Molecular model for nematic, smectic-*A*, and smectic-*C* liquid crystals

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We analyze a molecular model to describe the phase transitions between the isotropic, nematic, smectic-*A*, and smectic-*C* phases. The smectic phases are described by the use of a pair potential, which lacks the full rotational symmetry because of the cylindrical symmetry around the smectic axis. The tilt of the long molecules inside the smectic layers is favored by a biquadratic pair potential, which compete with the pair potential of the McMillan model. The part of the phase diagram showing the first three phases is similar to that of the McMillan molecular model. The smectic-*C* phase is separated from the nematic by a continuous phase transition line along which the tilt angle is nonzero. The tilt angle vanishes continuously when one reaches the line separating the smectic-*C* and the smectic-*A* line.

I. INTRODUCTION

The phase transition from the most prominent of the liquid crystal mesophases [1–4], the nematic, to the isotropic phase is well described by the molecular theory proposed by Maier and Saupe [5]. The fundamental assumption of their theory concerns the form of the potential energy of any molecule i, which they have assumed to be proportional to $q\mathcal{S}_i$ where $\mathcal{S}_i$ is defined by

$$\mathcal{S}_i = 1 - \tfrac{3}{2}\sin^2\theta_i, \tag{1}$$

where θ_i is the angle between the axis of the molecule and one of the axes of a frame of reference, and q is the mean field due to the neighboring molecules, given by

$$q = \langle \mathcal{S}_j \rangle, \tag{2}$$

assumed to be the same for all molecules and understood as the order parameter of the nematic phase. Maier and Saupe theory predicts a discontinuous phase transition with a jump of the order parameter.

The theory of Maier and Saupe was extended to the case of biaxial nematic phases by Freiser by using a quadrupole interactions between molecules [6]. The interaction between two molecules is assumed to be proportional to the trace of $\widehat{\Omega}^i\,\widehat{\Omega}^j$ where $\widehat{\Omega}^i$ is a quadrupole field variable associated to molecule i, represented by a tensor of the second rank. If the tensor has three distinct eigenvalues, it describes biaxial molecules, which is the case of the Freiser model. Following de Gennes [1], $\widehat{\Omega}^i$ is chosen to be a traceless tensor so that the nematic tensor order parameter is

$$\widehat{Q} = \langle \widehat{\Omega}^i \rangle. \tag{3}$$

The pair interaction, in accordance with the molecular theories, is assumed the be proportional to the trace of $\widehat{Q}\,\widehat{\Omega}^i$. The Freiser model predicts a discontinuous phase transition from the isotropic to each one of the two types of uniaxial nematic

phase, and a continuous phase transition from each one of the two phases to the biaxial nematic phase. It also predicts a multicritical point where the four phases meet, known as Landau point [7]. When two eigenvalues of $\widehat{\Omega}^i$ become equal, the model is reduced to the Maier and Saupe model, in which case $\widehat{\Omega}^i$ is an axially symmetric traceless tensor describing a uniaxial nematic phase.

A smectic liquid crystal is structured in layers with nematic order inside each layer. If the director **n**, a unit vector that defines the nematic orientation, in each layer is perpendicular to the layers, we are faced to a smectic-*A* structure. A molecular theory for the transition between nematic and smectic phases was formulated independently by Kobayashi [8,9] and by McMillan [10] and was based on the molecular theory of uniaxial nematic of Maier and Saupe [5]. The interaction is set up by coupling the field variable $\mathcal{S}_i$ of Maier and Saupe with a field variable $\cos\xi_i$ describing the modulation in density along the axis of the smectic layers.

The potential energy of a molecule i within the McMillan molecular theory is proportional to $q\mathcal{S}_i\cos\xi_i$ where

$$\sigma = \langle \mathcal{S}_j \cos\xi_j \rangle \tag{4}$$

is the McMillan order parameter describing the smectic-*A* phase [10]. The McMillan theory predicts a continuous transition between the nematic and smectic-*A* that ends on a tricritical point. Beyond this point, the transition between these two phases is discontinuous. It also predicts discontinuous transition lines between the isotropic and smectic-*A* and between the isotropic and nematic, which meet at triple point.

If the director in each layer is tilted with respect to the axis of the layers, the liquid crystal structure is called smectic-*C*. The smectic-*C* phase is appropriately characterized by the vector **s** which is the projection of the director **n** onto the smectic layer plane and may be understood as the order parameter of the smectic-*C* phase [11]. Several molecular models for the transition between the smectic-*C* and the

smectic-A have been proposed [11–21]. These transitions have also been treated by the Ginzburg-Landau theory [22–28] and the Landau theory [29–41]. Some of these models predict a continuous phase transition between the smectic-A and smectic-C phases. The transition between the nematic and smectic-C is also continuous but the tilt angle along the transition line is nonzero and vanishes at the point where the three phases meet.

In this paper we propose a molecular model for the smectic-C that is distinct from previous molecular models in the use of an appropriate treatment of the spatial symmetries related to the pair potential. In a nematic phase, the pair potential is symmetric under any spatial rotation, that is, the interaction

$$\mathrm{Tr}(\widehat{\Omega}^i\,\widehat{\Omega}^j) \tag{5}$$

is invariant under the simultaneous rotation of both $\widehat{\Omega}^i$ and $\widehat{\Omega}^j$. The nematic phase arises by a spontaneous symmetry breaking of this symmetry. In a smectic phase the pair interaction should not have the full rotation symmetry due to the presence of the smectic axis, the axis perpendicular to the smectic layers, but it holds the invariance under rotation around the smectic axis. In a smectic-A phase, this cylindrical symmetry is still present but in a smectic-C phase it is spontaneously broken.

If the invariance of the pair potential is valid only for rotations around the smectic axis then the appropriate form of the pair potential is either

$$(\widehat{\Omega}^i\,\widehat{\Omega}^j)_{xx} + (\widehat{\Omega}^i\,\widehat{\Omega}^j)_{yy}, \tag{6}$$

or

$$(\widehat{\Omega}^i\,\widehat{\Omega}^j)_{zz}, \tag{7}$$

where indices x, y, and z are used to denote the corresponding Cartesian components of the tensor $\widehat{\Omega}^i\,\widehat{\Omega}^j$, and we have elected the z axis of a frame of reference to be the smectic axis.

Considering that the pair potential in the smectic phases should hold the cylindrical symmetry, induced by the presence of the smectic axis, we develop here a molecular theory for the emergence of the smectic-C phase and its transitions to the smectic-A and the nematic phases. The pair potential is assumed to be a combination of two competing forces. One of these favors the alignment with the smectic axis and the other favors a tilt of the director with respect to this axis, and is chosen to be a term quadratic in the tensors.

II. MOLECULAR APPROACH

A molecular field theory is set up as follows. To each molecule one associates a *field variable*, with one or more component, such as a scalar, a vector, or a tensor. We denote by X_ν^i the several scalar variables that one associates to the molecule i, which might be the components of a vector or of a tensor field, or a combination of them.

The energy of interaction between two molecules i and j is taken to be a sum of terms of the type $a_\nu^{ij} X_\nu^i X_\nu^j$. The strength of the interaction a_ν^{ij} depends on the distance, and the total

energy function $\mathcal{H}$ will be a sum over all pairs ij

$$\mathcal{H} = -\sum_{ij}\sum_\nu a_\nu^{ij} X_\nu^i X_\nu^j. \tag{8}$$

We are assuming that a_ν^{ij} is nonzero only when the molecules of a pair belong to a small neighborhood of each other, and take the same value a_ν. The molecular approach we consider here consists of using an approximation in which the product $X_\nu^i X_\nu^j$ is replaced by the expression

$$X_\nu^i\langle X_\nu^j\rangle + \langle X_\nu^i\rangle X_\nu^j - \langle X_\nu^i\rangle\langle X_\nu^j\rangle. \tag{9}$$

We further assume that the system is homogeneous so that the average $\langle X_\nu^i\rangle = A_\nu$ is the same for all molecules, and expression (9) becomes

$$\left(X_\nu^i + X_\nu^j\right)A_\nu - A_\nu^2. \tag{10}$$

The resulting expression for the total energy function will be a sum of terms of the type

$$H_i = -\sum_\nu a_\nu \left(X_\nu^i A_\nu - \frac{1}{2}A_\nu^2\right) \tag{11}$$

for each molecule, that is,

$$\mathcal{H} = \sum_i H_i, \tag{12}$$

and $a_\nu \geqslant 0$ so that the pair potential is attractive. Since $\mathcal{H}$ becomes a sum of statistically independent terms H_i, it suffices to treat just one molecule whose energy function is given by Eq. (11). On account of this reduction we may drop the index i of the molecule, and write the molecule energy function (11) as

$$H = -\sum_\nu a_\nu \left(X_\nu A_\nu - \frac{1}{2}A_\nu^2\right), \tag{13}$$

and

$$A_\nu = \langle X_\nu\rangle. \tag{14}$$

It is useful to write the molecule energy function as composed of two parts, $H = \Phi - E$, where

$$\Phi = -\sum_\nu a_\nu X_\nu A_\nu, \tag{15}$$

which we call the pair potential, and

$$E = -\frac{1}{2}\sum_\nu a_\nu A_\nu^2, \tag{16}$$

which is half the average of the pair potential, $E = \Phi/2$. This quantity is in fact the average energy per molecule $E = \langle H\rangle$, a result that can be verified by taking the average of Eq. (13) and using $A_\nu = \langle X_\nu\rangle$.

The thermodynamic properties of equilibrium is determined by using the probability Gibbs distribution

$$P(x) = \frac{1}{Z}e^{-\beta\Phi(x)}, \tag{17}$$

where x is the space of states over which the field variables X_ν are defined, and β is proportional to the inverse of the

temperature. The normalization factor Z is

$$Z = \int e^{-\beta\Phi} dx, \qquad (18)$$

where $dx = \Pi_\nu \, dx_\nu$ and x_ν are the components of x.

The free energy per molecule F is obtained from the partition function

$$Z^* = \int e^{-\beta H} dx, \qquad (19)$$

and is given by $F = -(1/\beta) \ln Z^*$, or by

$$F = -E - \frac{1}{\beta} \ln Z, \qquad (20)$$

and will depend on temperature and on A_ν.

The first derivative of F with respect to A_ν gives

$$\frac{\partial F}{\partial A_\nu} = -a_\nu(\langle X_\nu \rangle - A_\nu). \qquad (21)$$

On account that A_ν is the mean value of X_ν, it follows at once that

$$\frac{\partial F}{\partial A_\nu} = 0. \qquad (22)$$

The second derivative of F is

$$\frac{\partial^2 F}{\partial A_\nu^2} = -\beta a_\nu^2 \left(\langle X_\nu^2 \rangle - \langle X_\nu \rangle^2 \right) + a_\nu. \qquad (23)$$

From the result (22), the free energy F may be interpreted as a functional of a set of parameters A_ν with respect to which it should be minimized. To check whether the solution is indeed a local minimum one may determine the second derivative by means of Eq. (23), if necessary. When there is more than one solution, that is, when there is more than one local minima, one should choose the one that gives the lowest value of the free energy F. In an equivalent manner, we may say that the actual free energy is the convex hull [42] of expression (20).

III. MAIER AND SAUPE MODEL

We start by considering the Maier and Saupe model that describes the transition from the nematic to the isotropic phase. To each molecule we associate a field variable which is the axially symmetric traceless tensor

$$\widehat{\Omega} = \mathbf{mm} - \frac{1}{3} \mathrm{I}, \qquad (24)$$

where I stands for the identity matrix and $\mathbf{m}$ is the vector

$$\mathbf{m} = m_1 \mathbf{x} + m_2 \mathbf{y} + m_3 \mathbf{z}, \qquad (25)$$

with Cartesian components

$$m_1 = \sin\theta\cos\phi, \quad m_2 = \sin\theta\sin\phi, \quad m_3 = \cos\theta, \qquad (26)$$

where θ is the polar angle and ϕ is the azimuthal angle that defines the unit vector $\mathbf{m}$ in spherical coordinates.

Following the molecular approach above we write the pair potential of the Maier and Saupe model as

$$\Phi = -a\mathrm{Tr}(\widehat{Q}\,\widehat{\Omega}), \qquad (27)$$

and the energy as

$$E = -\frac{1}{2} a \mathrm{Tr}(\widehat{Q}^2), \qquad (28)$$

where $a > 0$ is the strength of the interaction and

$$\widehat{Q} = \langle\widehat{\Omega}\rangle. \qquad (29)$$

In each phase, the probability distribution as well as the tensor order parameter $\widehat{Q}$ reflect the symmetry of the phase. In the isotropic phase, the full rotational symmetry takes place and $\widehat{Q}$ will vanish. In the nematic phase, the full rotational symmetry is broken but the cylindrical symmetry still remains. The probability distribution will be invariant under the rotation about a certain axis and the the order parameter $\widehat{Q}$ can be assumed to be an axially symmetric traceless tensor, represented by

$$\widehat{Q} = q\left(\mathbf{nn} - \frac{1}{3}\mathrm{I}\right), \qquad (30)$$

where $\mathbf{n}$ is a unit vector, the director, and q is the nematic order parameter. Both properties, the vanishing of the trace of $\widehat{Q}$ and the rotational symmetry of $\widehat{Q}$ around $\mathbf{n}$ are preserved by the process of taking the average. The average $\langle\widehat{\Omega}\rangle$ is traceless because $\widehat{\Omega}$ is traceless. The second property is a consequence of the invariance of the probability distribution under the rotation around the axis determined by $\mathbf{n}$.

Taking into account that the pair potential Φ is invariant under a spatial rotation of both $\mathbf{n}$ and $\mathbf{m}$, the director $\mathbf{n}$ may emerge in any direction. We choose the z direction in which case $\mathbf{n} = \mathbf{z}$, and $\widehat{Q} = q\mathbf{zz} - (q/3)\mathrm{I}$, which replaced into Eqs. (27) and (28) gives the simple expressions

$$\Phi = -aqS, \qquad (31)$$

where we are using the abbreviation

$$S = m_3^2 - \frac{1}{3} = \cos^2\theta - \frac{1}{3}, \qquad (32)$$

and

$$E = -\frac{1}{3} aq^2. \qquad (33)$$

The free energy is

$$F = \frac{1}{3} aq^2 - \frac{1}{\beta} \ln Z_0, \qquad (34)$$

where

$$Z_0 = \int e^{\beta aqS} \sin\theta \, d\theta \, d\phi. \qquad (35)$$

Differentiating F with respect to q and equating the result to zero yields

$$q = \frac{3}{2} \langle S \rangle, \qquad (36)$$

an equation that should be solved to find q, where the average should be taken by using the probability distribution $P(\mathbf{m}) = P(\theta, \phi)$,

$$P = \frac{1}{Z_0} e^{\beta aqS}. \qquad (37)$$

The phase transition from the isotropic phase, $q = 0$, to the nematic phase, $q \neq 0$, is discontinuous. The transition occurs when the free energy of the two phases becomes equal, a condition given by the equation

$$\frac{1}{3} \beta aq^2 = \ln Z_0. \qquad (38)$$

The numerical solution of Eqs. (36) and (38) give the transition point at a temperature $T = 1/\beta a = 0.146796$ and the jump on the order parameter at the transition equal to $q = 0.429029$.

IV. MCMILLAN MODEL

A. Pair potential

The McMillan model is described as follows. In addition to the tensor field variable $\widehat{\Omega}$, we associate to a molecule another field variable $\cos \xi$ describing the variation in density along the axis perpendicular to the smectic layers, which we take to be the z axis of a frame of reference. Along this axis, the density of the system is periodic, with a variation in density characterized by an amplitude of modulation and by a phase ξ. According to de Gennes, the order parameter of the smectic phase can be understood as a two-dimensional vector perpendicular to the axis of modulation with Cartesian components being $\cos \xi$ and $\sin \xi$. The description of the smectic-A phase is obtained by coupling the two field variables, $\widehat{\Omega}$ and $\cos \xi$. Accordingly, the molecule pair interaction is assumed to be

$$\Phi_b = -b \operatorname{Tr}(\widehat{\Omega}\,\widehat{\Lambda}) \cos \xi, \qquad (39)$$

where b is the strength of the McMillan interaction, and the energy is

$$E_b = -\tfrac{1}{2} b \operatorname{Tr}(\widehat{\Lambda}^2), \qquad (40)$$

where $\widehat{\Lambda} = \langle \widehat{\Omega} \cos \xi \rangle$, which implies that $\widehat{\Lambda}$ is a traceless tensor.

The pair potential Φ of the McMillan model is defined as the sum of the pair potential Φ_b and the nematic pair potential given by expression (27),

$$\Phi = -a \operatorname{Tr}(\widehat{\Omega}\,\widehat{Q}) - b \cos \xi \operatorname{Tr}(\widehat{\Omega}\,\widehat{\Lambda}), \qquad (41)$$

and the energy is the sum of Eqs. (40) and (28),

$$E = -\tfrac{1}{2} a \operatorname{Tr}(\widehat{Q}^2) - \tfrac{1}{2} b \operatorname{Tr}(\widehat{\Lambda}^2). \qquad (42)$$

Owing to the invariance of the potential Φ under a simultaneous rotation of $\widehat{Q}, \widehat{\Lambda}$, and $\widehat{\Omega}$ around any axis, we may choose the tensors $\widehat{Q}$ and $\widehat{\Lambda}$ to be uniaxial tensors. Accordingly, we choose $\widehat{Q}$ to have the form we have already used, given by Eq. (30),

$$\widehat{Q} = q\left(\mathbf{nn} - \tfrac{1}{3}\,\mathrm{I}\right). \qquad (43)$$

sThe tensor $\widehat{\Lambda}$ is chosen to have the same form,

$$\widehat{\Lambda} = \sigma\left(\mathbf{nn} - \tfrac{1}{3}\,\mathrm{I}\right), \qquad (44)$$

where σ is the order parameter of the smectic-A phase. Again, the director may arise in any direction due to the full rotational symmetry of the pair potential, and we choose the z direction in which case $\mathbf{n} = \mathbf{z}$. Using these results, expressions (41) and (42) acquire the forms

$$\Phi = -(aq + b\sigma \cos \xi)S, \qquad (45)$$

where we recall that $S = m_3^2 - 1/3$, and

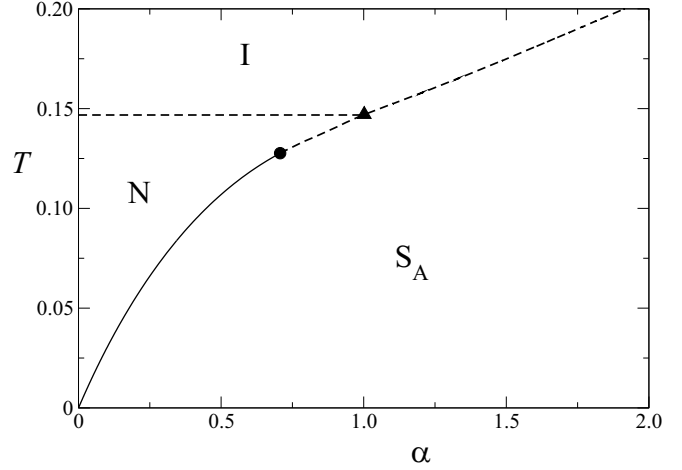$$E = -\tfrac{1}{3}(aq^2 + b\sigma^2). \qquad (46)$$

FIG. 1. Phase diagram of the McMillan model showing the isotropic (I), the nematic (N), and the smectic-A phases, in the plane temperature T versus the parameter α. The dashed and solid lines represent discontinuous and continuous transitions, respectively. The triangle and the full circle represent triple point and a tricritical point, respectively. The phase diagram corresponds also to the anisotropic model when $c = 0$.

The free energy per molecule is

$$F = \frac{1}{3}(aq^2 + b\sigma^2) - \frac{1}{\beta} \ln Z, \qquad (47)$$

where

$$Z = \int e^{\beta(aq + b\sigma \cos \xi)S} \sin \theta\, d\theta\, d\phi\, d\xi. \qquad (48)$$

Minimizing F with respect to the order parameters q and σ, we find the relations

$$q = \tfrac{3}{2}\langle S \rangle, \qquad (49)$$

and

$$\sigma = \tfrac{3}{2}\langle S \cos \xi \rangle, \qquad (50)$$

where the averages are calculated using the probability distribution $P(\mathbf{m}, \xi) = P(\theta, \phi, \xi)$,

$$P = \frac{1}{Z} e^{\beta(aq + b\sigma \cos \xi)S}. \qquad (51)$$

B. Phase transitions

The McMillan model has two order parameters, q and σ, associated to the nematic and smectic-A phases, respectively, and the parameters a, b, and β. Considering Eq. (47), the free energy F can be renormalized by the parameter a, so that the relevant parameters can be chosen to be the temperature $T = 1/\beta a$ and the ratio $\alpha = b/a$. The phase diagram expressed in terms of these two parameters is shown in Fig. 1. It was obtained by solving Eqs. (49) and (50), and by using the free energy (47) to find the absolute minimum.

The phase diagram shows the three regions, each one associated to a different phase:

  (a) isotropic, $q = 0$, $\sigma = 0$,
  (b) nematic, $q \neq 0$, $\sigma = 0$,
  (c) smectic-A, $q \neq 0$, $\sigma \neq 0$.

The transition from the isotropic to the nematic phase is a discontinuous transition. The line is found by setting $\sigma = 0$ in Eq. (47), the free energy becomes independent of b and is reduced to the free energy Eq. (34). In other words, the McMillan model is reduced to the Maier and Saupe model when $\sigma = 0$. As we have seen above a transition from isotropic to the nematic is discontinuous and occurs at $T = 0.146796$, and is thus represented by a horizontal line in the phase diagram of Fig. 1. A transition from the isotropic to the smectic-A phase is also possible and the transition is discontinuous, as can be seen in Fig. 1.

The transition line between the nematic and smectic-A phases has a tricritical point and is continuous up to this point becoming discontinuous beyond it. The continuous portion is obtained by setting $\sigma = 0$ in equation (49), which gives

$$q = \tfrac{3}{2}\langle S \rangle_0, \tag{52}$$

and by taking the limit $\sigma \to 0$ of the nonzero solution of equation (50). This task is accomplished by dividing the left and right hand side of equation (50) by σ and taking the limit $\sigma \to 0$. The result is

$$\frac{1}{\beta b} = \frac{3}{4}\langle S^2 \rangle_0. \tag{53}$$

The two averages above are calculated by using the probability distribution (37). The elimination of q in these two equations gives the critical line. A numerical calculation give the critical line shown in Fig. 1.

To find the tricritical point we observe that in the neighborhood of this point, both σ and the deviation $v = q_a - q$ of the nematic order parameter of the smectic-A phase from its value in the nematic phase are small quantities. This observation allows us to use an expansion of the free energy in powers of σ and v. In our analysis it suffices to write down an expansion up to fourth order in σ and up to second order in v because it turns out that v is of the order of σ^2.

Performing the expansion of the free energy we find

$$F = F_n + a_1 v^2 + a_2 \sigma^2 + a_3 v\sigma^2 + a_4 \sigma^4, \tag{54}$$

where F_n and the coefficients a_1, a_2, a_3, and a_4 depend on q. If we differentiate F with respect to v and set the result to zero, we find $v = -a_3\sigma^2/2a_1$, showing that v is of the order of σ^2. Replacing this result into the free energy (54), we get an expansion in σ which has only the powers σ^2 and σ^4. When the coefficient of σ^2 vanishes we get the condition for the critical line, which is the condition (53) already found. The condition for the tricritical point is found when the coefficient of σ^4 vanishes. This condition together with the equations (53), and (52) give the location of the tricrital point. A numerical calculation gives the location of the tricritical point, $T = 0.12765$, $r = 0.70701$, and the value of $q = 0.65778$ at this point.

V. ANISOTROPIC MODEL

A. Modified McMillan potential

The pair interaction $\mathrm{Tr}(\widehat{\Omega}^i \widehat{\Omega}^j)$ between two neighboring molecules is invariant under a simultaneous rotation of $\widehat{\Omega}^i$ and $\widehat{\Omega}^j$. When the invariance is broken, as in the nematic phase, the director may arise in any direction due to the full

rotational invariance of the pair potential. If one wishes to describe the smectic-A phase, the director should arise in the direction of the modulation. In this case the pair potential cannot have the full rotational symmetry but should hold the rotational symmetry around the smectic axis as is the case of the pair potential $(\widehat{\Omega}^i \widehat{\Omega}^j)_{zz}$. In accordance with the molecular theory this potential is replaced by $(\widehat{\Omega} \widehat{\Lambda})_{zz}$. Thus instead of the interaction (39) we consider the following pair interaction

$$\Phi_b = -\bar{b}\cos\xi (\widehat{\Omega} \widehat{\Lambda})_{zz}. \tag{55}$$

Accordingly, the corresponding energy is

$$E_b = -\tfrac{1}{2}\bar{b}(\widehat{\Lambda}^2)_{zz}. \tag{56}$$

Using the expression (55), the pair interaction of the modified McMillan model becomes

$$\Phi = -a\mathrm{Tr}(\widehat{Q}\,\widehat{\Omega}) - \bar{b}\cos\xi (\widehat{\Omega}\,\widehat{\Lambda})_{zz}, \tag{57}$$

and the corresponding energy becomes

$$E = -\tfrac{1}{2}a\mathrm{Tr}(\widehat{Q}^2) - \tfrac{1}{2}\bar{b}(\widehat{\Lambda}^2)_{zz}. \tag{58}$$

Assuming that the director will arise in the z direction, as desired, the tensors $\widehat{Q}$ and $\widehat{\Lambda}$ have the forms

$$\widehat{Q} = q\big(\mathbf{zz} - \tfrac{1}{3}\mathrm{I}\big), \tag{59}$$

$$\widehat{\Lambda} = \sigma\big(\mathbf{zz} - \tfrac{1}{3}\mathrm{I}\big), \tag{60}$$

and the pair potential (57) and the energy (58) become

$$\Phi = -(aq + b\sigma\cos\xi)\big(m_3^2 - \tfrac{1}{3}\big), \tag{61}$$

$$E = -\tfrac{1}{3}(aq^2 + b\sigma^2), \tag{62}$$

where b is related to $\bar{b}$ by $\bar{b} = (3/2)b$. Notice that these two expressions are identical to the expressions for the pair potential and energy of the McMillan model that we have discussed above and given by Eqs. (45) and (46), respectively. These results allow us to say that the modification just introduced does not change the results obtained for the McMillan model, reproducing the same phase diagram.

It is worth mentioning that the model as defined originally by McMillan is represented by the pair potential in the form (45), which is identical with Eq. (61). Since this expression can be derived from the pair potential either in the form (41) or in the form (57), each one of these two forms can be said to represent the McMillan model. However, the form (57) induces the appearance of the director in the z direction, which defines a smectic-A phase, whereas the form (41) does not do that and the director may arise in any direction. In this case the phase is smectic-A only by a declaration. In any case, it is immaterial whether we call the McMillan model the one represented by the pair potential in the form (41) or in the form (57).

B. Biquadratic pair potential

The pair potential (55) induces the appearance of the director in direction of the smectic axis, an thus the emergence of the smectic-A phase. The smectic-C may emerge if one introduces a pair potential which favors the tilting of the molecules with respect to the smectic axis, the z direction.

Govind and Madhusudana [21] have proposed a mechanism of tilt in smectic-C layers based on the relative shift of molecules due to presence of off-axis lateral dipoles in the molecules. This mechanics is represented by a pair potential which contribute with an energy that decreases with increasing tilt and is relevant only when the smectic layers are presence, implying that the tilt potential should be coupled to the smectic order parameter.

A second requirement concerns the rotational symmetry of the pair potential. Induced by the existence of an axis of symmetry, the pair potential should be invariant by a rotation around the axis but not by any rotation, as is the case of the pair potential $(\widehat{\Omega}^i \widehat{\Omega}^j)_{zz}$ considered above. This pair potential, however, yields only a tilt of ninety degrees. In order to obtain a tilt other than ninety degrees, we propose a biquadratic pair potential of the type $(\widehat{\Omega}^i \widehat{\Omega}^j)^2_{zz}$, which also holds a cylindrical symmetry.

In accordance with these considerations the pair potential describing the smectic phase will be a sum of two competing terms. The first is the pair potential (55), which favors the molecules to be in the z direction, which we write more explicitly as

$$\Phi_b = -\bar{b}\cos\xi(\Omega_{xz}\Lambda_{xz} + \Omega_{yz}\Lambda_{yz} + \Omega_{zz}\Lambda_{zz}), \qquad (63)$$

where $\Omega_{\mu\nu}$ and $\Lambda_{\mu\nu}$ are the elements of the matrices $\widehat{\Omega}$ and $\widehat{\Lambda}$, respectively, which are related by

$$\Lambda_{\mu\nu} = \langle\Omega_{\mu\nu}\cos\xi\rangle. \qquad (64)$$

The corresponding energy is

$$E_b = -\tfrac{1}{2}\bar{b}\left(\Lambda^2_{xz} + \Lambda^2_{yz} + \Lambda^2_{zz}\right). \qquad (65)$$

The second term, which favors the tilt of the molecules with respect to the z direction is the biquadratic potential introduce above, which, in accordance with the molecular theory, is given by,

$$\Phi_c = \bar{c}\cos\xi\left(L_{xx}\Omega^2_{xz} + L_{yy}\Omega^2_{yz} + L_{zz}\Omega^2_{zz}\right.$$
$$\left. + 2L_{xy}\Omega_{xz}\Omega_{yz} + 2L_{xz}\Omega_{xz}\Omega_{zz} + 2L_{yz}\Omega_{yz}\Omega_{zz}\right), \qquad (66)$$

where

$$L_{\mu\nu} = \langle\Omega_{\mu z}\Omega_{\nu z}\cos\xi\rangle. \qquad (67)$$

The corresponding energy is

$$E_c = \tfrac{1}{2}\bar{c}\left(L^2_{xx} + L^2_{yy} + L^2_{zz} + 2L^2_{xy} + 2L^2_{xz} + 2L^2_{yz}\right). \qquad (68)$$

The pair potential Φ of the anisotropic model is

$$\Phi = \Phi_a + \Phi_b + \Phi_c, \qquad (69)$$

which is the sum of Φ_c given above with the pair potential of the modified McMillan model Φ_b, given by Eq. (55), and the pair potential of the Maier and Saupe model,

$$\Phi_a = -a(Q_{xx}\Omega_{xx} + Q_{yy}\Omega_{yy} + Q_{zz}\Omega_{zz}$$
$$+ 2Q_{xy}\Omega_{xy} + 2Q_{yz}\Omega_{yz} + 2Q_{xz}\Omega_{xz}), \qquad (70)$$

where

$$Q_{\mu\nu} = \langle\Omega_{\mu\nu}\rangle. \qquad (71)$$

The corresponding energy is

$$E = E_a + E_b + E_c, \qquad (72)$$

which is the sum of E_c given above, the energy (56), and the energy of the Maier and Saupe model,

$$E_a = -\tfrac{1}{2}a\left(Q^2_{xx} + Q^2_{yy} + Q^2_{zz} + 2Q^2_{xy} + 2Q^2_{xz} + 2Q^2_{yz}\right). \qquad (73)$$

The free energy is

$$F = -E_a - E_b - E_c - \frac{1}{\beta}\ln Z, \qquad (74)$$

$$Z = \int e^{-\beta(\Phi_a+\Phi_b+\Phi_c)}\sin\theta\,d\theta\,d\phi\,d\xi, \qquad (75)$$

and the averages (64), (67), and (71) are determined by using the probability density $P(\mathbf{m}, \xi) = P(\theta, \phi, \xi)$, given by

$$P = \frac{1}{Z}e^{-\beta(\Phi_a+\Phi_b+\Phi_c)}. \qquad (76)$$

The pair potential Φ_c compels the director to be tilted with a certain angle ω, which is the polar angle of the director with respect to the z direction. However, due to the rotational invariance of Φ around the z direction, the director may arise with any azimuthal angle. We choose the azimuthal angle in such a way that the director will lie in the xy plane. As a consequence, some of the quantities $Q_{\mu\nu}$, $\Lambda_{\mu\nu}$, and $L_{\mu\nu}$ vanish and the pair potentials acquire the simpler forms

$$\Phi_a = -a(Q_{xx}\Omega_{xx} + Q_{yy}\Omega_{yy} + Q_{zz}\Omega_{zz} + 2Q_{xz}\Omega_{xz}), \qquad (77)$$

$$\Phi_b = -\bar{b}\cos\xi(\Omega_{xz}\Lambda_{xz} + \Omega_{zz}\Lambda_{zz}), \qquad (78)$$

$$\Phi_c = \bar{c}\cos\xi\left(L_{xx}\Omega^2_{xz} + L_{zz}\Omega^2_{zz} + 2L_{xz}\Omega_{xz}\Omega_{zz}\right). \qquad (79)$$

The corresponding energies will be

$$E_a = -\tfrac{1}{2}a\left(Q^2_{xx} + Q^2_{yy} + Q^2_{zz} + 2Q^2_{xz}\right), \qquad (80)$$

$$E_b = -\tfrac{1}{2}\bar{b}\left(\Lambda^2_{xz} + \Lambda^2_{zz}\right), \qquad (81)$$

$$E_c = \tfrac{1}{2}\bar{c}\left(L^2_{xx} + L^2_{zz} + 2L^2_{xz}\right). \qquad (82)$$

C. Phase transitions

The present anisotropic model is defined by the pair potential $\Phi = \Phi_a + \Phi_b + \Phi_c$ and has three parameter a, $\bar{b}$, $\bar{c}$, and β. For convenience we define $\bar{a} = (3/2)a$ and $c = (2/3)\bar{c}$, because the factor $3/2$ appears very often. Considering Eq. (74), the free energy F can be renormalized by the parameter a, so that the relevant parameters can be chosen to be the temperature $T = 1/\beta a$, and the ratios $\alpha = b/a$ and c/a. The quantities related to the order parameters are Q_{xx}, Q_{yy}, Q_{zz}, Q_{xz}, and Λ_{zz}, Λ_{xz}, L_{xx}, L_{zz}, L_{xz}, which are averages given by Eqs. (71), (64), and (67). The averages are determined self-consistently by using the probability distribution (76).

The order parameter q of the nematic phase and the tilt angle are determined from Q by the representation

$$\widehat{Q} = q_1\mathbf{nn} + q_2\mathbf{yy} + q_3\mathbf{pp}, \qquad (83)$$

as explained in the Appendix, where the director $\mathbf{n}$ is related to the tilt angle by

$$\mathbf{n} = \mathbf{x}\sin\omega + \mathbf{z}\cos\omega. \qquad (84)$$

In accordance with the choice we have made above, the director $\mathbf{n}$ is chosen to lie in the xz plane. From q_1, one obtains the
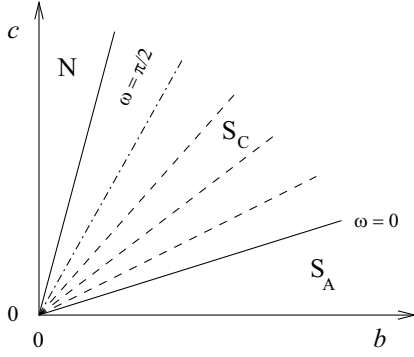
FIG. 2. Ground state or zero temperature phase diagram showing the nematic (N) and the two smectic phases. The smectic-C occurs between the two solid lines. The dashed lines are lines of constant tilt angle ω. In the region between the dot-dashed line and the solid line the tilt angle is $\omega = \pi/2$.

nematic order parameter

$$q = \tfrac{3}{2} q_1. \tag{85}$$

The order parameter s of the smectic-C is related to the tilt angle by

$$s = \sin \omega. \tag{86}$$

In an analogous way the tensor Λ is represented by

$$\widehat{\Lambda} = \sigma_1 \mathbf{n}' \mathbf{n}' + \sigma_2 \mathbf{y} \mathbf{y} + \sigma_3 \mathbf{p}' \mathbf{p}', \tag{87}$$

and the order parameter σ is obtained from

$$\sigma = \tfrac{3}{2} \sigma_1. \tag{88}$$

The four phases predicted by the present model are as follows:
  (a) isotropic, $q = 0$, $\sigma = 0$,
  (b) nematic, $q \neq 0$, $\sigma = 0$,
  (c) smectic-A, $q \neq 0$, $\sigma \neq 0$ s=0;
  (d) smectic-C, $q \neq 0$, $\sigma \neq 0$, $s \neq 0$.

At zero temperature, the possible thermodynamic phases are obtained by the minimization of the energy (72) whose results are shown in Fig. 2. If c is nonzero, the two smectic phases as well as the nematic phase may be present depending on the value of the parameter b. The transition between the smectic-A and smectic-C is described by the straight line $c = (9/8)b$, whereas that of the transition between the smectic-C and the nematic is $c = 9b$. in the region between the lines $c = (9/2)b$ and $c = 9b$, the tilt angle is $\pi/2$.

When $c = 0$, the anisotropic model reduces to the McMillan model, and the phase diagram is that shown in Fig. 1, which shows no smectic-C phase. As the parameter c becomes nonzero, the smectic-C phase emerges as can be seen in Fig. 3 for the case of $c/a = 2$.

The transition from the isotropic to the nematic is obtained by setting $\Lambda_{\mu\nu} = 0$ and $L_{\mu\nu} = 0$. The pair potential becomes independent of b and c and the model reduces to the Maier and Saupe. The transition from nematic to the isotropic is independent of the parameter b and c and is represented by a horizontal straight line in the phase diagram of Fig. 3.

The transition lines from the smectic-A to the isotropic and from the smectic-A to the nematic are obtained by taking into
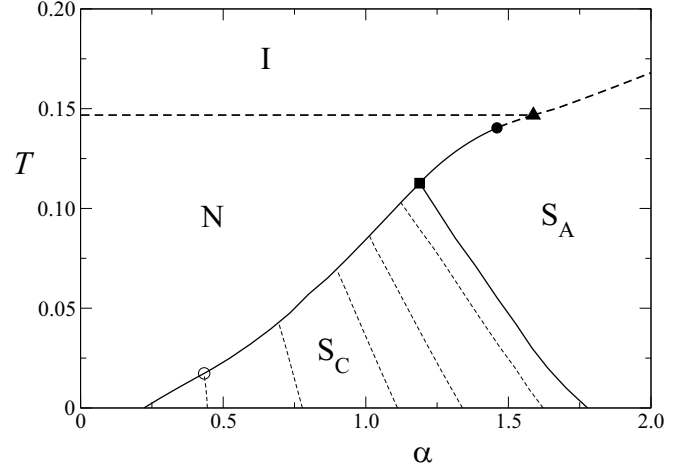

FIG. 3. Phase diagram of the anisotropic model showing the isotropic (I), the nematic (N), the smectic-A, and the smectic C phases, in the plane temperature T versus the parameter α for $c/a = 2$. The heavy dashed line and the solid line represent discontinuous and continuous transitions, respectively. The triangle and the full circle represent a triple point and a tricritical point, respectively, whereas the square represents a Lifshitz point. The light dashed lines are lines of constant tilt angle ω. Along the line separating the smectic-C and the smectic-A, $\omega = 0$. Along the critical line separating the N and S_C phases the tilt angle ω decreases from $\omega = \pi/2$ at the empty circle to $\omega = 0$ at the Lifshitz point. In the smectic-C domain, the triangle region with the open circle has tilt angle $\omega = \pi/2$.

account that in the smectic-A phase, $\widehat{Q}$ and $\widehat{\Lambda}$ will be uniaxial of the form

$$\widehat{Q} = q \left(\mathbf{nn} - \tfrac{1}{3} \mathbf{I} \right), \tag{89}$$

$$\widehat{\Lambda} = \sigma \left(\mathbf{nn} - \tfrac{1}{3} \mathbf{I} \right), \tag{90}$$

as we have considered in the case of the McMillan model. In an equivalent form we may say that the probability distribution (76) is independent of ϕ. As a consequence, $Q_{xz} = 0$, $\Lambda_{xz} = 0$, and $L_{xz} = 0$, and the pair potential becomes

$$\Phi = -(\bar{a} Q_{zz} + \bar{b} \cos \xi \, \Lambda_{zz}) \Omega_{zz}$$
$$+ \bar{c} \cos \xi \left(L_{xx} \Omega_{xz}^2 + L_{zz} \Omega_{zz}^2 \right), \tag{91}$$

and the corresponding energy is

$$E_a = -\tfrac{1}{2} \bar{a} Q_{zz}^2 - \tfrac{1}{2} \bar{b} \Lambda_{zz}^2 + \tfrac{1}{2} \bar{c} \left(L_{xx}^2 + L_{zz}^2 \right). \tag{92}$$

The transition from the nematic to the smectic-A is similar to that of the McMillan model. It has a tricritical point and is continuous up to this point, becoming discontinuous beyond it as shown in Fig. 3. The continuous portion, which occurs when σ vanishes continuously, can be found by a manner similar to that employed in the case of the McMillan model. The other transition lines shown in Fig. 3 are obtained by solving numerically Eqs. (71), (64), and (67). To locate the discontinuous transition one compares the free energy of each phase.

The phase diagram of the anisotropic model differs from the phase diagram of the McMillan model by the presence of the smectic-C region. The smectic-C phase is separated from

the nematic phase by a continuous transition. As one crosses the transition line from the smectic-*C* region, where the tilt angle is nonzero, the order parameter σ vanishes continuously. However, the tilt angle approaches a nonzero value except at the Lifshitz point. Along the transition line the tilt angle is nonzero and vanishes as one reaches the Lifshitz point. A Lifshitz point is here understood as the point at which both σ and s vanish and is located at the point where the three phases, nematic, smectic-*A*, and smectic-*C*, meet.

The transition from the smectic-*C* to the smectic-*A* phase is also continuous. As one crosses this line coming from the smectic-*C* region the tilt angle ω vanishes continuously so that the whole transition line is a line of $\omega = 0$.

VI. DISCUSSION AND CONCLUSION

We have considered a molecular model for the phase transitions between the isotropic, nematic, smectic-*A*, and smectic-*C* phases. The part of the phase diagram showing the first three phases is similar to that of the McMillan molecular model. The transition from the smectic-*A* phase has a continuous and a discontinuous portion with a tricritical point. The transition from the nematic to the isotropic is discontinuous as well as from the smectic-*A* to the isotropic phase. The smectic-*C* region of the phase diagram occurs between the nematic and smectic-*A* phases, that is, the smectic-*C* borders the nematic and the smectic-*A* phase.

As one crosses the transition line from the smectic-*C* to the nematic region, the order parameter σ vanishes continuously but the tilt angle has a finite value at the transition, with the exception of the Lifshitz point at which the tilt angle vanishes. As one crosses the transition line from the smectic-*C* to the smectic-*A* the tilt angle vanishes continuously and the order parameter σ remains finite, except at the Lifshitz point at which σ vanishes.

The tilt angle of the director in the smectic-*C* phase may take any value, depending on the value of the parameters. If one varies the parameters T and α in such a way that the tilt angle remains constant, a line is described, as shown in Fig. 3. However, if the tilt angle is 90°, as one varies the parameters, an extended region is described. This region is shown in Fig. 3 as the triangle with an empty circle. In other words, a smectic-*C* phase with a tilt angle of 90° is stable against arbitrary variation of the parameter.

To understand how the smectic-*C* phase emerges, it is helpful to analyze the Landau free energy that one would obtain from the present molecular model by an expansion of the free energy in powers of the order parameter. If such an expansion is performed one finds, up to fourth order in σ,

$$F = F_n + (a_0 + a_1 s^2 + a_2 s^4)\sigma^2 + a_3\sigma^4, \qquad (93)$$

where F_n and the coefficients a_0, a_1, a_2, may depend on q but not on s and a_3 may depend on q and s. At the transition from the smectic-*C* to the nematic phase, the value of s, which is related to the tilt angle by $s = \sin\omega$, is determined by the minimum of the expression that multiply σ^2. Due to the presence of the term $a_4 s^4$, the value of s may be distinct from zero, giving rise to the smectic-*C* phase. In the present molecular model this crucial term is a consequence of the use of the biquadratic pair potential $(\Omega_i\Omega_j)^2_{zz}$. It is worth mentioning

that if the biquadratic pair potential is replaced by $(\Omega_i\Omega_j)_{zz}$ then the expression multiplying σ^2 would have only the two terms $a_0 + a_1 s^2$, in which case the minimum would be either $s = 0$ ($\omega = 0$) or $s = 1$ ($\omega = \pi/2$), and we would not get a smectic-*C* phase with a tilt distinct from 90°.

The phase diagram of Fig. 3 has the same topology of the phase diagrams obtained by other authors but is particularly similar to the one obtained by Drossinos and Ronis [16] by a molecular-field approach distinct from ours. The main similarities include the presence of the tricritical point on the line separating the smectic-*A* and smectic-*C* phases and the presence of the NAC point with the following geometric properties. Near the point NAC, the lines NA and NC belong to the same straight line whereas the line AC meet this line at a nonzero angle. It should be mentioned that a biaxial, but translationally disordered phase has been predicted by a dislocation-loop theory, which is located near the NAC point and interposed between the nematic and smectic-*C* phases [43].

As a final remark, the results obtained here should be understood as valid within a mean field theory, which neglects fluctuations. If one goes beyond mean field theory, and includes fluctuations effects, some qualitative results might change. For instance, if fluctuations are taken into account, the phase transition from an isotropic state to a periodic structure turns out to be a discontinuous phase transition [44,45].

APPENDIX: TENSOR REPRESENTATION

A symmetric tensor $\widehat{Q}$ can be represented by

$$\widehat{Q} = q_1\mathbf{nn} + q_2\mathbf{rr} + q_3\mathbf{pp}, \qquad (A1)$$

where $\mathbf{n}$, $\mathbf{r}$, and $\mathbf{p}$ are three mutually perpendicular unit vectors such that $\mathbf{n} \times \mathbf{r} = \mathbf{p}$, and hold the property

$$\mathbf{nn} + \mathbf{rr} + \mathbf{pp} = I, \qquad (A2)$$

where I is the identity matrix. It is easily shown that the unit vectors are the eigenvector of $\widehat{Q}$ and q_1, q_2, and q_3 the corresponding eigenvalues. It suffices to observe that $\widehat{Q}\mathbf{n} = q_1\mathbf{n}$, $\widehat{Q}\mathbf{r} = q_2\mathbf{r}$, and $\widehat{Q}\mathbf{p} = q_3\mathbf{p}$, which follows from the orthogonality of the unit vectors.

If the three eigenvalues are distinct, the tensor is a biaxial tensor. If two eigenvalues are equal and distinct from the third, the tensor is a uniaxial tensor. In this case, letting $q_3 = q_2$, the representation becomes

$$\widehat{Q} = (q_1 - q_2)\mathbf{nn} + q_2 I, \qquad (A3)$$

where we used the property (A1). This tensor is invariant under rotation around the vector $\mathbf{n}$ and for this reason it is also called an axially symmetric tensor.

If $\widehat{Q}$ is traceless, which means that $q_2 = -q_1/2$, the representation becomes

$$\widehat{Q} = q\left(\mathbf{nn} - \tfrac{1}{3}I\right), \qquad (A4)$$

where $q = 3q_1/2$.

If the tensor has the three eigenvalues equal, in which case $q_3 = q_2 = q_1$, then it is represented by

$$\widehat{Q} = q_1 I, \qquad (A5)$$

and if in addition it is traceless then $q_1 = 0$, and the tensor vanishes identically.

Let us consider a traceless tensor such that one of its eigenvector has the y direction, that is,

$$\widehat{Q} = q_1 \mathbf{nn} + q_2 \mathbf{yy} + q_3 \mathbf{rr}, \qquad (A6)$$

where $q_1 + q_2 + q_3 = 0$, and

$$\mathbf{n} = \mathbf{x} \sin \omega + \mathbf{z} \cos \omega, \qquad (A7)$$

$$\mathbf{r} = \mathbf{x} \cos \omega - \mathbf{z} \sin \omega. \qquad (A8)$$

The Cartesian components $Q_{xy} = Q_{yx} = Q_{yz} = Q_{zy} = 0$ of the tensor $\widehat{Q}$ vanish and the other are

$$Q_{xx} = q_1 \sin^2 \omega + q_3 \cos^2 \omega, \qquad (A9)$$

$$Q_{zz} = q_1 \cos^2 \omega + q_3 \sin^2 \omega, \qquad (A10)$$

$$Q_{yy} = q_2, \qquad (A11)$$

$$Q_{xz} = Q_{zx} = (q_1 - q_3) \sin \omega \cos \omega. \qquad (A12)$$

The eigenvalues q_1, q_2, and q_3, and the angle ω are obtained from the relation

$$q_1 = \tfrac{1}{2}\left(\sqrt{(Q_{zz} - Q_{xx})^2 + 4Q_{xz}^2} - Q_{yy} \right), \qquad (A13)$$

$$q_3 = -\tfrac{1}{2}\left(\sqrt{(Q_{zz} - Q_{xx})^2 + 4Q_{xz}^2} + Q_{yy} \right), \qquad (A14)$$

$$q_2 = Q_{yy}, \qquad (A15)$$

$$\tan 2\omega = \frac{2Q_{xz}}{Q_{zz} - Q_{xx}}. \qquad (A16)$$

We recall that

$$Q_{xx} + Q_{yy} + Q_{zz} = 0, \qquad (A17)$$

and remark that

$$\mathrm{Tr}(\widehat{Q}^2) = Q_{xx}^2 + Q_{yy}^2 + 2Q_{xz}^2 + Q_{zz}^2 = q_1^2 + q_3^2 + q_2^2. \quad (A18)$$

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