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Critical slowing down near the smectic-A-hexatic-B transition

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Résumé. — Nous avons fait des mesures de capacité calorifique et conductivité thermique, avec une grande résolution, sur un échantillon de n-propyl-4'-n-heptyloxybiphenyl-4'-carboxylate (370BC) au voisinage de la transition smectique A-hexatique B. La conductivité thermique a une forte décroissance près de la transition, ce qui montre clairement et confirme le ralentissement critique des fluctuations thermiques, déjà observé sur des échantillons de séries homologues. On vérifie que l’anomalie est en accord quantitatif avec la théorie classique de la dynamique des phénomènes critiques.

Abstract. — We have performed high-resolution heat-capacity and thermal-conductivity investigations on the same sample in the vicinity of the smectic-A-hexatic-B transition of n-propyl-4'-n-heptyloxybiphenyl-4-carboxylate (370BC). The thermal diffusivity shows a pronounced drop near the transition. This clearly demonstrates and confirms the critical slowing down of the thermal fluctuations observed in the other member of the homologous series. The anomaly is found to be in quantitative agreement with the conventional theory of critical dynamics.

Halperin and Nelson [1] formulated a two-stage dislocation mediated melting theory which would take a two-dimensional (2D) solid to a 2D liquid via two phase transitions instead of one. This is a dislocation unbinding transition, first proposed by Kosterlitz and Thouless [2] followed by a disclination unbinding transition. These transitions can be continuous, unlike the first order melting transition of bulk materials.

Intermediate between the transitions a hexatic phase is predicted which has short range positional order and algebraically decaying bond-orientational order (order in the local lattice orientation). Birgeneau and Litster [3] argued that the stacking of such hexatic layers would
produce a kind of smectic liquid-crystal mesophase which would have three-dimensional long
range bond-orientational order due to weak intra-layer coupling, while both inter- and intra-
layer positional orders remain short range. Without long range positional order, the layer
structures in both the smectic-A(SmA) and this intermediate phase (the hexatic-B(HexB)
phase) undergo large fluctuations. The HexB phase was first detected through X-ray
diffraction studies by Pindak et al. [4] in 650BC (n-hexyl-4'-n-pentyloxybiphenyl-4-carboxy-
late). High-resolution calorimetry investigations by Huang et al. [5] show that the SmA-HexB
transition in 650BC is continuous with a heat-capacity anomaly described by the critical
exponent \( \alpha = 0.60 \). Employing an experimental technique which is an extension of the ac
calorimetry method [6], Nounesis and coworkers reported a strong anomaly associated with
the thermal conductivity of 650BC in the vicinity of the SmA-HexB transition [7]. This
is described by a critical exponent \( a = 0.51 \pm 0.04 \) and a critical amplitude ratio \( \Lambda^+ / \Lambda^- = 0.93 \).
In this paper we report on thermal conductivity studies for the SmA-HexB transition in
370BC, another nmOBC compound (n-alkyl-4'-n-alkoxybiphenyl-4-carboxylate). The SmA-
HexB transition of 370BC has a similar anomaly in the thermal conductivity. The heat
capacity of 370BC over the same temperature region is consistent with that found for other
nmOBC compounds with critical exponent \( \alpha = 0.60 \). Fitting the thermal diffusivity data to a
simple scaling model [8] allows us to determine another critical exponent (\( \eta \)) associated with
the SmA-HexB transition. Furthermore, we demonstrate that three experimental available
critical exponents (\( \alpha, \eta \) and \( \beta \)) for the SmA-HexB transition satisfy the scaling relations. Here
critical exponent \( \beta \) characterizes the temperature variation of the order parameter.

Details of the experimental technique and its motivation have been reported [7]. Due to the
relatively poor thermal conductivity of liquid-crystal compounds (about one-fifth that of
glass) a special sample cell has been designed to significantly reduce heat loss by conduction
through the sample container. The cell consists of a thin sample of liquid-crystal compound
housed between two chemically etched glass slides [6]. To determine thermal conductivity,
the apparent heat capacity per unit area, \( \tilde{C}_A = \frac{\Delta P_A}{\omega \Delta T} \) is measured as a function of
temperature throughout the transition region. \( \Delta P_A \) is the ac power oscillation amplitude per
unit area applied to the bottom side of the sample cell, \( \omega \) the angular frequency of this
oscillation, and \( \Delta T \) the resulting temperature oscillation amplitude detected on the top side of
the sample cell. This variation of the apparent heat capacity was measured with high data
density (~1200 data for each frequency) for eleven different frequencies. Through
interpolation of the data, the frequency response curve, i.e. \( \tilde{C}_A^{-1} = \frac{\omega \Delta T}{\Delta P_A} \) vs. \( f \left( = \frac{\omega}{2 \pi} \right) \), is
obtained for each of the 106 different temperatures. A linear fitting [7] was done for

\[
\tilde{C}_A^2 = C_A^2 \left( 1 + \left( \frac{\omega}{\omega_H} \right)^2 \right).
\]

This determines \( \omega_H \), the high cutoff frequency which is directly related to the effective
thermal diffusivity of the entire sample cell, and can be used to determine the thermal
conductivity of the liquid-crystal sample through the expression

\[
\frac{1}{\omega_H} = \frac{1}{3 \sqrt{10}} (C_A) \left( \frac{h_L}{K_L} + \frac{2 h_G}{K_G} \right)
\]

where \( C_A = 2 h_G C_G + h_L C_L \) is the total heat capacity per unit area. The quantity \( h \) refers to
thickness, \( C \) to heat capacity, and \( K \) to thermal conductivity. The subscripts G and L refer to
glass and liquid crystal, respectively. Separate thermal conductivity and heat capacity
measurements were done for the glass slides used to hold the sample over the relevant temperature region to determine the glass contribution to equation (2).

Other methods used to measure thermal conductivity of liquid-crystal mesophases, e.g., the steady state method [9], thermal lens effect [10], and forced Rayleigh light scattering technique [11, 12], require a fairly large temperature gradient inside the sample to obtain a measurable signal. Our technique requires only a small amount of sample (~ 15 mg) with a temperature oscillation of about 3 mK rms over the sample. Both are important factors in studying critical phenomena.

The measurements of Nounesis and coworkers [7] showed a peak in the thermal conductivity and a drop in the thermal diffusivity, $D_T = K/C_P$, of 65OBC near the transition temperature ($T_c$). Our results on the heat capacity, thermal conductivity and thermal diffusivity near the SmA-HexB transition of 37OBC show the same behavior as that of 65OBC. The heat capacity data have been published in reference [13]. The transition temperature for our sample was 70.960 °C, and remained stable, with a $T_c$ shift less than 5 mK/d during the course of the measurements.

The drop in thermal diffusivity in both 37OBC and 65OBC illustrates critical slowing down of the thermal fluctuations. For smectic liquid crystals, thermal studies by Rondelez and coworkers [11] show that heat transport is essentially governed by orientational ordering and molecular properties, but not by long range positional ordering, or the smectic layer order. This suggests a direct coupling between thermal and hexatic order fluctuations near the transition in our system.

Recently Hobbie and Huang [8] proposed a simple scaling model for smectic liquid crystals that predicts the thermal diffusivity to be given by

$$\frac{1}{D_T} \sim \frac{1}{C_P} \left[ \frac{1}{\Gamma_{\phi}} \chi \left( \frac{\partial \chi}{\partial t} \right)^2 \frac{1}{\xi^5} + B \right]$$

where $\chi$ is the order parameter susceptibility, $\xi \sim \chi^{1/(2-\eta)}$ the « bulk » correlation length, $t$ the reduced temperature and $\Gamma_{\phi}$ the kinetic coefficient associated with the order parameter. $B$ is a background term that should be a relatively smooth function of temperature. For the conventional theory of the critical dynamics of nonconserved order parameter fluctuations ($z = 2 - \eta$), $\Gamma_{\phi}$ will be independent of the correlation length. Taking $\chi = |t|^{-\gamma}$ and using static scaling, the above expression for $D_T^{-1}$ predicts $C_P/D_T = A^z |t|^{-z\gamma + z\eta} + B$, where

Fig. 1. — The singular part of the ratio $C_P/D_T$ as measured (dots) and as predicted by the conventional theory (line).
Fig. 2. — Temperature variation of thermal conductivity (a) and thermal diffusivity (b) in the vicinity of the SmA-HexB transition of 37OBC. The dots and line represent the measured and calculated behavior, respectively.

\[ A^+/A^- = (\chi^-/\chi^+)^{(3+\eta)/(2-\eta)} \]. A power-law fit of the ratio \( C_P/D_T \) was carried out with a weakly linear background term. The results are shown in figure 1. From this exponent and the previously determined value of \( \alpha \) we find \( \nu \eta = -0.10 \pm 0.03 \) and \( \chi^+ / \chi^- = 1.13 \), in very good agreement with similar fits of the 65OBC data [8]. Employing the scaling relations (\( d\nu = 2 - \alpha \), \( 2 \nu - \eta \nu = 2 - 2 \beta - \alpha \)), we obtained \( \beta = 0.18 \), which is consistent with the value measured by Ho and Rosenblatt [14] for 65OBC. The fits of the measured thermal diffusivity and conductivity are constructed according to \( D_T = C_P/(A^{\pm}|T|^{-\alpha+\eta\nu+B}) \) and \( K = C_P/(A^{\pm}|T|^{-\alpha+\eta\nu+B}) \) using the fitted expression for \( C_P \). These fits are shown in figure 2a and 2b, respectively. The fact that the heat capacity (\( C \)) has a sharper rise than the drop in the thermal diffusivity (\( D_T \)) near the transition temperature leads to a divergence in the thermal conductivity (\( K = C \times D_T \)). Although we know that the drop in \( D_T \) is related to the critical slowing down of thermal fluctuations, we do not have microscopic explanations for the divergence in thermal conductivity. This agreement of the data with the conventional theory of critical dynamics (\( z = 2 - \eta \)) depends strongly on the validity of the inferred \( \beta \).

Although the value of \( \eta \) is unusually large and negative (\( \eta = -0.21 \pm 0.03 \)), it should be noted that the exponents \( \gamma \) and \( \nu \) are only slightly removed from their mean field values (\( \gamma = 1.04 \pm 0.05 \) and \( \nu = 0.47 \pm 0.01 \)).

In light of this strange value of \( \eta \), it is worthwhile to consider some other possible dynamic schemes. For \( z \) unknown, dynamic scaling gives \( \Gamma_\phi \sim \xi^{2-\eta-z} \) which, when substituting into the above expression for \( D_T^{-1} \), gives the singular part of \( C_P/D_T \) proportional to \( |T|^{-\alpha+\eta(2-z)} \). This implies \( D_T \sim \xi^{2-z} \) which is what one gets by extending the dynamic scaling assumption to the thermal diffusion mode \( \omega_q = D_T k^2 \). The fact that \( \omega_q \) softens weakly near \( T_c \) implies that \( z \) is slightly larger than 2. Renormalization group calculations of \( z \) for an auxiliary conserved density that couples to the order parameter fluctuations like the temperature have been carried out by Hohenberg and Halperin [16]. For a one component order parameter, which would be an incomplete description of hexatic ordering, they find that \( z = 2 + \alpha / \nu \), which would imply a softening of \( D_T \) with an exponent \( \alpha \). In that case the thermal conductivity is predicted to be smooth through the transition. For a two component order parameter, which in this case would be more realistic, they find that there are difficulties with the recursion relations at the appropriate fixed point and hence the correct
value of \( z \) is not clear. The situation can be made more complicated by nondissipative couplings between the order parameter and other hydrodynamic modes of the system that arise from the Poisson bracket relations between these quantities. Such a coupling between the phase of the order parameter and the energy density gives rise to the anomalous transport of heat above the lambda transition of \(^4\)He. In smectic liquid crystals, however, none of these couplings involve thermal fluctuations directly, and the thermal diffusion mode is purely diffusive in both the SmA and HexB phases. In addition, it is most likely fluctuations in the modulus of the order parameter below \( T_c \) that are relevant in determining \( z \), as opposed to the case in superfluid \(^4\)He where amplitude fluctuations are frozen out in the ordered state. There has been speculation that the SmA-HexB transition is tricritical, so it is worth mentioning that the critical exponent \( z \) has been calculated to be 2 for relaxational models at a tricritical point \([16]\). Hence extended dynamic scaling predicts that the thermal diffusivity would not soften at \( T_c \). Whether or not the softening that is observed would arise a finite distance away from such a point is not clear. At any rate, the value of \( \beta \) that has been measured for 65OBC along with the similarity between the behavior observed for both 65OBC and 37OBC suggest that the conventional theory is adequate. A direct experimental determination of the exponent \( \eta \) would shed more light on this.

For 37OBC the fitting range for the heat capacity extended to about \( |T - T_c| \leq 20 \text{ mK} \), showing a power-law behavior closer to the transition temperature than the ratio \( C_p/D_T \), which becomes rounded for \( |T - T_c| \leq 30 \text{ mK} \). Similar behavior was observed for the 65OBC. One may speculate that the rounding in \( \omega_H \) (and hence \( C_p/D_T \)) is due to our unique measurement technique \([17]\). Recently, Hobbie and Huang have investigated the temperature variation of thermal conductivity in the vicinity of the SmA-smectic-C (SmC) transition of one liquid-crystal compound \([18]\). They have found that both heat capacity and thermal conductivity show sharp jumps at the mean-field SmA-SmC transition. Furthermore, judging from the 10 \%-90 \% width of the jump, they obtained a sharper jump for the thermal conductivity than that for the heat capacity. Thus, this result indicates that our measurement technique will not increase the rounding region of the thermal conductivity in comparison with that for the heat-capacity anomaly.

In conclusion, we have performed high resolution thermal conductivity studies on the SmA-HexB transition of 37OBC, confirming the results of Nounesis \textit{et al.} \([7]\) with 65OBC. Our results once again show a dip in the thermal diffusivity, demonstrating the critical slowing down of the thermal fluctuations consistent with a conventional theory of the dynamics of the hexatic order parameter fluctuations. Another critical exponent (i.e. \( \eta \)) is obtained. Its value satisfies the scaling relation with the other two critical exponents, namely, \( \alpha \) and \( \beta \). A clear picture of the fundamental nature of the SmA-HexB transition is still lacking.

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The thermal diffusivity, $D_T$, can be related to the thermal conductivity, $K$, by $D_T = K/\rho CP$, where $\rho$ is the specific gravity. Both the smectic-A and hexatic-B phase do not have long-range positional order, so the temperature variation of the nearest neighbor spacing can give us approximately the density change through the transition. According to the X-ray measurements (DAVEY S. C., BUDAI J., GOODBY J. W., PINDAK R. and MONCTON D. E., Phys. Rev. Lett. 53 (1984) 53), there exists no anomaly in the nearest-neighbor spacing through this transition. Thus we expect no anomaly in $\rho$ through this phase transition.