# Stability and phase transitions of single-molecular-layer free-standing liquid-crystal films

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We have successfully prepared stable one-layer films of 54COOBC [*n*-pentyl-4′-*n*-pentanoyloxy biphenyl-4-carboxylate] in a small film hole ($\approx 0.7$ mm in diameter) and conducted high-resolution optical reflectance measurements near the smectic-*A*–hexatic-*B* transition. The stability of these films is contrary to experiences with all other compounds and also to heuristic understanding. We propose a modification to such understanding. Within the resolution of our measurements, data are in good agreement with those of two-layer films. The result gives a confirmation of two-dimensional behavior of two-layer films. [S1063-651X(97)03408-9]

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Ever since Young *et al.* [1] successfully demonstrated a clever technique to prepare uniform free-standing liquid-crystal films in phases which possess a layer structure, i.e., smectic phases, such films have been utilized to investigate physical properties of various smectic phases and explore the two-dimensional physical properties of substrate-free systems [2,3]. Our detailed calorimetric studies of such films near the smectic-*A*–hexatic-*B* (Sm-*A*–Hex-*B*) and smectic-*C*–smectic-*I* transitions of various liquid-crystal compounds [2,4,5] suggest that two-layer films ($N=2$), which exhibit a single heat-capacity anomaly, can be viewed as a two-dimensional (2D) system. Thicker films ($N>2$), however, show more than one heat-capacity anomaly and are definitely not simple 2D systems. Because single-layer films have proven to be extremely rare and unstable, a direct comparison of the behavior of one- and two-layer films through a phase transition has previously never been performed. Our study also raises questions about the present understanding of the stability of free-standing films. We will address these issues.

According to electron-diffraction studies [6], the order parameter associated with the Sm-*A*–Hex-*B* transition is the bond-orientational order [$\Psi\ \exp(i6\theta)$] placing this transition in the *xy* universality class. Thus in a 2D system, theoretical advances [7] predicted a Kosterlitz-Thouless-type heat-capacity hump [8]. Our simultaneous heat capacity and optical reflectivity measurements near the Sm-*A*–Hex-*B* transition in two-layer films of two different types of liquid-crystal compounds [4] give diverging heat-capacity anomalies which can be characterized by the heat-capacity critical exponent $\alpha=0.30$. Such studies have raised the experimentally challenging question ‘‘Can one prepare a stable one-layer film and characterize its physical properties?’’

Through experience, we [9] know that by choosing an appropriate liquid-crystal compound and taking proper care, preparation of a uniform two-layer film (diameter $\approx 1$ cm) is not unreasonably difficult. In 1980, Rosenblatt *et al.* [10] measured the light scattering intensity from a one-layer DOBAMBC film with its lifetime shorter than several minutes. Recently, Pang and Clark [11] reported the observation of stable one-layer film regions in a low temperature smectic phase of a perfluorinated compound and Ho [12] studied electron-diffraction from one-layer films prepared in a small hole. Despite these instances, preparation of a stable one-layer film has proven to be an almost insurmountable task. The stability of thin free-standing films has been discussed by many scientists [13]. The following heuristic reasoning was provided by Prost [14] to argue the stability of liquid-crystal free-standing films and offers a qualitative explanation of the difficulties in preparing one-layer films. The energy required to create a hole of radius $R$ through an $N$-layer film consists of two major parts,

$$E_R \approx 2\pi(\gamma_L N l_0 R - \gamma_S R^2). \tag{1}$$

Prost took $\gamma(=\gamma_L=\gamma_S)$ to be the film-vapor interfacial tension. $l_0$ is the smectic layer thickness. The first term is due to the positive line tension of the hole. The second term comes from the surface tension of the film (there are two surfaces). This equation yields an energy barrier, $E_c \approx [\pi\gamma(Nl_0)^2]/2$ and hence the frequency of thermally creating holes of critical radius $R_c(\approx Nl_0/2)$ per unit area will be $f\approx f_0\exp(-E_c/k_BT)$. Taking $\gamma=21$ dyn/cm [15], $l_0=25$ Å and assuming that $f_0\approx$ (speed of sound)/[(molecular diameter) (molecular cross section)], one obtains

$$f \approx 2\times10^{27}\exp(-42N^2)(\sec\ \mathrm{cm}^2)^{-1}. \tag{2}$$

For $N=1$, $f\approx10^{9}$ $(\sec\ \mathrm{cm}^2)^{-1}$ while for $N=2$, $f\approx10^{-46}$ $(\sec\ \mathrm{cm}^2)^{-1}$. Thus the $N$ term in the exponent is of tremendous consequence. Although it is a ‘‘back of the envelope’’ calculation, the result suggests that while a one-layer film is extremely unstable and very difficult to prepare, thicker films ($N\geq2$) will last effectively forever. This heuristic argument does not include the surface enhanced layer order which increases very rapidly in the thin film limit [16]. The discovery of layer-by-layer thinning transitions in two perfluorinated

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compounds [17,18] by our group has demonstrated that two-layer films are the most stable.

Our recent experimental studies yield a very different scenario. In order to enhance the chance of preparing a one-layer film and promote its stability, we employed a very small film hole ($\approx 0.7$ mm in diameter). We chose 54COOBC [$n$-pentyl-4′-$n$-pentanoyloxy biphenyl-4-carboxylate], which exhibits the Sm-$A$–Hex-$B$ phase transition near 65 °C in two-layer free-standing films. It also exhibits the unusual thinning transition in which the films spontaneously thin as temperature is increased above the bulk Sm-$A$–isotropic transition. In searching for compounds exhibiting this unusual layer thinning transition [18] above the bulk Sm-$A$–isotropic or Sm-$A$–nematic transition, we and other research groups have studied more than 20 conventional and perfluorinated liquid-crystal compounds. Although these transitions are highly irregular in 54COOBC [19], it is one of two hydrogenated compounds [20], thus far, shown to exhibit this. Such behavior suggests that in the Sm-$A$ phase, the smectic layer structure of 54COOBC is better organized than the majority of the other nonperfluorinated compounds. It is also an important indication that we will have a greater chance of preparing one-layer films from 54COOBC than from the other nonperfluorinated compounds.

As expected, it is extremely rare to obtain a one-layer film even with such a small film hole. The success rate is only about one in 500 tries even after taking extreme care in manufacturing the film plate and preparing the films. To our surprise, one-layer films could last for more than 4 h for our detailed experimental runs. A significant modification that (a) follows from reasonable physical arguments and (b) changes the results in a direction consistent with our observations can be made in the prediction of the stability of one-layer films. Through our detailed surface tension investigations of free-standing films [15], we have realized the following important difference between $\gamma_S$ and $\gamma_L$. It is well established that a surface consisting of -CH$_3$ molecular groups has a lower surface energy ($\gamma \approx 21$ dyn/cm) than a surface with -CH$_2$- or aromatic molecular groups ($\gamma \approx 32$ dyn/cm). For the 54COOBC compound, the film-vapor interface which mainly consists of -CH$_3$ end group should have $\gamma_S \approx 21$ dyn/cm. On the other hand, $\gamma_L$ is mainly contributed by -CH$_2$- groups and the molecular core residing in the film-hole interface and thus has a higher surface energy ($\gamma_L \approx 32$ dyn/cm) [21]. Here we make a reasonable assumption that before the film ruptures, a hole ($R_c \approx N l_0/2$) is created without changing the layer structure. Employing different values for $\gamma_S$ and $\gamma_L$ in Eq. (1), one can rewrite Eq. (2) as

$$f \approx 2 \times 10^{27} \exp(-98N^2)(\sec \mathrm{cm}^2)^{-1}. \quad (3)$$

For $N=1$, now $f=10^{-15}$ $(\sec \mathrm{cm}^2)^{-1}$, instead of $f \approx 10^9$ $(\sec \mathrm{cm}^2)^{-1}$. Thus this predicts stability for a one-layer film once it can be prepared. Because there are many mechanisms that can rupture a film, this is at best a lower bound for $f$ [22].

An additional wrinkle in this issue was found, however, when we tried to prepare a one-layer film in a hole of twice the area ($\approx 1$ mm in diameter). If the above stability argument also applies to the preparation of films, the frequency of preparing one-layer films should decrease only by a factor of two. After spreading roughly 5000 films over a period of ten days, loading a new sample each day, no one-layer films were observed. This suggests that film preparation has more factors than the above argument would indicate. Thus it remains to be addressed, "Is the difficulty in preparing one-layer films closely related to the fact that such a film is less stable?"

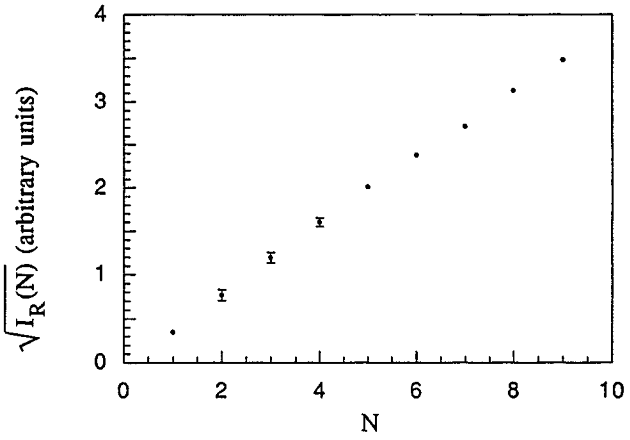

FIG. 1. A plot, used to calibrate film thickness, demonstrating a direct proportionality between the square root of the optical reflectance ($\sqrt{I_R}$) and the film thickness ($N$) in a number of layers. Due to the small film hole diameter (roughly the incident beam size), intensity scattering from the meniscus contributes measurably to the total signal. Thus, there is an unusually large uncertainty in the values of $I_R$ as compared to film much larger than the incident beam. The error bars for the two-, three-, and four-layer films display the range of values observed for these thicknesses. Since there is clearly no overlap of the error bars, we are assured that this noise does not compromise the film thickness calibration.

We [19] have experimentally realized that both heat capacity and optical reflectivity signals from two-layer 54COOBC films are noisier than those of $nm$OBC compounds. To date, we do not have a good explanation for this difference. Here $nm$OBC refers to $n$-alkyl-4′-$n$-alkyloxy biphenyl-4-carboxylate. We have also discovered a strong relationship between the temperature dependences of the heat capacities and optical reflectivities through the Sm-$A$–Hex-$B$ transitions in these compounds [4,19]. Thus, the optical reflectivity is a good probe of the thermodynamic nature of this transition in such films. Although a 0.7 mm diameter hole is too small for our calorimetric experiment, by properly focusing our amplitude-stabilized He-Ne laser beam, we have conducted detailed optical reflectance measurements in 54COOBC. Figure 1 shows our characterization of film thickness. In the thin film limit, the optical reflectance ($I_R$) is proportional to $N^2$ [23]. A linear relation between $(I_R)^{1/2}$ and $N$ is well established in Fig. 1 for $1 \leqslant N \leqslant 9$.

Figure 2 displays the temperature variation of $I_R$ obtained from two-layer films for the two hole diameters, 0.7 and 1.0 mm. The overall signal from two-layer films is noisier than our previous results from a 1 cm free-standing film [19]. The following may be the major sources of additional noise: large film curvature for the small diameter films, stray light reflected from the meniscus, etc. The good agreement between the two, however, assures us that the shape of the curve is not affected by these complications. Figure 3 exhibits the

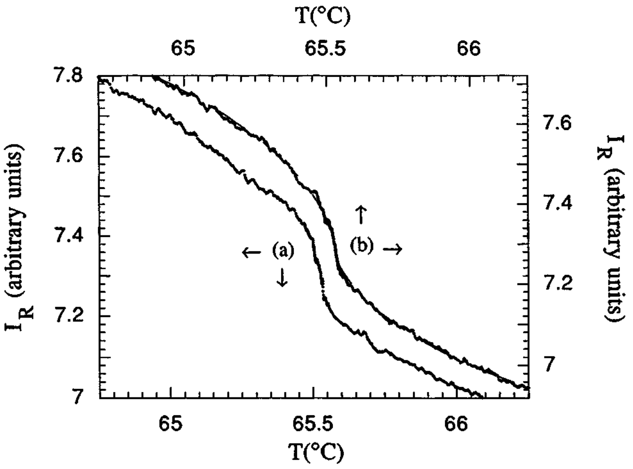

FIG. 2. Optical reflectance ($I_R$) as a function of temperature ($T$) through the Sm-$A$–Hex-$B$ transition for two-layer films of diameters (a) 0.7 mm and (b) 1.0 mm. The consistency between the two data sets indicates that complications associated with the small diameter of the films are not affecting the shape of the curves. The fit, shown as a continuous line, for the 1.0 mm film yields $\alpha=0.34\pm0.04$ and $A^+/A^-=0.86\pm0.05$. These parameters were consistent for $|T-T_c|_{\max}=2$ K, 1.5 K, and 1 K. The plots are offset for clarity [24].

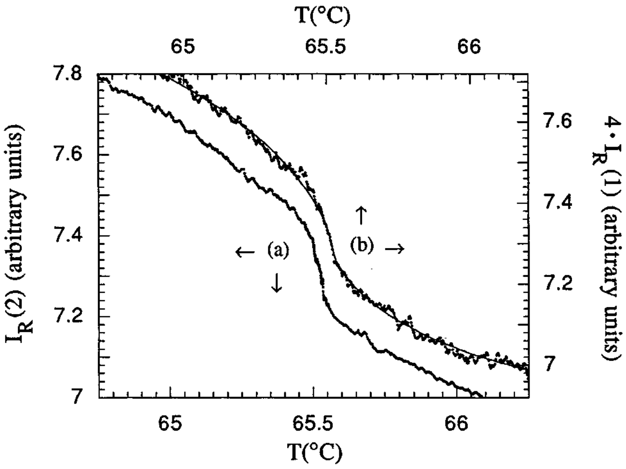

FIG. 3. Optical reflectance ($I_R$) as a function of temperature ($T$) through the Sm-$A$–Hex-$B$ transition for (a) a two-layer and (b) a one-layer film, both of diameter 0.7 mm. The fit, shown as a continuous line, for the one-layer film yields $\alpha=0.30\pm0.06$ and $A^+/A^-=0.79\pm0.10$. These parameters were consistent for $|T-T_c|_{\max}=2$ K and 1.5 K. The good agreement supports the prediction that both one-layer and two-layer films possess two-dimensional behavior. The plots are offset for clarity [24].

overlay of $I_R(N=2)$ and $4I_R(N=1)$ for 0.7 mm diam films. We have fit the data to the following expression:

$$I_R=B+DT\pm A^{\pm}|t|^{1-\alpha}, \tag{4}$$

where $t=(T-T_c)/T_c$. Our results give $\alpha=0.34\pm0.04$ and $A^+/A^-=0.86\pm0.05$ for two-layer data and $\alpha=0.30\pm0.06$ and $A^+/A^-=0.79\pm0.10$ for one-layer data. Thus, within our resolution, both sets of data agree well with each other. The exponent is also consistent with our two-layer heat-capacity results for a 1 cm diam. film [4,19].

In summary, we have successfully prepared uniform one-layer 54COOBC films which are stable over sufficient time for our detailed optical reflectance measurement through the Sm-$A$–Hex-$B$ transition. The good agreement between the results from the one-layer and two-layer films supports the prediction that both one-layer and two-layer films possess two-dimensional behavior. Based on the observed layer thinning transition, we argue that 54COOBC should give us a better chance to obtain one-layer films. If such an argument holds, some of the perfluorinated liquid-crystal compounds exhibiting a sequence of regular layer-by-layer thinning transitions should be better candidates for preparing one-layer films. Our preliminary results and those by Pang and Clark [11] support such a prediction. Further effort to prepare and characterize one-layer films is in progress.

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[22] The dramatic effect of our modification (a 50% change in surface tension changes $f$ by 24 orders of magnitude) calls the validity of this calculation into question. One wonders whether an alternative approach is necessary to reasonably predict free-standing film stability.

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[24] The scale for the vertical axes has a large background term (approximately 95% of the total signal) subtracted from it. The anomaly shown is actually a $<1\%$ effect.