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Molecular order in the smectic *E* phase*

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A Landau theory of the smectic *B*-*E* transition at constant volume is proposed. The coupling constants of this theory are then derived from a previously published microscopic theory. Coupling between the orientational order and the lattice-strain tensor is then introduced, and it is shown that this causes the *B*-*E* transition to be first order. Elastic neutron scattering is discussed as an experimental test of the microscopic theory. Finally, interlayer interactions are included.

I. INTRODUCTION

In recent years there has been a great deal of research in the more highly ordered smectic phases of liquid crystals. In a number of these more highly ordered phases it is found the two-dimensional smectic *A* liquid freezes to form a two-dimensional hexagonal lattice characterizing the smectic *B* phase. If the long molecular axes of the molecules are tilted with respect to the normal to the smectic plane, the phase is called the smectic *H*.

A model of the *B*-*H* transition based on a soft-core repulsive potential and a dipole-dipole intermolecular interaction has been proposed by McMillan and the author.[1] This model, giving freeze-out of rotation around the long molecular axis, is still a subject of controversy.

Recent x-ray studies[2] have shown that the smectic *E* phase is characterized by a two-dimensional approximately hexagonal lattice and herringbone symmetry (see Fig. 1). The molecules are normal to the smectic plane. There is also evidence[2,3] that the smectic VI phase has the same structure as the smectic *E* phase, except that the molecules are tilted with respect to the normal to the smectic plane.

In a previous paper the author[4] formulated a microscopic theory for the *E*, *H*, and VI phases by introducing a phenyl-phenyl interaction in addition to the previously discussed dipole-dipole term. This phenyl-phenyl interaction was composed of multipole-multipole, Van der Waals, and soft-core repulsive interaction terms. In that calculation an ideal two-dimensional hexagonal lattice was assumed, and the possibility of both dipolar and herringbone order was considered in the self-consistent-field approximation. It was found that two order parameters, $\langle 2\cos\phi\sin\phi\rangle$ and $\langle 2\cos^2\phi - 1\rangle$, reflect the herringbone order in the *E*, *H*, and VI phases. The rotational freeze-out model has been verified in the smectic VI phase.[5]

In this paper a Landau theory of the smectic *E* phase is presented. As will be obvious, this theory bears formal similarity to both de Gennes's theory of the nematic phase[6] and Landau's theory of the antiferromagnet.[7] The relevant parameters of the Landau theory at constant volume are derived from the previously discussed microscopic theory.[4] Coupling with the lattice is then introduced, and it is shown that this invariably makes the *B*-*E* transition first order. Elastic neutron scattering is then discussed as an experimental test of the microscopic theory of the *E* phase. Finally, interlayer interactions are shown to change the transition temperature but leave the order of the transition unchanged.

II. SMECTIC *B*-*E* TRANSITION AT CONSTANT VOLUME

The model of the smectic *E* phase proposed by Doucet *et al.*[2] suggests the molecular model shown in Fig. 2. The molecule is represented by a plate of length approximately 30 Å and width 6 Å. The rotational symmetry of this molecular model necessitates the use of a second-rank tensor order parameter. In this paper only rotations in the *x*-*y* plane around the long molecular axis will be considered; so our tensor order parameter has dimension 2.

In the microscopic theory[4] two order parameters reflected herringbone symmetry, $\langle 2\cos\phi\sin\phi\rangle$

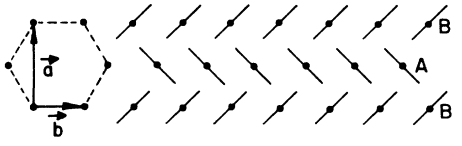

FIG. 1. Molecular order in the smectic *E* phase showing the two types of lattice sites. The line represents the "axis of symmetry" perpendicular to the plane of the phenyl rings.

and $\langle 2\cos^2\phi - 1\rangle$. Generalizing, our tensor order parameter takes the form

$$Q_{ij}^{\alpha\beta} = \langle 2i_\alpha j_\beta - \delta_{ij}\delta_{\alpha\beta}\rangle, \tag{1}$$

where $\vec{i}$ and $\vec{j}$ are two orthonormal vectors linked to the molecule, while α and β are indices referring to a frame fixed to the two-dimensional hexagonal lattice. We shall use a lattice coordinate system corresponding to the $\vec{a}$ and $\vec{b}$ vectors of the lattice as in Fig. 1. The superscripts α and β will henceforth be dropped. Because of definition (1), our order parameter is symmetric and traceless; so only Q_{11} and Q_{12} are of interest.

This order parameter is similar to the tensor order parameter $\langle 3i_\alpha j_\beta - \delta_{ij}\delta_{\alpha\beta}\rangle$ used by de Gennes[6] for the nematic phase.

As in the case of the antiferromagnet,[7] we have two types of lattice sites, A and B, as shown in Fig. 1. The free energy of the lattice of A sites interacting with its neighbors is given by

$$F_A = \tfrac{1}{4}aQ_{ij}^A Q_{ji}^A + \tfrac{1}{16}b(Q_{ij}^A Q_{ji}^A)^2 + \tfrac{1}{2}C_1(\partial Q_{11}^A/\partial x)^2 + \tfrac{1}{2}C_2(\partial Q_{11}^A/\partial y)^2 + \tfrac{1}{2}C_1(\partial Q_{12}^A/\partial x)^2 + \tfrac{1}{2}C_2(\partial Q_{12}^A/\partial y)^2. \tag{2}$$

In the above expression, and throughout this paper, repeated indices are summed over. There is an identical expression F_B for the free energy of the B sites. The two lattices interact in two ways, first by

$$F_3 = \tfrac{1}{2}AQ_{ij}^A Q_{ji}^B. \tag{3}$$

The terms a and A are actually the $\zeta\zeta\eta\eta$ components of a fourth-rank tensor; however, it is not necessary to take this into account.[8]

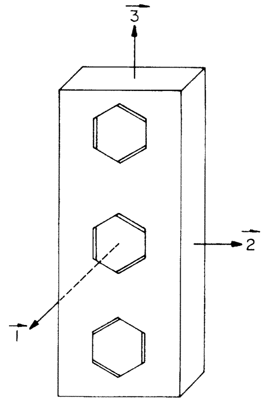

FIG. 2. Molecular model: a plate of length L and diameter D. The phenyl rings lie in the plane of the plate.

There is also an interaction of the form

$$F_4 = \frac{1}{2}C_3\left(\frac{\partial Q_{11}^A}{\partial x}\frac{\partial Q_{11}^B}{\partial x} + \frac{\partial Q_{12}^A}{\partial x}\frac{\partial Q_{12}^B}{\partial x}\right) + \frac{1}{2}C_4\left(\frac{\partial Q_{11}^A}{\partial y}\frac{\partial Q_{11}^B}{\partial y} + \frac{\partial Q_{12}^A}{\partial y}\frac{\partial Q_{12}^B}{\partial y}\right). \tag{4}$$

If there is a magnetic field present, there is also a term

$$F_H = -\tfrac{1}{2}\chi_a\left[\tfrac{1}{2}(H_x^2 - H_y^2)(Q_{11}^A + Q_{11}^B) + H_xH_y(Q_{12}^A + Q_{12}^B)\right], \tag{5}$$

where $\chi_a = \chi_{11} - \chi_{22}$. The total free energy is then given by

$$F = \tfrac{1}{2}(F_A + F_B + F_3 + F_4 + F_H). \tag{6}$$

The expression for the free energy can be simplified by making the substitutions

$$Q_{ij}^A = m_{ij} + l_{ij} \quad\text{and}\quad Q_{ij}^B = m_{ij} - l_{ij}. \tag{7}$$

The free energy is then given by $F = F_m + F_l + F_{\text{int}}$ where

$$F_m = \tfrac{1}{2}(a+A)(m_{11}^2 + m_{12}^2) + \tfrac{1}{4}b(m_{11}^4 + m_{12}^4 + 2m_{11}^2 m_{12}^2) + \tfrac{1}{2}(C_1 + C_3)[(\partial m_{11}/\partial x)^2 + (\partial m_{12}/\partial x)^2] + \tfrac{1}{2}(C_2 + C_4)[(\partial m_{11}/\partial y)^2 + (\partial m_{12}/\partial y)^2] - \tfrac{1}{2}\chi_a[\tfrac{1}{2}(H_x^2 - H_y^2)m_{11} + H_xH_y m_{12}], \tag{8}$$

$$F_l = \tfrac{1}{2}(a - A)(l_{11}^2 + l_{12}^2) + \tfrac{1}{4}b(l_{11}^4 + l_{12}^4 + 2l_{11}^2 l_{12}^2) + \tfrac{1}{2}(C_1 - C_3)[(\partial l_{11}/\partial x)^2 + (\partial l_{12}/\partial x)^2] + \tfrac{1}{2}(C_2 - C_4)[(\partial l_{11}/\partial y)^2 + (\partial l_{12}/\partial y)^2], \tag{9}$$

$$F_{\text{int}} = \tfrac{3}{2}b(m_{11}^2 l_{11}^2 + m_{12}^2 l_{12}^2) + \tfrac{1}{2}b(l_{11}^2 m_{12}^2 + m_{11}^2 l_{12}^2 + 4m_{11}m_{12}l_{11}l_{12}). \tag{10}$$

In a smectic E material with no applied magnetic field $m_{ij} = 0$. In this case we need only consider the contribution to the free energy given in Eq. (9). Below T_c we have $l_{ij}l_{ji} = -2(a-A)/b$. As usual in Landau theory, we have $a - A = 2kT_c \times (1 - T_c/T)$. Fluctuations in l_{11} and l_{12} are given above the B-E transition temperature by

$$\langle l_{ij,\vec{q}}^2\rangle = \int l_{ij,\vec{q}}^2 e^{-F_{\vec{q}}/kT}\, dl_{ij,\vec{q}} \Big/ \int e^{-F_{\vec{q}}/kT}\, dl_{ij,\vec{q}}, \tag{11}$$

where $F_{\vec{q}} = \tfrac{1}{2}A_{\vec{q}} l_{ij,\vec{q}}^2$. It follows in the long-wavelength limit that $l_{ij}^2 = kT/(a-A)$. Fluctuations in both l_{11} and l_{12} are infinite through the B-E transition.

It should be pointed out here that this Landau theory predicts that the *B*-*E* transition is of second order and is completely isotropic with respect to diagonal and off-diagonal terms in the order parameter (neglecting spacial variation terms). This holds true only when the lattice is constrained to the hexagonal lattice of the *B* phase. This constraint will later be removed.

III. DERIVATION FROM MICROSCOPIC THEORY

The interactions between molecules in the smectic *E* phase have been discussed previously.[4] The result of this discussion could be viewed as a phenomenological two-body potential of the form

$$U_{12}(\phi_1, \phi_2, \xi) = A_1(r_{12})\cos^2(\phi_1 - \phi_2) + A_2(r_{12})\cos(4\xi)\cos 2(\phi_1 + \phi_2). \tag{12}$$

The angles ϕ_1, ϕ_2, and ξ are defined in Fig. 3. For a hexagonal lattice in two dimensions, keeping only nearest-neighbor interactions, the radial dependence can be absorbed into the two constants A_1 and A_2.

On all type-*A* sites the molecules feel the average potential

$$V_A(\phi) = \tfrac{1}{2}V_0 Q_{11}^A(2\cos^2\phi - 1) + \tfrac{1}{2}V_1 Q_{12}^A(2\cos\phi\sin\phi). \tag{13}$$

The potentials on type-*A* and -*B* sites are related by $V_A(\phi) = V_B(-\phi)$. It can be shown that $V_0 = 6A_1$ and $V_1^A = -(2A_1 + 8A_2)$.[4] The partition function is given by

$$Z = \int_{-\pi}^{\pi} d\phi \exp[-V_A(\phi)/kT]. \tag{14}$$

To derive the coupling constants of the Landau theory, the response of the order parameter Q_{ij}^A to an external field $\vec{H}$ is calculated according to both the Landau and microscopic theories, and the responses are equated. We first calculate the response function using the Landau theory. Apply a spacially varying magnetic field in the $\hat{y}$ direction. We write

$$\vec{H} = \hat{y}He^{i\vec{q}\cdot\vec{r}}. \tag{15}$$

The free energy is then

$$F = F_l + \tfrac{1}{2}(a+A)m_{11}^2 + \tfrac{1}{2}m_{11}^2[(C_1 + C_3)q_x^2 + (C_2 + C_4)q_y^2] + \tfrac{1}{2}\chi_a H^2 m_{11}. \tag{16}$$

There is no direct coupling to m_{12}. Minimizing F with respect to m_{11}, we find

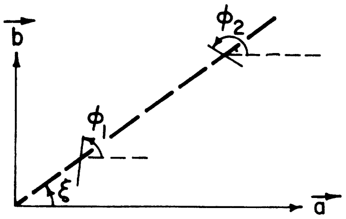

FIG. 3. The coordinate system is fixed to the hexagonal lattice vectors $\vec{a}$ and $\vec{b}$. The coordinates *x* and *y* are parallel to the $\vec{a}$ and $\vec{b}$ axes of the crystal respectively. The angle ξ gives the angle of the 1-2 intermolecular vector and the $\vec{a}$ axis.

$$m_{11} = -\tfrac{1}{4}\chi_a H^2[(a+A) + (C_1 + C_3)q_x^2 + (C_2 + C_4)q_y^2]^{-1}. \tag{17}$$

Q_{ij}^A can then be found from Eq. (7).

Similarly, for $\vec{H} = H(\hat{x} + \hat{y})e^{i\vec{q}\cdot\vec{r}}$ we find

$$m_{12} = \tfrac{1}{2}\chi_a H^2[(a+A) + (C_1 + C_3)q_x^2 + (C_2 + C_4)q_y^2]^{-1}. \tag{18}$$

We now calculate the response function according to the microscopic theory. With the external field in the $\hat{y}$ direction the external potential is

$$V_{\text{ext}}(\phi) = \tfrac{1}{4}\chi_a H^2 e^{i2\vec{q}\cdot\vec{r}}\cos 2\phi \tag{19}$$

where $\vec{r}$ is the position of the molecule and ϕ is the angle between the normal to the face of the molecule and the $\vec{a}$ axis of the lattice. The self-consistent-field method is used. Assume a single-particle potential on a type I site of

$$V(\vec{r}, \phi) = \tfrac{1}{2}V_1 Q_{12}^{\text{I}}\sin 2\phi - V_q e^{i2\vec{q}\cdot\vec{r}}\cos 2\phi. \tag{20}$$

For convenience assume $Q_{11}^{\text{I}} = 0$. The single-particle distribution function is then

$$f(\vec{r}, \phi) = Z^{-1}e^{-V(\vec{r},\phi)/kT}. \tag{21}$$

As usual, one calculates the average potential which one molecule feels due to the interactions (19) and (12). For self-consistency this calculated potential must equal the assumed potential (20). This self-consistency equation is

$$V(\vec{r}, \phi) = \sum_{\vec{r}_2}\int_{-\pi}^{\pi} d\phi_2 f(\vec{r}_2, \phi_2)U_{1,2}(\vec{r}_{12}, \phi_1, \phi_2) + V_{\text{ext}}(\vec{r}_1, \phi_1), \tag{22}$$

where the sum is over nearest neighbors only. To perform the necessary operation, $f(\vec{r}_2, \phi_2)$ is expanded to first order in V_q and then $e^{i2\vec{q}\cdot\vec{r}}$ is expanded to second order in $\vec{q}$. This gives

$$
\begin{aligned}
&\tfrac{1}{2}V_1 Q_{12}^A \sin 2\phi_1 - V_q e^{i2\vec{q}\cdot\vec{r}_1}\cos 2\phi_1 \\
&\quad = -\tfrac{1}{2}(2A_1+4A_2)\langle \sin 2\phi_2\rangle \sin 2\phi_1 \\
&\qquad + (V_q/kT)\langle \cos^2 2\phi_2\rangle[3A_1-(3A_1+3A_2)(q_x^2D^2)+(3A_2-3A_1)(q_y^2D^2)]e^{2i\vec{q}\cdot\vec{r}_1}\cos 2\phi_1 + \tfrac{1}{4}\chi_a H^2 e^{2i\vec{q}\cdot\vec{r}}\cos 2\phi_1, \qquad (23)
\end{aligned}
$$

where

$$\langle g(\phi)\rangle = Z_0^{-1}\int_{-\pi}^{\pi} d\phi\, g(\phi)\exp\left(-\frac{V_1Q_{12}^A \sin 2\phi}{2kT}\right) \qquad (24)$$

and

$$Z_0 = \int_{-\pi}^{\pi} d\phi \exp\left(-\frac{V_1Q_{12}^A\sin 2\phi}{2kT}\right). \qquad (25)$$

D is the nearest-neighbor distance within the smectic plane.

Equating coefficients of $\cos 2\phi$ and $\sin 2\phi$ gives the self-consistency equations for V_1 and V_q. Calculating $\langle \cos^2 2\phi\rangle$ and substituting it into Eq. (23) gives

$$
\begin{aligned}
m_{11} &= \tfrac{1}{2}(V_q/kT) \\
&= -\tfrac{1}{4}\chi_a H^2[(2kT_c+\tfrac{3}{2}A_1)+3D^2(A_1+A_2)q_x^2 \\
&\qquad + 3D^2(A_1-A_2)q_y^2]^{-1}. \qquad (26)
\end{aligned}
$$

Comparing coefficients in (17) and (26) gives

$$a + A = 2kT_c + \tfrac{3}{2}A_1, \qquad (27)$$

$$C_1 + C_3 = 3D^2(A_1+A_2), \qquad (28)$$

$$C_2 + C_4 = 3D^2(A_1 - A_2), \qquad (29)$$

where $kT_c = -\frac{1}{4}(2A_1 + 8A_2)$.[4]

A similar calculation can be done for the l_{ij} mode by using an artificial magnetic field that is different on the A and B sites, giving $V_{\text{ext}}^A(\phi) = -V_{\text{ext}}^B(\phi)$. The details of the calculation are almost identical to those above, and will not be repeated here. The results are

$$a - A = 2kT_c(1 - T_c/T), \qquad (30)$$

$$C_1 - C_3 = 3D^2(A_1 + A_2), \qquad (31)$$

$$C_2 - C_4 = D^2(5A_2 - A_1). \qquad (32)$$

This completes the derivation of the Landau theory of the smectic E phase from the microscopic theory. The lattice has been assumed to be rigid in this derivation. This restriction will be removed in the next section.

IV. COUPLING TO THE LATTICE

In this section we will show how lattice distortions modify the nature of the smectic B-E transition. In particular, it will be shown that lattice distortions make the B-E transition first order and anisotropic in the diagonal and off-diagonal terms in l_{ij}.

In this section it will be assumed that there is no external magnetic field, and so $m_{ij}=0$. Neglecting spacial variations, F_l is given as usual by

$$F_l = \tfrac{1}{2}(a-A)(l_{11}^2 + l_{12}^2) + \tfrac{1}{4}b(l_{11}^4 + l_{12}^4 + 2l_{11}^2 l_{12}^2). \qquad (33)$$

Note that this expression is isotropic in l_{11} and l_{12}.

For small distortions of the hexagonal lattice the free energy is given by[8]

$$F_{el} = 2\lambda_1(U_{xx}+U_{yy})^2 + \lambda_2(U_{xx}-U_{yy})^2 + 4\lambda_2 U_{xy}^2 \qquad (34)$$

where U_{ij} is the two-dimensional strain tensor.

Finally, there are the cross terms which couple the angular order parameter l_{ij} to the strain tensor U_{ij}:

$$F_c = \tfrac{1}{2}K_1(\operatorname{tr}U_{ij})(l_{ij}l_{ji}) + U_{ij}M_{jr}l_{ri}. \qquad (35)$$

The tensor coupling constant M_{jr} is symmetric and of rank 2, dimension 2. Define

$$K_2 = \tfrac{1}{2}M_{ii} \qquad (36)$$

and

$$K_3 = \tfrac{1}{2}(M_{11} - M_{22}). \qquad (37)$$

The total free energy is given by $F = F_l + F_{el} + F_c$. Minimizing F with respect to $U_{xx}+U_{yy}$, $U_{xx}-U_{yy}$, and U_{xy}, we find

$$U_{xx} + U_{yy} = -(4\lambda_1)^{-1}(\tfrac{1}{2}K_1 l_{ij}\, l_{ji} + K_3 l_{11} + M_{12} l_{12}), \qquad (38)$$

$$U_{xx} + U_{yy} = -(2\lambda_2)^{-1}K_2 l_{11}, \qquad (39)$$

$$U_{xy} = -(4\lambda_2)^{-1}K_2 l_{12}. \qquad (40)$$

These expressions can be substituted in the equation for F. When we set $l_{12}=0$, we find

$$
\begin{aligned}
F(l_{12}=0) &= \tfrac{1}{2}l_{11}^2[(a-A) - (2\lambda_2)^{-1}K_2^2 - (4\lambda_1)^{-1}K_3^2] \\
&\quad + \tfrac{1}{3}l_{11}^3(-\tfrac{3}{4}\lambda_1^{-1}K_1K_3) + \tfrac{1}{4}l_{11}^4(b - \tfrac{1}{2}\lambda_1 K_1^2). \qquad (41)
\end{aligned}
$$

From the presence of the third-order term in l_{11} it follows that the phase transition is first order.

Setting $l_{11}=0$ we find

$$F(l_{11}=0)=\tfrac{1}{2}l_{12}^2[(a-A)-(2\lambda_2)^{-1}K_2^2-(4\lambda_1)^{-1}M_{12}^2]$$
$$+\tfrac{1}{3}l_{12}^3(-\tfrac{3}{4}\lambda_1^{-1}K_1M_{12})+\tfrac{1}{4}l_{12}^4(b-\tfrac{1}{2}\lambda_1^{-1}K_1^2). \tag{42}$$

By comparing Eqs. (41) and (42) we see that as long as $K_3 \neq M_{12}$ the phase transition is anisotropic in l_{11} and l_{12}. The case $l_{12}=0$ is that found experimentally by Doucet *et al.*[2] In the case $U_{xy}=0$ and $U_{xx}\neq U_{yy}$, the hexagonal lattice deforms to give an orthorhombic lattice. Another possible deformation due to $l_{11}=0$ gives $U_{xx}-U_{yy}=0$, $U_{xy}\neq 0$. The hexagonal lattice deforms to give a monoclinic lattice, in which the vectors $\vec{a}$ and $\vec{b}$ in the smectic plane are not orthogonal.

It should also be noted that $U_{xx}+U_{yy}=(V_E-V_B)/V_B$, and Eq. (38) implies a volume change associated with the B-E phase transition, regardless of which of the components of l_{ij} is nonzero.

V. ELASTIC NEUTRON SCATTERING

Elastic neutron scattering has recently been used as a tool to investigate the molecular order in the smectic H and VI phases.[5,9] The results of that analysis can easily be extended to the smectic E phase. The self-correlation function at infinite time is give by[10]

$$G_s^\infty(\vec{r})=N^{-1}\sum_{i=1}^{N}\int p_i(\vec{r}\,'-\vec{r})p_i(\vec{r}\,')\,d^3r', \tag{43}$$

where $p_i(\vec{r}\,')$ is the probability per unit volume of finding particle i at $\vec{r}\,'$.

The incoherent elastic structure factor is given by

$$A_0(\vec{q})=\left\langle \int G_s^\infty(\vec{r}-\vec{r}_0)e^{i\vec{q}\cdot\vec{r}}\,d^3r\right\rangle_{r_0}, \tag{44}$$

where the average is over the initial position $\vec{r}_0$. Equation (44) reduces to

$$A_0(\vec{q})=[MI_0^2(\alpha)]^{-1}\sum_{j=1}^{M}\frac{\sin[2qa\sin(\pi j/M)]}{2qa\sin(\pi j/M)}$$
$$\times I_0[2\alpha\cos(2\pi j/M)], \tag{45}$$

where $\alpha=V_1l_{12}/2kT$.

This result is almost identical to that for the smectic H phase.[9] $A_0(q)$ is plotted in Fig. 4 for the smectic B and E phases. This plot shows that the elastic neutron scattering increases as we go through the B-E transition. Although the theory is not good enough to give quantitative agreement with experiment, the trend of increased elastic scattering as we go down through the phase transition should be valid. This trend has been found in the H phase,[5] although it has been suggested that it is a pretransition effect of the H-VI transition. Quantitative agreement with theory is not found for reasonable values of a, and it is necessary to treat a as a variable parameter.

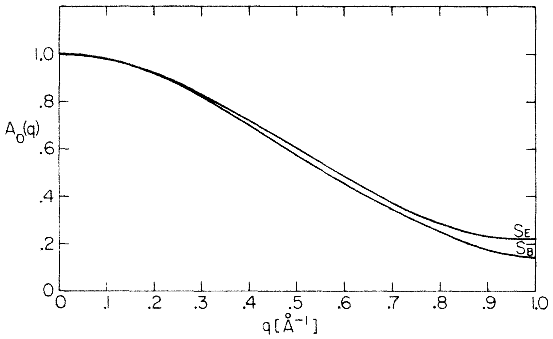

FIG. 4. Incoherent elastic structure factor as a function of q in the smectic B and E phases for values of $M=6$, $a=2.50$ Å, and $\alpha=1.4\cong 20_{12}^{A}T_c/T$. The plot for the B phase comes from Eq. (6) of Ref. 10.

VI. INTERLAYER INTERACTIONS

The introduction of weak interlayer interactions has little effect on the nature of the B-E transition. This is easily shown in two simple layer configurations: that in which each molecule of type A in one layer has an A-type molecule above and below it, and the configuration in which each A-type molecule has a type-B molecule above and below it. These are the most likely sequences although there are other possibilities.

The interaction between adjacent layers 1 and 2 in the lowest order can be written as

$$F_{\text{int}}=\tfrac{1}{2}\alpha l_{ij}^{(1)}l_{ji}^{(2)}, \tag{46}$$

where the arabic superscripts refer to layer number. Then the free energy for the liquid crystal is given by

$$F=F^{(1)}+F^{(2)}+F_{\text{int}}, \tag{47}$$

where $F^{(1)}$ and $F^{(2)}$ are from Eq. (9).

The free energy can be diagonalized in lowest order by making the substitutions

$$l_{ij}^{(1)}=n_{ij}+p_{ij} \tag{48a}$$

and

$$l_{ij}^{(2)}=n_{ij}-p_{ij}. \tag{48b}$$

The free energy then takes the form

$$F=(a-A+\alpha)(n_{11}^2+n_{12}^2)+(a-A-\alpha)(p_{11}^2+p_{12}^2), \tag{49}$$

where the p order parameter describes the layer sequence 121212... and the n order parameter describes the sequence 1111... . Thus it is easily seen that the introduction of interlayer interactions changes the transition temperature but leaves the order of the transition unchanged. More complicated layer sequences of the form 123123... have Hamiltonians that can be diagonalized by transformations similar to Eq. (48), and our conclusions are unchanged.

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