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Simple explanation of the anomalous transport of heat near two smectic liquid-crystal phase transitions

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A detailed scaling argument is used to derive an expression for the thermal diffusivity in terms of the heat capacity, correlation length, and susceptibility. This simple model gives good fits to our experimental data near the smectic-A–hexatic-B transition of one liquid-crystal compound and the smectic-A–smectic-C transition of another. The critical dynamics of both transitions is assumed to be described by the conventional theory.

Recently we reported high-resolution thermal conductivity measurements near the smectic-A (Sm-A) to hexatic-B transition for a bulk sample of a liquid-crystal compound.[1] In that report, we found that the thermal diffusion mode showed a critical slowing down at T_c, which was demonstrated by a weak power-law singularity in the thermal diffusivity. We also recently reported high-resolution thermal conductivity data taken near the Sm-A–smectic-C (Sm-C) transition for bulk samples of another liquid-crystal compound, where we found anomalous behavior in the thermal diffusivity that was quite different from that reported for the Sm-A–hexatic-B transition.[2] In general, thermal transport in liquid-crystal systems is via orientational entropy fluctuations induced by fluctuations in the local molecular orientation.[3] For both of the transitions mentioned above, the order parameter in the usual Ginzburg-Landau free energy coarsely represents a degree of the local molecular orientation; the fluctuations of that part having an anomalously large relaxation time at T_c. Hence any singularities that are present in the thermal diffusivity should be directly linked to the critical slowing down of the order-parameter relaxation mode near T_c. As a first approximation, the order-parameter fluctuations and the thermal diffusion mode are coupled directly via the functional form of the Landau free energy and the thermodynamic relation between free energy and entropy. This simple model is unique to systems in which the order-parameter fluctuations are a strong thermal mode of the system. In the critical regime, it reduces to the extended dynamic scaling result for the thermal diffusivity ($D_T \sim \xi^{2-z}$ for a dynamic exponent z). For the extended mean-field Sm-A–Sm-C transition the heat capacity is not a simple power law, and it gives the temperature dependence of D_T in terms of C_p, χ, and ξ. For both transitions the critical dynamics of the order-parameter fluctuations is assumed to be described by the conventional theory,[4] although other possibilities are considered for the Sm-A–hexatic-B transition.

We measure the thermal diffusivity by measuring the time for a small heat pulse to diffuse across a thin liquid-crystal sample.[5] Hence there are no additional static temperature gradients in our system. In the presence of a quasistatically changing background temperature T, then, the thermal current density is given by $J_q^i \approx -TD_T^{ik}\partial_k s(\mathbf{x},t)$, where D_T^{ij} is the total thermal diffusivity tensor of an aligned, monodomain sample and $s=-\partial f(\mathbf{x},t)/\partial T$ is a field describing fluctuations in the local entropy density around thermodynamic equilibrium. Summation over repeated indices is assumed. Although the measurements were done on bulk, unaligned samples, it is simplest to first consider heat transport in some direction $\hat{\mathbf{n}}$ relation to a common layer normal $\hat{\mathbf{z}}$ of an aligned geometry. The quantity f, the free energy due to fluctuations, is obtained by expanding the appropriate static free-energy density in terms of the small fluctuating variables of the system. Since we are interested in singularities in the temperature dependence, we consider first fluctuations around the static order parameter, $\Psi \rightarrow \Psi + \psi(\mathbf{x},t)$. Here ψ is a real field describing local fluctuations in the order-parameter amplitude. For the Sm-A–Sm-C transition, ψ represents fluctuations in the tilt angle. For the Sm-A–hexatic-B transition, ψ represents the density of appearing and disappearing little islands of hexatic order in the Sm-A phase, and small deviations from hexatic order in the hexatic-B phase. In terms of ψ the free energy density is, in a renormalized Gaussian approximation,

$$f(\mathbf{x},t)=\tfrac{1}{2}\chi^{-1}\psi^2+\tfrac{1}{2}c_\perp(\partial_\perp\psi)^2+\tfrac{1}{2}c_\parallel(\partial_\parallel\psi)^2 +g(\mathbf{x},t)\ , \tag{1}$$

where g is the contribution from orientational fluctuations other than ψ, χ is the order-parameter susceptibility, and the second and third terms are a generalized smectic elastic energy density, the first term representing spatial fluctuations within the smectic planes ($\perp$) and the second representing fluctuations along the layer normal $\hat{\mathbf{z}}$ ($\parallel$). We assume that the elastic constants $c_\perp$ and $c_\parallel$ are nonsingular functions of temperature. We have also assumed that the modes associated with g are either sufficiently weak or smooth enough functions of temperature, such that the leading singular behavior will come from $\chi(T)$. The fact that the order parameter is in general complex for both of these inherently XY-like transitions gives rise to an "azimuthal" degree of freedom

$\phi(\mathbf{x},t)$ associated with the broken rotational symmetry (about $\hat{\mathbf{z}}$) in each of these low-temperature phases. The leading contribution to the free energy from this mode will be $\frac{1}{2}K_i|\partial_i\phi|^2$, where the elastic constants K_i are unspecified functions of temperature. The relevance of such terms depends on the strength of the K_i relative to the leading term in Eq. (1). In general, the ϕ mode is soft and energetically favorable in the hydrodynamic limit, and the correlation function for ϕ will have power-law decay at large distances, whereas the correlation function for ψ will decay exponentially. If the amplitude fluctuations were truly frozen out below T_c, then the leading term in the free energy would be from the phase fluctuations. Here we assume that amplitude fluctuations are important in the ordered state. The optical ψ mode is much stiffer and less easily excited than the hydrodynamic ϕ mode. Hence by tracking thermal excitations of the amplitude ψ we will follow the main stream of the thermal current and get the leading singular behavior of the thermal transport coefficients. There will be some higher-order structure in the thermal transport coefficients from the ϕ mode fluctuations. Whether or not these contributions are measurable in light of the leading term is a question requiring further investigation. With these assumptions understood, the thermal current density and the corresponding Kubo expression[6] for the thermal conductivity in the previously defined direction $\hat{\mathbf{n}}$ are, respectively,

$$\mathbf{J}_q\cdot\hat{\mathbf{n}}\approx TD_T(\hat{\mathbf{n}})\left[\frac{\partial\chi^{-1}}{\partial T}\psi\partial_{\hat{\mathbf{n}}}\psi-\partial_{\hat{\mathbf{n}}}S_b\right], \qquad (2)$$

$$\kappa(\hat{\mathbf{n}})=\lim_{\omega\to 0}\lim_{k\to 0}\frac{1}{6k_BT^2}\int\int dt\, d\mathbf{x}\, e^{i\omega t-i\mathbf{k}\cdot\mathbf{x}} \times\langle \mathbf{J}_q(\mathbf{x},t)\cdot\hat{\mathbf{n}}\mathbf{J}_q(0,0)\cdot\hat{\mathbf{n}}\rangle. \qquad (3)$$

Here S_b is the background entropy density arising from g. Since the order-parameter fluctuations are coupled to the background fluctuations, the appropriate equation of motion[4] for ψ is of the form $\partial\psi/\partial t=-\Gamma_\psi\delta f/\delta\psi+\rho$, where we have introduced Γ_ψ, the kinetic coefficient associated with ψ, and ρ is a Langevin white-noise source. The thermal diffusivity $D_T(\hat{\mathbf{n}})$ and the thermal conductivity $\kappa(\hat{\mathbf{n}})$ are related by $\kappa(\hat{\mathbf{n}})=C_pD_T(\hat{\mathbf{n}})$, where C_p is the total heat capacity per unit volume of the liquid-crystal sample at constant pressure. After substituting the expression (2) into Eq. (3), evaluating the ensuing correlation function in the usual effective Gaussian approximation, and rescaling all of the residual temperature dependence in the Kubo integral onto ω and $\mathbf{k}$, one is left with, after taking the hydrodynamic limit, $D_T^{-1}(\hat{\mathbf{n}})=C_p^{-1}[F_s^{-1}(\hat{\mathbf{n}})+B]$. Here $F_s^{-1}(\hat{\mathbf{n}})$, the singular part of the ratio $C_p/D_T(\hat{\mathbf{n}})$, is derived in terms of χ, Γ_ψ, $\hat{\mathbf{n}}$, $\xi_\perp$, and $\xi_\parallel$.[7] For a bulk, unaligned sample of approximately 50 μm in thickness, all directions $\hat{\mathbf{n}}$ relative to some molecular orientation will be probed.[8] Since the anisotropy of the thermal diffusivity tensor is not severe for smectic liquid crystals,[3] what we have measured in this paper is $D_T=(4\pi)^{-1}\int d\Omega\, D_T(\hat{\mathbf{n}})$. For the Sm-$A$ and hexatic-B phases there are two independent thermal diffusivity parameters $D_T^\parallel$ and $D_T^\perp$ and the angular average is $\frac{1}{3}(D_T^\parallel+2D_T^\perp)$. For the Sm-$C$ phase there are, neglecting the biaxiality of the molecules, three independent thermal diffusivity parameters $D_T^\parallel$, $D_T^{\perp(1)}$, and $D_T^{\perp(2)}$. For the purposes of this paper we neglect the difference between the (1) and (2) directions. Then the measured quantity is again $\frac{1}{3}(D_T^\parallel+2D_T^\perp)$. The expressions we obtain for $F_s^{-1}(\perp)$ and $F_s^{-1}(\parallel)$ are

$$\begin{aligned} F_s^{-1}(\perp)&=\frac{C_p}{D_T^\perp}-B_\perp\sim\frac{1}{\Gamma_\psi\chi}\left[\frac{\partial\chi}{\partial r}\right]^2\frac{1}{\xi_\parallel\xi_\perp^4}\,,\\ F_s^{-1}(\parallel)&=\frac{C_p}{D_T^\parallel}-B_\parallel\sim\frac{1}{\Gamma_\psi\chi}\left[\frac{\partial\chi}{\partial r}\right]^2\frac{1}{\xi_\parallel^3\xi_\perp^2}\,, \end{aligned} \qquad (4)$$

where r is the reduced temperature $(T-T_c)/T_c$. Here the correlation lengths $\xi_\perp\sim(C_\perp\chi)^{1/(2-\eta)}$ and $\xi_\parallel\sim(C_\parallel\chi)^{1/(2-\eta)}$ have the same temperature dependence and we define a bulk correlation length $\xi\sim\chi^{1/(2-\eta)}$. Note that this is not a valid assumption for the nematic–Sm-A transitions of compounds that display an anisotropic divergence in ξ ($\xi_\perp\sim|r|^{-\nu_\perp}$ and $\xi_\parallel\sim|r|^{-\nu_\parallel}$). We assume it is good for the two transitions considered here, although more measurements on aligned samples are needed to verify it (beyond the success of the fits obtained using this assumption in the present paper). To obtain an expression for the ratio of the two measured quantities, C_p/D_T where $D_T=\frac{1}{3}(D_T^\parallel+2D_T^\perp)$, we need only note that the thermal transport anisotropy is governed by the molecular shape anisotropy and the molecular orientation.[3] Hence the anisotropy of the background will be the same as the anisotropy of the leading singular term, and the appropriate expression is $C_p/D_T=F_s^{-1}+B$ where

$$F_s^{-1}\sim\frac{1}{\Gamma_\psi\chi\xi^5}\left[\frac{\partial\chi}{\partial r}\right]^2 .$$

The background B contains all contributions from higher-order modes and Γ_ψ is a nonsingular function of temperature.[4]

Our previously published data for the thermal diffusivity of a bulk, unaligned sample of N-(4-n-heptyloxybenzylidene)-4′-n-butylaniline (70.4) near its Sm-A–Sm-C transition[2] should fit the expression for F_s derived above, with the appropriate theoretical expressions for χ and ξ. From the extended mean-field theory of the Sm-A–Sm-C transition proposed by Huang and Viner,[9] one obtains an expression for the susceptibility χ in terms of the two parameters t_0 and T_c.[10] These two parameters are determined independently from a fit of the heat capacity data and are hence fixed.[2] For a mean-field transition, $\xi\sim\chi^{1/2}$, and we may fit the value of F_s determined from the data, $(C_p/D_T-B)^{-1}$, to the calculated value. The fitting results are shown in Fig. 1. The only free parameters are an overall factor A and a constant background $B^\pm$ with a step at T_c. It is not possible to fit the data without a step in B such that the background diffusivity is roughly 15% larger just below T_c. The ori-

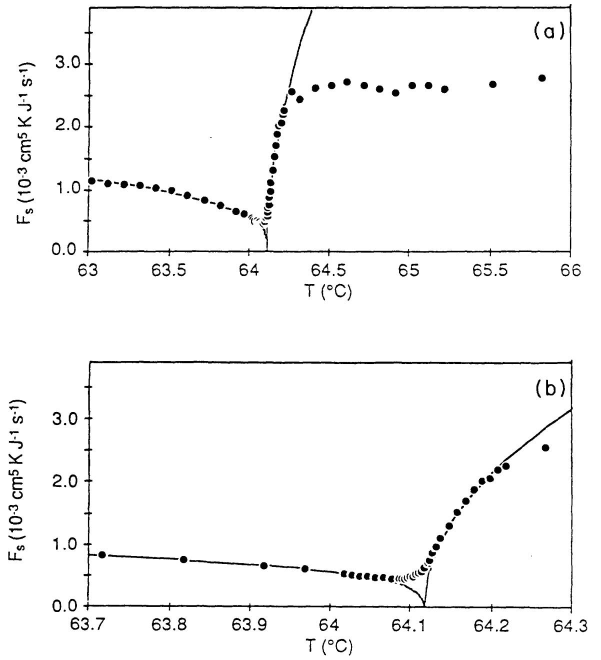

FIG. 1. (a) Experimental value of $F_s(T)$ for the 70.4 compound (dots) plotted with the theoretical value of $F_s(T)$ (line). (b) Experimental and theoretical values of $F_s(T)$ close to T_c.

gin of this step is not yet clear, although a few possible explanations exist.[11] The small peak near T_c in the measured value of D_T that was reported by our group in Ref. 2 is due to the coupling of the thermal diffusivity to the heat capacity via the nonzero (rounded) value of F_s at T_c (experimentally) and the finite background B at T_c. The saturation of D_T at around 4.6×10^{-4} cm^2/s on the high-temperature side of the transition is reflected by the flattening of F_s at about 64.2 °C, and is not presently understood, although it would be explained by a saturation of the tilt relaxation time at some finite value in the Sm-A phase. Overall, the data can only be fit for about 1.5 decades (4 mK$\rightarrow$150 mK) above T_c and for slightly more than 1.5 decades (20 mK$\rightarrow$1.1 K) below the transition, due to the transition to crystal-G phase occurring roughly 3° below T_c. Hence it would be useful to take data near the Sm-A–Sm-C transition of another compound with a much larger Sm-C range. The reason we chose 70.4 is that this compound shows the sharpest Sm-A–Sm-C transition[2,12] among all the reported Sm-A–Sm-C (or –Sm-C^*) transitions.

In contrast to the mean-field behavior of the Sm-A–Sm-C transition, the static properties of the Sm-A–hexatic-B transition are well described by power laws in the reduced temperature. For the compound n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate (65OBC), detailed heat capacity studies on unaligned samples by our group suggest that the anomalous part of C_p diverges with an exponent $\alpha=0.60\pm0.03$,[1] and birefringence measurements by Ho and Rosenblatt suggest that the critical exponent $\beta=0.19\pm0.03$.[13] The thermal diffusivity data previously published by our group for a bulk, unaligned sample of 65OBC near its Sm-A–hexatic-B transition[1] should fit the derived expression for D_T, provided that the critical dynamics for 65OBC near its Sm-A–hexatic-B critical point is described by the conventional theory (i.e., Γ_ψ independent of ξ). Taking $\chi\sim|r|^{-\gamma}$ and $\xi\sim|r|^{-\nu}$, it follows from the theoretical expression for F_s that $F_s^{-1}\sim|r|^{-\alpha+\nu\eta}$. Since F_s^{-1} describes the singular behavior of the ratio C_p/D_T, the singular part of the thermal diffusivity is predicted to be proportional to $|r|^{-\nu\eta}$. This result also follows directly from an extended

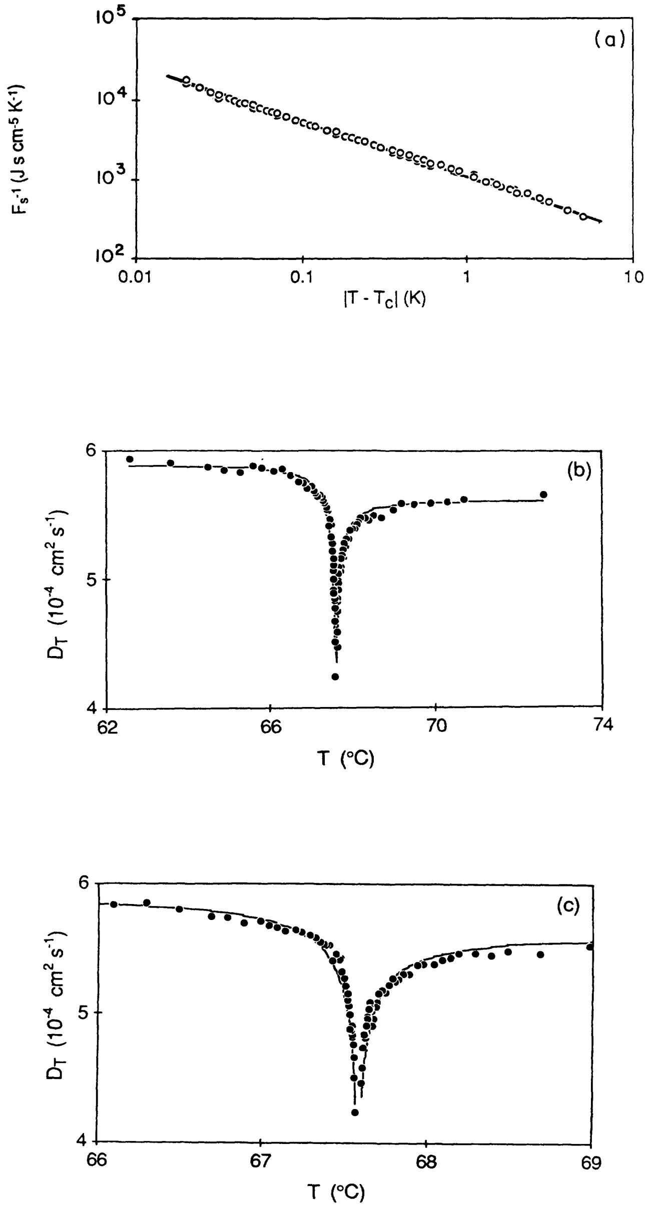

FIG. 2. (a) Log-log plot of F_s^{-1} vs $|T-T_c|$ for the 65OBC compound. Open dots are experimental values and the line is the calculated value. Measured (dots) and calculated (line) thermal diffusivity for 65OBC (b) over the whole temperature range and (c) close to T_c.

dynamic scaling assumption, since $\omega_q \sim D_T k^2$ scaling like $k^z\Omega(k\xi)$ implies $D_T \sim \xi^\eta$ (the dynamic exponent z is equal to $2-\eta$ for a nonconserved order parameter described by a conventional dynamic theory).[4] Since in general the model predicts $D_T \sim \Gamma_\psi \xi^\eta$, we can obtain an expression for the leading singular behavior of D_T for any dynamic critical exponent z. From dynamic scaling we must have (for a nonconserved order parameter) $\Gamma_\psi \sim \xi^{2-\eta-z}$, where z is now unspecified. We then get the general result $D_T \sim \xi^{2-z}$ which is what one gets directly from extended dynamic scaling for any z. Hence the idea presented here is just a more detailed statement of the extended dynamic scaling hypothesis. From static scaling one finds that $\nu\eta = \alpha/3 + 2\beta - \frac{2}{3}$, and from the measured values of α and β, D_T is predicted to slow down at T_c with an exponent $b = 0.09 \pm 0.05$. This is in very good agreement with the value reported by our group in Ref. 1. Figure 2(a) shows a fit of the experimental value of $F_s^{-1} = C_p/D_T - B$ to the calculated value of F_s^{-1}, which diverges with an exponent $-\alpha + \nu\eta = -0.69 \pm 0.05$. The fit is for over two decades (20 mK→5 K) both above and below T_c. Since the exponent is fixed, the only free parameters are $A^\pm$ [the amplitude for $T > T_c$ (+) and $T < T_c$ (−)], and a constant background $B^\pm$ with a step at T_c. Again, the best fit requires a step in B such that the contribution of the background to D_T is about 10% higher in the low-temperature phase. From the fitted values of $A^\pm$ it follows that the amplitude ratio for the static susceptibility for 65OBC is $\chi_0^+/\chi_0^- \approx 1$. Figures 2(b) and 2(c) show both the measured total thermal diffusivity and the calculated value, $D_T = C_p(F_s^{-1} + B)^{-1}$.

Although the static behaviors of the Sm-A–Sm-C and the Sm-A–hexatic-B transitions are strikingly different, the thermal diffusivity of both compounds reported here can be described by a conventional dynamic theory. It should be pointed out that for a dynamic model analogous to superfluid ^{4}He with $z = d/2 + \alpha/2\nu$ one has $D_T \sim \xi^{1/2-\alpha/2\nu}$, which, for the 65OBC critical exponents specified above, gives behavior quite close to that reported here for $z = 2-\eta$ (see footnote 21 in Ref. 1). This must be coincidental, since the value of z for ^{4}He comes directly from the existence of a propagating critical mode below T_c, and there is no analogy to second sound in the hexatic phase. The conventional dynamic theory, which we assume to be correct for both the transitions considered here, is believed to hold for a relaxational model near a tricritical point, where $z \to 2$ ($\eta \to 0$). The Sm-A–Sm-C transition is known to be very close to a mean-field tricritical point, and there has been speculation that the Sm-A–hexatic-B transition of 65OBC is also near a tricritical point, although the detailed nature of this transition is not clear. The model presented here fits both transitions down to $|T - T_c| \sim 10$ mK, which is near the limit of our resolution using this technique. For 65OBC, experimental error in the exponents specified from other measurements limits any singularity in Γ_ψ to have an exponent with absolute value less than 0.05. Although the temperature dependence of D_T through the mean-field Sm-A–Sm-C transition of 70.4 is not predicted by an extended dynamic scaling assumption,[2] such an argument does seem to work for the Sm-A–hexatic-B transition of 65OBC. This is because the hyperscaling does not hold for mean field systems. One can use the idea presented here to calculate contributions to D_T from modes whose leading term in the free energy is of the form $\frac{1}{2}K_i|\partial_i\phi|^2$, provided the temperature dependence of the K_i are known. The way we have coupled the thermal diffusion mode to the softening order-parameter fluctuations via an effective (in that it gives the correct static behavior) Gaussian free energy may not work for higher-order hydrodynamic modes, however. We are currently pursuing this idea in analyzing thermal diffusivity data we have taken near the smectic-C to smectic-I transition of a liquid-crystal compound for which the temperature dependence of the elastic constants has been measured.[14]

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[1] G. Nounesis, C. C. Huang, and J. W. Goodby, Phys. Rev. Lett. **56**, 1712 (1986).

[2] E. K. Hobbie and C. C. Huang, Phys. Rev. A **36**, 5459 (1987).

[3] F. Rondelez, W. Urbach, and H. Hervet, Phys. Rev. Lett. **41**, 1058 (1978).

[4] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[5] C. C. Huang, J. M. Viner, and J. C. Novak, Rev. Sci. Instrum. **56**, 1390 (1985).

[6] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin/Cummings, New York, 1975), p. 85.

[7] For an aligned geometry, an expression for $F_s(\hat{n})$ in terms of $\xi_\perp$, $\xi_\parallel$, and $\hat{n}$ is easy to derive, and we are currently studying the anisotropic nature of D_T for the Sm-A and Sm-C phases of 70.4.

[8] For a probed volume of roughly 0.15 mm^3, on the order of 10^3 domains are within the region of measurement, making this a good approximation.

[9] C. C. Huang and J. M. Viner, Phys. Rev. A **25**, 3385 (1982).

[10] C. C. Huang and J. M. Viner, *Liquid Crystals and Ordered Fluids*, edited by A. Giffin and J. F. Johnson (Plenum, New York, 1984), Vol. 4, p. 643.

[11] It is possible that a sudden change in the thermal contact resistance between the glass and the liquid-crystal sample could account for the step in the background. The contribution to the total diffusivity from the surface diffusivity, which we have not subtracted, would be contained in the term B. Such a change could arise from a preferential orientation of the molecules on the surface; however, it is not clear why such a change would appear discontinuous. It is also possible that the step is the anomalous contribution of the hydro-

dynamic ϕ mode to the background B. For example, a sudden change at T_c in the kinetic coefficient Γ_ϕ associated with this mode would make a step in B. One final possibility is that the change in the background would go away if higher-order terms were taken into account. Such small "correction to scaling" terms are needed to fit C_p for 65OBC without a step in the background at T_c. These scenarios are purely speculative and all three may or may not be relevant.

[12] Recently, we have found that another compound has a continuous Sm-A–Sm-C transition with a very sharp heat capacity anomaly [H. Y. Liu, C. C. Huang, Ch. Bahr, and G. Heppke, Phys. Rev. Lett. **61**, 345 (1988)]. We plan to perform thermal conductivity studies on this compound.

[13] C. Rosenblatt and J. T. Ho, Phys. Rev. A **26**, 2293 (1982).

[14] S. Sprunt and J. D. Litster, Phys. Rev. Lett. **59**, 2682 (1987).