Simultaneous calorimetric and optical reflectivity measurements of extremely thin liquid crystal films

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Simultaneous calorimetric and optical reflectivity measurements of extremely thin liquid crystal films

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An extremely sensitive measuring system has been developed to obtain simultaneously heat capacity and optical reflectivity data from thin free-standing liquid crystal films. Results from 3(10)OBC near the smectic A to hexatic B transition will be reported and discussed in the context of recent theory regarding phase transitions in two dimensions.

1. Introduction

Theoretical advances [1] in describing two dimensional (2D) melting introduced a novel, thermodynamically stable phase of matter (the hexatic phase) intermediate between the solid and liquid phases. The 2D hexatic phase is characterized by pseudo-long range bond orientational order and short range positional order. As a result, the scattering profile of this phase should exhibit a diffuse six-fold modulation, in contrast to the symmetric ring characteristic of the liquid phase and the sharp spots indicative of the solid phase. The unique features of the hexatic phase provided substantial physical insight into several liquid crystal mesophases. Subsequently, experimental identification of the diffuse six-fold modulation from X-ray [2] and electron diffraction studies [3] of the hexatic B (HexB) phase of several members of the nmOBC (n-alkyl 4′-n-alkoxybiphenyl-4-carboxylate) homologous series has seemingly confirmed the existence of this phase in nature. Another interesting feature of the 2D hexatic phase is that it should melt into the 2D liquid phase via a Kosterlitz–Thouless (KT) type transition [4] at a finite temperature. The heat capacity associated with such a transition is expected to exhibit a broad, asymmetric anomaly at some temperature $T > T_{KT}$ reflecting the presence of an essential singularity at the KT transition temperature, T_{KT}. By simultaneously measuring the heat capacity and some quantity sensitive to the essential singularity at T_{KT}, as a function of temperature, of extremely thin liquid crystal films, a crucial test of these theoretical predictions concerning the liquid–hexatic transition in liquid crystals could be performed.

2. Results and discussion

Because free-standing liquid crystal films only two molecular layers in thickness can be prepared with relative ease from a number of different liquid crystal compounds, they are excellent physical systems with which to investigate physical properties related to substrate free two dimensional systems. To provide data on the liquid–hexatic transition in liquid crystals, during the past several years, we have constructed not only

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a high resolution AC differential calorimeter [5], but also a high sensitivity optical reflectivity measurement system [6]. Both probes are capable of performing very high resolution studies on a number of phase transitions as a function of temperature and film thickness. Furthermore, they can be used to obtain simultaneous data on both physical quantities.

The success of our AC calorimeter relies, in part on a rather remarkable coincidence. The alkyl end chains of many liquid crystal molecules strongly absorb $3 \cdot 39 \, \mu$m radiation due primarily to vibrational modes of their CH_2 and CH_3 groups. This is fortunate, because He–Ne lasers with stable output intensity operating on the $3 \cdot 39 \, \mu$m emission line are commercially available. Consequently mechanically chopped $3 \cdot 39 \, \mu$m radiation from a He–Ne laser has proved to be the most effective AC heating source for our AC calorimeter. To further enhance its output stability, the He–Ne laser is placed in a temperature regulated aluminium housing. Without such a stable AC heating source, it would have been impossible to obtain heat capacity data from thin free-standing liquid crystal films. Furthermore, to achieve high mechanical and thermal stability of our probing system over a long measuring time (>8 h), the principal part of the calorimeter has been redesigned and replaced by a fairly compact package made of stainless steel. The package consists of a film plate for preparing free-standing films and mounts for two tiny thermocouple junctions which are essential for our differential AC calorimetric approach [5]. As a result of this modification, the long term drift in the heat capacity signal, presumably caused by the slight displacement of the thermocouple junctions and the liquid crystal film as a function of temperature, has been significantly reduced.

The optical reflectivity is probed by another He–Ne laser operating in an amplitude stabilized mode at $0 \cdot 63 \, \mu$m. It is also mechanically chopped, but at a frequency (675 Hz) that is much higher than the chopping frequency used for the calorimetric studies (42·5 Hz). As in the case of the heat capacity measurements, the signal to noise ratio of the reflectivity measurement is greatly enhanced by operating the lock-in amplifier in a differential mode between the beam reflected by the film and the signal from a laser intensity monitor. Relative resolution of one part in 5×10^4 has been achieved. By focusing the $0 \cdot 63 \, \mu$m laser beam to a small spot ($<350 \, \mu$m in diameter) and directing it to intersect the film less than one thermal diffusion length ($l_d \approx 0 \cdot 7$ mm at our 42·5 Hz operating frequency) from the tiny thermocouple junction that senses the films' response to the AC heat input, we can simultaneously measure the heat capacity and optical reflectivity as a function of temperature.

The liquid crystal compound used for this study was 3(10)OBC (a member of the nmOBC homologous series). Bulk samples of 3(10)OBC exhibit the smectic A–hexatic B transition near 66°C. Thin films of 3(10)OBC exhibit surface ordering due to the stabilizing effects of the film–vapour interfaces. The temperature variation of the heat capacity (C_p) and optical reflectivity (R) associated with these liquid–hexatic transitions is shown in figures 1, (a), (b), and (c) for two, three, and four layer films, respectively. The heat capacity anomalies near 74°C signal the liquid–hexatic transition in only the two outermost layers, while the lower temperature anomalies in figures 1, (b) and (c) correspond to the hexatic ordering in the interior layer(s). Unlike the broad humps theoretically predicted [7], the heat capacity data display sharp anomalies associated with both the surface and interior transitions.

The curvature of the reflectivity data exhibits a change in sign near the peak positions of all the heat capacity anomalies. Assuming that the film thickness and molecular polarizability remain constant through the transitions, the Lorentz–Lorenz
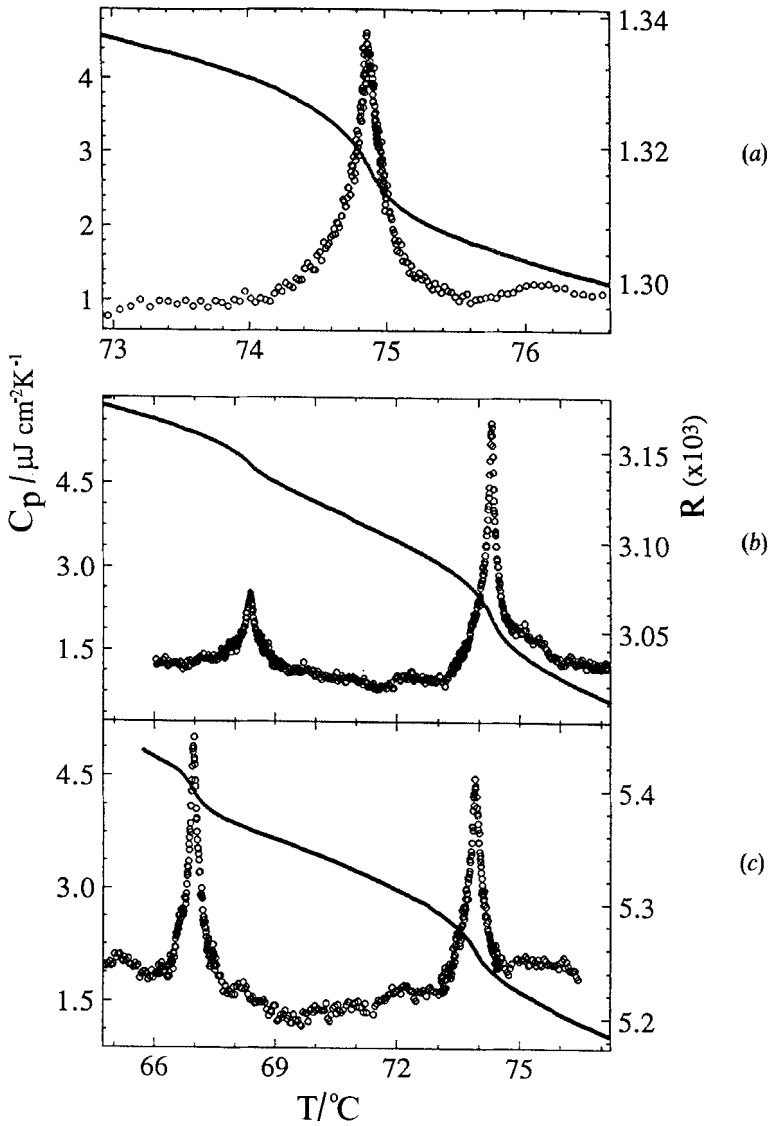
Figure 1. Temperature variation of heat capacity and reflectivity of a (*a*) two, (*b*) three, and (*c*) four layer film of 3(10)OBC (see [11]).

relation [8] can be used to relate the reflectivity data (*R*) and the in-plane molecular density (ρ_A) through the expression:

$$\rho_A = c/\{1 + 3hk/(2R^{1/2})\},$$

where *c* is a constant, *h* is the film thickness and *k* is the wave-vector of the red laser light. Details of this derivation have been presented in [6]. Actually, the temperature dependence of in-plane molecular density is very similar to that of reflectivity (see figure 1 in [6]). The fact that the high resolution reflectivity data can be taken with high
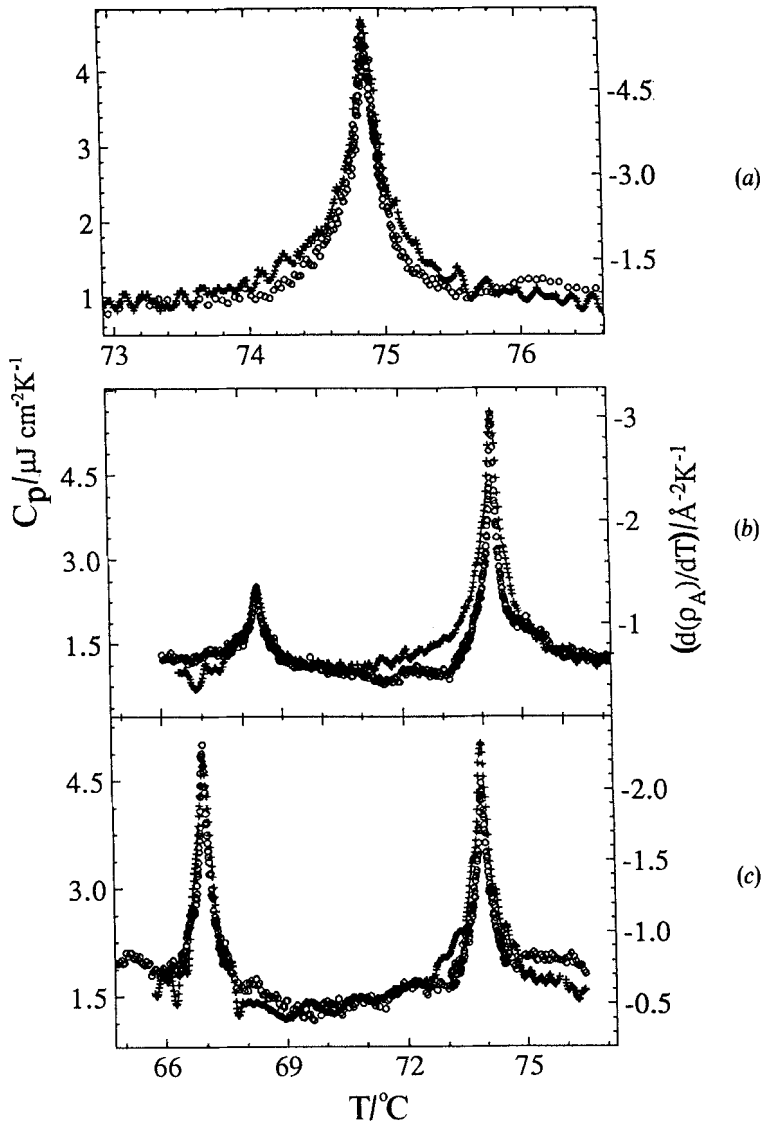
Figure 2. Comparison of the temperature dependence of the heat capacity and the temperature derivative of the in-plane density $(d\rho_A/dT)$ of a (a) two, (b) three, and (c) four layer film of 3(10)OBC.

data density enables us to take temperature derivatives of the in-plane density data. Figures 2(a), (b), and (c) show the comparison of heat capacity data (C_p) with the temperature derivative of in-plane density $(d\rho_A/dT)$. Theoretical advances [9] have suggested a direct relation between ρ_A and the hexatic order parameter. We would therefore expect the derivative $(d\rho_A/dT)$ to reveal the onset of the hexatic order at T_{KT}. On the contrary, the C_p and $d\rho_A/dT$ data look strikingly similar. In fact, the peak positions of the C_p and $d\rho_A/dT$ data are in excellent agreement up to our experimental resolution (7 mK).

3. Conclusions

In conclusion, we have observed sharp heat capacity anomalies associated with the smectic A–hexatic B transitions in two, three, and four layer films of 3(10)OBC. In particular, the two layer film heat capacity data can be well-described by a power law fitting expression with critical exponent $\alpha = 0.25 \pm 0.05$ [6]. In order to reconcile the following three experimental facts: (i) the lack of any additional feature in the $d\rho_A/dT$ data to signal the onset of the hexatic order at T_{KT}, (ii) the six-fold modulated diffraction patterns from X-ray and electron beam scattering experiments, and (iii) the sharpness of the heat capacity peak which can be described by a power law expression, we suggest that another type of long range order (for example herring-bone) is established along with the bond orientation order in the immediate vicinity of the liquid–hexatic transition found in the *nm*OBC compounds. Under this circumstance, the hexatic B phase in these liquid crystals cannot be characterized as the simple stacked hexatic phase suggested by Birgeneau and Litster [10].

References

[1] HALPERIN, B. I., and NELSON, D. R., 1978, *Phys. Rev. Lett.*, **41**, 121. NELSON, D. R., and HALPERIN, B. I., 1979, *Phys. Rev.* B, **19**, 2457. YOUNG, A. P., 1979, *Phys. Rev.* B, **19**, 1855.

[2] PINDAK, R., MONCTON, D. E., DAVEY, S. C., and GOODBY, J. W., 1981, *Phys. Rev. Lett.*, **46**, 1135. DAVEY, S. C., BUDAI, J., GOODBY, J. W., PINDAK, R., and MONCTON, D. E., 1984, *Phys. Rev. Lett.*, **53**, 2129.

[3] CHENG, M., HO, J. T., HUI, S. W., and PINDAK, R., 1987, *Phys. Rev. Lett.*, **59**, 1112.

[4] KOSTERLITZ, J. M., and THOULESS, D. J., 1973, *J. Phys.* C, **6**, 1181.

[5] GEER, R., STOEBE, T., PITCHFORD, T., and HUANG, C. C., 1991, *Rev. scient, Instrum.*, **62**, 415.

[6] STOEBE, T., HUANG, C. C., and GOODBY, J. W., 1992, *Phys. Rev. Lett.*, **68**, 2944.

[7] BERKER, A. N., and NELSON, D. R., 1979, *Phys. Rev.* B, **19**, 2488. SOLLA, S. A., and REIDEL, E. K., 1981, *Phys. Rev.* B, **23**, 6008.

[8] JACKSON, J. D., 1975, *Classical Electrodynamics* (Wiley), p. 155.

[9] AEPPLI, G., and BRUINSMA, R., 1984, *Phys. Rev. Lett.*, **53**, 2133.

[10] BIRGENAU, R. J., and LITSTER, J. D., 1978, *J. Phys., Lett., Paris*, **39**, 399.

[11] The determination of the absolute heat capacity scale is non-trivial and further experimental work is necessary and is in progress to confirm the preliminary values shown here.