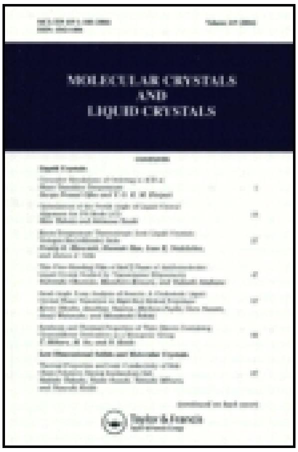

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Layer-By-Layer Transitions Found in Free-Standing Liquid-Crystal Films

T. Stoebe [a], A. J. Jin [a], P. Mach [a] & C. C. Huang [a]

[a] School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota, 55455, U.S.A.

To cite this article: T. Stoebe, A. J. Jin, P. Mach & C. C. Huang (1995): Novel Layer-By-Layer Transitions Found in Free-Standing Liquid-Crystal Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 511-520

To link to this article: http://dx.doi.org/10.1080/10587259508038725

Mol. Cryst. Liq. Cryst. 1995, Vol. 260, pp. 511–520
Reprints available directly from the publisher
Photocopying permitted by license only

NOVEL LAYER-BY-LAYER TRANSITIONS FOUND IN FREE-STANDING LIQUID-CRYSTAL FILMS

T. STOEBE, A. J. JIN, P. MACH, AND C. C. HUANG
School of Physics and Astronomy, University of Minnesota,
Minneapolis, Minnesota 55455, U.S.A.

Abstract By utilizing our state-of-the-art ac differential *free-standing film calorimetric system*, three remarkable surface enhanced layer-by-layer transitions in several liquid-crystal compounds have been investigated. Each of these transitions can be well-described by the simple power-law expression: $L = L_0 t^{-\nu}$. This demonstrates that these surface enhanced transitions occur on the smooth "substrate" with long-range interactions.

INTRODUCTION

Thermotropic liquid crystals are elongated organic molecules which display one or more mesophases between the crystalline state and the isotropic liquid. An important class of these mesophases are the smectics (derived from the Greek σμηγμα (= soap)). The smectic phases exhibit layered structures in which the interlayer interaction is relatively weak. Because the layers are not coupled strongly, interesting surface effects are apparent and the phase behavior of liquid crystals is strongly influenced by the proximity of interfaces. Moreover, much like a soap film on a ring, free-standing smectic liquid-crystal films can be prepared and suspended over a hole cut into a film plate. These substrate-free films constitute a highly intriguing physical system. Provided the appropriate compounds are chosen, sample thickness can easily be varied from two to a few hundred molecular layers (each layer is ≈ 25 Å thick, roughly the dimension of the long axis of the molecule) in a matter of seconds by simply spreading new films until the desired thickness is obtained.

Numerous interesting experiments [1] (e.g., calorimetric studies, light-scattering, mechanical measurements, optical observations, optical reflectivity, x-ray and electron diffraction, etc.) have been conducted on free-standing liquid-crystal films to investigate inter- and intra-layer molecular order, the evolution of phase transitions as the system is taken from the thick-film to thin-film limit, as well as to study substrate-free two-dimensional physical phenomena and the effect of free surfaces.

The atoms or molecules at the surfaces of the vast majority of bulk solids are in a somewhat less ordered state than those in the interior. Consequently, the melting process usually begins at the surface and progresses inwards as the transition is approached from below [2]. Unlike conventional solids, the surface tension associated with the liquid-crystal/vapor interface tends to reduce layer fluctuations due to the fundamental nature of one-dimensional density wave and promote order near the surface of liquid-crystals. This effectively enhances the surface transition temperature. Consequently, ordering transitions tend to start at the liquid-crystal/vapor interface and proceed inwards as the transition is approached from above. The fact that the surface enhanced transitions progress in a layer-by-layer fashion indicates that the "substrates" for the transitions are smooth. Significant insight into this behavior has been provided by recent experimental investigations [3-6] and theoretical work [7].

Ocko *et al.* [3] measured the angular dependence of the x-ray specular reflectivity from the liquid-crystal free surface as a function of temperature above the bulk SmA-isotropic transition of 12CB (dodecylcyano-biphenyl). The reflectivity data can be described in terms of a sinusoidal density modulation, starting at the surface and abruptly terminating after an integral number of layers. The data are therefore consistent with the discrete penetration of the bulk isotropic phase by an increasing number of SmA layers as the temperature is reduced. This work represents the first experimental observation of a layer transition involving smectic liquid crystals. Employing an elegant computer-enhanced polarized video microscope, Swanson *et al.* [4], studied the layer-by-layer surface ordering transition of free-standing films of 9O.4. Here 9O.4 is a member of the *n*O.*m* (4-(n-*alkyl*oxy) benzylidene-4-(n-*alkyl*) aniline) homologous series. Excellent resolution of this optical technique enabled them to observe 28 separate layering transitions. The transition temperatures of the first ten layers were found to be well-characterized by the simple power-law form, $L = L_0 t^{-\nu}$, with $\nu = 0.37$, indicating that a van der Waals-like force dominates the interlayer coupling.

Here we will report other three remarkable layer-by-layer transitions identified in liquid-crystal films. Again each of these transitions can be well-characterized by the simple power-law expression. The data associated with the layer-by-layer transitions found near the SmA-hexatic-B and SmA-crystal-B transitions can be fitted to the exponent $\nu \approx 1/3$, indicating that a van der Waals-like force is responsible for the interlayer interaction. The third one is the novel layer-by-layer *thinning* transition which has been found above the bulk SmA-isotropic transition of a perfluorinated liquid-crystal compound. The value of the exponent obtained, $\nu \approx 3/4$, cannot be explained utilizing familiar models.

RESULTS AND DISCUSSIONS

In order to give a crucial test of the applicability of the novel two-dimensional (2D) melting theory to describe the SmA-HexB transition in liquid crystals, we have established a state-of-the-art high-resolution ac differential calorimetric system [8,9]. The system enables us to simultaneously measure both heat capacity and optical reflectivity of free-standing films even only two molecular layer in thickness. *The resolution of both probes is better than a few parts in 10^5!* The fact that 2-layer films exhibit only a single heat-capacity anomaly while thicker films show more than one peak associated with the SmA-HexB transition in the *nm*OBC compounds, supports the assertion that 2-layer films possess 2D thermodynamic behavior [10]. Here *nm*OBC refers to members of the n-*alkyl*-4'-n-*alk*oxy-biphenyl-4-carboxylate homologous series.

Two-layer films appear to be two-dimensional. Surprisingly, however, even films just three molecular layers thick clearly display distinct anomalies corresponding to separate transitions in the surface and interior layers. Upon cooling these thicker *nm*OBC films, the SmA-HexB transition has been observed to originate at the outermost surface layers and progress into the film in a layer-by-layer fashion [5]. Among the nine *nm*OBC compounds that exhibit the SmA-HexB transition, 3(10)OBC possesses the longest total alkyl chain length. The increased separation between the biphenyl-carboxylate cores may further reduce the interlayer coupling. Such reduced coupling is consistent with the observation that 3(10)OBC not only shows the most pronounced heat-capacity peaks but also displays up to five (rather than four) separate heat-capacity anomalies near the SmA-HexB transition for sufficiently thick films [5]. Heat capacity as a function of temperature in the vicinity of the bulk SmA-HexB transition in (a) 60-, (b) 30-, and (c) 6-layer 3(10)OBC free-standing films is shown in Fig. 1. For clarity, the temperature axes are expanded in the insets of (a) and (b), to better illustrate the surface transitions near the large interior anomalies. Despite the impressive resolution of our calorimeter, we are unable to resolve additional heat-capacity peaks. It is therefore unclear whether the transition continues in a layer-by-layer fashion throughout the entire film (complete wetting) or is terminated by a single bulk transition involving the rest of the interior layers (incomplete wetting).

The results exhibited in Fig. 1 are quite remarkable. Previous to this work, layering transitions had been theoretically addressed and experimentally investigated only in systems exhibiting a first order transition [11]. However, none of the heat-capacity anomalies in Fig. 1 exhibit measurable ($<$ 10 mK) thermal hysteresis [5, 12]. Moreover, the well separated heat-capacity anomalies can be successfully fit to a simple power law [13-15]. These two observations are strongly indicative of the continuous nature of these transitions. In principle, the predicted divergence of the order-parameter susceptibility (χ) makes the discussion of a layer-by-layer transition near a continuous transition appear inappropriate. However, it can be shown [16] that if the critical exponent η associated with the corresponding 2D transition is greater than 2, the interlayer coupling becomes irrelevant and the layer-by-layer transition is feasible.

The ordering effects of the surface tension inherent in the liquid-crystal/vapor interface have been clearly demonstrated by x-ray diffraction measurements [17]. It was found that the molecular fluctuation amplitudes increased sharply as a function of increasing

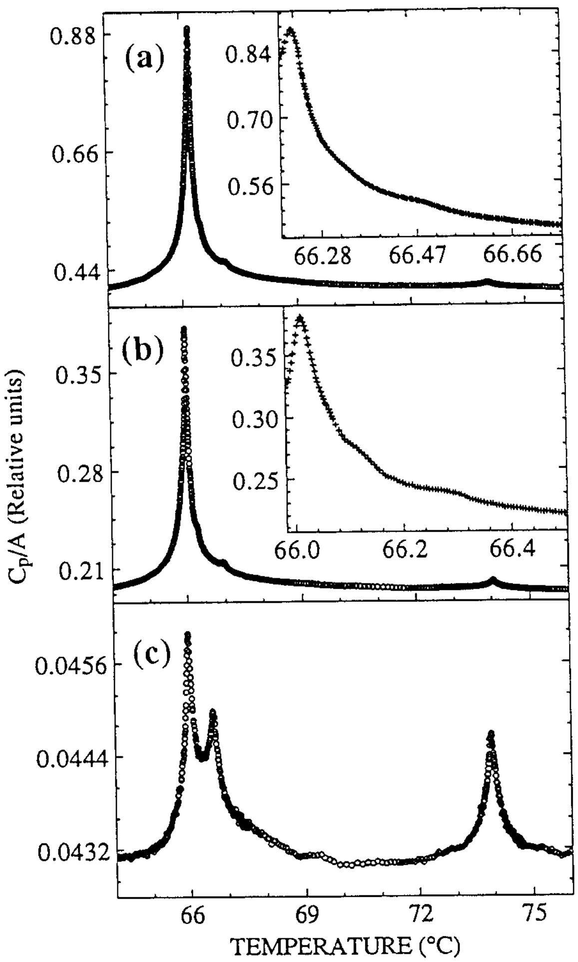

FIG. 1. Temperature variation of heat capacity for (a) 60-, (b) 30-, and (c) 6-layer 3(10)OBC free-standing films near the SmA-HexB transition. To make the layer transition more apparent near the large interior anomaly, the temperature axes are expanded in the insets.

depth into the film, strongly supporting the hypothesis that the ordering originates at the free surfaces. Furthermore, this study suggests that there may be a variation of in-plane molecular density $(\rho_A(L))$ between the outermost layers and the interior. Because the SmA-HexB transition can probably also be density driven, it is reasonable to assume that the transition temperature of each molecular layer is a function of $\rho_A(L)$. The outermost layers, having the highest density due to the surface tension, would exhibit the highest transition temperature and the transition would progress inwards upon decreasing temperature. Unfortunately, despite the high resolution of our optical reflectivity probe (which is sensitive to the index of refraction and, hence, density), we have not yet been able to measure any variation of the in-plane density as a function of film thickness. The transition temperatures may be strongly dependent on small changes of the in-plane density, however, and this failure does not greatly weaken the above argument.

The transition temperature ($T_c(L)$) of the individual layer (L) can be measured with high resolution. Here L gives the separation (measured in units of layers) between the nearest film/vapor interface and the layer in question. Figure 2 displays the temperature variation of the penetration depth (L versus $[T_c(L)-T_0]/T_0$) of the surface ordering transitions for the three different films introduced in Fig. 1. The data can be described by the simple power-law expression: $L = L_0\ ([T_c(L)-T_0]/T_0)^{-\nu}$ with the exponent $\nu = 0.32 \pm 0.01$, coefficient $L_0 = 0.30$ and $T_0 = T_c$, the bulk transition temperature. By utilizing standard wetting calculations [18], the value of the exponent ν leads us to conclude that the interlayer interaction is dominated by van der Waals-like forces. The results also show that the interlayer interaction does not change within our experimental resolution over the range of film thickness studied.

In contrast to the case of the SmA-HexB transition, the SmA-CryB transition establishes long-range positional order both within and between the layers. Because enhanced surface ordering has now been observed in many liquid-crystal systems, it was not a complete surprise when surface transitions near the first-order SmA-CryB transition were also identified. Nevertheless, it is the first layer-by-layer transition involving a liquid-crystal crystalline phase to be identified experimentally [19]. Employing our high-resolution free-standing film calorimetric system, we have identified up to six separate heat-capacity peaks associated with the SmA-CryB transition of 40.8 films [19]. The temperature dependence of the surface CryB penetration into the SmA substrate can again be well-characterized by the power law form: $L = L_0\ ((T_c(L)-T_0)/T_0)^{-\nu}$, where T_0 is again the bulk transition temperature. Fitting yields the

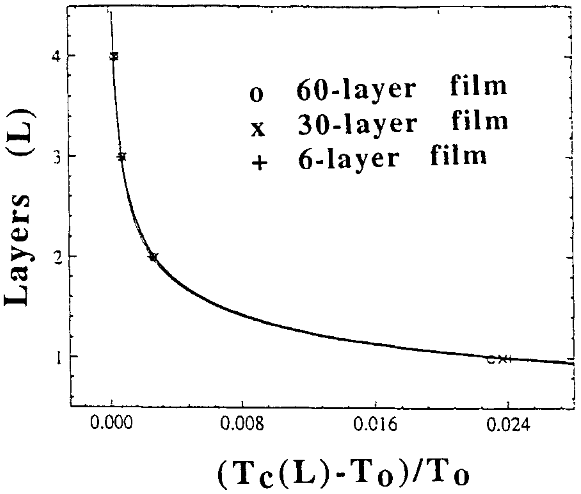

FIG. 2. Plot of L vs. $[T_c(L)-T_0]/T_0$ of the layer transition temperature, $T_c(L)$, obtained from Fig. 1. The solid line is the fit to the power law expression.

exponent $\nu = 0.36$. Similar to the SmA-HexB transition, this value of the exponent ν again indicates that the interlayer interaction is van der Waals-like.

In our laboratory, another layer-by-layer transition exhibited by liquid crystals has been recently observed above the SmA-isotropic transition of H(10)F(5) [5-n-decyl-2-(4-n-(perfluoropentyl-metheleneoxy) phenyl) pyrimidine]. These molecules consist of a phenyl-pyrimidine core separating hydro-alkyl and fluoro-alkyl end chains. The perfluorination seems to have a profound impact on the behavior exhibited by this class of compounds. These end groups are expected (and have been observed) to enhance the tendency of such compounds to favor layered phases [20, 21]. Not only are the smectic phase ranges greatly enhanced but the layer structure might also be expected to be much more well developed in the perfluorinated analogues of the more common hydro-alkyl terminated compounds. This observation becomes important in the discussion of the novel results obtained above the SmA-isotropic transition of H(10)F(5). To date, when free-standing films of ordinary hydro-alkyl liquid-crystal compounds are heated, the films invariably rupture at or below the bulk isotropic transition temperature (T_{AI}) or the bulk nematic transition temperature (T_{AN}). It was therefore very surprising when H(10)F(5) films were observed to exhibit an extremely interesting layer-by-layer *thinning* transition well above the bulk T_{AI} (see Fig. 3) [22]. Both our optical reflectivity and heat capacity data indicate that the films thin as the interior layer(s) become isotropic and are progressively squeezed out of the film. The temperature dependence of this effect is extremely intriguing. Let $T_{hc}(L)$ denote the highest temperature at which a film of thickness L is stable. The film thickness is again found to obey the simple power-

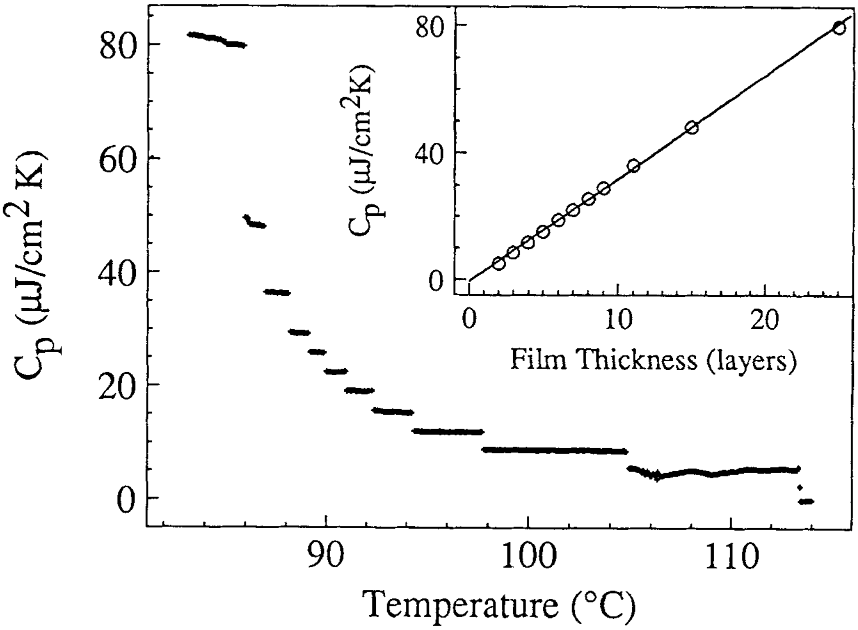

FIG. 3. Heat capacity data associated with the SmA-isotropic transition of an initially 25-layer thick H(10)F(5) film. The melting occurs as a series of discrete transitions in which interior layers become progressively disordered and drain out of the film. The resultant thinning continuous until the films become only two layers thick and eventually rupture near 112 °C. The inset demonstrates that the plateau values are consistent with the expected linear dependence on film thickness, confirming our hypothesis that the melting occurs as a series of layer-thinning transitions.

law form: $L = L_0((T_{hc}(L)-T_0)/T_0)^{-v}$ with $T_0 = T_{AI}$ and a very different value for the exponent v (≈ 3/4). To the best of our knowledge, no theory can explain this observed *thinning* transition. Moreover, it is truly amazing that two-layer SmA films remain stable more than 25 K above the bulk SmA-isotropic transition temperature (84 °C). Evidently the enhanced intralayer coupling is strong enough to preserves the layer structure and prevent film rupture as interior layers drain into the surrounding reservoir of sample at the film plate edge. Unlike the previous two examples layer-by-layer transitions discussed above, this film *thinning* transition is monotropic so that the film thickness does not increase upon cooling.

In conclusion, in our laboratory, three distinct layer-by-layer transitions in various liquid-crystal free-standing film systems have been characterized. The progression of both the SmA-HexB and SmA-CryB transitions has been shown to be well described by a simple power law resulting from a standard wetting calculation assuming the interlayer interaction to be van der Waals-like. Although a similar power law has been found to describe the fascinating SmA-isotropic *thinning* transition in perfluorinated liquid-crystal compounds, there does not appear to be any theory that can account for the extremely large value of the exponent (v ≈ 3/4) obtained. Thus far, all the surface enhanced ordering transitions found in liquid crystals exhibit layer-by-layer transitions and are well-characterized by the simple power-law expression. This indicates that the observed surface "freezing" transitions occur on smooth "substrates" through long-range interlayer interactions.

This work was supported in part by the National Science Foundation, Solid State Chemistry Program, Grant No. DMR93-00781.

REFERENCES

1. T. Stoebe and C.C. Huang "Physical properties of thin substrate free liquid crystal films," to be published in Int. J. Mod. Phys. B.
2. J.W.M. Frenken and J.F. van der Veen, Phys. Rev. Lett. 57, 94 (1986).
3. B.M. Ocko, A. Braslau, P.S. Pershan, J. Als-Nielson, and M. Deutsch, Phys. Rev. Lett. 57, 94 (1986).

4. B.D. Swanson, H. Stragier, D.J. Tweet, and L.B. Sorensen, Phys. Rev. Lett. 62, 909 (1989).
5. T. Stoebe, R. Geer, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett. 69, 2090 (1992).
6. J. Als-Nielsen, Physica A 140, 376 (1986); E.B. Sirota, P.S. Pershan, S. Amador, and L.B. Sorensen, Phys. Rev. A 35, 2283 (1987); B.M. Ocko, Phys. Rev. Lett. 64, 2160 (1990).
7. J.V. Selinger and D.R. Nelson, Phys. Rev. A 37, 1736 (1988); Z. Pawlowska, T.J. Sluckin, and G.F. Kventsel, *ibid.* 38, 5342 (1988); A.M. Somoza, L. Mederos, and D.E. Sullivan, Phys. Rev. Lett. 72, 3674 (1994).
8. R. Geer, T. Stoebe, T. Pitchford, and C.C. Huang, Rev. Sci. Instrum. 62, 415 (1991).
9. T. Stoebe, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett. 68, 2944 (1992).
10. R. Geer, T. Stoebe, C.C. Huang, R. Pindak, J.W. Goodby, M. Cheng, J.T. Ho and S.W. Hui, Nature 355, 152 (1992).
11. A number of excellent review articles on wetting have been presented including work by M. Schick in *Liquids at Interfaces*, edited by J. Charvolin, J.F Joanny, and J. Zinn-Justin, (Elsevier Science Publishers B.V., 1990) and P.G. de Gennes, Rev. Mod. Phys. 57, 827 (1985).
12. R. Geer, T. Stoebe, and C.C. Huang, Phys. Rev. E 48, 408 (1993).
13. R. Geer, Ph.D. thesis (University of Minnesota) 1991.
14. T. Stoebe, I.M. Jiang, S.N. Huang, A.J. Jin, and C.C. Huang, Physica A. 205, 108 (1994).
15. T. Stoebe, Ph.D. thesis (University of Minnesota) 1993.
16. T.C. Lubensky, private communication.
17. D.J. Tweet, R. Holyst, B.D. Swanson, H. Stragier, and L.B. Sorensen, Phys. Rev. Lett. 65, 2157 (1990).
18. J.G. Dash, Contemporary Physics 30, 89 (1989).
19. A.J. Jin, T. Stoebe, and C.C. Huang, Phys. Rev. E 49, R4791 (1994).
20. E.P. Janulis, D.W. Osten, M.D. Radcliffe, J.C. Novack, M. Tristani-Kendra, K.A. Epstein, M. Keyes, G.C. Johnson, P.M. Savu, and T.D. Spawn, SPIE-Int. Soc. Opt. Eng. 1665, 143 (1992).
21. W.H. deJeu, private communication.
22. T. Stoebe, P. Mach, and C.C. Huang, (preprint).