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Matthew A. Marcus [a] & Bell Laboratories [a]
[a] Murray Hill, N.J., 07974

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LACK OF SECOND-ORDER PHASE TRANSITIONS IN CUBIC "BLUE" PHASES IN LANDAU THEORY

Matthew A. Marcus
Bell Laboratories
Murray Hill, N.J. 07974

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ABSTRACT

The possibility of second-order transitions among body-centered or simple cubic "blue" phases is investigated with the assumption that Landau theory, as used by Brazovskii, Hornreich and Shtrikman and others, is valid. In all cases, any phase transitions that exist are found to be first-order. This result is independent of the structure within the unit cell of either phase.

I. INTRODUCTION

In many cholesterogens that have a "blue" phase (BP), there are actually two or three different BP's, all within 2°C of the isotropic point[1]. Two of these BP's have three-dimensionally periodic order-parameter fields, and hence have the symmetries of crystals[2–4]. The other (fog) phase is not periodic[2,3], and will not be discussed here. In many systems, both BP's are simple or body-centered cubic[3,4]. Recent evidence shows that the symmetries in at least two compounds are body-centered cubic (bcc) for BPI (the lower-temperature phase), and simple cubic (sc) for BPII (higher temperature)[5].

The BPI↔BPII transition is usually first-order, as can be seen microscopically and spectroscopically[1,2,4,5]. However, there have been claims for a second-order transition, either between BPI and BPII or between two forms of BPI[4]. Evidence has been put forward strongly suggesting that the putative second-order transition is actually an artifact of the use of mixtures[6], so it is not clear that such a phase transition actually can be second order. In this paper, I show that within the framework of Landau theory there can be no second-order transition between sc phases, bcc phases, or between a bcc and a simple cubic phase.

II. METHOD

The proof starts with the assumption that Landau theory, as applied by Brazovskii, et. al., Hornriech and Shtrikman, and others[7,8], is appropriate to this problem. I therefore invoke a tensor order parameter, which is broken up into two parts. The first is the bcc-symmetry part appropriate to the higher-symmetry phase. To this part is added another part of sc symmetry which is zero in one phase and non-zero in the other.

I define "bcc symmetry" and "sc symmetry" by reference to the non-zero Fourier components of Q, $\tilde{Q}_{hkl}$, with hkl being Miller indices. A "bcc" tensor is defined by $\tilde{Q}_{hkl}=0$ for $h+k+l=odd$, and a "pure sc" one by $\tilde{Q}_{hkl}=0$ for $h+k+l=even$. A "sc" tensor is anything else. Therefore, face-centered cubic is treated as a subset of simple cubic. The importance of this notation is that there are no invariant products involving an odd number of "pure sc"'s and any number of bcc's.

For convenience in labeling, I assume that the phase without the "extra" term is the BPI, as it probably is. The BPI solution is considered to be a solution even in the BPII region. However, the complete order-parameter field, with the "extra" term is the lowest-energy solution. The amplitude of the "extra" part is taken to be an order parameter of the transition. Also, the inverse lattice parameter $2\pi/a_0$ is separated into a BPI part, and a BPII part which is zero in the BPI phase, and is another order parameter.

The free energy is written in terms of the two new order parameters (sc part and change in inverse lattice parameter), and the possible second-order transitions searched for. I will then show that at these transition points, there is a combination of order parameters that make the free energy lower than that of the BPI phase. It will develop that if the "extra" ordering is "pure sc", then the transition may be second-order, but it is always possible to add a bcc part and lower the free energy, thus ending up with a first-order transition again. This result shows that there can be no second-order transitions, since all possible ones are "masked" by first-order transitions. The extensions to other crystal structures will be discussed.

III. THE CALCULATION

We write the free energy F in the following form[7,8]:

$$F = a\,\mathrm{Tr}Q^2 - b\,\mathrm{Tr}Q^3 + c\,\mathrm{Tr}Q^4 + q\,\mathrm{Tr}(Q:T:Q) + q^2\mathrm{Tr}(Q:G:Q) \qquad 1)$$

where Q is the tensor order parameter (a function of position), a, b, and c are

the coefficients in the Landau power-series expansion, $q=2\pi/a_0$, a_0 is the lattice parameter, and T and G are fourth-rank tensor-valued linear differential operators. In these equations, spatial averaging over the unit cell is to be understood. It is easy to show that G, which represents elastic strain energy, is positive-definite in the sense that $\mathrm{Tr}Q{:}G{:}Q>0\ \forall Q$. Also, a, b, and c must be positive for the usual stability reasons.

We expand Q and q as explained above:

$$Q = Q_0+\epsilon Q_1$$
$$q = q_0+q_1 \qquad 2)$$

where Q_0 and Q_1 are unspecified tensors. Q_0 has bcc symmetry, and Q_1 is sc. As special cases, Q_1 can have "pure sc" or bcc symmetry, which is a special case of simple cubic. The Q_0 tensor may vary with temperature, and setting $Q=Q_0$ makes F an extremum, provided that $q=q_0(T)$. Further, q_0 is the value of q (also temperature-dependent) that makes F extremal. In other words, the functional derivatives of F w.r.t. Q and q vanish when $Q=Q_0$ and $q=q_0$. This condition makes sure that $Q=Q_0;q=q_0$ represents a solution, which may be stable, metastable, or unstable.

We now substitute the forms (2) for Q and q into (1), and subtract the free energy of BPI ($\epsilon=q_1=0$ by definition):

$$F-F(0) = K_1\epsilon^2+K_2q_1\epsilon+K_3q_1^2+L_1\epsilon^3+L_2\epsilon^2q_1+L_3\epsilon q_1^2+M_1\epsilon^4+M_2\epsilon^2q_1^2 \qquad 3)$$

The K's, L's, and M's are coefficients that can be written in terms of Q_0, Q_1, and q_0. Solutions are determined by the condition that the partial derivatives of F w.r.t. ϵ and q_1 vanish. Since the coefficients vary with Q_0 and q_0, they also depend on temperature. Also K_1 depends on a which is temperature-dependent. This temperature dependence is what makes a phase transition possible.

When can we get a second-order phase transition (2PT)? The usual Landau-theory rules apply here*, and tell us that the condition is:

$$D \equiv K_1K_3-K_2^2/4 = 0\,. \qquad 4)$$

The second-order terms vanish if

$$\epsilon = -\frac{K_2}{2K_1}q_1\,. \qquad 5)$$

this condition is satisfied near the 2PT when ϵ and q_1 are small. However, if we assume this condition everywhere, we will only overestimate the free energy. This approach is equivalent to examining a line in order-parameter space. If when the condition (4) is satisfied, we find values of q_1 and ϵ which make $F<F(0)$, we shall have found a first-order phase transition (1PT), since the

stable-equilibrium values of the order parameters are non-zero, implying a phase transition, which cannot be second-order, since all such transitions are "accounted for". Therefore, we plug (5) into (3), and find

$$F-F(0) = Wq_1^3+Xq_1^4 \qquad 6)$$

where W and X are coefficients, and $W=0$ if $K_2=0$. If $W\neq 0$, then it is trivial to show that there is a value of q_1 (hence ϵ) that makes $F<F(0)$.

So far this proof is a standard demonstration of the role of third-order terms in producing a 1PT. However, if Q_1 is of the "pure sc" type, then K_2, L_1, and L_3 all vanish. The proof is then incomplete because $F-F(0)\geq 0$ if we just use the result (7). It can be shown that if one restricts Q_1 to "pure sc" components, then the transition may indeed be second-order. However, this result is irrelevant unless it can be shown that the free energy can't be lowered by the addition of a bcc part to Q_1, while keeping the temperature fixed.

Consider the condition for a 2PT, $D=0$ (4). It can be shown that the "ordered" phase exists for $D<0$. Now, if we sit at a constant temperature, and "turn on" a bcc part to Q_1, the K's will change, and so will D. Suppose that the addition of a bcc part B to Q_1 causes D to decrease. Then, there will be a temperature T^* at which D was positive before the addition, and negative afterwards. Now T^* is a temperature at which the "disordered" phase was in equilibrium before the addition ($D>0$), which implies that if on adding the bcc term the "ordered" phase becomes the one in equilibrium ($D<0$), then this phase will also be present at the temperature at which D was zero before the bcc part was added. In other words, the original $D=0$ 2PT will be "masked" by whatever appears at T^*. After the addition, the transition will be first order, since there is now a bcc part, $K_2\neq 0$, and the proof up to Eq. (6) is in force. To sum up, if D can be made to decrease at constant temperature by the addition of a bcc part, then the 2PT associated with a "pure sc" Q_1 is "masked" by a 1PT, so that the only transition is a 1PT.

Consider a Q_1 with a bcc addition as follows:

$$Q_1 = S+\lambda B \qquad 7)$$

where λ is a coefficient used to "turn on" the bcc part B, and S is the "pure sc" part. Now, K_3 is independent of Q_1, but K_1 and K_2 are given by:

$$\begin{aligned} K_1(Q_1) &= Q_1:\frac{\delta^2 F}{\delta Q^2}:Q_1 = K_1(S)+\lambda^2 K_1(B) \\ K_2(Q_1) &= \mathrm{Tr}(Q_1:T:Q_0+Q_0:T:Q_1)+2q_0\mathrm{Tr}(Q_1:G:Q_0+Q_0:G:Q_1) \\ &= \lambda K_2(B)\ . \end{aligned} \qquad 8)$$

Since there are no invariant products of odd numbers of S's, we find that

$$D = \lambda^2\left(K_1(B)K_3 - \frac{K_2^2(B)}{4}\right)\ . \qquad 9)$$

Suppose we make B something with a very rapid variation with position, meaning that it has components with large Miller indices. Then, since G is a positive-definite, second-order differential operator, $K_2(B)^2$, which is related to the strain energy, will increase as h^4 (h=typical Miller index in B), while $K_1(B)$ increases only as h^2. Therefore, the admission of a small admixture of this rapidly-varying component replaces the 2PT with a 1PT.

The above proof assumed that Q_0 had bcc symmetry. If it had sc symmetry instead, there would have been a third-order term in Q_1, even if Q_1 were "pure sc". This term would have come from the $c\mathrm{Tr}Q^4$ term in Eq. (1). Such a term would guarantee a 1PT. Therefore, we have covered the cases sc→sc, bcc→sc, and bcc→bcc, finding 1PT's in each.

IV. CONCLUSIONS

I have proven that within the framework of Landau theory, there are no second-order transitions among simple-cubic or body-centered cubic "blue" phases. This exclusion arises partly from the appearance of Fourier components of Q from which odd-order invariants can be made, and partly from the coupling of the lattice parameter to the unit-cell structure. This proof is structure-independent (except for specifying the translation group).

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*The rule is that the second-order part of the free energy must be zero at a 2PT. Consider ϵ, q_1 as components of a "vector" $V=(\epsilon, q_1)$. Then, the second-order part is $V:\begin{bmatrix} K_1 & K_2/2 \\ K_2/2 & K_3 \end{bmatrix}:V$ which is zero only if the determinant of the above 2×2 matrix is zero.