong 0.3$. It has been shown that in two dimensions $\sigma(n) = n^2$ [11] or $\lambda = 1$ if one fits the data to Eq. (3). Hence the scaling parameter λ is a good indicator of the effective dimensionality of the system under study.

From the experimentally determined bond-orientational order parameters C_{6n} , the scaling exponents $\sigma(n)$ were calculated using Eq. (2). The values of $\sigma(n)$ were then compared with Eq. (3) to obtain the value of λ that best described the data. The results are shown in Fig. 3(a). It can be seen that the data in the temperature range where long-range Hex- B order was observed are all consistent with $\lambda = 1$, indicating that the scaling relation $\sigma_n = n^2$ expected in a 2D XY system is obeyed in our one-layer 54COOBC film.

By comparing the scaling relation among the C_{6n} 's obtained in our one-layer film with that reported previously in a

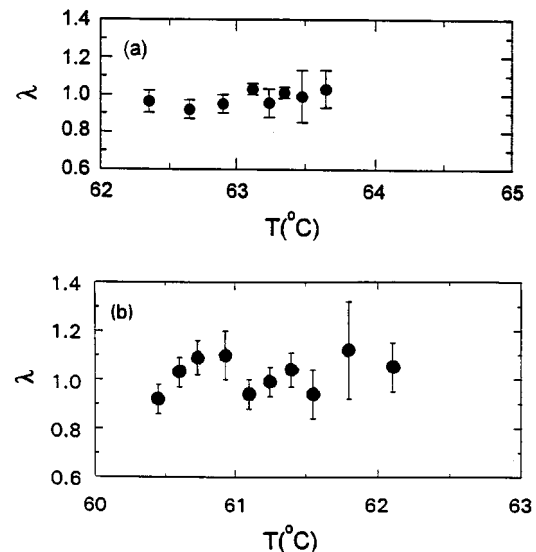


FIG. 3. Temperature dependence of the scaling parameter λ from (a) a one-layer and (b) a two-layer 54COOBC film (from Ref. [9]).

two-layer 54COOBC film in its Hex-*B* phase [9], as shown in Fig. 3(b), we conclude that a *two-layer film behaves essentially the same as a one-layer film*, implying that the two-layer film indeed approaches the 2D limit. This affirmation is important because it is known that multilayer films can exhibit departure from 2D behavior [12] as well as layer-by-layer transitions [13].

Our measurements also lead to the following observations. The fact that the single-domain Hex-*B* phase is preceded by a phase that we call Hex-*B*₁, with hexaticlike positional correlation length but no long-range bond-orientational order, has also been seen in other materials, including 4O.8 [14]. The true nature of the Sm-*A*–Hex-*B*₁ phase transition remains an open question. The Hex-*B*₁ phase could be a multiple-domain Hex-*B* phase spatially averaged by the electron beam of diameter 50 μm. On the other hand, from a theoretical point of view, there is no reason why we could not have a transition from a 2D isotropic liquid with short-range positional and bond-orientational correlations to another isotropic phase (i.e., *nonhexatic*) with longer-range positional correlations [15]. If this is the case, since there is no symmetry breaking, the Sm-*A*–Hex-*B*₁ transition must be first order. In other words, it will not be a Kosterlitz-Thouless (KT) transition [16] as described in the 2D defect-mediated melting theory [17]. The fact that the heat-capacity anomaly in a two-layer 54COOBC film [3] and

the optical-reflectivity change in a one-layer film [18] in the vicinity of this transition suggest a weakly first-order transition with strong pretransitional effects could be interpreted as supporting this argument.

The discovery of the hexatic phase in a liquid-crystal system [19] was a benchmark verifying the defect-mediated theory of 2D melting. However, the expected KT-type behavior associated with its transitions has never been observed in 2D liquid-crystal films, despite having been observed in the superfluid transition of thin helium films [20] and in the roughening transition of equilibrium crystal surfaces [21]. Since our electron-diffraction data have unambiguously demonstrated 2D hexatic behavior in one- and two-layer 54COOBC films, the Hex-*B*–Cry-*B* transition in these films would appear to be an excellent candidate to exhibit KT-type pretransitional properties. Unfortunately, both high-resolution heat-capacity and optical-reflectivity measurements so far have not been able to reveal any resolvable changes in these properties near the Hex-*B*–Cry-*B* transition in 2D 54COOBC films [3].

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- [1] C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978).
- [2] For recent reviews see C. C. Huang and T. Stoebe, *Adv. Phys.* **42**, 343 (1993); I. Lyuksyutov, A. G. Naumovets, and V. Pokrovsky, *Two-Dimensional Crystals* (Academic, San Diego, 1992).
- [3] A. J. Jin, M. Veum, T. Stoebe, C. F. Chou, J. T. Ho, S. W. Hui, V. Surendranath, and C. C. Huang, *Phys. Rev. Lett.* **74**, 4863 (1995).
- [4] I. M. Jiang, T. Stoebe, and C. C. Huang, *Phys. Rev. Lett.* **76**, 2910 (1996).
- [5] V. Surendranath, D. Fishel, A. de Vries, R. Mahmood, and D. L. Johnson, *Mol. Cryst. Liq. Cryst.* **131**, 1 (1985).
- [6] A. J. Jin, M. Veum, T. Stoebe, C. F. Chou, J. T. Ho, S. W. Hui, V. Surendranath, and C. C. Huang, *Phys. Rev. E* **53**, 3639 (1996).
- [7] C. Rosenblatt and N. Amer, *Appl. Phys. Lett.* **36**, 432 (1980).
- [8] A one-layer film of the compound DOBAMBC was reportedly seen only once in the laboratory, lasting for about 2 h [C. Rosenblatt (private communication)]; see C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).
- [9] C. F. Chou, J. T. Ho, S. W. Hui, and V. Surendranath, *Phys. Rev. Lett.* **76**, 4556 (1996).
- [10] A. Aharony, R. J. Birgeneau, J. D. Brock, and J. D. Litster, *Phys. Rev. Lett.* **57**, 1012 (1986).
- [11] M. Paczuski and M. Kardar, *Phys. Rev. Lett.* **60**, 861 (1988).
- [12] M. Cheng, J. T. Ho, S. W. Hui, and R. Pindak, *Phys. Rev. Lett.* **61**, 550 (1988).
- [13] R. Geer, T. Stoebe, C. C. Huang, R. Pindak, J. W. Goodby, M. Cheng, J. T. Ho, and S. W. Hui, *Nature (London)* **355**, 152 (1992).
- [14] C. Y. Chao, C. F. Chou, J. T. Ho, S. W. Hui, A. J. Jin, and C. C. Huang, *Phys. Rev. Lett.* **77**, 2750 (1996).
- [15] D. R. Nelson (private communication).
- [16] J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1973).
- [17] B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); A. P. Young, *Phys. Rev. B* **19**, 1855 (1979).
- [18] M. Veum, P. Mach, and C. C. Huang (private communication).
- [19] P. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, *Phys. Rev. Lett.* **46**, 1135 (1981).
- [20] I. Rudnick, *Phys. Rev. Lett.* **40**, 1454 (1978); D. J. Bishop and J. Reppy, *ibid.* **40**, 1727 (1978).
- [21] P. E. Wolf, F. Gallet, S. Balibar, and E. Rolley, *J. Phys. (France)* **46**, 1987 (1985).