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# X-ray scattering in smectic-*A* liquid crystals

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The two-dimensional (2*D*) crystal and the 3*D* smectic-*A* liquid crystal are examples of Landau-Peierls systems, where long-wavelength fluctuations wash out long-range order of the order parameter. However, the decay of the order-parameter correlation functions is of the power-law type, rather than exponential. The result is that in x-ray scattering characteristic power-law singularities appear instead of the usual Bragg peaks. The details of these singularities, which have recently been observed experimentally in a smectic-*A* liquid crystal by Als-Nielsen *et al.*, are analyzed for the smectic-*A* case. A new *scaling* property of the structure factor is derived as a function of the momentum-transfer components parallel ($\kappa$) and perpendicular ($K_\perp$) to the smectic layers. Very close to the Bragg points, *finite-size effects* become important, including a new and unusual effect when $K_\perp$ is proportional to the inverse square root of the finite thickness of the specimen. The *crossover* in the Bragg peaks due to order-restoring effects of an *external magnetic field* is presented.

## I. INTRODUCTION: LARGE FLUCTUATIONS IN LOWER-DIMENSION LANDAU-PEIERLS SYSTEMS

As early as the thirties, Peierls[1] and Landau[2] argued that bodies whose density is periodic in one or two dimensions cannot exist. This is due to the important role of large long-wavelength fluctuations which, in a sense, wash out the assumed long-range periodicity. Similarly, Bloch had shown earlier[3] that ferromagnetism does not exist in two-dimensional (2D) Heisenberg systems. In modern terminology one knows quite generally[4] that strict long-range order does not exist at and below two dimensions for systems where the order parameter has a continuous symmetry. In the case of the 2D lattice or the smectic liquid crystal[5] (a liquid having a 1D density wave) the fluctuations are such that each atom performs a motion around its assumed equilibrium position whose extent is much larger (and is in fact weakly divergent in the thermodynamic limit) than the average periodicity length. However, these large motions are still performed around *well-defined equilibrium positions* and it turns out that *macroscopically large parts of the system move almost in unison*. Alternatively, it follows that *macroscopically large, finite systems* can show an effective long-range ordering.[6] Related to this is the fact that the displacement correlation functions decay *weakly enough* as functions of distance, so that the appropriate susceptibilities may diverge.[7] Those weakly decaying fluctuations result in anomalous singular scattering around the Bragg positions of the assumed lattice[8] as well as in dynamic effects, such as a Mössbauer spectrum[8(b),9] and sharp peaks in the inelastic neutron-scattering cross section.[9] These effects have been treated for the case of the 2D lattice[10] as well as quasi-1D and quasi-2D lattices[11] and experiments have been made for 2D overlayers.[12] The case of the smectic-*A* liquid crystal, which is analogous but not identical to the above because the 1D density wave involves macroscopic layers, deserves careful study. Caillé[13] has given some results for the static structure factor, and a beautiful experimental demonstration of the anomalous thermal diffuse structure has been recently given.[14]

It is the purpose of this paper, after a short review of the 2D lattice, to present a theory of the static structure factor near the Bragg points of the smectic-*A* liquid crystal. Caillé's results for the static structure factor $S(\vec{K})$ will be augmented: Finite-size effects will be taken into account. The effect of an external magnetic field will be discussed. And finally, though a closed form for $S(\vec{K})$ will not be given, $S(\vec{K})$ will be shown to exhibit certain scaling properties. We do not discuss dynamic effects, which should also exist.

## II. SUMMARY OF THE RESULTS FOR THE TWO-DIMENSIONAL LATTICE

The 2D harmonic lattice[7(c),8-10] is the simplest Landau-Peierls 2D system which, although not having strict long-range ordering due to large fluctuations, displays a slow decay of the appropriate correlation functions. This slow decay results in many observable properties which differ only slightly from those of strictly ordered systems. These slight differences are well defined and uniquely characterize the quasi-long-range order of such 2D systems. One of these important observable quantities is the static (e.g., x-ray) structure factor, which does not have strict Bragg peaks for an infinite 2D lattice. However, it turns out that strong thermal diffuse scattering exists near the Bragg positions with a characteristic singular structure. High resolution experiments are required to distinguish between these singular structures and the usual Bragg scattering. In addition, true Bragg peaks also appear, on top of the above singularities, for realistic *finite-size* systems. It can also be shown[7(c),8,10] that the harmonic approximation in 2D is useful for real systems in spite of the large fluctuations. This result, which seemed surprising at first, follows from the fact that the large fluctuations occur over long distances, while the short-range fluctuations, which determine the validity of the harmonic approximation, are not anomalously large in 2D. Here we briefly review the results for the structure factor of the 2D lattice. (Analogous, but more complicated results follow for the smectic liquid crystal, which will be considered in Secs. III and IV.)

The static structure factor $S(\vec{K})$ is given in the harmonic approximation by

$$S(\vec{K}) = \sum_{n,m} \exp\left\{[i\vec{K}\cdot(\vec{R}_n - \vec{R}_m)] - \tfrac{1}{2}\langle[\vec{K}\cdot(\vec{u}_n - \vec{u}_m)]^2\rangle\right\}, \qquad (2.1)$$

where $\vec{u}_n$ signifies the displacement of the $n$th atom from its equilibrium position $\vec{R}_n$. The displacement-displacement correlation function is given by

$$h_n \equiv \tfrac{1}{2}\langle[\vec{K}\cdot(\vec{u}_n - \vec{u}_0)]^2\rangle \xrightarrow[r\to\infty]{} \text{constant} + \ln r^{-2T/T_K}, \qquad (2.2)$$

where $r \equiv |\vec{R}_n - \vec{R}_0|/a$, and $a$ is the lattice spacing. In the Debye approximation,

$$k_B T_K = 4\pi m c^2/a^2K^2, \qquad (2.3)$$

$c$ being the sound velocity and $m$ the mass of an atom. Since $h_n$ does not tend to a finite limit as $|\vec{R}_n - \vec{R}_0| \to \infty$ for an infinite system, no "true" Bragg scattering exists. However, due to the weak power-law decay in (2.1) obtained by using (2.2), $S(\vec{K})$ behaves singularly around the Bragg positions $\vec{K} = \vec{G}$. For $T < T_G$, defining $\vec{\kappa} \equiv \vec{K} - \vec{G}$, with $|\vec{\kappa}| \ll a^{-1}$,

$$S(\vec{\kappa}) \propto 1/\kappa^{2(1-T/T_G)}. \qquad (2.4)$$

Relevant expressions can be found in Ref. 10. Some representative curves are given in Fig. 1. [This figure corrects Fig. 4(a) of Ref. 11.] Notice that $T_G$ decreases with $G$ as $1/G^2$. Therefore, the anomalous scattering around higher-order Bragg points becomes observable at lower temperatures.

The picture which emerges is that the lattice, in principle, exhibits Bragg peaks with singularities of all orders at absolute zero. As the temperature is raised, the singularities disappear, one by one, in order of decreasing reciprocal-lattice vector. The last one corresponds to a reciprocal-lattice vector $|\vec{G}| = 2\pi/a$ and disappears at a temperature $T_{max}$ of order $mc^2$, corresponding to a temperature of a few thousand degrees Kelvin in a typical case.

Two important processes modify the above picture: First, and most obviously, anharmonic effects will become important well below $T_{max}$.[10] Second, Kosterlitz and Thouless[7(a)] have pointed out that dislocations play a special role in the melting of 2D lattices: Below and not too close to the melting point, the above picture is adequate. Dislocations tend to pair off and produce only qualitative modifications in the correlation functions. However, as we approach the melting point, the dislocations tend to dissociate and the weak power-law behavior is modified: Above the melting point it decays exponentially.[15] Recently, Halperin and Nelson[15] studied the melting of the 2D crystal mediated by the dissociation of paired dislocations. Melting was found to occur in two stages, with an intermediate phase having only orientational order. They also found that the dislocation pairs affect a renormalization of the elastic constants,

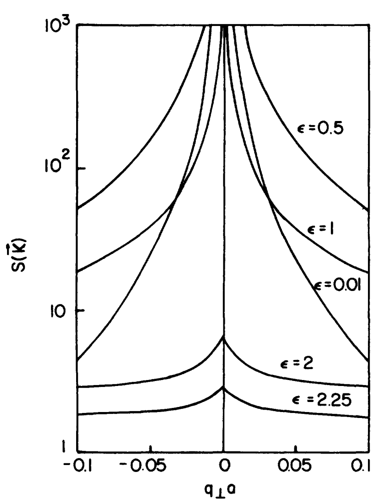


FIG. 1. $S(K)$ near the Bragg position of the 2D harmonic lattice. [This figure replaces the erroneous Fig. 4(a) of Ref. 11.]

and hence of $T_G$, without changing the basic power-law structure.

Equation (2.4) is valid for the infinite lattice. For a finite lattice with a characteristic linear size $L \gg a$, (2.4) is valid only for $\kappa \gg L^{-1}$. On the other hand, the correlation function (2.2) is finite for $|\vec{R}_n - \vec{R}_0| \sim L$, and therefore, a Bragg peak, with a typical width of $O(L^{-1})$ exists. This can also be looked at[6(a),8,10] as a manifestation of the finiteness of the Debye-Waller factor due to the $1/L$ lower cutoff on $\vec{k}$-space integrations which limits the logarithmic infrared divergences.

It is worthwhile to note that in Ref. 8(b) it was believed that the simple power-law behavior of Eq. (2.4) broke down for temperatures $T < T_G/4$. This result stemmed from the divergence of the integral corresponding to Eq. (2.1) in this temperature regime [Eq. (B5) of Ref. 8(b)]. The oscillatory behavior of $S(\vec{K})$ which we obtained in this regime [Eq. (B8)] is indicative of the need to insert a factor $\exp(-\epsilon R_n)$ into the integral. We may then let the range of $R_n$ extend to infinity and *afterwards* let $\epsilon \to 0$. When this is done, the power-law behavior is found to hold all the way down to absolute zero.[11,16] Physically, this factor may represent the presence of perturbations (e.g., for some types of coupling of the 2D lattice with a substrate) which weaken the $\ln R_n$ behavior so little as not to affect the power-law behavior of $S(\vec{K})$, but are large enough so that $\exp(-\epsilon L) \ll 1$. In our treatment of the liquid crystal, a similar divergence occurs in the integral expression of $S(\vec{K})$. In addition, we will see that finite-size effects can occur for values of transverse momentum transfer $K_\perp \gg L^{-1}$.

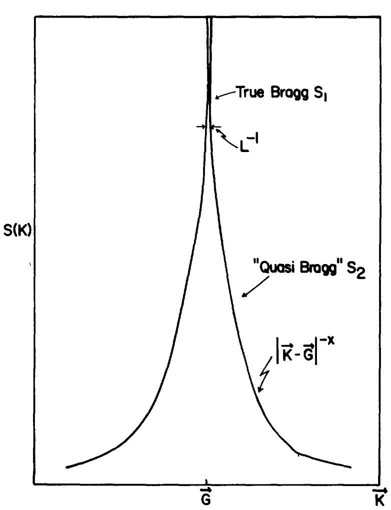


FIG. 2. The true Bragg part $S_1$ of $S(K)$ and the thermal diffuse quasi-Bragg part $S_2$ (schematic).

In sum, a very high resolution experiment should display the structure schematized in Fig. 2, with the characteristic singular "thermal diffuse" part $S_2(K)$ and the "true Bragg" part $S_1(K)$. The intensity of the former is $O[(T/T_G)(\kappa a)^{-2(1-T/T_G)}]$ for $T \ll T_G$, while that of the latter is on the order of $N^{(1-T/T_G)}$ and thus becomes dominant at very low temperatures. Note that the above picture does not take into account finite experimental resolution. It can also be observed with $k$-space resolutions that are much better than $1/L$. For example, to observe $S_2$ distinctly from $S_1$ for $T \ll T_G$, one would need a resolution $\Delta K$ satisfying $(\Delta K a)^2 \ll 1$, which means that $\Delta K$ has only to be very small on the scale of $1/a$.

## III. SCALING PROPERTIES OF THE STRUCTURE FACTOR OF THE INFINITE SMECTIC-$A$ LIQUID CRYSTAL

A smectic-$A$-type liquid crystal is presumably characterized by an array of layers of elongated molecules one molecule thick. The axes of the molecules are perpendicular to the layers. We will denote the spacing between the layers by $d$. We will further align these layers parallel to the $xy$ plane, denoting positions in the plane by the coordinate $\vec{\rho} \equiv (x, y)$. The significant fluctuations are in the $\hat{z}$ direction and are characterized by the displacement function $u_n(\vec{\rho})$ for the $n$th layer. We will let $a^2$ be the mean area per molecule within a given layer.

The x-ray scattering intensity for momentum transfer $\vec{K}$ is proportional to the structure factor

$$S(\vec{K}) = \sum_n \int \frac{d^2\rho}{a^2} \exp(iK_z nd + i\vec{K}_\perp \cdot \vec{\rho}) \times \langle \exp\{iK_z[u_n(\vec{\rho}) - u_0(0)]\}\rangle, \quad (3.1)$$

where we decomposed $\vec{K}$ into its parallel ($K_z$) and perpendicular ($K_\perp$) components relative to the direction of the layer displacements. The bracketed term represents a thermal average which we denote by $G_n(\vec{\rho})$.

Since the most significant details of $S(\vec{K})$ depend upon long-wavelength fluctuations, we can well replace the sum $\sum_n$ over the layers by an integral $d^{-1}\int dz$. $G_n(\vec{\rho})$ is then expressed as a function $G(\vec{r} \equiv (\vec{\rho}, z))$. The $K_z$ in $\exp(iK_z nd)$ must be expressed modulo a reciprocal-lattice vector.

In the harmonic approximation,

$$G(\vec{\rho}, z) = \exp[-\tfrac{1}{2}K_z^2\langle|u_n(\vec{\rho}) - u_0(0)|^2\rangle], \quad (3.2)$$

where in the Debye approximation,

$$\langle |u_n(\vec{\rho}) - u_0(0)|^2\rangle = \frac{1}{\pi^2}\int_{-\pi/d}^{\pi/d} dq_z \int_0^{1/a} dq_\perp q_\perp \int_0^{2\pi} d\theta_q (1 - e^{i\vec{q}\cdot\vec{r}})\langle |U_{\vec{q}}|^2\rangle , \tag{3.3}$$

and, in turn,

$$\langle |U_{\vec{q}}|^2\rangle = \frac{k_B T}{\bar{B} q_z^2 + K_1 q_\perp^4} . \tag{3.4}$$

The parameter $\bar{B}$ is the interlayer "spring constant" and vanishes at the smectic-nematic phase transition temperature $T_{AN}$. $K_1$ is the Frank constant. The interlayer distance $d$ is typically ~20 Å, while $a$ is on the order of the intermolecular distance and is typically ~5 Å. The characteristic length $\lambda \equiv (K_1/\bar{B})^{1/2}$ is typically $\sim d$, but diverges at $T_{AN}$.

For $z \gg d$, we find

$$\langle |u_n(\rho) - u_0(0)|^2\rangle \cong \frac{k_B T\lambda}{4\pi k_1}\left[\ln\left(\frac{\gamma\rho}{2a}\right)^2 + E_1\left(\frac{\rho^2}{4\lambda z}\right) - f\left(\frac{\lambda d}{\pi a^2}\right)\right], \tag{3.5}$$

where $\ln\gamma = 0.577\cdots$ is Euler's constant, $E_1(x)$ is the exponential integral function

$$E_1(x) = \int_x^\infty dt \frac{e^{-t}}{t},$$

and the function $f(\lambda d/\pi a^2)$ is given by

$$f(x) = \frac{2}{\pi}\int_0^x dy \frac{\tan^{-1} y}{y}. \tag{3.6}$$

It is in this function where our result differs essentially from that of Caillé. Typically, $\lambda d/\pi a^2 = O(1)$ and so is $f(\lambda d/\pi a^2)$. However, as $T \to T_{AN}$, $\lambda \to \infty$, and $f$ diverges logarithmically:

$$f(\lambda d/\pi a^2) \to \ln(\lambda d/\pi a^2) . \tag{3.7}$$

We obtain for the correlation function

$$G(\vec{r}) = \left(\frac{2a}{\rho}\right)^{2x} \exp(-2M) \exp\left[-xE_1\left(\frac{\rho^2}{4\lambda z}\right)\right], \tag{3.8}$$

where

$$x \equiv x(T) = \frac{k_z^2 \lambda k_B T}{8\pi K_1} \tag{3.9}$$

and

$$2M = x(T)[2\ln\gamma - f(\lambda d/\pi a^2)] . \tag{3.10}$$

The asymptotic behavior of $G(\vec{r})$ is given by

$$G(\vec{r}) \propto \begin{cases} (a^2/\lambda z)^x , & \rho \ll (\lambda z)^{1/2} \\ (2a/\rho)^{2x} , & \rho \gg (\lambda z)^{1/2} . \end{cases} \tag{3.11}$$

As Caillé[13] has shown, this asymptotic behavior of $G(\vec{r})$ results in singularities of $S(\vec{K})$ about $K_z = 2\pi m/d \equiv K_m$, where $m$ is an integer. With $\kappa \equiv |K_z - K_m|$, we have

$$S(\vec{K}) \propto \frac{1}{\kappa^{2-x}} \text{ when } K_\perp = 0 , \tag{3.12a}$$

in agreement with Caille[13]; and

$$S(\vec{K}) \propto \frac{1}{K_\perp^{4-2x}} \text{ when } \kappa = 0 , \tag{3.12b}$$

a result[5(a)] which disagrees with Caillé.[13] (However, see the discussion of Sec. IV.) When $\kappa \ll a^{-1}$, we may evaluate $x(T)$ with $K_z = K_m$.

The *scaling property* of $S(\vec{K})$ results from the peculiar scaling property of $G(\vec{r})$. Let us introduce the new variables of integration

$$z' \equiv \kappa z \text{ and } w \equiv \rho^2/4\lambda z$$

into the integral expression of $S(\vec{K})$ in terms of $G(\vec{r})$. We obtain

$$S(\vec{K}) = (da^2)^{-1} e^{-2M} \int d\vec{r} \left(\frac{2a}{\rho}\right)^{2x} \exp[i\kappa z + i\vec{K}_\perp \cdot \vec{\rho} - E_1(\rho^2/4\lambda z)]$$
$$= \frac{(\pi a/d)(4\lambda/a)^{1-x} e^{-2M}}{(\kappa a)^{2-x}} \int_{-\infty}^{\infty} dz' e^{iz'} z'^{(1-x)} \int_0^\infty dw\, w^{-x} J_0\left(2K_\perp\left(\frac{\lambda w z'}{\kappa}\right)^{1/2}\right) e^{-xE_1(w)} . \tag{3.13}$$

The integral over $w$ is a function only of the variable $\lambda K_\perp^2 z'/\kappa$. Therefore, the integral over $z'$ is a function only of the variable $(\lambda K_\perp^2/\kappa)$. We can thus write

$$S(\vec{K}) = \frac{(4\lambda/a)^{1-x}}{(\kappa a)^{2-x}} e^{-2M} F\left(\frac{\lambda K_\perp^2}{\kappa}\right). \tag{3.14}$$

Thus $\kappa^{2-x} S(\vec{K})$ is a function of the single variable $(\lambda K_\perp^2/\kappa)$. As $y \to 0$, $F(y) \to$ constant; as $y \to \infty$, $F(y) \to (\text{constant}) y^{x-2}$. This behavior of $F(y)$ accounts for the singular behavior of Eqs. (3.12). Note, finally, that Eqs. (3.12a) and (3.12b) are also valid in the cases $\lambda K_\perp^2 \ll \kappa$ and $\lambda K_\perp^2 \gg \kappa$, respectively.

## IV. FINITE-SIZE EFFECTS IN THE STRUCTURE FACTOR OF SMECTIC-A LIQUID CRYSTAL

In Sec. III we discussed $G(\rho, z)$ for an infinite system. Likewise, we discussed $S(\vec{K})$ for the case that the x-ray beam samples the entire infinite system. In practice, experiments are made on *finite* samples and the x-ray beam may sample the *whole* system or a *subvolume* thereof. The general case is relatively complicated to analyze. We will consider in this section, the case when the subvolume sampled is much smaller than the size of the entire system. In this case, we can use $G(\rho, z)$ for an infinite system, but restrict our integral for $S(\vec{K})$ in Eq. (3.1) to that subvolume.

It is to be expected that to sense the finiteness of the subvolume, one needs $\kappa^{-1}>$ (subvolume dimension) when $K_\perp=0$, and $K_\perp^{-1}>$ (subvolume dimension) when $\kappa=0$. As we will see in this section, an *unusual finite-size effect* appears when $(K_\perp^2\lambda)^{-1}>$ (subvolume dimension). It is reasonable to expect that the results we present will be qualitatively valid for the case of a beam sampling an entire finite sample having the dimensions of the subvolume. The qualitative reason for this expectation is that the correlation functions for the finite system should not be very sensitive to the small wave vectors (wavelengths much greater than the size of the finite system) that exist only in the infinite system.

While we are not able to obtain exact results for a finite sample, we can obtain the leading terms when $\kappa \ll d^{-1}$ and $K_\perp \ll a^{-1}$. We may, therefore, replace our sum over $n$ by an integral. We will consider a subvolume whose dimensions are $L$ along the optical axis and $L' \times L'$ along the two other directions. Then,

$$S(\vec{K}) = (da^2)^{-1}e^{-2M} \times \int_{-L}^{L} dz \int^{L} d^2\rho \exp(i\kappa z + i\vec{K}_\perp \cdot \vec{\rho})G(\rho, z), \quad (4.1)$$

with $G(\rho, z)$ defined by Eq. (3.2). For our purposes, it is sufficient to replace $G(\rho, z)$ by

$$G(\rho, z) \to \begin{cases} (2a/\rho)^{2x}, & \rho \geq (4\lambda z)^{1/2} \\ (a^2/\lambda z)^x, & \rho \leq (4\lambda z)^{1/2}. \end{cases} \quad (4.2)$$

The integration over $\rho$ is then carried out in two corresponding parts, followed by the integration over $z$. Our results are summarized below.

(a) $K_\perp=0$, $\kappa \neq 0$. We have

$$S(\kappa, 0) \sim \frac{A\lambda^{1-x}}{\kappa^{2-x}} + \begin{cases} \delta(\kappa)L'^{(2-2x)}, & x<1 \\ \delta(\kappa)(\lambda L)^{1-x}, & x>1. \end{cases} \quad (4.3)$$

The first term is the anomalous thermal diffuse part [cf. Eq. (3.12)] characteristic of the quasi-long-range order of the system. The expression is valid only when $\kappa \gg L^{-1}$. When $\kappa \to L^{-1}$, the first term "saturates" at $A\lambda^{1-x}L^{2-x}$, where $A$ is a numerical constant of order unity.

In the second term $\delta(\kappa)$ represents a peak of height $L$ and a width $L^{-1}$. This is a "true," albeit weakened, Bragg peak.

The word "weakened" refers to the fact that a conventional Bragg peak for a 3D crystal behaves as $L'^2\delta(\kappa)$. While the exponent of $L'$ is reduced in this case [as well as in the case of the 2D crystal, cf. Refs. 8(a) and 8(b)], this Bragg peak is observable at very low temperatures, when $x \ll 1$.

$S(\kappa, K_\perp=0)$ looks schematically like the sketch in Fig. 1. We see that for $x<1$, $S(\kappa, 0)$ is dominated by a "true" Bragg peak of width $L^{-1}$ and maximum value $LL'^{(2-2x)}$, with a relatively weak thermal diffuse part whose maximum value is $L^{(2-x)}$. When $x \ll 1$, this result can be compared with the ordinary separation of a Bragg peak in a *three-dimensional* crystal into a sharp part of height $L^3$ and width $L^{-1}$ and a thermal diffuse part of height $L^2$. However, as we will point out later in this paper, under typical experimental conditions, finite resolution results in the diffuse part of the peak dominating over the "true" Bragg peak.

While the true Bragg peak appears to be larger than the thermal diffuse part (due to the $L'^{2(1-x)}$ factor), it turns out that this results from our setting $K_\perp=0$. *For finite $K_\perp$, the relative strength of the two parts is changed radically.*

(b) $\kappa=0$, $K_\perp \gg L'^{-1}$. This case is more complicated than case (a). Results depend upon whether $K_\perp$ is larger or smaller than $(\lambda L)^{-1/2}$. We find for the leading terms

$$S(0, K_\perp) \propto \begin{cases} \dfrac{1}{\lambda K_\perp^{(4-2x)}} \quad \text{for } K_\perp \gg (\lambda L)^{-1/2} & (4.4a) \\ \left.\begin{matrix} L/K_\perp^{2-2x}, & x<1 \\ \lambda^{1-x}L^{2-x}, & x>1 \end{matrix}\right\} \text{for } K_\perp \ll (\lambda L)^{-1/2}. & (4.4b) \end{cases}$$

When $K_\perp \lesssim L'^{-1}$, $K_\perp$ must be replaced by $L'^{-1}$ in Eq. (4.4b) so that $S(0, K_\perp) \propto LL'^{2-2x}$ for $x<1$ when $K_\perp \lesssim L'^{-1} \ll (\lambda L)^{-1/2}$. Note, further, the sharp drop when $x$ increases through unity.

The result for $K_\perp \gg (\lambda L)^{-1/2}$ corresponds to the infinite sample result of Sec. III. Caillé's[13] paper has $S(0, K_\perp) \propto K_\perp^{2x-2}$, but without the factor $L$. de Gennes[5(a)] corrected this result with $S(0, K_\perp) \propto K_\perp^{2x-4}$.

The correct state of affairs is, however, that both results, $LK_\perp^{2x-2}$ and $K_\perp^{2x-4}$, apply in their respective ranges of validity—$K_\perp \ll (\lambda L)^{-1/2}$ and $x<1$ on the one hand, and $K_\perp \gg (\lambda L)^{-1/2}$ on the other. This is an interesting finite-size effect, characteristic of a Landau-Peierls system which is, on the average, periodic in one direction; quasi-long-range order is achieved through the soft (via the $q_\perp^4$ term in the free energy) interaction in the 2D lateral dimensions. As far as the authors know, this sort of effect has not been obtained before. When both $\kappa$ and $K_\perp$ are nonzero, we must consider two regimes.

(c) $L'^{-1} \lesssim K_\perp \ll (\kappa/\lambda)^{1/2}$. $L'$ is replaced by $K_\perp^{-1}$ in the Bragg part:

$$S(\kappa, K_\perp) \sim \frac{A\lambda^{1-x}}{\kappa^{2-x}} + \begin{cases} \delta(\kappa)/K_\perp^{2-2x}, & x<1 \\ \delta(\kappa)(\lambda L)^{1-x}, & x>1. \end{cases} \quad (4.5)$$

(d) $L^{-1} \lesssim \kappa \ll \lambda K_\perp^2$. We have $K_\perp \gg (\lambda L)^{-1/2}$ and Eq. (4.4a) applies.

If $\kappa \ll L^{-1}$, $S(\kappa, K_\perp) \cong S(0, K_\perp)$ and either Eq. (4.4a) or (4.4b) holds in the appropriate regimes. The scaling relation (3.14) holds as long as $\kappa \gg L^{-1}$ and $K_\perp \gg L'^{-1}$. When either of these strong inequalities breaks down, the scaling relation does not hold and size effects are significant.

There is also a crossover at $x=1$ in the integrated peak intensities measured by experiments as a result of finite resolution. See Sec. VII for its relevance on the observability of higher-order peaks. Results when $K_\perp \gg L'^{-1}$ can be summarized as follows:

$$S(\vec{K}) \propto \begin{cases} \lambda^{1-x}/\kappa^{2-x} & \text{when } \kappa \gg (K_\perp^2\lambda, L^{-1}) \\ 1/K_\perp^{4-2x} & \text{when } K_\perp^2\lambda \gg (\kappa, L^{-1}) \\ \left.\begin{matrix} L^{2-x}/\lambda^{1-x}, & x>1 \\ L/K_\perp^{2-2x}, & x<1 \end{matrix}\right\} & \text{when } L^{-1} \gg (K_\perp^2\lambda, \kappa). \end{cases} \quad (4.6)$$

## V. VALIDITY OF THE "HARMONIC" APPROXIMATION

Exactly as in the case of the 2D lattice,[8,10] the condition for the validity of the harmonic approximation is *not* that each of the displacements $u_n$ be small, but that the *relative fluctuation* in the displacements of *neighboring layers* be small compared to the interlayer spacing $d$. Now

$$\frac{\langle |u_{n+1}(0) - u_n(0)|^2\rangle}{d^2} \cong \frac{k_B T}{\pi} \int d^3q \frac{q_z^2}{q_z^2 + \lambda^2 q_\perp^4} \sim x_{m=1}, \quad (5.1)$$

where $x_m$ is the value of the exponent $x$ for $K_z = K_m$. Therefore, the condition for the validity of the harmonic approximation is that

$$x_{m=1} \ll 1. \quad (5.2)$$

This is reminiscent of the analogous condition[10] for the 2D lattice. The result for $\langle |u_{n+1} - u_n|^2\rangle$ can be understood physically in terms of an effective harmonic spring between adjacent layers with a force constant $\lambda\bar{B}$. As $T \to T_{AN}$, $x_m$ diverges and the harmonic approximation must become invalid. However, as the temperature is lowered enough below the transition to the nematic phase, the harmonic approximation gains validity. In practice, of course, the material may, prior to that, make a phase transition to a more ordered phase than smectic-$A$. It is possible that, in analogy with the failure of the usual Gaussian approximation for critical phenomena, the scaling properties of $S(\vec{K})$ may still be valid, with changed exponents, even in the critical region.

## VI. THE EFFECT OF AN EXTERNAL MAGNETIC FIELD

The presence of an external magnetic field $H$ (sometimes used to align the director of the smectic-$A$ liquid crystal) introduces a "strong" coupling between the layers[5(a)]: In Eq. (3.4),

$$(\bar{B}q_z^2 + K_1 q_\perp^4) \to (\bar{B}q_z^2 + \chi_a H^2 q_\perp^2 + K_1 q_\perp^4).$$

The anistropy susceptibility $\chi_a$ is $O(10^{-7}\text{cgs})$.[5a] As noted by de Gennes,[5a] the extra term brings about full long-range order. We expect to have a true Bragg peak [of width $O(L^{-1})$ and of height $L^3$]. The Debye-Waller factor for these true Bragg peaks is given by

$$e^{-2W} = \exp[-K_m^2\langle u_n(\vec{\rho})^2\rangle], \quad (6.1)$$

which can be expressed as

$$e^{-2W} = (c\xi_1/d)^{-2x}. \quad (6.2)$$

Here, $\xi_1 \equiv (K_1/\chi_a H^2)^{1/2}$ is the magnetic coherence length[5(a)] of $O(1\ (\text{cm})/H\ (\text{gauss}))$ and $c$ is a dimensionless constant of order unity. Thus, the Debye-Waller factor vanishes as $H^{2x}$ as $H \to 0$. It also vanishes, as expected, when $T \to T_{AN}$ (since $x \to \infty$).

In practice, the effect of a small magnetic field is analogous to the effect of weak coupling between stacked 2D harmonic lattices, a system which was treated in some detail in Ref. 11. It is also analogous in some ways to the stabilization of the fluctuations of the surface of a liquid by gravity, with $K_1$ being the counterpart of the surface tension and $\chi_a H^2$ the counterpart of the weight density. It is to be expected that the $H=0$ results of the body of this paper hold for finite $\kappa$ and $K_\perp$ outside a small region about $K=0$ which vanishes as $H \to 0$. First, we have a true 3D Bragg peak at $K=0$. In the perpendicular direction of a liquid crystal, stabilization by the magnetic field occurs over distances greater than $\xi_1$. Thus, we expect

$$S(\kappa=0, K_\perp) \sim 1/\lambda K_\perp^{4-2x} \to \xi_1^{4-2x}/\lambda$$

when $K_\perp \ll \xi_1^{-1}$. In the direction of the optical axis, stabilization occurs over distances greater than $\xi_1^2/\lambda$. Therefore, we expect

$$S(\kappa, K_\perp=0) \sim \lambda^{1-x}/\kappa^{2-x} \to \xi_1^{4-2x}/\lambda$$

when $\kappa \ll \lambda/\xi_1^2$. In the former case, the width of the crossover region is proportional to $H$, while in the latter case, the width is proportional to $H^2$ and is much less accessible.[17]

## VII. DISCUSSION OF OUR RESULTS FOR SMECTIC-*A* LIQUID CRYSTALS

The principal results of this paper are the scaling form of the thermal diffuse scattering and the clarification of the behavior of $S(\vec{K})$ as a function of $\vec{K}$ [which differs according to whether $K_\perp \gg (\lambda L)^{-1/2}$ or $K_\perp \ll (\lambda L)^{-1/2}$]. Systematic experiments to check these predictions would be extremely desirable. The inverse-power-law dependence of $S(\kappa, K_\perp = 0)$ has been observed in recent experiments[14]—but only for the first-order ($m=1$) peak. Though the experiment was carried out very close to $T_{AN}$ [$(T_{AN}-T)/T_{AN} = O(10^{-3})$], independent light-scattering measurements provide values of $\bar{B}$ and $K_1$ which lead to a value $x = 0.12$. This value of $2-x$, close to two, is consistent with theoretical estimates.[14,5(a)] The factor $\exp(-2M)$ is, therefore, of order unity. It is also reasonable (cf. Sec. V) to expect the harmonic approximation to be adequate.

It is important to understand the absence of higher-order peaks in the experiments of Ref. 14: There was no evidence for a peak at either $m=2$ or 3 on a relative intensity scale of $10^{-4}$. For $m=2$, $x = 4(0.12) = 0.48$. The factor $\exp(-2M)$ is, therefore, still of order unity. In addition, there is no reason to expect that the molecular form factor is so sharply peaked as to make the higher-order peaks unobservable. While anharmonic effects are expected to be quite significant, we have no reason to expect the $m=2$ peak to be so completely washed out on that account.

It might have been thought that the nonappearance of higher-order peaks in the experiments of Ref. 14 was due to the smectic density wave's being purely sinusoidal. We would like to point out that there exist two factors, each of which should substantially reduce the intensity of the higher-order peaks.

First, it should be noted that even the absence of higher-order peaks in the scattering does not imply the absence of higher-order Fourier components in the density. (In fact, the theory presented in this paper predicts the disappearance of the $m$th-order peak when $x_m > 2$.) On the other hand, a major source of reduction of the intensity of the higher-order peaks is the small amplitude of the higher-order Fourier components of the density close to $T_{AN}$: A Landau free-energy functional of the density is expected to have cubic terms in the density. In the mean-field approximation, the $2\pi/d$ component of the density will be proportional to $(T_{AN}-T)^{1/2}$. The higher-order components are "induced" by the $2\pi/d$ component via the cubic and higher-order terms. As a result, it can easily be seen[18] that the $4\pi/d$ component of the density will be proportional to $(T_{AN}-T)$. In the temperature range $(T_{AN}-T)/T_{AN} \sim 10^{-3}$ of the Als-Nielsen *et al.* experiment,[14] the second-order component will have an amplitude of order $[(T_{AN}-T)/T_{AN}]^{1/2} \sim \frac{1}{30}$ times the amplitude of the first-order component. Since the scattering intensity is proportional to the square of the density, the ratio of the intensities of the corresponding $m=2$ and $m=1$ peaks will be $O[(T_{AN}-T)/T_{AN}] \sim 10^{-3}$ due to this factor alone.

A second important source of reduction of the intensity of the higher-order peaks, which might be relevant in the Als-Nielsen *et al.* experiment, follows from the results of Sec. IV. Suppose the experimental resolution in $\vec{K}$ is $\Delta$ with $\lambda\Delta \ll 1$, $L\Delta \gg 1$, and $\lambda L \Delta^2 \gg 1$. [This would hold true if $\lambda = 10$ Å, $L = 1$ cm, and $\Delta = 10^5$ cm$^{-1}$.] Then the experimentally observed peak value is an *integrated intensity* over $\vec{K}$. We find that the integrated *diffuse* part of the peak behaves as $\lambda L/a^2)^{1-x}/\Delta$ for $x<1$ and $(\lambda/a^2\Delta)^{1-x}/\Delta$ for $x>1$. This contribution to the integrated intensity dominates over the *Bragg* contribution, $[a^{2-2x}\Delta^3(\lambda L)^x]^{-1}$, for all $x$, for both $x<1$ and $x>1$. Furthermore, the integrated diffuse part drops sharply as $x$ increases. Taking $x_{m=1} = 0.12$ would make $x_{m=2} = 0.48$ and $x_{m=3} = 1.1$.[19] This effect would result in integrated intensities of the $m=2$ and 3 peaks smaller than that of the $m=1$ peak by factors of $10^2$ and $10^6$, respectively. Smaller reductions would be expected with different experimental resolutions.[20]

Improvements in experimental techniques which would allow for studies at lower temperatures (and hence smaller values of $x$) would be very useful. Theoretical work on anharmonic effects is clearly very much needed. One may speculate that the scaling form for $S(\vec{K})$ might still hold in the "critical region" where anharmonic effects are important, albeit with modified exponents. This speculation is based only on an analogy with other critical phenomena and the results of Ref. 15.

Any real experiment will have a finite resolving power which should be taken into account. An important example is the ratio between the Bragg-type and the singular thermal diffuse parts of Eq. (4.3). While the former is dominant if $K_\perp \equiv 0$, the discussion of Sec. IV shows that the latter part can be dominant for resolutions much worse than $O(L^{-1})$. Finally, in order for the magnetic field to have a significant effect, the resolution must be better than the inverse magnetic coherence length $\xi_1^{-1}$.

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[16]Equation (B8) of Ref. 8(b) is thus incorrect. Furthermore, Eq. (B6) of Ref. 8(b), which gives the structure factor [symbolized therein by $I(K)$] for $\kappa L \ll 1$, should read

$$I(\kappa)/I(G)=1-(\kappa L)^2(1-T/T_G)/8(1-T/2T_G)+\dots .$$

[17]A more detailed analysis of the effect of a magnetic field on the structure factor is in progress and will be reported elsewhere.

[18]The development of such a Landau free-energy functional and the analysis of its consequences is presently in progress. Results will be reported elsewhere.

[19]It is worthwhile noting that to have $x_{m=1}>1$ in the Als-Nielsen *et al.*[14] experiment would require the temperature to be so close to $T_{AN}$ that one would probably have to take into account fluctuations in the density. These fluctuations were ignored in the model used in this paper and may destroy the crossover effect at $x_{m=1}=1$.

[20]R. J. Birgeneau and P. E. Cladis have each recently reported the observation of the $m=2$ peak, albeit on a scale of only $10^{-4}$ in intensity. We are grateful to them for communicating to us their results.