Temperature dependence of *XY*-like order parameters in thin free-standing smectic liquid-crystal films

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The in-plane projection of the director in smectic-*C* liquid crystals and the hexatic order parameter in hexatic smectic liquid crystals are both analogous to the magnetization in an *XY* ferromagnet. Recent experimental results and theoretical arguments suggest that two-dimensional *XY* ferromagnets have a universal finite-size-induced effective magnetization exponent $\beta \approx 0.23$ [S. T. Bramwell and P. C. W. Holdsworth, J. Phys. Condens. Matter **5**, L53 (1993)]. From these results, we predict that *XY*-like order parameters in thin free-standing smectic liquid-crystal films should behave as $\propto (T_C - T)^{\beta}$ in an intermediate temperature range below the relevant transition temperature T_C if they exhibit a Kosterlitz-Thouless transition of a single *XY*-like order parameter.

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There exist several smectic phases in nature in which the thin and elongated liquid-crystal molecules organize themselves into a stack of two-dimensional (2D) liquid layers [1,2]. Some of the smectic phases are actually solid phases while others are anisotropic liquids which display various types of molecular and/or nearest-neighbor bond orientational order [1]. In the liquid phases discussed below, the relevant type of order is characterized by a two-component order parameter which is analogous to the magnetization M of an *XY* ferromagnet [1].

In the smectic-*A* phase, the long axis of the molecules points on average along a common direction $\hat{\mathbf{n}}$, which is parallel to the normal of the layers, $\hat{\mathbf{z}}$. Upon cooling, smectic-*A* liquid crystals often undergo a transition to a smectic-*C* phase or to a smectic-B_H phase [1]. Both the smectic-*C* and the smectic-B_H phases are characterized by an *XY*-like magnetization order parameter. In the smectic-*C* phase, $\hat{\mathbf{n}}$ is tilted with respect to $\hat{\mathbf{z}}$, and $\hat{\mathbf{n}}_p$, the in-plane projection of $\hat{\mathbf{n}}$ onto the smectic layers, makes an angle ϕ with $\hat{\mathbf{x}}$, a fixed axis parallel to the smectic layers. One defines $\Phi = \exp\{i\phi\}$ as the *XY*-like order parameter for the smectic-*A* to smectic-*C* transition [1]. The hexatic smectic-B_H phase is characterized by order in the nearest-neighbor bond orientation, which is an order among local hexagonal lattice orientations. The hexatic order parameter for the smectic-*A* to smectic-B_H transition is $\Psi_6 = \exp(i6\theta_6)$, where θ_6 is the angle of one of the six nearest-neighbor bonds with respect to $\hat{\mathbf{x}}$ [1,3–5].

A free-standing smectic liquid-crystal film (FSSLCF) is obtained by spreading a smectic liquid-crystal material across a hole in a glass, steel, or copper sheet [1]. Depending upon the speed at which the liquid is spread, it is possible to vary the number of molecular layers between two and several hundred. The lack of substrate makes FSSLCF's particularly suitable for studying 2D phase transitions. Hence, one can investigate both the 2D and the three-dimensional (3D) behavior of these systems as well as their 2D-to-3D crossover. The thermal average of *XY*-like order parameters in FSSLCF's can in principle be determined from experiments. For example, $\langle \Phi \rangle$ could be extracted from optical polarization measurements [6] ($\langle\ \rangle$ indicates a Boltzmann average). $\langle \Psi_6 \rangle$ is the amplitude of the first harmonic of the Fourier-series expansion of the angular-dependent scattered intensity in electron- [7,8] and x-ray- [9] diffraction experiments. From symmetry and universality class arguments one expects thin FSSLCF's characterized by an *XY* order parameter to display a defect-unbinding "Kosterlitz-Thouless" (KT) transition [10–12], such as that which occurs in the 2D *XY* ferromagnet. Indeed, a study of the smectic-*A* to smectic-*C* transition in a thin (2D) FSSLCF suggests a behavior compatible with an underlying KT transition [13].

The magnetization M of a 2D *XY* ferromagnet is zero for a system of infinite size [14]. However, it has been understood for some time that the slow power-law decay of M with the system size makes the thermodynamic limit very difficult to reach in any real 2D *XY* system [15]. For example, in the liquid-crystal material 65OBC (n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate), a sizeable value of the $\langle \Phi_6 \rangle$ can be measured below the smectic-*A* to smectic-*B* transition [8]. Recently, two of us showed that M approximates to power-law behavior below the ordering temperature T_C, $M \sim (T_C - T)^{\beta}$, with $\beta = 3\pi^2/128 \approx 0.231$, a universal constant intimately related to the occurrence of a KT transition in the 2D *XY* model [16]. This result resolves a long-standing paradox in the field of layered magnetism where materials well described by a 2D *XY* magnet show a universal critical exponent $\beta \approx 0.23$ [17–20]. In this paper we exploit the analogy between the liquid-crystal and ferromagnetic *XY* systems to propose that order-parameter measurements can be used as a sensitive test for KT behavior in thin FSSLCF's.

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We define the magnetization M of a 2D XY system of N spins as

$$M(N,T)=\left\langle \left| \frac{1}{N}\sum_{i=1}^{N}\mathbf{S}_i \right| \right\rangle , \quad (1)$$

where $\mathbf{S}_i$ is a two-component classical spin vector of unit length at site i. At low temperatures M is given by the linear spin-wave expression

$$M(N,T)=\left[\frac{a}{L\sqrt{2}}\right]^{1/4\pi K} , \quad (2)$$

where L is the system size, a is the spacing for a square lattice, and $K=J/k_BT$, with J the coupling constant [21]. For purely harmonic interactions, Eq. (2) exactly describes the magnetization at all temperatures. The effect of bound vortex pairs is simply to renormalize K to an effective stiffness K_{eff}. Near T_{KT}, vortex pairs are thermally generated in ever-increasing numbers which rapidly reduce K_{eff} [10,11,22]. In the infinite system K_{eff} reaches the universal value $2/\pi$ at T_{KT} and then jumps discontinuously to zero [23]. In the finite system, the exclusion of length scales greater than L implies that the universal jump is rounded [16]. $K_{\text{eff}}(L)$ reaches the value $2/\pi$ at a higher temperature T^* ($T^*>T_{\text{KT}}$) and continues to decrease smoothly with temperature. In this regime the magnetization may be accurately calculated by substituting K for $K_{\text{eff}}(L)$ in (1). It is found that at T^* the magnetization scales universally both with system size, as $\sim L^{-1/8}$, and with temperature, as $\sim(T_C-T)^{\beta}$, where $\beta=3\pi^2/128\approx0.231$. Monte Carlo simulations of the 2D XY [16] and the Villain model [24] have been used to determine the system-size dependence of the temperature regime where the value $\beta\approx0.23$ can be measured. We define the effective transition temperature T_C as the point where the spin-spin correlation length ξ falls below the system size [11], causing the magnetization to approach zero. Figure 1 shows the result for the temperature dependence of the magnetization M for a Monte Carlo simulation of a 2D XY system of 10^4 spins. The data were averaged over five runs, each consisting of 10^5 Monte Carlo steps per particle per temperature. The first 20 000 steps at each temperature were used for equilibration. Power-law behavior is observed over an extensive range of temperature centered around T^*, as shown by the solid line $M=B(T_C-T)^{3\pi^2/128}$ in Fig. 1. The amplitude B is *not* a fitting parameter; rather, its value is determined precisely by equating this expression at $T=T^*$ with the scaling result $M(T^*)=(a/L\sqrt{2})^{1/8}$. The power-law regime is shown to be due to the approximate scaling behavior of thermally generated vortex pairs [24]. Even at low temperatures, where the vortex-pair density is negligibly small, the magnetization falls below that of the spin-wave result (dotted curve) because of the anharmonic nature of the cosine interaction. Unlike the XY model, the Villain model is harmonic by definition [22]. As a consequence, $M(N,T)$ can be fitted by the spin-wave result for $T\le T_{\text{cr}}$ and by $M(N,T)=B(T_C-T)^{3\pi^2/128}$ for $T\ge T_{\text{cr}}$, where T_{cr} is an extremely sharp crossover temperature. In this case, there is no intermediate region of anharmonic spin-wave behavior, as occurs in the XY model [24].

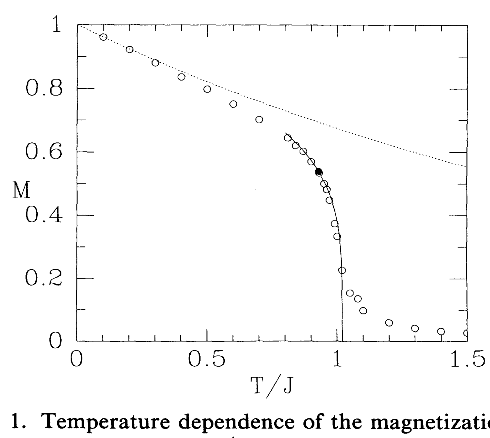

FIG. 1. Temperature dependence of the magnetization M in a 2D XY model of size $N=10^4$. The open circles are the Monte Carlo data and the solid circle is the theoretical value $M(T^*)=(a/L\sqrt{2})^{1/8}$. The solid curve is a fit to power-law behavior (see text) and the dashed curve is the spin-wave result of Eq. (2).

The value $\beta=0.23$ is well defined and easily observable in experiments and in simulations because the shift (T_C-T^*) is logarithmic as a function of L. This puts T^* well outside the temperature range affected by either the asymptotic 3D critical region in the case of layered magnets [17–19] or finite-size rounding in the case of numerical work [16,24] and thin-film experiments [25]. In the latter case our predictions have been quantitatively confirmed by recent experiments on purely 2D magnetic monolayers that exhibit clear signatures of a KT transition [25].

The universality of $\beta\approx0.23$ has been demonstrated in a statistical survey of over 30 quasi-2D magnetic systems, nearly all of which can be classified either as Ising-like with $\beta\approx\frac{1}{8}$ or XY-like with $\beta\approx0.23$ [20]. Results on many magnetic systems show that the nonobservation of $\beta\approx0.23$ is sufficient evidence to reject the hypothesis of a KT transition. We therefore propose that in experiments on FSSLCF systems showing a KT transition of a single XY-like order parameter, M should display a temperature dependence $M\sim(T_C-T)^{0.23}$ close to and below the transition temperature T_C.

Finally, we note that in magnetic systems, there is another possible 2D universality class, that of the three-state Potts model, with $\beta=\frac{1}{9}$. This third class is of interest, as renormalization-group calculations predict threefold symmetry to be a relevant perturbation to the 2D XY model [22]. Threefold anisotropy is unusual in magnetic materials, and three-state Potts behavior has not, to our knowledge, been observed. The three-state Potts model may, however, be relevant to FSSLCF's. Heat-capacity measurements on the smectic-A to smectic-B_H transition in the nmOBC homologous series [26,27] show a divergent peak with an exponent α consistent with the value $\alpha=\frac{1}{3}$ of the three-state Potts model, rather than the broad bump characteristic of the 2D XY system [21,28]. At first sight these data suggest an

XY-like system with a threefold perturbation. Such an observation poses a puzzle, as there is no imposed three-state symmetry in a FSSLCF, and the mechanism for hexatic ordering in these systems is rather mysterious [29]. It has been suggested that the coupling between local herringbone molecular packing and hexatic order may be at the origin of the three-state Potts-like value of α [26,27,29]. It would hence be of particular interest to compare the results for β obtained for the smectic-A to smectic-C transition, which is generally accepted to be a "good" realization of an XY transition, to those obtained for the smectic-A to smectic-B_H transition.

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