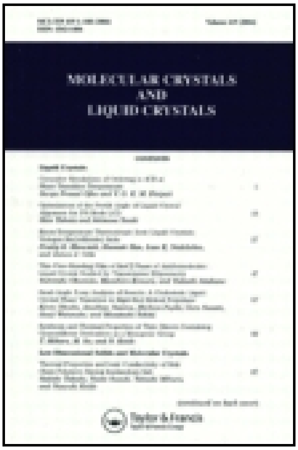

Molecular Crystals and Liquid Crystals

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Symmetry Considerations for Plastic Crystal–Crystal Phase Transitions†

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Molecular and lattice symmetry effects on the order of plastic crystal-crystal phase transitions are discussed in the context of Landau theory.

I INTRODUCTION

"It is the general rule that, when the envelope of the molecule becomes an oblate sphere, or is pear-shaped, the rotational transition becomes of the first order."[1] Such phenomenological rules relating molecular symmetry and the order of plastic crystal phase transitions are not especially useful in understanding symmetry effects on the order of phase transitions. In this letter, Landau theory will be used to explore the role of molecular and lattice symmetry in determining the order of plastic crystal-crystal transitions. Specific examples will not be considered except where they are useful in illustrating a specific point. It is not the purpose of this paper to construct a general theory of plastic crystal transitions, rather to illustrate steps necessary in forming a theory of any particular transition.

In the second section, the relation between molecular rotational and inversion symmetry and the form of the tensor order parameter will be discussed. In section III the construction of a Landau theory, and the relation between the form of the free energy expansion and the order of the phase transition will be discussed. The similarity between the theory of plastic crystal transitions and the Cauchy theory of elasticity[2] will be noted. The interplay between molecular and lattice symmetry and phase transition order

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will be stressed. In section IV the direct inspection method[3,4] of tensor coupling constant determination will be briefly discussed for a simple two dimensional phase transition. Finally, in the last section, lattice effects on phase transitions for molecules consistent with more than one order parameter symmetry will be briefly noted.

II THE ORDER PARAMETER

In a plastic crystal phase molecules are arranged so that their centers lie on a crystal lattice, however the molecules remain free to perform random rotations at each lattice site.[5,6] In a crystalline phase this rotational motion is frozen out, giving complete order at each lattice site. A quantity called the order parameter specifies the orientation of the molecule, or groups of molecules in some cases, with respect to the fixed lattice of the crystal.

In the context of mean field theory[7] the order parameter is found by factoring the two body intermolecular potential into a part which only depends on the Euler angles of molecule 1 with respect to the crystal lattice and another part which only depends on the coordinates of molecule 2. A statistical average over the coordinates of molecule 2 gives the order parameter of the system. In order to proceed in this manner however, it is necessary to use a model two-body interaction.

Another method, the Landau theory approach,[8] avoids the complications of Euler angles, and relys only on relatively simple molecular rotational and inversion symmetry arguments to obtain the order parameter. This method will be used here.

The order parameter must (i) be able to completely specify the orientation of the molecule with respect to the crystal axes, and (ii) have sufficient symmetry that when the molecule is rotated through a set of Euler angles into itself, this transformation applied to the order parameter tensor leaves it unchanged.

Objects which have the rotational and inversion symmetry of the spherical harmonic Y_{LM} or Wigner $D^L_{MM'}$ function transform as a tensor of rank L.[9] An M-fold axis of the molecule means the molecule has the rotational properties of $e^{iM\phi}$. The molecule must be assigned L even (odd) if it goes to itself (or not) upon inversion through its center. The tensor order parameter is the lowest rank tensor consistent with both the inversion and rotation symmetries of the molecule.

Just as a second rank tensor has two symmetries; symmetric and antisymmetric, so a tensor of rank L can have a number of symmetries which give relations between different elements of the tensor related by permutations of the indices. These different tensor symmetries can be constructed by the use of the Young tableaux.[10] A highly symmetrical molecule is generally only consistent with a few tensor symmetries of those possible for a tensor of rank L, as can be shown by the direct inspection method. These allowed tensor symmetries depend only on the molecular configuration and are independent of the orientation of the molecule with respect to the crystal axes.

The order parameter for a plastic crystal-crystal phase transition, as discussed previously, is the lowest rank tensor consistent with molecular symmetry that will completely specify the orientation of the molecule relative to the crystal axes. Because there are no lower rank tensors which can uniquely determine the molecular orientation, all tensors formed from the order parameter tensor by contractions of pairs of indices must vanish. This simplifies the free energy expansion, as will be shown in the next section, but also adds a constraint to the variational problem.

III THE FREE ENERGY EXPANSION

The free energy of a thermal system is a scalar, i.e. independent of the coordinate system used for a calculation. Therefore, we can express the free energy in terms of the order parameter tensor $\mathbf{Q}$ by summing all invariants of all orders in $\mathbf{Q}$ consistent with symmetry.[8]

For plastic crystals in which there is only one type of lattice site in the ordered phase the free energy expansion takes the form

$$\begin{aligned} F = {} & \tfrac{1}{2}a_{(ijk\ldots)(lmn\ldots)}Q_{(ijk\ldots)}Q_{(lmn\ldots)} \\ & + \tfrac{1}{3}b_{(ijk\ldots)(lmn\ldots)(pqr\ldots)}Q_{(ijk\ldots)}Q_{(lmn\ldots)}Q_{(pqr\ldots)} \\ & + \textit{higher order terms} + \textit{gradient terms} \end{aligned} \tag{1}$$

where repeated indices are assumed to be summed. Equation (1) is analogous to the Cauchy theory of elasticity,[2] where the order parameter plays the role of the strain tensor, and the coupling constants are analogous to the elastic modulus tensor. As was shown in the previous section, all coupling constant terms giving contractions of pairs of indices on one order parameter must be dropped.

If there is more than one type of lattice site in the low temperature, ordered phase, then the free energy can be diagonalized in lowest order by taking linear combinations of order parameters similar to those for the antiferromagnet.[11–13] In this paper we will only consider one order parameter, $\mathbf{Q}$, in the low temperature phase.

In doing a variational calculation making use of the free energy expansion (1), the constraints may be included by a Lagrange multiplier. For methane the order parameter is a completely symmetric third rank tensor.[12] The quantity to be minimized is

$$F + \lambda_\varepsilon Q_{\varepsilon\eta\eta} \tag{2}$$

where λ_x, λ_y, and λ_z are the Lagrange multipliers, and F is given by Eq. (1).

Although Eq. (2), in expanded form, is imposing, the physics is no different from any other phase transition. From mean field arguments we know that the components of $a_{(ijk\ldots)(lmn\ldots)}$ in Eq. (1) behave as:

$$a_{(ijk\ldots)(lmn\ldots)} = |A_{(ijk\ldots)(lmn\ldots)}|(T - T_c^{(ijk\ldots)(lmn\ldots)}) \tag{3}$$

One component, or set of components related by symmetry or connected by constraint relations, will have a phase transition while the other components of **Q** will be zero.

As is well known, the presence of a cubic term in **Q** in the free energy expansion (1) means the phase transition from plastic crystal to crystal must be of first order, i.e. having a latent heat.[14] The presence or absence of such a term can be determined by molecular and lattice symmetry arguments, as shown below. If there is no cubic term in **Q**, then the order of the phase transition is determined by the details of the intermolecular potential and no general statements can be made.

From the previous discussion we know that if the molecule has even parity, then the order parameter **Q**, and the coupling constants **a** and **b** must have even rank.

The tensor coupling constants **a**, **b**, etc., must be consistent with the rotational and inversion symmetry of the lattice of the high temperature, disordered phase. If the lattice of the high temperature phase has inversion symmetry, then all odd-ranked coupling constants in Eq. (1) vanish. This argument is identical to that for piezoelectric materials.[3] Thus, if the order parameter is an odd-rank tensor, reflecting an odd parity molecule, and the lattice has inversion symmetry, all odd terms in (1) vanish. In this case the phase transition may be of either order, as in methane.[13]

There are two other cases of interest (i) Q odd rank and the lattice has no inversion symmetry (as in some cases of a Bravais lattice with basis) and (ii) Q even rank and any lattice symmetry. At first glance it appears that these latter cases allow a cubic term in Eq. (1) and must have a first order phase transition. However, lattice rotational symmetry and order parameter constraint conditions must be examined carefully in these two cases to see if cubic terms of interest vanish. To illustrate the care that must be exercised, in the next section we will discuss the smectic B—smectic E liquid crystal phase transition. This transition can be viewed as a two dimensional plastic crystal-two dimensional crystal phase transition.

IV THE DIRECT INSPECTION METHOD

As was previously mentioned, the free energy expansion (1) is analogous to that used in the theory of elasticity. Therefore it should not be surprising that we can determine the independent elements of the coupling tensors by the same symmetry arguments used to determine the elastic modulus tensor.[2]

The coupling constant tensors must have the symmetry of the high temperature, disordered, phase. All tensors T_{ijk} transform under rotation, reflection, and inversion according to the well-known relations[3]

$$T'_{ijk} = a_{il}a_{jm}a_{kn}T_{lmn}, \tag{4}$$

and similarly for tensors of arbitrary rank. If we know how the product of crystal axes transforms under crystal reflection and inversion, we know how the corresponding tensor coupling constant element transforms. For example, if the crystal is unchanged under the reflection $y \to -y$, then the tensor term $xyz \to -xyz$. Since the crystal is unchanged $xyz = -xyz = 0$. Similarly $T_{xyz} = -T_{xyz} = 0$, if **T** is to have the same symmetry as the lattice. Inversions are treated identically.[4]

Rhombohedral systems[2] with 3-fold axes and hexagonal systems with 6-fold axes can also be handled by direct inspection. For a 3-fold axis parallel to the z-axis perpendicular to a vertical mirror plane, choose a new coordinate system

$$\begin{aligned} \zeta &= x + iy \\ \eta &= x - iy \\ z& \end{aligned} \tag{5}$$

When the crystal is rotated through $2\pi/3$ around z, $\zeta \to \zeta e^{2\pi i/3}$, $\eta \to \eta e^{-2\pi i/3}$, $z \to z$. Only those tensor elements unchanged by this rotation can be non-zero, i.e. those containing ζ three times, η three times, or ζ and η in the same number of times. Also, under the operation $y \to -y$ we have $\zeta \to \eta$, and $\eta \to \zeta$. Therefore, tensor terms with $\zeta\zeta\zeta$ are identical to those with $\eta\eta\eta$, and $\zeta\eta = \eta\zeta$.

By using these simple arguments, virtually all tensor coupling constant elements for **a** and **b** in Eq. (1) may be found without difficulty for a known lattice. Also, for a given molecular orientation, tensor order parameter elements may be obtained by identical means.

As an example, consider the case of the liquid crystal phase transition: smectic B → smectic E.[15–19] This can be viewed as a two dimensional plastic crystal–two dimensional crystal transition. Imagine a two dimensional hexagonal lattice, and at each lattice site we have a benzene ring rotating around its para-axis, which is perpendicular to the plane. In the spectic B phase the molecules have free rotation around the para-axis. In the smectic E phase this rotation freezes out at each lattice site. The order parameter for this transition has been shown to be a symmetric second rank tensor of dimension two.

Consider first the coupling tensor **a** for the second order term in **Q**. From the previous discussion, direct inspection shows we have only two distinct elements to $a_{ijkl}Q_{ij}Q_{kl}$:

$$a_{\zeta\eta\zeta\eta}Q_{\zeta\eta}Q_{\zeta\eta} = a_{\zeta\eta\zeta\eta}(Q_{xx} + Q_{yy})^2 \tag{6a}$$

and

$$a_{\zeta\zeta\eta\eta}Q_{\zeta\zeta}Q_{\eta\eta} = a_{\zeta\zeta\eta\eta}[(Q_{xx} - Q_{yy})^2 + 4Q_{xy}^2]. \tag{6b}$$

From the constraint condition $Q_{ii} = 0$ we see the contribution in (6a) vanishes.

From the discussion in Section III, we would be tempted to conclude that the even order parameter and lattice parity would force this phase transition to be of first order due to the presence of a cubic term in Eq. (1). However, as we shall see, this isn't true. The tensor **b** in Eq. (1) has two distinct elements:

$$b_{\zeta\zeta\zeta\eta\eta\eta}Q_{\zeta\zeta}Q_{\zeta\eta}Q_{\eta\eta} = b_{\zeta\zeta\zeta\eta\eta\eta}[(Q_{xx} - Q_{yy})^2 + 4Q_{xy}][Q_{xx} + Q_{yy}] \tag{7a}$$

and

$$b_{\zeta\eta\zeta\eta\zeta\eta}Q_{\zeta\eta}Q_{\zeta\eta}Q_{\zeta\eta} = b_{\zeta\eta\zeta\eta\zeta\eta}[Q_{xx} + Q_{yy}]^3. \tag{7b}$$

The constraint condition $Q_{ii} = 0$ causes both terms in Eq. (7) to vanish, *and the order of the phase transition must be determined by the details of* the intermolecular force. Thus the order of a plastic crystal-crystal phase transition is determined by a variety of symmetry considerations of both the molecule and the lattice.

V DISCUSSION AND CONCLUSIONS

Thus far only order parameters of one symmetry have been considered. However, for molecules that are consistent with order parameters of more than one symmetry there are additional considerations. For a molecule consistent with two tensor symmetries Q^{I} and Q^{II} the free energy to lowest order can be expressed in the form

$$\mathbf{F} = \mathbf{a}^{\mathrm{I}}\mathbf{Q}^{\mathrm{I}}\mathbf{Q}^{\mathrm{I}} + \mathbf{a}^{\mathrm{II}}\mathbf{Q}^{\mathrm{II}}\mathbf{Q}^{\mathrm{II}} + \mathbf{a}^{\mathrm{I-II}}\mathbf{Q}^{\mathrm{I}}\mathbf{Q}^{\mathrm{II}} + \lambda^{\mathrm{I}}\mathbf{Q}^{\mathrm{I}} + \lambda^{\mathrm{II}}\mathbf{Q}^{\mathrm{II}} \tag{8}$$

where λ^{I} and λ^{II} are Lagrange multipliers for the various constraint equations. If the lattice has sufficient symmetry such that the $\mathbf{a}^{\mathrm{I-II}}$ tensor vanishes, then the phase transition must be to a phase in which the order parameter has symmetry I or symmetry II, but not to the general tensor.

An example of such a case, in principle, occurs in the case of the smectic B → smectic E phase transition. If the benzene ring rotates around an axis which is at a slight angle to the para-axis of the ring, then symmetry is consistent with either a symmetric or an antisymmetric second rank tensor order parameter.[10] However, it is easily seen that the hexagonal lattice requires the $\mathbf{a}^{\mathrm{I-II}}$ term in Eq. (8) to vanish, and so the phase transition can in principle only go the state of the symmetric tensor or the antisymmetric tensor, but not a general tensor of mixed symmetry. Actually, the antisymmetric order parameter is unphysical because it rotates as a scalar, and cannot have a phase transition. However, this example illustrates the interplay of lattice and molecular symmetry effects.

This concludes the discussion of symmetry effects on the order of phase transitions in plastic crystals. The purpose of this discussion has been to explore the wide range of symmetry interactions that go into determining phase transition order. Obviously, simple rules concerning molecular oblateness, etc., are inadequate to give an understanding of these phase transitions. The symmetry of the molecule as well as that of its environment must be investigated in detail to make predictions.

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