Theory of phase transitions and modulated structures in ferroelectrics

D. Blankschtein
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

R. M. Hornreich
*Department of Theoretical Physics, Oxford University, Oxford OX1 3NP, United Kingdom and Department of Electronics, Weizmann Institute of Science, 76100 Rehovot, Israel**

(Received 8 March 1985)

For ferroelectric systems described by an $n>1$ polar vector order parameter $\mathbf{p}$, a new term in the free-energy density, $\beta[\mathbf{p}^2\nabla\cdot\mathbf{p}-\mathbf{p}\cdot\nabla(\mathbf{p}^2)]$, is allowed. Considering an isotropic, centrosymmetric model and using Landau theory, we show that as a result the ferroelectric phase becomes locally unstable when $|\beta|$ is sufficiently large. For $|\beta|$ values above the critical one, the ordered phase has a modulated antiferroelectric structure. Several alternative structures are considered, and it is argued that for $n=3$ the most likely phase is a cubic one (space group O_h^9). Immediately above the critical value of $|\beta|$, the transition to the ordered phase is of second order. When $|\beta|$ is further increased, a tricritical point is reached above which the transition is first order. The effect of fluctuations on the above results is analyzed by using renormalization-group theory and expanding to $O(\epsilon)$ in $4-\epsilon$ dimensions. The new term is found to be relevant when $n<n_0=4-11\epsilon/4+O(\epsilon^2)$, in which case no stable fixed points exist for $1.86\lesssim n<n_0$. Thus ferroelectrics and ferromagnets are not necessarily in the same universality class. An examination of the renormalization-group flows, together with the results of the classical Landau analysis, indicates that modulated structures are possible immediately below the order-disorder transition regardless of the magnitude of $\beta(\neq 0)$. Some experimental data which appear to agree with the theoretical results are discussed.

I. INTRODUCTION

In both its classical[1] and modern[2] versions, the theory of phase transitions is based upon the choice of an appropriate order parameter, which depends fundamentally upon the particular system being modeled. Typical examples are density (a scalar) to describe the liquid-solid transition,[3,4] magnetization or polarization (vectors) to characterize spin ordering[5] or ferroelectricity,[6] and dielectric constant or quadrupolar moment (second-rank tensors) to study transitions in thermotropic liquid crystals.[7] The systems characterized by a vector order parameter may be further divided into two classes: those in which the order parameter is a true or polar vector; and those in which it is a pseudovector, or axial vector. (The former changes sign under inversion while the latter does not.) Axial vectors are relevant to the entire spectrum of magnetic systems and have been extensively studied.[2,5] Systems belonging to the former (polar vector) class had, in general, been expected to exhibit critical properties identical to those of their axial vector counterparts; thus no separate analysis of their phase transitions and their critical behavior was believed to be necessary. For example, the simplest case of a phase transition in a fully isotropic centrosymmetric system characterized by a polar vector order parameter $\mathbf{p}(\mathbf{r})$ was modeled in Landau theory by the average free-energy density,[6]

$$F=V^{-1}\int dV[\alpha\mathbf{p}^2+\gamma(\mathbf{p}^2)^2+a(\nabla\mathbf{p})^2+\cdots]\,, \tag{1}$$

where the integration is over a representative volume V, α is proportional to a reduced temperature $t=(T-T_c)/T_c$, and γ, a are regarded as positive and t independent in the neighborhood of the phase transition. The terms given explicitly in (1) are sufficient to describe the phase transition classically.[1] Clearly, (1) is entirely equivalent to its magnetic counterpart, which is customarily described using precisely the same free-energy expression [with $\mathbf{p}$ replaced by the axial vector $\mathbf{m}(\mathbf{r})$].[2,5]

However, as was first pointed out by Michelson[8] and by Aslanyan and Levanyuk,[9] (1) is *not* a complete description for the case of a polar vector order parameter as an additional term, of the form

$$V^{-1}\int dV\beta[\mathbf{p}^2\nabla\cdot\mathbf{p}-\mathbf{p}\cdot\nabla(\mathbf{p}^2)]\,, \tag{2}$$

is then allowed.[10] Here β is a phenomenological, temperature-independent coefficient. Note that symmetry under time reversal would always result in such a term vanishing in a magnetic system. In addition, it will vanish in a centrosymmetric system with an axial vector order parameter since only ∇ changes sign under inversion. However, since *both* $\mathbf{p}$ *and* ∇ change sign under inversion, (2) is symmetry allowed in the case of a centrosymmetric system and polar vector order parameter. The consequences of including (2) in the free energy were first analyzed within a Landau-theory framework by Alexander *et al.*[11] and, using a different approach, by Korzhenevskii,[12] who also considered fluctuation effects using low-order perturbation theory. The results of a more gen-

eral renormalization-group treatment were given by us independently.[13]

Our objective here is to present a detailed analysis of the effect of (2) on phase transitions and critical behavior of systems described by polar vector order parameters. We shall restrict our treatment to the specific case of isotropic systems characterized by short-range interactions only. We thus exclude crystalline anisotropy and long-range (e.g., dipolar) interactions. The latter, in particular, can be significant in practical cases and we shall return to this point in the concluding section. We begin, in Sec. II, with a comprehensive treatment of the Landau theory of polar vector ordering. In particular, a rigorous linear stability analysis of the uniformly ordered (e.g., ferroelectric) state is given. We then extend the treatments of both Alexander *et al.*[11] and Korzhenevskii[12] and argue that the prediction of an ordered phase having a cubic structure[11] for sufficiently large $|\beta|$ is the more plausible one. Next, in Sec. III, we consider the effect of fluctuations on the phase transition within a renormalization-group framework in $d=4-\epsilon$ dimensions. We show rigorously that this results in a first-order phase transition for *all* $\beta\neq 0$ and argue that this could result in cubic structures occurring in certain physically realizable cases. In the concluding section, we explore the experimental implications of our results and comment upon the limitations of the particular model studied.

II. LANDAU THEORY OF POLAR VECTOR ORDERING

Since the two terms in (2) differ only by a surface integral, we shall consider a total average free energy having the form

$$F=V^{-1}\int dV[\alpha\mathbf{p}^2+\beta\mathbf{p}^2\nabla\cdot\mathbf{p}+\gamma(\mathbf{p})^2+a(\nabla\mathbf{p})^2] . \quad (3)$$

This functional is appropriate for fully isotropic systems characterized by short-range interactions. We assume that $a>0$ and note that the last term in (3) is necessary in order to obtain a finite equilibrium value for $\nabla\cdot\mathbf{p}$.

A. Instability of the uniform phase

The uniformly (u) ordered phase is described by

$$\mathbf{p}=\mu_u\hat{\mathbf{i}}_3 , \quad (4)$$

with μ_u independent of $\mathbf{r}$ and $\hat{\mathbf{i}}_3$ the (arbitrary) axis along which the system orders. Substituting (4) into (3) gives

$$F=F_u=\alpha\mu_u^2+\gamma\mu_u^4 , \quad (5)$$

and, from $\partial F_u/\partial\mu_u=0$, $\partial^2F_u/\partial\mu_u^2>0$, we obtain

$$\mu_u^2=-\alpha/2\gamma, \quad F_u=-\alpha^2/4\gamma, \quad \text{for } \alpha<0 . \quad (6)$$

A necessary (and, when the transition is of second order, sufficient) condition for (4) and (6) to describe the ordered state is that the uniform state be stable with respect to small perturbations. This *local stability* can be tested by letting

$$\mathbf{p}(\mathbf{r})=\mu_u\hat{\mathbf{i}}_3+\boldsymbol{\sigma}(\mathbf{r}), \text{ with } \sigma\ll\mu_u . \quad (7)$$

Substituting (7) into (3), keeping only contributions up to second order in $\boldsymbol{\sigma}$, using (6), and neglecting surface terms, we obtain

$$F=F_u+V^{-1}\int dV[-2\alpha\sigma_3^2+2\beta\mu_u\sigma_3(\partial\sigma_1/\partial x+\partial\sigma_2/\partial y)+a(\nabla\boldsymbol{\sigma})^2] . \quad (8)$$

Setting $\delta F/\partial\sigma_j=0$ gives the linear Euler-Lagrange equations

$$\begin{aligned} &a\nabla^2\sigma_1+\beta\mu_u(\partial\sigma_3/\partial x)=0 ,\\ &a\nabla^2\sigma_2+\beta\mu_u(\partial\sigma_3/\partial y)=0 ,\\ &a\nabla^2\sigma_3+2\alpha\sigma_3-\beta\mu_u(\partial\sigma_1/\partial x+\partial\sigma_2/\partial y)=0 . \end{aligned} \quad (9)$$

Letting $\boldsymbol{\sigma}=\mathbf{A}\exp(i\mathbf{q}\cdot\mathbf{r})$, (9) has solutions other than $\boldsymbol{\sigma}=\mathbf{A}=0$, if and only if

$$\begin{vmatrix} -q^2a & 0 & i\beta\mu_u q_1 \\ 0 & -q^2a & i\beta\mu_u q_2 \\ -i\beta\mu_u q_1 & -i\beta\mu_u q_2 & -q^2a+2\alpha \end{vmatrix}=0 . \quad (10)$$

Introducing the normalized wave-vector magnitude $\kappa=(-2\alpha/a)^{-1/2}q$ and direction cosines $\gamma_j\equiv q_j/q$, and noting that the $q=0$ solutions of (10) are Goldstone modes associated with the arbitrary breaking of the O(3) symmetry, we obtain from (10)

$$B\equiv\beta^2/a\gamma=4(1+\kappa^2)/(\gamma_1^2+\gamma_2^2) . \quad (11)$$

The *minimum* value of B for which a $\boldsymbol{\sigma}=0$ solution of (9) exists is obtained by taking $\kappa\to 0$ and $\gamma_1^2+\gamma_2^2=1$ (i.e., $\mathbf{q}$ in the $\hat{\mathbf{i}}_1-\hat{\mathbf{i}}_2$ plane). This gives

$$B(\kappa\to 0;\gamma_3=0)\equiv B_0=4 . \quad (12)$$

Thus, for $B>4$, the uniformly ordered phase is locally *unstable* with respect to a long wavelength longitudinal mode transverse to the ordering direction. It follows that in this region of the phase diagram there necessarily exists an ordered phase characterized by a *nonuniform* order parameter. Also, while (12) was obtained by taking $\mathbf{p}$ to be an $n=3$ (three-component) order parameter the result is the same for the $n=2$ case and also for two-dimensional systems. The nature of the instability mode is also unchanged. Finally, note that (12) is valid in the entire region $\alpha<0$. That is, the uniform phase is not stable at *any* temperature when $B>4$. This is due to our not including higher-order [e.g., $(\mathbf{p}^2)^3$] terms in (3).

Given that the uniform phase is not thermodynamically stable, the question of the nature of the ordered phase or phases in the $B>4$ region of the phase diagram naturally arises. We therefore now consider several alternative structures, all having $\nabla\cdot\mathbf{p}\neq 0$.

B. Cubic phase

The structurally simplest phases with $\nabla\cdot\mathbf{p}\neq 0$ are those characterized by a set $j=1,\ldots,n$ of wave vectors $\mathbf{k}_j$

satisfying $k_j=k$. In this case the $\mathbf{p}^2\nabla\cdot\mathbf{p}$ term in (3) will contribute to F whenever the $\mathbf{k}_j$ form equilateral triangles. This is a well-known result which has been used to study solidification[3,4,14] and blue phases in cholesterics.[15]

For an $n=3$ order parameter in three dimensions, the simplest structure is composed of a regular tetrahedron of wave vectors, which can be aligned with the $\langle 110\rangle$ directions in $\mathbf{k}$ space. The order parameter is then[11]

$$\mathbf{p}_{c1}(\mathbf{r})=\frac{1}{2\sqrt{6}}\mu_{c1}\left[\sum_{j=1}^{3}\{(\hat{\mathbf{i}}_j+\hat{\mathbf{i}}_{j+1})\exp[ik(x_j+x_{j+1})+i\xi_j]+\text{c.c.}\}+\sum_{j=1}^{3}\{(i_j-i_{j+1})\exp[ik(x_j-x_{j+1})+i\eta_j]+\text{c.c.}\}\right], \tag{13}$$

where $\mu_{c1}>0$, ξ_j and η_j are phases, c.c. denotes complex conjugate, and all subscripts are modulo 3. The calculation of the free energy F_{c1} associated with $\mathbf{p}_{c1}$ is simplified by noting that the structure has a threefold symmetry axis about [111]; by placing the origin at a suitable point on this axis, we can, without loss of generality, set $\xi_j=-\eta_j=-\eta$. Then (13) becomes

$$\mathbf{p}_{c1}(\mathbf{r})=(\tfrac{2}{3})^{1/2}\mu_{c1}\sum_{j=1}^{3}\{\hat{\mathbf{i}}_j[(\cos\eta)(C_jC_{j+1}-S_jS_{j+2})+(\sin\eta)C_j(S_{j+1}+S_{j+2})]\}, \tag{14}$$

where $C_j\equiv\cos(kx_j)$, $S_j\equiv\sin(kx_j)$. Note that the part of $\mathbf{p}_{c1}(\mathbf{r})$ proportional to $\cos\eta$ changes sign under spatial inversion while that proportional to $\sin\eta$ does not. They thus belong to different representations of the O(3) (disordered phase) rotation group which implies that $\eta=0$, π, or $\pm\pi/2$. As the former cannot have a β-dependent contribution to F we set $\eta=\pm\pi/2$.

Substituting (14) into (3) and integrating over a unit cell gives

$$F_{c1}=\alpha\mu_{c1}^2\mp(\tfrac{2}{3})^{1/2}\beta k\mu_{c1}^3+\tfrac{19}{12}\gamma\mu_{c1}^4+2ak^2\mu_{c1}^2 . \tag{15}$$

Clearly, F_{c1} is minimum when $\eta=+\pi/2$. Setting $\partial F_{c1}/\partial k=0$ yields

$$k=\tfrac{1}{4}(\tfrac{2}{3})^{1/2}\mu_{c1}\beta/a , \tag{16}$$

with

$$F_{c1}=\alpha\mu_{c1}^2+\tfrac{1}{12}\gamma[19-(\beta^2/a\gamma)]\mu_{c1}^4 . \tag{17}$$

Comparing (17) with (5), we see that $F_{c1}<F_u$ when[11]

$$\tfrac{1}{12}(19-B)<1 , \tag{18a}$$

or

$$B>B_{c1}=7 . \tag{18b}$$

Further, the transition from the disordered to the cubic phase is necessarily *first order* when

$$B>\bar{B}_{c1}=19 . \tag{18c}$$

Thus, $\bar{B}_{c1}$ is a tricritical point.

While (18) is in accord with the rigorous result that the uniform phase becomes unstable when $B>B_0=4$ the threshold obtained $B_{c1}=7$ is considerably larger. This, we believe, is due to choosing an order parameter having nonzero Fourier components with $|\mathbf{k}|=k$ only. To demonstrate this quantitatively, we add to $\mathbf{p}_{c1}(\mathbf{r})$ in (14) (with $\eta=\pi/2$) the next symmetry-allowed harmonic, obtaining

$$\mathbf{p}_{c2}(\mathbf{r})=(\tfrac{2}{3})^{1/2}\mu_{c1}\sum_{j=1}^{3}\hat{\mathbf{i}}_jC_j(S_{j+1}+S_{j+2})+(\tfrac{2}{3})^{1/2}\mu_{c2}\sum_{j=1}^{3}\hat{\mathbf{i}}_j\cos(2kx_j+\psi) , \tag{19}$$

with μ_{c1} and $\mu_{c2}>0$. Again invoking inversion symmetry, we have $\psi=\pm\pi/2$. Substituting into (3) and integrating over a unit cell gives

$$F_{c2}=\alpha(\mu_{c1}^2+\mu_{c2}^2)-(\tfrac{2}{3})^{1/2}\beta k(\mu_{c1}^3\mp2\mu_{c1}^2\mu_{c2})+\gamma(\tfrac{19}{12}\mu_{c1}^4+4\mu_{c1}^2\mu_{c2}^2+\tfrac{7}{6}\mu_{c2}^4)-2ak^2(\mu_{c1}^2+2\mu_{c2}^2) . \tag{20}$$

We minimize F_{c2} by taking $\psi=-\pi/2$ and setting $\partial F_{c2}/\partial k=0$. Letting $\mu_{c1}=\mu_c\cos\theta=\mu_c c$, $\mu_{c2}=\mu_c\sin\theta=\mu_c s$, we find

$$k=-\tfrac{1}{4}(\tfrac{2}{3})^{1/2}(\beta\mu_c/a)[c^2(c+2s)/(1+s^2)] , \tag{21}$$

and

$$F_{c2}=a\mu_c^2+8\mu_c^4\left[\tfrac{19}{12}c^4+4c^2s^2+\tfrac{7}{6}s^4-\tfrac{1}{12}B\frac{c^4(c+2s)^2}{1+s^2}\right] . \tag{22}$$

It follows that the uniform phase becomes thermodynamically unstable with respect to the two harmonic cubic phase when

$$B>B_{c2}=\left[\frac{(19c^4+48c^2s^2+14s^2-12)(1+s^2)}{c^4(c+2s)^2}\right]_{\min} , \tag{23a}$$

where the quantity on the right-hand side of (23a) is to be minimized with respect to θ. A simple numerical calculation yields $\theta_{\min}=16.03°$ and

$$B_{c2}=4.227 , \tag{23b}$$

much closer to the rigorous threshold of 4. As before, further increasing B eventually results in a first-order phase transition which now necessarily occurs when B exceeds the tricritical value,

$$\bar{B}_{c2}=\left[\frac{(19c^4+48c^2s^2+14s^2)(1+s^2)}{c^4(c+2s)^2}\right]_{\min}$$

$$=10.778\,|_{\theta=17.90^\circ}\,. \tag{24}$$

Clearly, introducing additional harmonics into the order parameter $\mathbf{p}_c(\mathbf{r})$ will result in further reductions in B_c and $\bar{B}_c$. However, in view of the closeness of B_{c2} to $B_0=4$, these will be small, We close by noting that $\mathbf{p}_c(\mathbf{r})$ is invariant under the body-centered space group O_h^9, which thus characterizes the cubic phase.[10]

C. Hexagonal phase

The two-dimensional analog of the basic cubic phase discussed in Sec. II B is obtained by taking a set of *three* wave vectors which form a *single* equilateral triangle. In this case we have

$$\mathbf{p}_{h1}(\mathbf{r})=\frac{1}{2\sqrt{3}}\mu_{h1}\sum_{j=1}^{3}\{(\hat{\mathbf{i}}_j-\hat{\mathbf{i}}_{j+1})\exp[ik(x_j-x_{j+1})+i\eta_j]+\text{c.c.}\}\,. \tag{25}$$

Setting our origin at the center of the triangle we have $\eta_j=\eta$ and, from invariance under inversion, $\eta=\pm\pi/2$. Then

$$\mathbf{p}_{h1}(\mathbf{r})=\frac{\mp1}{\sqrt{3}}\mu_{h1}\sum_{j=1}^{3}\hat{\mathbf{i}}_j\{\sin[k(x_j-x_{j+1})]+\sin[k(x_j-x_{j+2})]\}\,. \tag{26}$$

Substituting into (3) gives

$$F_{h1}=\alpha\mu_{h1}^2\mp\frac{1}{\sqrt{3}}\beta k\mu_{h1}^3+\tfrac{3}{2}\gamma\mu_{h1}^4+2ak^2\mu_{h1}^2\,. \tag{27}$$

Thus, $\eta=+\pi/2$. Setting $\partial F_{h1}/\partial k=0$, we have[11]

$$k=\frac{1}{4\sqrt{3}}(\beta\mu_{h1}/a)\,, \tag{28}$$

$$F_{h1}=\alpha\mu_{h1}^2+\gamma\mu_{h1}^4(\tfrac{3}{2}-\tfrac{1}{24}B)\,, \tag{29}$$

and

$$B_{h1}=12,\bar{B}_{h1}=36\,. \tag{30}$$

As in the cubic case, these results can be significantly improved by incorporating higher harmonics in the order parameter. When a second harmonic is included, we have

$$\mathbf{p}_{h2}(\mathbf{r})=-\frac{1}{\sqrt{3}}\mu_{h1}\sum_{j=1}^{3}\hat{\mathbf{i}}_j\{\sin[k(x_j-x_{j+1})]+\sin[k(x_j-x_{j+2})]\}$$
$$\mp\frac{1}{\sqrt{3}}\mu_{h2}\sum_{j=1}^{3}\hat{\mathbf{i}}_j\{\sin[k(x_j+x_{j+1}-2x_{j+2})]-2\sin[k(x_{j+1}+x_{j+2}-2x_j)]+\sin[k(x_{j+2}+x_j-2x_{j+1})]\}\,. \tag{31}$$

The phases in the second harmonic term have been chosen so that $\mathbf{p}_{h2}(\mathbf{r})=\mathbf{p}_{h2}(-\mathbf{r})$. Taking the upper sign, the free energy (3) becomes

$$F_{h2}=\alpha(\mu_{h1}^2+\mu_{h2}^2)-\beta k\left[\frac{1}{\sqrt{3}}\mu_{h1}^3+\mu_{h1}^2\mu_{h2}+\mu_{h2}^3\right]$$
$$+\gamma(\tfrac{3}{2}\mu_{h1}^4+\tfrac{14}{3}\mu_{h1}^2\mu_{h2}^2+\tfrac{3}{2}\mu_{h2}^4)+2ak^2(\mu_{h1}^2+3\mu_{h2}^2)\,. \tag{32}$$

Setting $\mu_{h1}=\mu_h\cos\theta=\mu_h c$, $\mu_{h2}=\mu_h\sin\theta=\mu_h s$, and $\partial F_{h2}/\partial k=0$, we find

$$B_{h2}=\left[\frac{4(1+\frac{10}{3}c^2s^2)(c^2+3s^2)}{[(1/\sqrt{3})c^3+c^2s+s^3]^2}\right]_{\min}$$

$$=8.825\,|_{\theta=11.30^\circ}\,, \tag{33a}$$

$$\bar{B}_{h2}=\left[\frac{4(3+\frac{10}{3}c^2s^2)(c^2+3s^2)}{[(1/\sqrt{3})c^3+c^2s+s^3]^2}\right]_{\min}$$

$$=23.96\,|_{\theta=15.53^\circ}\,. \tag{33b}$$

While (33) is a significant improvement on (30), the results for B_h are still well above the rigorous stability limit $B_0=4$ which, as noted in Sec. II A, is valid for systems with two-component as well as three-component order parameters. We shall return to this point in Sec. IV.

D. Linearly modulated phase

Independently of Alexander *et al.*,[11] the consequences of a $\mathbf{p}^2\nabla\cdot\mathbf{p}$ invariant in the free energy were examined by Korzhenevskii.[12] Using Landau theory and Eq. (3), he compared the free energy of the uniform phase with that of a two-harmonic linearly modulated structure defined by the order parameter

$$\mathbf{p}_l(\mathbf{r})=\mu_l[\hat{\mathbf{i}}_1\sin(2kx)+\hat{\mathbf{i}}_2\cos(kx)]\,. \tag{34}$$

However, in order that both terms in $\mathbf{p}_l(\mathbf{r})$ transform identically under inversion, it is preferable to replace $\cos(kx)$ in (34) by $\sin(kx)$. Also, a slightly generalized version, having the form

$$\mathbf{p}_l(\mathbf{r})=\sqrt{2}\mu_l[\hat{\mathbf{i}}_1\sin\theta\sin(2kx)+\hat{\mathbf{i}}_2\cos\theta\sin(kx)]\,, \tag{35}$$

can be considered. Using (3) we obtain (with $c=\cos\theta$, $s=\sin\theta$)

$$F_l=\alpha\mu_l^2-\sqrt{2}c^2s\beta k\mu_l^3+\tfrac{3}{2}(1-\tfrac{2}{3}c^2s^2)\gamma\mu_l^4$$
$$+(c^2+4s^2)ak^2\mu_l^2\,, \tag{36}$$

and, after setting $\partial F_l/\partial k=0$,

$$B_l=\left[\frac{(1-2c^2s^2)(c^2+4s^2)}{c^4s^2}\right]_{\min}=7.480\,|_{\theta=34.19^\circ}\,, \tag{37a}$$

$$\bar{B}_l=\left[\frac{(3-2c^2s^2)(c^2+4s^2)}{c^4s^2}\right]_{\min}=32\tfrac{2}{3}\,|_{\theta=30^\circ}\,. \tag{37b}$$

Korzhenevskii,[11] with $\theta=45^\circ$ or $c=s=1/\sqrt{2}$, found (in our notation) $B_l=10$ and $\bar{B}_l=50$.

E. Discussion

In this section we have found, using Landau theory, that a ferroelectric phase cannot be thermodynamically stable in an isotropic system when the magnitude of the coefficient β of the $\mathbf{p}^2\nabla\cdot\mathbf{p}$ term in the free-energy density is sufficiently large. While this result is not new,[11,12] the value of $|\beta|$ at the stability limit had not been given previously.

The Landau theory phase diagram is shown in Fig. 1. When only the terms shown explicitly in (3) are considered, Fig. 1(a) is obtained. The uniform phase stability limit is reached at $B=\beta^2/a\gamma=4$ for *all* temperatures less than T_c. The order-disorder phase boundary is second order for all $B\le B_{\rm TC}$, which is a tricritical point. For $B>B_{\rm TC}$, the model is not thermodynamically stable at any finite value of $\mathbf{p}(\mathbf{r})$ and higher-order terms must be included in the free energy. When this is done by, e.g., adding a term proportional to $(\mathbf{p}^2)^3$ to the free-energy density (3), it is straightforward to show by an analysis similar to that in Sec. II A that the result is the phase diagram shown schematically in Fig. 1(b). Note that (i) the order-disorder phase boundary for $B>B_{\rm TC}$ is first order and the transition occurs at $T_c(B>B_{\rm TC})>T_c(B=0)$, and (ii) the boundary between the ordered phases is now T-dependent and the ferroelectric phase becomes thermodynamically stable at sufficiently low temperatures also for $B>4$.

In both parts of Fig. 1, the boundary between the uniform and modulated phases is shown as first order for $\alpha<0$. This is generally true whenever the modulated phase is periodic, in which case the order parameter can be formally written as a Fourier series with coefficients

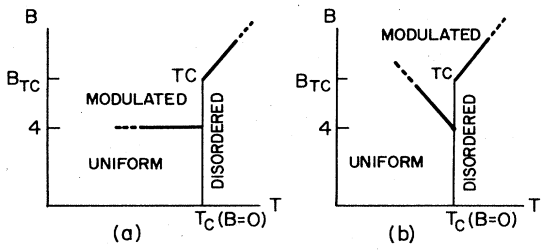

FIG. 1. Possible classical phase diagram for isotropic centrosymmetric ferroelectrics showing schematically the regions in which the disordered, uniform (ferroelectric), and modulated (antiferroelectric) phases are thermodynamically stable (a) based on analysis of Sec. II, (b) including the effect of sixth-order terms in the free energy. Thick (thin) lines denote first- (second-) order phase transitions. There is a tricritical point at TC.

μ_i. The average free-energy density of the modulated phase can then always be written in the form

$$F_m=\alpha\mu^2+\gamma[f(\Omega)-Bg(\Omega)]_{\min}\mu^4+\cdots\,,$$
$$=\alpha\mu^2+\gamma(\bar{f}-B\bar{g})\mu^4+\cdots\,, \tag{38}$$

after minimization with respect to k. Here $\mu^2=\sum_i\mu_i^2$ and the quantity in brackets is to be minimized with respect to orientation Ω, in the parameter space generated by the μ_i. Then

$$\partial F_m/\partial B=-\gamma\bar{g}\mu^4\,, \tag{39}$$

which is nonzero for $\alpha<0$. Since $\partial F_u/\partial B\neq 0$ always, it follows that this free-energy derivative is discontinuous on the uniform-modulated phase boundary for $\alpha<0$ and hence this boundary is first order in character.

III. FLUCTUATIONS: RENORMALIZATION-GROUP ANALYSIS

In a classical Landau-theory framework (such as used in Sec. II), the effect of thermodynamic fluctuations on the phase diagram and on the nature of the phase transitions is neglected. Our objective in this section is to treat these effects by means of a renormalization-group analysis[2] of the isotropic ferroelectric model system introduced earlier. While such an analysis is not directly applicable to three-dimensional systems it nevertheless provides strong indications as to the range of validity of the classical Landau approach.

A. Stability of the $\beta=0$ isotropic fixed point

To begin, we remind ourselves that when $\beta=0$, a system with short-range interactions is described by a free-energy functional (or Landau-Ginzburg-Wilson Hamiltonian) which is conventionally written in the form

$$\mathcal{H}_0/k_BT=\int d^dx\{\tfrac{1}{2}[r\mathbf{p}^2+(\nabla\mathbf{p})^2]+u(\mathbf{p}^2)^2\}\,, \tag{40}$$

with $\mathbf{p}$ generalized to be an n-component vector ($n>1$). In $d=4-\epsilon$ dimensions, the critical behavior of this system is given by the well-known Wilson-Fisher (WF) fixed point which, to $O(\epsilon^2)$, is characterized by[5]

$$u=u^*=[\epsilon/4K_4(n+8)][1+3(3n+14)\epsilon/(n+8)^2]\,,$$

with (41)

$$K_4=1/8\pi^2\,.$$

As has been noted, Michelson[8] and Aslanyan and Levanyuk[9] have pointed out that (40) is not necessarily an adequate description of ferroelectric systems. We may therefore ask whether the WF fixed point is *stable* or *unstable* when the additional symmetry-allowed term (2) is taken to be an infinitesimal perturbation of the initial Hamiltonian $\mathcal{H}_0$ in the neighborhood of its fixed point. In renormalization-group terms, this is equivalent to studying the *relevance* of the additional term

$$\mathcal{H}_1/k_BT=w\int d^dx\,\mathbf{p}^2\nabla\cdot\mathbf{p}\,, \tag{42}$$

for $u=u^*$ and $w\to 0$. The coefficient w is, of course, simply proportional to β in (2).

Using standard renormalization-group methods[2] and (41), we obtain to $O(\epsilon^2)$ the linearized recursion relation valid in the vicinity of the WF fixed point

$$w'=w\left[1+\left[\frac{(4-n)}{2(n+8)}\epsilon-\frac{3(n+2)(7n+16)}{4(n+8)^3}\epsilon^2\right]\ln b\right], \tag{43}$$

where b is the usual momentum rescaling factor. Setting $w'=b^{\lambda_w}w$, the eigenvalue exponent λ_w is found to be

$$\lambda_w=[(4-n)/2(n+8)]\epsilon -[3(n+2)(7n+16)/4(n+8)^3]\epsilon^2 . \tag{44}$$

For $n=d=4-\epsilon$, $\lambda_w=-(\frac{7}{96})\epsilon^2$ and therefore $\mathscr{H}_1$ is (weakly) irrelevant. However, for $n<n_0=-11\epsilon/4+O(\epsilon^2)$, λ_w is *positive* and $\mathscr{H}_1$ is relevant in $d=4-\epsilon$ dimensions. *Therefore the WF fixed point does not describe the critical behavior of isotropic ferroelectric systems in which* $w\neq 0$ *when* $n<n_0$. Extrapolating to $d=3$ we find $\lambda_w(\epsilon=1,n=3)=-0.059$, and $\lambda_w(\epsilon=1,n=2)=+0.01$, indicating that, particularly for $n=2$, the stability of the WF fixed point in three dimensions is doubtful. However, as is well-known from, e.g., the case of cubic anisotropy,[5] results obtained by extrapolating eigenvalue expansions to $\epsilon=1$ must be regarded cautiously.

B. General Landau-Ginzburg-Wilson Hamiltonian

Since we have found that the $d=4-\epsilon$ WF fixed point is *unstable* for $w\neq 0$, a search for other possible fixed points is in order. We must therefore consider more generally the choice of an appropriate effective Hamiltonian in order to model isotropic ferroelectric systems with $n<d$. The appropriate choice is not simply $\mathscr{H}_0+\mathscr{H}_1$ but rather

$$\mathscr{H}/k_BT=\int d^dx\{\tfrac{1}{2}\{r\mathbf{p}^2+\Delta_1[(\nabla_n\times\mathbf{p})^2+(\nabla\cdot\mathbf{p})^2]+\Delta_2[(\nabla_n\times\mathbf{p})^2-(\nabla\cdot\mathbf{p})^2] +\Delta_3[(\nabla\times\mathbf{p})^2-(\nabla_n\times\mathbf{p})^2]\}+w\mathbf{p}^2\nabla\cdot\mathbf{p}+u(\mathbf{p}^2)^2\} , \tag{45}$$

where the gradient operators ∇ and ∇_n have d and n components, respectively. The new quadratic terms in (45) arise since in isotropic systems, characterized by ($n<d$) component order parameters, one can construct *three* invariant operators which are quadratic in the spatial derivatives. These are $(\nabla\cdot\mathbf{p})^2$, $(\nabla_n\times\mathbf{p})^2$, or their symmetrized versions $\Theta_\pm=(\nabla_n\times\mathbf{p})^2\pm(\nabla\cdot\mathbf{p})^2$ (note that $\nabla\cdot\mathbf{p}=\nabla_n\cdot\mathbf{p}$), and $[(\nabla\times\mathbf{p})^2-(\nabla_n\times\mathbf{p})^2]$. Note that if, initially, $\Delta_1=\Delta_3=1$ and $\Delta_2=0$, the quadratic terms in (15) reduce to $r\mathbf{p}^2+(\nabla\mathbf{p})^2$, where $(\nabla\mathbf{p})^2=(\nabla\times\mathbf{p})^2+(\nabla\cdot\mathbf{p})^2$. When $w=0$, the Δ_i are marginal to $O(\epsilon)$ (see below), and full isotropy is maintained under the renormalization-group (RG) transformation [(45) reduces to (40)].[5] The situation is different when $w\neq 0$ and $n<n_0$. In this case, w is relevant and generates contributions of $O(w^2)$, with $w=O(\epsilon^{1/2})$, to the Δ_i. Although it is possible to maintain $\Delta_1=\Delta_3=1$ via anisotropic rescaling of the momenta (see below), a nonzero value of Δ_2 inevitably emerges under the RG transformation. It is therefore necessary to have $\Delta_2\neq 0$ *ab initio*.

To carry out a RG analysis of (45), it is useful to rewrite $\mathscr{H}$ in terms of momentum-space coordinates. We then have

$$\mathscr{H}/k_BT=\tfrac{1}{2}\int_{\mathbf{Q}}U^{\alpha\beta}(\mathbf{Q})p^\alpha(\mathbf{Q})p^\beta(-\mathbf{Q})+iw\int_{\mathbf{Q}}\int_{\mathbf{Q}_1}q^\alpha p^\alpha(\mathbf{Q})p^\beta(\mathbf{Q}_1)p^\beta(-\mathbf{Q}-\mathbf{Q}_1) +u\int_{\mathbf{Q}}\int_{\mathbf{Q}_1}\int_{\mathbf{Q}_2}p^\alpha(\mathbf{Q})p^\alpha(\mathbf{Q}_1)p^\beta(\mathbf{Q}_2)p^\beta(-\mathbf{Q}-\mathbf{Q}_1-\mathbf{Q}_2) , \tag{46a}$$

with

$$U^{\alpha\beta}(\mathbf{Q})=[r+(\Delta_1+\Delta_2)q^2+\Delta_3k^2]\delta_{\alpha\beta}-2\Delta_2q^\alpha q^\beta , \tag{46b}$$

$\int_{\mathbf{Q}}\equiv(2\pi)^{-d}\int d^dQ$, $1<\alpha,\beta\leq n$, and the usual summation convention (over repeated indices) applies. In (46b), $\mathbf{q}$ is an n-component vector in the same space as $\mathbf{p}$, and $\mathbf{k}$ is a $(d-n)$-component vector in the remaining subspace. In general, $\mathbf{Q}=\mathbf{q}+\mathbf{k}$. Upon defining the propagator $[G]=[U]^{-1}$, we obtain

$$G^{\alpha\beta}(\mathbf{Q})=\frac{1}{r+(\Delta_1+\Delta_2)q^2+\Delta_3k^2}\times\left[\delta_{\alpha\beta}+\frac{2\Delta_2q^\alpha q^\beta}{r+(\Delta_1-\Delta_2)q^2+\Delta_3k^2}\right] . \tag{47}$$

In addition to $u>0$, we must have $\Delta_1\pm\Delta_2>0$ and $\Delta_3>0$ in order for $\mathscr{H}$ to be thermodynamically stable.

C. Renormalization-group recursion relations

We now carry out a renormalization-group calculation in order to obtain $O(\epsilon)$ recursion relations for the parameters Δ_1, Δ_2, Δ_3, w, and u appearing in $\mathscr{H}$ (it is necessary to consider the parameter r only at stable fixed points of the other Hamiltonian parameters). The following procedure is used: (i) We assume that the parameters Δ_i ($i=1,2,3$), w, and u are $O(1)$, $O(\epsilon^{1/2})$, and $O(\epsilon)$, respectively. (ii) We use an *anisotropic rescaling*[16] of the momentum $\mathbf{Q}$, i.e., we rescale $\mathbf{q}$ by a factor b and $\mathbf{k}$ by a factor a with $a/b=1+O(\epsilon)$. This permits us to impose constraints independently on Δ_1 and Δ_3, i.e., we can require that $\Delta_1=\Delta_3=1$ under renormalization. As usual,[3] we take the $\mathbf{Q}$ integrals in (46a) to be over the region $|\mathbf{Q}|\leq 1$. (iii) The order parameter is rescaled by a factor φ, i.e., $\mathbf{p}(\mathbf{q},\mathbf{k})=\varphi\mathbf{p}(b\mathbf{q},a\mathbf{k})$.

Starting from the expression (46a) for $\mathscr{H}$, we obtain a sequence of renormalized Hamiltonians $\mathscr{H}'$ having the same form, but with new parameters r', Δ_1', Δ_2', Δ_3', w',

and u' replacing the originals at each step. The terms with coefficients w and u can be considered as small perturbations in $d=4-\epsilon$ dimensions, and their contributions are evaluated by means of a diagrammatic expansion using the propagator (47). The third- and fourth-order vertices (iw and u, respectively) used in the evaluation of the various graphs are shown in Fig. 2. Note that the wavy α leg of the third-order vertex has a factor q^α associated with it.

We first investigate the $O(\epsilon)$ renormalized pair interaction $[U^{\alpha\beta}(\mathbf{Q})]'$. From the diagrams in Fig. 3, we obtain

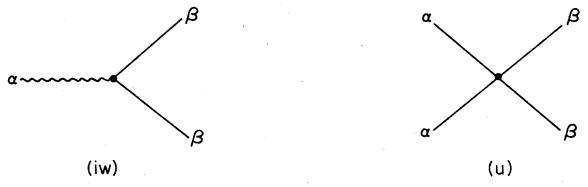

FIG. 2. Third- (iw) and fourth- (u) order vertices. The wavy α leg of the third-order vertex has a factor q^α associated with it.

$$
\begin{aligned}
[U^{\alpha\beta}(\mathbf{Q})]' = \varphi^2 b^{-n} a^{-d+n} \Big[& [r+(\Delta_1+\Delta_2)b^{-2}q^2+\Delta_3 a^{-2}k^2]\delta_{\alpha\beta} - 2\Delta_2 b^{-2} q^\alpha q^\beta + 4u \left[\int_{Q_1}^{>} G^{\gamma\gamma}(\mathbf{Q}_1) + 2\int_{Q_1}^{>} G^{\alpha\beta}(\mathbf{Q}_1) \right] \\
& - 2w^2 \Big[b^{-2} q^\alpha q^\beta \int_{Q_1}^{>} G^{\gamma\delta}(\mathbf{Q}_1) G^{\gamma\delta}(\mathbf{Q}_1 + b^{-1}\mathbf{q} + a^{-1}\mathbf{k}) \\
& + 4 b^{-1} q^\alpha \int_{Q_1}^{>} G^{\gamma\delta}(\mathbf{Q}_1) G^{\gamma\beta}(\mathbf{Q}_1 + b^{-1}\mathbf{q} + a^{-1}\mathbf{k}) q_1^\delta \\
& + 2 \int_{Q_1}^{>} G^{\gamma\delta}(\mathbf{Q}_1) G^{\alpha\beta}(\mathbf{Q}_1 + b^{-1}\mathbf{q} + a^{-1}\mathbf{k}) q_1^\gamma q_1^\delta \\
& - 2 \int_{Q_1}^{>} G^{\gamma\beta}(\mathbf{Q}_1) G^{\alpha\delta}(\mathbf{Q}_1 + b^{-1}\mathbf{q} + a^{-1}\mathbf{k}) q_1^\gamma (q_1^\delta + b^{-1} q^\delta) \Big] + O(u^2) \Big] ,
\end{aligned}
\tag{48}
$$

where $\int_Q^>$ denotes the integration $(2\pi)^{-d}\int d^dQ$ in the range between the sphere $q^2+k^2=1$ and the ellipsoid $b^2q^2+a^2k^2=1$, and the usual summation convention applies. Since all the integrals in (48) are multiplied by either u or w^2, both of which are taken to be $O(\epsilon)$, it is sufficient in an $O(\epsilon)$ calculation to set $r=0$ and $a=b$ (this implies an integration over $1>|\mathbf{Q}|>b^{-1}$) in the various integrals and evaluate them at $d=4$. Clearly, the terms proportional to u coming from Figs. 3(a) and 3(b) do not affect the Q-dependent part of $[U^{\alpha\beta}(\mathbf{Q})]'$ and can therefore be ignored (they contribute to r'). The four terms proportional to w^2 [Figs. 3(c)–3(f)] do, however, contribute to the Q-dependent part of $[U^{\alpha\beta}(\mathbf{Q})]'$. Since we are interested only in those terms containing q^2, k^2, and $q^\alpha q^\beta$, it is sufficient to study the integrals in (48) for very small values of $|\mathbf{Q}_1|$. In the range of integration $0<b^{-1}<|\mathbf{Q}_1|<1$ the various propagators in (48) are analytic in $\mathbf{Q}_1$ for small $|\mathbf{Q}_1|$, and we can therefore expand them about $\mathbf{Q}_1=0$ to obtain contributions proportional to $q^\alpha q^\beta$, q^2, and k^2. The first $O(w^2)$ term in (48) [Fig. 3(c)] contains a factor $q^\alpha q^\beta$, hence one can set $\mathbf{q}=\mathbf{k}=0$ in the propagator $G^{\gamma\delta}$ and calculate the integral $\int_{Q_1}^{>}[G^{\gamma\delta}(\mathbf{Q}_1)]^2$. As an example, we evaluate this integral explicitly. Using the expression (47) for the propagator with $r=0$ and summing over γ and δ gives

$$
[G^{\gamma\delta}(\mathbf{Q}_1)]^2 = (n-1)/[(\Delta_1+\Delta_2)q_1^2+\Delta_3 k_1^2]^2 + 1/[(\Delta_1-\Delta_2)q_1^2+\Delta_3 k_1^2]^2 . \tag{49}
$$

The integration of (49) over $\mathbf{Q}_1$ is given in the Appendix. Using (A10) and (A11) we obtain

$$
\int_{Q_1}^{>}[G^{\gamma\delta}(\mathbf{Q}_1)]^2 = (n-1)I_2 + I_3 , \tag{50}
$$

where I_2 and I_3 are given in (A11) and (A10), respectively. The second $O(w^2)$ term in (48) [Fig. 3(d)] is proportional to

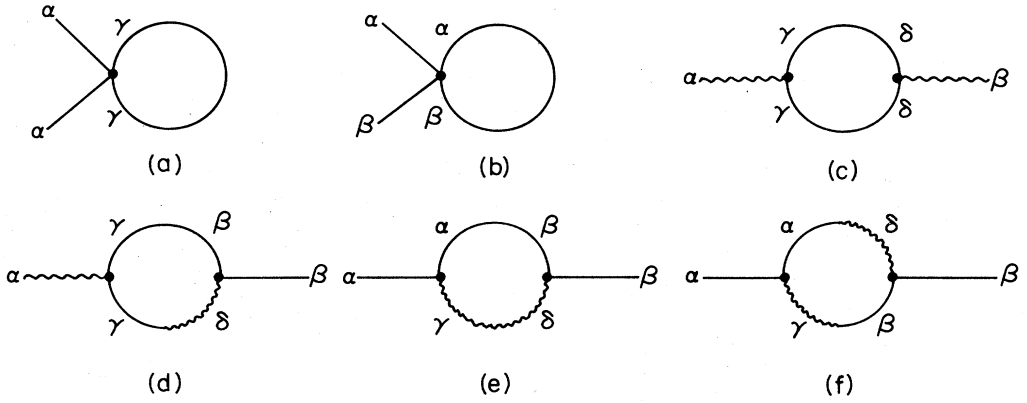

FIG. 3. Diagrams contributing to the $O(\epsilon)$ renormalization of the two-particle interaction $U^{\alpha\beta}(\mathbf{Q})$. The indices on the various legs are labeled in order to clarify the various contractions which appear in Eq. (48).

q^α, hence, we can set $\mathbf{k}=0$ in $G^{\gamma\beta}$ (note that terms odd in $\mathbf{k}$ do not contribute, see the Appendix), and expand the propagator to first order in $\mathbf{q}$. Several contributions proportional to q^β are generated (giving a contribution to $q^\alpha q^\beta$). A typical contribution is

$$\int_{Q_1}^{>} \frac{(q_1^\alpha q_1^\beta/q_1^2)q^\alpha}{[(\Delta_1+\Delta_2)q_1^2+\Delta_3 k_1^2][(\Delta_1-\Delta_2)q_1^2+\Delta_3 k_1^2]}$$
$$= K_n K_{4-n}\langle(q_1^\alpha q_1^\beta/q_1^2)\rangle q^\alpha \int\int_{\substack{b^{-1}\le q_1^2+k_1^2\le 1,\\ k_1\ge 0, q_1\ge 0}} \frac{q_1^{n-1}k_1^{3-n}}{[(\Delta_1+\Delta_2)q_1^2+\Delta_3 k_1^2][(\Delta_1-\Delta_2)q_1^2+\Delta_3 k_1^2]} dq_1 dk_1 = (I_1/n)q^\beta \quad (51)$$

where the angular integration $\langle(q_1^\alpha q_1^\beta/q_1^2)\rangle=\delta_{\alpha\beta}/n$ and I_1 are given in (A3) and (A12), respectively. In the third $O(w^2)$ term in (48) [Fig. 3(e)], it is necessary to expand the propagator $G^{\alpha\beta}$ to second order in $\mathbf{q}$ and $\mathbf{k}$. This generates contributions proportional to q^2, k^2, and $q^\alpha q^\beta$. A typical contribution to q^2 and $q^\alpha q^\beta$ is

$$8\Delta_2(\Delta_1+\Delta_2)^2\langle(q_1^\gamma q_1^\delta q_1^\alpha q_1^\beta/q_1^4)\rangle \int_{Q_1}^{>} \frac{q_1^6}{[(\Delta_1+\Delta_2)q_1^2+\Delta_3 k_1^2]^3[(\Delta_1-\Delta_2)q_1^2+\Delta_3 k_1^2]^2} q^\gamma q^\delta$$
$$= 8\Delta_2(\Delta_1+\Delta_2)^2 \frac{(\delta_{\alpha\beta}\delta_{\gamma\delta}q^\gamma q^\delta+\delta_{\alpha\gamma}\delta_{\beta\delta}q^\gamma q^\delta+\delta_{\alpha\delta}\delta_{\beta\gamma}q^\gamma q^\delta)}{n(n+2)}\left[-\frac{1}{2}\frac{\partial^3 I_1}{\partial^2(\Delta_1+\Delta_2)\partial(\Delta_1-\Delta_2)}\right]$$
$$= -\frac{4\Delta_2(\Delta_1+\Delta_2)^2}{n(n+2)}\frac{\partial^3 I_1}{\partial^2(\Delta_1+\Delta_2)\partial(\Delta_1-\Delta_2)}(q^2\delta_{\alpha\beta}+2q^\alpha q^\beta) . \quad (52)$$

The angular integral $\langle(q_1^\gamma q_1^\delta q_1^\alpha q_1^\beta/q_1^4)\rangle$ and the integral I_1 are given in (A9) and (A12), respectively. In the last $O(w^2)$ term in (48) [Fig. 3(f)] we again expand the propagator $G^{\alpha\beta}$ to second order in $\mathbf{q}$ and $\mathbf{k}$ (note that there is also a contribution proportional to q^δ for which it is sufficient to set $\mathbf{k}=0$ in $G^{\alpha\beta}$ and expand to first order in $\mathbf{q}$), which generates new contributions to q^2, k^2, and $q^\alpha q^\beta$. A typical contribution to $q^\alpha q^\beta$ is

$$-2(\Delta_1-\Delta_2)\langle(q_1^\gamma q_1^\beta/q_1^2)\rangle \int_{Q_1}^{>} \frac{q_1^2}{[(\Delta_1-\Delta_2)q_1^2+\Delta_3 k_1^2]^3} q^\alpha q^\gamma$$
$$= -2(\Delta_1-\Delta_2)\delta_{\gamma\beta}q^\gamma q^\alpha\left[-\frac{1}{2}\frac{\partial(I_3}{\partial(\Delta_1-\Delta_2)}\right]$$
$$= (\Delta_1-\Delta_2)\frac{\partial I_3}{\partial(\Delta_1-\Delta_2)}q^\alpha q^\beta . \quad (53)$$

The angular integral $\langle(q_1^\gamma q_1^\beta/q_1^2)\rangle$ and I_3 are given in (A8) and (A10), respectively.

Collecting terms proportional to q^2, $q^\alpha q^\beta$, and k^2, we obtain the following recursion relations for $(\Delta_1+\Delta_2)$, Δ_2, and Δ_3, respectively,

$$\Delta_1'+\Delta_2' = \varphi^2 b^{-n-2}a^{-d+n}(\Delta_1+\Delta_2-X_0 w^2 \ln b) , \quad (54)$$
$$\Delta_2' = \varphi^2 b^{-n-2}a^{-d+n}\Delta_2(1-X_2 w^2\ln b) , \quad (55)$$
$$\Delta_3' = \varphi^2 b^{-n}a^{-d+n-2}\Delta_3(1-X_3 w^2\ln b) , \quad (56)$$

with X_0, X_2, and X_3 given in Table I. Substracting (55) from (54) gives

$$\Delta_1' = \varphi^2 b^{-n-1}a^{-d+n}\Delta_1(1-X_1 w^2\ln b) , \quad (57)$$

with $X_1=X_0-X_2$ given in Table I.

We next consider the recursion relation for w. The diagrams in Fig. 4 give the following contributions

TABLE I. Coefficients entering into renormalization-group recursion relations. $K_4=1/8\pi^2$ is the usual angular integral in $d=4$ dimensions (see Ref. 2). $X_i=\alpha_i K_4(x_i\bar{I}_1+y_i\bar{I}_2+z_i\bar{I}_3)$; $S=-(\Delta_1+\Delta_2)/2\Delta_2$. $\bar{I}_1=[(\Delta_1-\Delta_2)\bar{I}_3-(\Delta_1+\Delta_2)\bar{I}_2]/(n-2)\Delta_2$; $\bar{I}_2=(\Delta_1+\Delta_2)^{-n/2}\Delta_3^{-(4-n)/2}$; $\bar{I}_3=(\Delta_1-\Delta_2)^{-n/2}\Delta_3^{-(4-n)/2}$. Note that $\bar{I}_i=I_i/K_4\ln b$ (see Appendix A).

i	α_i	x_i	y_i	z_i
0	$2/n(n+2)$	$2(n-2)+2(n^2+n+2)S+8(n+1)S^2$	$-4S-8(n+1)S^2$	4
1	$2/n(n+2)\Delta_1$	$n(2-3n)+2(n^2-n+2)S+8nS^2$	$\frac{1}{2}n(n-1)(n+2)-2(2-n)S-8nS^2$	$2n^2$
2	$2/n(n+2)\Delta_2$	$3n^2-4+4nS+8S^2$	$-\frac{1}{2}n(n-1)(n+2)-2nS-8S^2$	$2(2-n^2)$
3	$2(n-1)/n(4-n)\Delta_2$	$n+4S$	$-4S$	0
4	$8/n$	$-2(1+S)$	$\frac{1}{2}(n-1)(n+2)$	$n+3+2S$
5	$2/n\Delta_2$	1	$-n+1-2S$	$2(n-1+S)$
6	$4(n-1)/n(n+2)\Delta_2$	$2n$	$-(3n+4)$	$n+4$
7	$(n^2-1)/n(n+2)\Delta_2^2$	-2	1	1
8	$4/n(n+2)$	$8(n-1)$	$(n-1)(n^2+10n+12)$	$n^2+6n+20$

$$
\begin{aligned}
\varphi^2 b^{-2n} a^{-2(d-n)} \Big[& iw \int_Q \int_{Q_1} b^{-1} q^\alpha p^\alpha(\mathbf{Q}) p^\beta(\mathbf{Q}_1) p^\beta(-\mathbf{Q}-\mathbf{Q}_1) \\
& -4iwu \int_Q \int_{Q_1} \int_{Q_2}^{>} [b^{-1} q^\alpha p^\alpha(\mathbf{Q}) p^\beta(\mathbf{Q}_1) p^\beta(-\mathbf{Q}-\mathbf{Q}_1) G^{\gamma\delta}(\mathbf{Q}_2) G^{\gamma\delta}(\mathbf{Q}_2+b^{-1}\mathbf{q}+a^{-1}\mathbf{k}) \\
& \quad +2b^{-1} q^\alpha p^\alpha(\mathbf{Q}) p^\beta(\mathbf{Q}_1) p^\delta(-\mathbf{Q}-\mathbf{Q}_1) G^{\gamma\beta}(\mathbf{Q}_2) G^{\gamma\delta}(\mathbf{Q}_2+b^{-1}\mathbf{q}+a^{-1}\mathbf{k}) \\
& \quad +2p^\alpha(\mathbf{Q}) p^\beta(\mathbf{Q}_1) p^\beta(-\mathbf{Q}-\mathbf{Q}_1) G^{\gamma\delta}(\mathbf{Q}_2) G^{\gamma\alpha}(\mathbf{Q}_2+b^{-1}\mathbf{q}+a^{-1}\mathbf{k}) q_2^\delta \\
& \quad +4p^\alpha(\mathbf{Q}) p^\gamma(\mathbf{Q}_1) p^\beta(-\mathbf{Q}-\mathbf{Q}_1) G^{\gamma\delta}(\mathbf{Q}_2) q_2^\delta G^{\beta\alpha}(\mathbf{Q}_2+b^{-1}\mathbf{q}+a^{-1}\mathbf{k})] \\
& -4iw^3 \int_{Q_1} \int_{Q_2} \int_Q^{>} \{p^{\alpha_1}(\mathbf{Q}_1) q_1^{\alpha_1} p^{\beta_2}(\mathbf{Q}_2) p^{\beta_3}(-\mathbf{Q}_1-\mathbf{Q}_2) G^{\beta_1\beta_2}(\mathbf{Q}) G^{\beta_1\beta_3}(\mathbf{Q}+b^{-1}\mathbf{q}_1+a^{-1}\mathbf{k}_1) \\
& \quad \times G^{\alpha_2\alpha_3}(\mathbf{Q}-b^{-1}\mathbf{q}_2-a^{-1}\mathbf{k}_2)[(q^{\alpha_2}-b^{-1}q_2^{\alpha_2})(b^{-1}q_2^{\alpha_3}-q^{\alpha_3})] \\
& \quad +2p^{\alpha_1}(\mathbf{Q}_1) q_1^{\alpha_1} p^{\beta_3}(\mathbf{Q}_2) p^{\beta_2}(-\mathbf{Q}_1-\mathbf{Q}_2) G^{\beta_1\beta_3}(\mathbf{Q}) G^{\beta_1\alpha_2}(\mathbf{Q}+b^{-1}\mathbf{q}_1+a^{-1}\mathbf{k}_1) \\
& \quad \times G^{\alpha_3\beta_2}(\mathbf{Q}-b^{-1}\mathbf{q}_2-a^{-1}\mathbf{k}_2)[(q^{\alpha_2}-b^{-1}q_1^{\alpha_2})(q^{\alpha_3}-b^{-1}q_2^{\alpha_3})] \\
& \quad +p^{\alpha_1}(\mathbf{Q}_1) q_1^{\alpha_1} p^{\beta_3}(\mathbf{Q}_2) p^{\beta_2}(-\mathbf{Q}_1-\mathbf{Q}_2) G^{\beta_1\alpha_3}(\mathbf{Q}) G^{\beta_1\alpha_2}(\mathbf{Q}+b^{-1}\mathbf{q}_1+a^{-1}\mathbf{k}_1) \\
& \quad \times G^{\beta_2\beta_3}(\mathbf{Q}-b^{-1}\mathbf{q}_2-a^{-1}\mathbf{k}_2)[(-q^{\alpha_3})(q^{\alpha_2}+b^{-1}q_1^{\alpha_2})] \\
& \quad +2p^{\beta_1}(\mathbf{Q}_1) p^{\beta_2}(\mathbf{Q}_2) p^{\beta_3}(-\mathbf{Q}_1-\mathbf{Q}_2) G^{\alpha_1\beta_2}(\mathbf{Q}) G^{\beta_3\beta_1}(\mathbf{Q}+b^{-1}\mathbf{q}_1+a^{-1}\mathbf{k}_1) \\
& \quad \times G^{\alpha_2\alpha_3}(\mathbf{Q}-b^{-1}\mathbf{q}_2-a^{-1}\mathbf{k}_2)[(q^{\alpha_1})(q^{\alpha_2}-b^{-1}q_2^{\alpha_2})(b^{-1}q_2^{\alpha_3}-q^{\alpha_3})] \\
& \quad +\tfrac{2}{3} p^{\beta_1}(\mathbf{Q}_1) p^{\beta_2}(\mathbf{Q}_2) p^{\beta_3}(-\mathbf{Q}_1-\mathbf{Q}_2) G^{\beta_1\alpha_3}(\mathbf{Q}+b^{-1}\mathbf{q}_1+a^{-1}\mathbf{k}_1)[q^{\alpha_3}+b^{-1}q_1^{\alpha_3}] \\
& \quad \times G^{\beta_3\alpha_2}(\mathbf{Q}-b^{-1}\mathbf{q}_2-a^{-1}\mathbf{k}_2) G^{\beta_2\alpha_1}(\mathbf{Q})[q^{\alpha_1}]\} \Big] .
\end{aligned} \tag{58}
$$

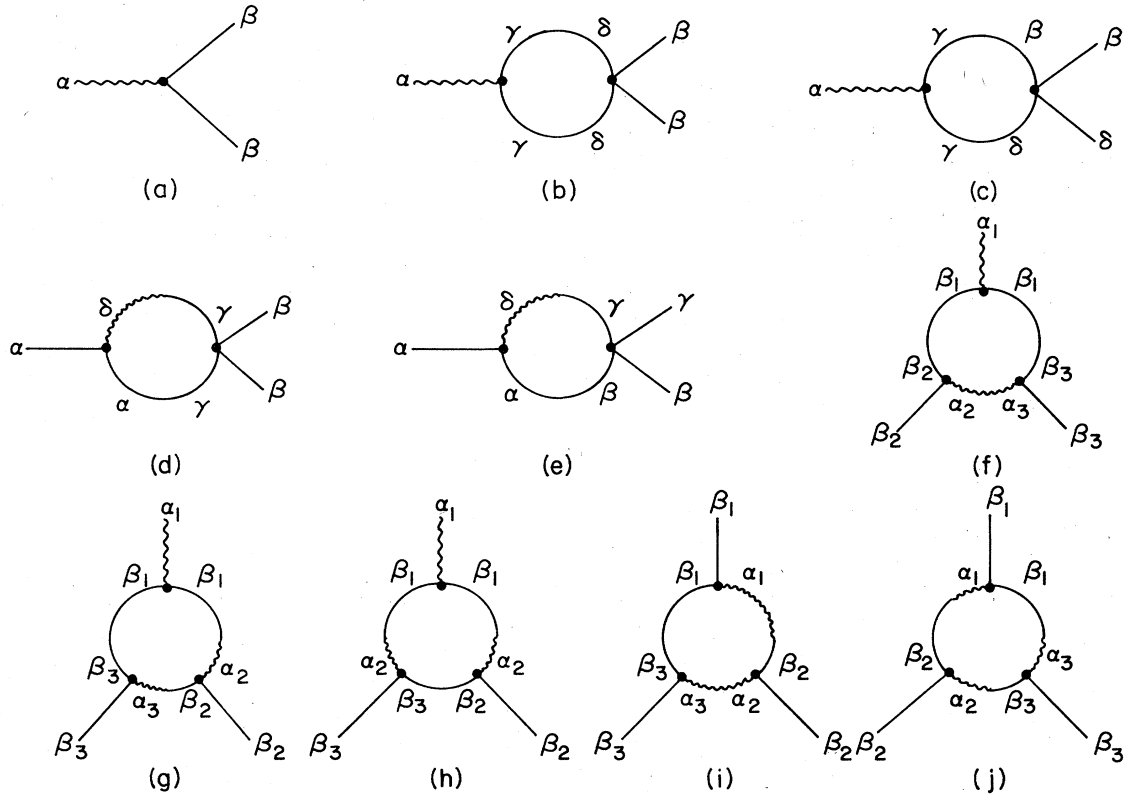

FIG. 4. Diagrams contributing to the $O(\epsilon)$ renormalization of w. The indices on the legs are labeled in order to clarify the various contractions which appear in Eq. (58).

The $O(w)$ term [Fig. 4(a)] in (58) is trivial and results from the rescaling of spin and momenta. There are four $O(wu)$ terms [Figs. 4(b)—4(e)] and five $O(w^3)$ terms [Figs. 4(f)—4(j)] in (58). In all the diagrams, wavy legs carry a momentum component factor; for example, in Fig. 4(h) leg α has a factor $q_1^{\alpha_1}$ associated with it. In principle, the integrals $\int_Q^>$ should be calculated in the range between the sphere $q^2+k^2=1$ and the ellipsoid $b^2q^2+a^2k^2=1$. However, as all the integrals in (58) are multiplied by either wu or w^3 which are $O(\epsilon^{3/2})$, it is sufficient in an $O(\epsilon)$ calculation to set $a=b$ [recall that $a=b+O(\epsilon)$] and integrate as usual over $1>|\mathbf{Q}|>b^{-1}$. We also set $r=0$ in the propagators and calculate the various integrals at $d=4$. As the first and second $O(wu)$ terms in (58) [Figs. 4(b) and 4(c)] are explicitly proportional to q^α, we set $\mathbf{q}=\mathbf{k}=0$ in $G^{\gamma\delta}$ when calculating the integrals. In the last two terms of $O(wu)$ [Figs. 4(d) and 4(e)] we expand $G^{\gamma\alpha}$ and $G^{\beta\alpha}$ to first order in $\mathbf{q}$ and $\mathbf{k}$ (in fact, the $\mathbf{k}$ contribution vanishes after the angular integration, see the Appendix). Collecting all contributions of $O(wu)$ we obtain X_4, see Table I.

The first three $O(w^3)$ terms [Figs. 4(f)—4(h)] are explicitly proportional to $q_1^{\alpha_1}$; we therefore set $\mathbf{q}_1=\mathbf{k}_1=0$ and $\mathbf{q}_2=\mathbf{k}_2=0$ when calculating these integrals. In the final two $O(w^3)$ terms [Figs. 4(i) and 4(j)] we expand to first order in $(\mathbf{q}_1,\mathbf{k}_1)$ and $(\mathbf{q}_2,\mathbf{k}_2)$. Note that there are some contributions explicitly proportional to $\mathbf{q}_2$ or $\mathbf{q}_1$, in these cases the external momenta are set to zero in the propagators. Due to the angular integration, all contributions proportional to $\mathbf{k}_1$ or $\mathbf{k}_2$ vanish (see the Appendix). Collecting the $O(w^3)$ terms, we obtain X_5, see Table I. The recursion relation for w is thus

$$w'=\varphi^3 b^{-2n-1}a^{-2(d-n)}(w-X_4 wu\ln b+X_5 w^3\ln b)\ . \tag{59}$$

Finally, we consider the $O(\epsilon)$ recursion relation for u. The set of diagrams needed for the calculation is given in Fig. 5. Since we are looking for contributions to u (which is momentum independent) we set all external momenta equal to zero in the various propagators and wavy legs. As before, we set $r=0$ in (47), take the range of integrations to be $1>|\mathbf{Q}|>b^{-1}$ when calculating $\int_Q^>$ and evaluate at $d=4$. The contributions to u' are then

$$\begin{aligned}
\varphi^4 b^{-3n}a^{-3(d-n)}\Big[&u\int_{Q_1}\int_{Q_2}\int_{Q_3}p^\alpha(\mathbf{Q}_1)p^\alpha(\mathbf{Q}_2)p^\beta(\mathbf{Q}_3)p^\beta(-\mathbf{Q}_1-\mathbf{Q}_2-\mathbf{Q}_3)\\
&-8w^2u\int_{Q_1}\int_{Q_2}\int_{Q_3}\int_{Q_4}\delta(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3+\mathbf{Q}_4)\\
&\times\int_Q^>[p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\delta(\mathbf{Q}_4)G^{\beta_1\beta_2}(\mathbf{Q})G^{\alpha_2\gamma}(\mathbf{Q})G^{\alpha_1\gamma}(\mathbf{Q})q^{\alpha_1}(-q^{\alpha_2})\\
&+2p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\gamma(\mathbf{Q}_4)G^{\beta_1\beta_2}(\mathbf{Q})G^{\alpha_2\delta}(\mathbf{Q})(-q^{\alpha_2})G^{\alpha_1\gamma}(\mathbf{Q})q^{\alpha_1}\\
&+p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\delta(\mathbf{Q}_4)G^{\alpha_1\alpha_2}(\mathbf{Q})q^{\alpha_1}(-q^{\alpha_2})G^{\beta_2\gamma}(\mathbf{Q})G^{\beta_1\gamma}(\mathbf{Q})\\
&+2p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\gamma(\mathbf{Q}_4)G^{\alpha_1\alpha_2}(\mathbf{Q})q^{\alpha_1}(-q^{\alpha_2})G^{\beta_2\delta}(\mathbf{Q})G^{\beta_1\gamma}(\mathbf{Q})\\
&+2p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\delta(\mathbf{Q}_4)G^{\alpha_1\gamma}(\mathbf{Q})q^{\alpha_1}G^{\alpha_2\beta_1}(\mathbf{Q})q^{\alpha_2}G^{\beta_2\gamma}(\mathbf{Q})\\
&+4p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\gamma(\mathbf{Q}_4)G^{\alpha_1\gamma}(\mathbf{Q})q^{\alpha_1}G^{\alpha_2\beta_1}(\mathbf{Q})q^{\alpha_2}G^{\beta_2\delta}(\mathbf{Q})]\\
&-4w^4\int_{Q_1}\int_{Q_2}\int_{Q_3}\int_{Q_4}\delta(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3+\mathbf{Q}_4)p^{\beta_1}(\mathbf{Q}_1)p^{\beta_2}(\mathbf{Q}_2)p^{\beta_3}(\mathbf{Q}_3)p^{\beta_4}(\mathbf{Q}_4)\\
&\times\int_Q^>[G^{\alpha_1\alpha_4}(\mathbf{Q})q^{\alpha_1}(-q^{\alpha_4})G^{\alpha_2\alpha_3}(\mathbf{Q})q^{\alpha_2}(-q^{\alpha_3})G^{\beta_1\beta_2}(\mathbf{Q})G^{\beta_3\beta_4}(\mathbf{Q})\\
&+2G^{\alpha_1\alpha_4}(\mathbf{Q})q^{\alpha_1}q^{\alpha_4}G^{\beta_1\alpha_2}(\mathbf{Q})q^{\alpha_2}G^{\beta_4\alpha_3}(\mathbf{Q})(-q^{\alpha_3})G^{\beta_2\beta_3}(\mathbf{Q})\\
&+4G^{\alpha_1\alpha_4}(\mathbf{Q})q^{\alpha_1}(-q^{\alpha_4})G^{\alpha_3\beta_4}(\mathbf{Q})(-q^{\alpha_3})G^{\alpha_2\beta_3}(\mathbf{Q})(-q^{\alpha_2})G^{\beta_1\beta_2}(\mathbf{Q})\\
&+G^{\alpha_1\beta_4}(\mathbf{Q})q^{\alpha_1}G^{\alpha_2\beta_1}(\mathbf{Q})q^{\alpha_2}G^{\alpha_3\beta_2}(\mathbf{Q})q^{\alpha_3}G^{\alpha_4\beta_3}(\mathbf{Q})q^{\alpha_4}]\\
&-4u^2\int_{Q_1}\int_{Q_2}\int_{Q_3}\int_{Q_4}\delta(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3+\mathbf{Q}_4)\\
&\times\int_Q^>[p^\alpha(\mathbf{Q}_1)p^\alpha(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\delta(\mathbf{Q}_4)G^{\beta\gamma}(\mathbf{Q})G^{\beta\gamma}(\mathbf{Q})\\
&+4p^\alpha(\mathbf{Q}_1)p^\alpha(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\gamma(\mathbf{Q}_4)G^{\gamma\beta}(\mathbf{Q})G^{\beta\delta}(\mathbf{Q})\\
&+4p^\alpha(\mathbf{Q}_1)p^\beta(\mathbf{Q}_2)p^\delta(\mathbf{Q}_3)p^\gamma(\mathbf{Q}_4)G^{\alpha\gamma}(\mathbf{Q})G^{\beta\delta}(\mathbf{Q})]\Big]\ ,
\end{aligned} \tag{60}$$

where the delta function $\delta(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3+\mathbf{Q}_4)$ ensures momentum conservation. The $O(u)$ term [Fig. 5(a)] in (60) is trivial and follows from the rescaling of spin and momenta. There are six $O(w^2u)$ terms [Figs. 5(b)—5(g)], four $O(w^4)$ terms [Figs. 5(h)— 5(k)], and three $O(u^2)$ terms [Figs. 5(e)—5(n)] in (60). The same type of analysis carried out earlier gives the recursion relation for u as

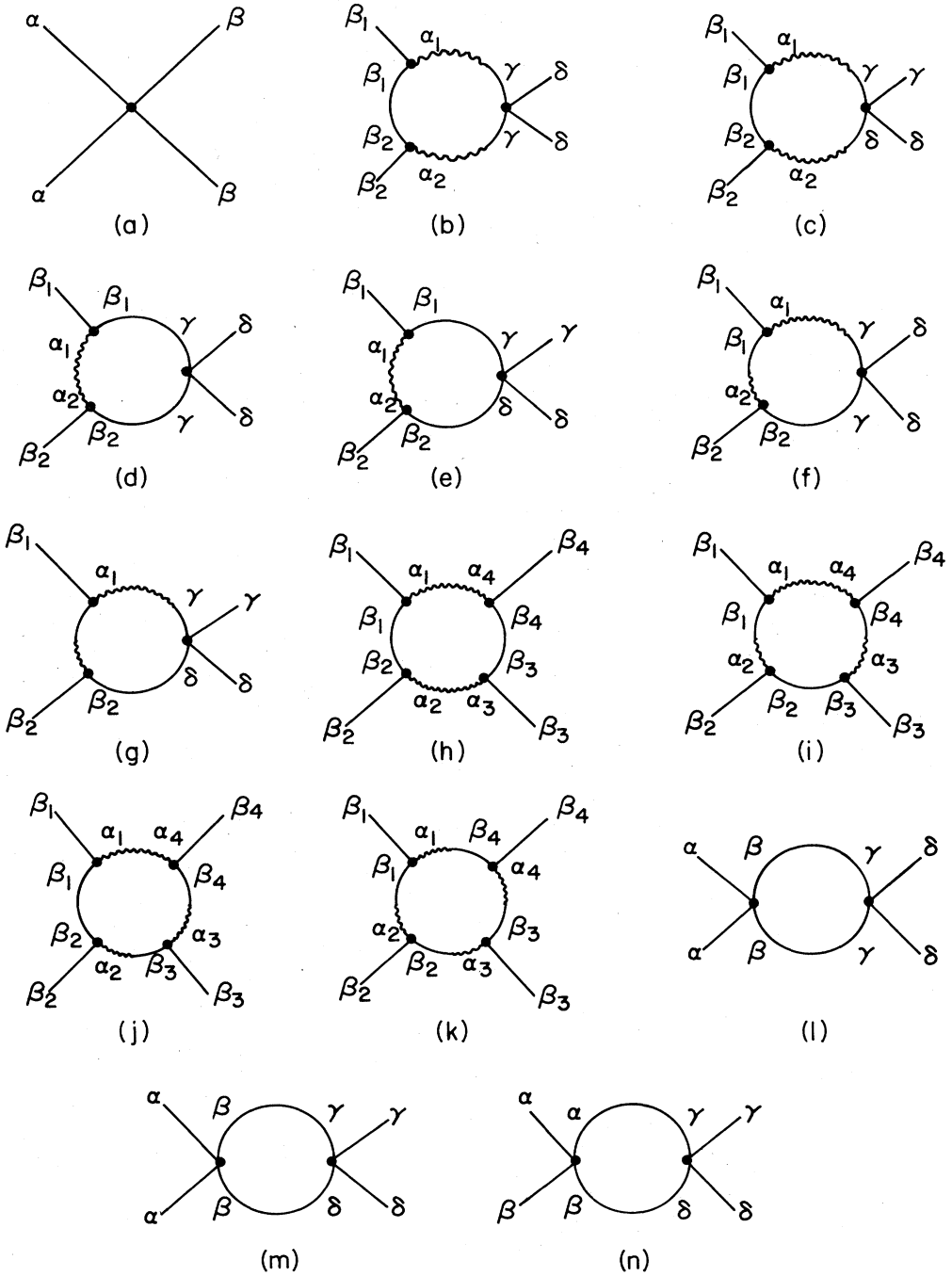

FIG. 5. Diagrams contributing to the $O(\epsilon)$ renormalization of u. The indices on the legs are labeled in order to clarify the various contractions which appear in Eq. (60).

$$u'=\varphi^4 b^{-3n} a^{-3(d-n)}(u+X_6 u w^2 \ln b - X_7 w^4 \ln b - X_8 u^2 \ln b), \tag{61}$$

with X_6, X_7, and X_8 given in Table I.

D. Fixed points and renormalization-group flows

As discussed earlier, the use of anisotropic rescaling[16] enables us to fix the ratio a/b and the order-parameter rescaling factor φ so as to maintain both Δ_1 and Δ_3 equal to unity. We are then left with just three renormalizable coefficients Δ_2, w, and u. Further, the quantities in Table I become functions of Δ_2 and n only. Dividing (57) by (56) (with $\Delta_1=\Delta_3=\Delta_1'=\Delta_3'=1$) and exponentiating, we find that to $O(\epsilon)$

$$a=b^{1+(X_1-X_3)w^2/2}, \tag{62}$$

so that $a/b=1+O(\epsilon)$ for $w=O(\epsilon^{1/2})$. Substituting (62) into (56) and exponentiating gives

$$\varphi^2=b^{(d+2)+[X_1+(4-n)(X_1-X_3)/2]w^2} . \quad (63)$$

Consider now Δ_2. Dividing (55) by (57) and exponentiating gives, to $O(\epsilon)$

$$\Delta_2'=\Delta_2 b^{(X_1-X_2)w^2} . \quad (64)$$

All $w^*\neq 0$ fixed points of (64) are therefore necessarily solutions of

$$X_1(n,\Delta_1=\Delta_3=1,\Delta_2^*)=X_2(n,\Delta_1=\Delta_3=1,\Delta_2^*) , \quad (65)$$

and are independent of w^* and u^* (see Table I). Given a solution $\Delta_2^*(n)$ of (65), it is convenient to consider the quantity $z=(w^2/u)$. Note that when $\Delta_2=\Delta_2^*$ this quantity is essentially $B=\beta^2/a\gamma$, which was introduced in Sec. II. To $O(\epsilon)$, z satisfies the recursion relation

$$z'=zb^{[X_7z^2+(X_1+2X_5-X_6)z+(X_8-2X_4)]u} , \quad (66)$$

and the $w^*,u^*\neq 0$ fixed-point equation

$$X_7^*(z^*)^2+(X_1^*+2X_5^*-X_6^*)z^*+(X_8^*-2X_4^*)=0 , \quad (67)$$

with $X_i^*\equiv X_i(n,\Delta_1=\Delta_3=1,\Delta_2^*)$.

By numerical analysis, we find that (65) has no $|\Delta_2^*|<1$ real solutions for $1.86\lesssim n\lesssim 4$. It follows that $\mathscr{H}$ has no $w^*\neq 0$ fixed points in this region of n. For $1<n\lesssim 1.85$, on the other hand, (65) has two real solutions. From (67), we find that $z^*(\Delta_2^*)$ is real and positive and, using (59), that there are two fixed points in the first quadrant of the (u,w^2) plane. Since, however, the $n<2$ region is not of physical interest, we did not analyze these fixed points further.

The Hamiltonian (45) thus has only (unstable) Gaussian ($u^*=w^*=0$) and WF ($u^*\neq 0$, $w^*=0$) fixed points to $O(\epsilon)$ in $d=4-\epsilon$ dimensions when $n\gtrsim 1.86$. We therefore examined the flows of the coefficients Δ_2, w, and u for various values of ϵ and $n\geq 2$ [chosen such that λ_w in (44) is positive] under repeated renormalization-group operations. This was done by using a small value of b and integrating the recursion relations numerically. Clearly, the region of parameter space of physical interest is $w^2\geq 0$ and $|\Delta_2|<1$ (recall that for stability $\Delta_1\pm\Delta_2>0$ and we have set $\Delta_1=1$). In addition, from the classical analysis carried out in Sec. II, we know that if after the Hamiltonian coefficients are renormalized to include fluctuation effects the quantity $B=\beta^2/a\gamma\sim w^2/(1-\Delta_2)u$ is greater than some numerical value, the transition will be of first order. Thus the relevant parameter space is bounded by three surfaces: $S_1(\Delta_2=-1)$, $S_2(w^2=0)$, and $S_3[w^2/u(1-\Delta_2)=\text{const}]$. These are shown in Fig. 6. Note that the usual WF fixed point at $w=\Delta_2=0$ becomes, at $O(\epsilon)$, a line of fixed points and that $u^*_{\rm WF}$ is Δ_2 dependent. For *all* initial points in the physical region, we find that the renormalization-group flows terminate on the surface S_3.

E. Discussion

In this section we have shown by a renormalization-group analysis that isotropic systems characterized by short-range forces and polar vector order parameters can behave quite differently from otherwise identical systems with axial vector order parameters (e.g., magnets). While the critical behavior of the latter, in $d=4-\epsilon$ dimensions, is described by the WF fixed point, that of polar vector systems is not. In fact, we have shown that the $n\geq 2$ ferroelectric model has *no* stable fixed points for $d=4-\epsilon$. This implies that the transition to an ordered state will always be of first order.[17] By examining the flow, we found that all renormalization-group trajectories within the physically relevant region reached the bounding surface $[w^2/u(1-\Delta_2)]=\text{const}$. This, together with the classical analysis of Sec. II, implies that the ordered state of the model system will not be ferroelectric, but rather antiferroelectric, most probably with a cubic unit cell.

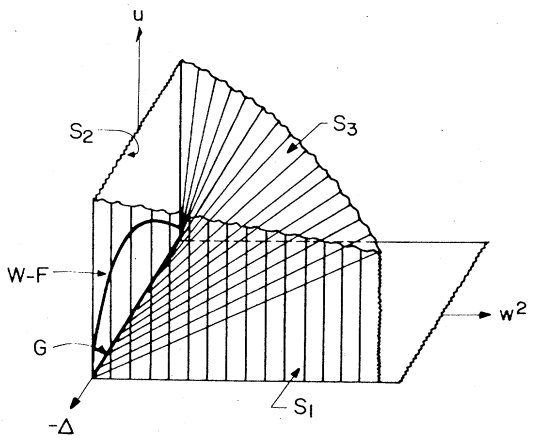

FIG. 6. Parameter subspace in which the renormalization-group flows occur for $n\geq 2$. The physical region is bounded by $S_1(\Delta_2=-1)$, $S_2(w^2=0)$, and $S_3[w^2/u(1-\Delta_2)=\text{const}]$. To $O(\epsilon)$ the Wilson-Fisher (WF) fixed point is Δ_2 dependent while the Gaussian is not. These points appear as line segments in the figure.

IV. SUMMARY AND CONCLUSIONS

In this paper, we have considered the implications of the additional symmetry-allowed term (2) in the free-energy density of systems described by polar vector order parameters. The most simple case, that of an isotropic centrosymmetric system with short-range interactions, was treated in detail using both classical Landau-theory and renormalization-group approaches. The Landau-theory analysis showed that a ferroelectric phase is thermodynamically stable only when the magnitude of the coefficient β multiplying the $\mathbf{p}^2\nabla\cdot\mathbf{p}$ term in the free-energy density is sufficiently small. Above the threshold (12), the ferroelectric phase is unstable and a modulated (antiferroelectric) phase appears as the temperature is lowered. The transition between the disordered and modulated phases may be either first or second order, depending upon the magnitude of β (see Fig. 1).

The nature of the modulated phase was investigated by calculating and comparing the free energies of alternative configurations. For $d=n=3$, i.e., a three-dimensional

system with a vector order parameter, the analysis in Sec. II clearly favors a cubic phase with space-group symmetry O_h^9. Other cases, however, are less clear. In particular, for $d=2$, $n=2$ or 3, it is difficult to choose between the hexagonal and linearly modulated structures analyzed in Secs. II C and II D. Here a further extension of the calculation appears to be necessary. Also, $d=3$, $n=2$, which may be of physical interest, was not considered explicitly. However, the configurations treated in Secs. II C and II D are possible candidates.

Turning to the renormalization-group analysis, we found that to $O(\epsilon)$ in $d=4-\epsilon$ dimensions, the model system has only Gaussian ($u^*=w^*=0$) and WF ($u^*\neq 0$, $w^*=0$) fixed points when $n \gtrsim 1.86$. For $d<4$ the former is, as usual, unstable while the latter is unstable for $n<n_0=4-11\epsilon/4+O(\epsilon^2)$ or, more generally, when the eigenvalue exponent λ_w in (44) is positive. In this case, all the renormalization-group flows leave the physical region (in which a classical analysis results in the model system undergoing a second-order phase transition) by reaching the surface

$$S_3=w^2/u(1-\Delta_2)=\text{const}\ . \tag{68}$$

Integrating the free energy over the renormalization-group trajectory eventually brings us to a regime in which mean-field theory will be applicable. Here we can use classical methods to analyze the free-energy expression and, from Sec. II, we expect that the system will undergo a first-order transition to a modulated ordered state. Thus, in so far as the renormalization-group analysis is applicable in three-dimensional systems (see below), we would expect the triple point in Fig. 1 to occur at $\beta=0$ and a modulated phase to appear immediately below the disordered phase for all β. Note, as indicated in Fig. 1(b), that the modulated structure may be stable only over a narrow temperature range. This result is in agreement with that obtained by Korzhenevskii,[11] who analyzed the case $n=d=3$ using low-order perturbation theory and concluded that a first-order transition to a modulated phase will occur.

We stress, however, that our analysis does not preclude the existence of a direct disordered-ferroelectric phase transition. For example, if we modify our Hamiltonian by taking $u<0$ and adding a $v(\mathbf{p}^2)^3$ term ($v>0$) to (45), a *first-order* transition to a ferroelectric state becomes possible. What we *have* rigorously shown is that a *second-order* transition to such a state cannot occur for systems modeled by (45) in $d=4-\epsilon$ dimensions when $1.86 \lesssim n<n_0$, even though this is allowed by mean-field (Landau) theory. The situation for $d=3$ is clearly more delicate, but it is likely that here also there exists a critical value n_c of n below which the WF fixed point is unstable. The discussion following (44) indicates that $n_c(d=3)>2$, thus our analysis could be relevant to XY ($n=2$) and possibly also to Heisenberg ($n=3$) ferroelectric systems in three dimensions. Note that $n_c(d=3)>3$ is supported by the results of Korzhenevskii.[11] We therefore conclude that simple ferroelectric and ferromagnetic systems do not necessarily belong to the same universality class[2] in $d=3$.

Experimentally, a search for noncommensurate phases in ferroelectrics should, as we have indicated, concentrate on systems with $n=2$ or 3 order parameters. The temperature region of interest is near the order-disorder phase boundary and the modulated phase is expected to exhibit a long-wavelength superstructure. This should be reflected in anomalies in the dielectric constant.

Such an anomaly has been reported by Smolenskii *et al.*,[18] who conducted a careful study of the multiple phase transitions which occur in cadmium pyroniobate $Cd_2Nb_2O_7$. At room temperature this compound has a cubic crystallographic structure (space group O_h^7) and undergoes a transition to a ferroelectric phase at 201 K. However, between 201 and 205 K there apparently exists a different ordered phase. As noted by the authors, their observations are consistent with this phase having a superstructure with a large period. This, of course, agrees with the theoretical results obtained by us. Further studies of this and similar compounds will be necessary in order to make a more detailed comparison with theoretical predictions. A useful experimental technique for such studies could be measurements of the velocity and absorption of *longitudinal* ultrasonic waves as a function of temperature, since the modulated structures are characterized by $\nabla\cdot\mathbf{p}\neq 0$ polarization waves. This technique has been shown to be an effective way of resolving multiple phase transitions occurring in ferroelectrics within narrow temperature intervals.[19] Measuring the electric field dependence of these transitions should help in determining whether they are first or second order. Such studies would clarify the nature of phase transitions in ferroelectric systems.

ACKNOWLEDGMENTS

We are grateful to A. Aharony, S. Alexander, E. Domany, D. Mukamel, and S. Shtrikman for helpful discussions. We are indebted to R. G. Petschek (see Ref. 13) for his comments. This work was supported in part by a grant from the United States—Israel Binational Science Foundation. One of us (R.M.H.) acknowledges support by the Science and Engineering Research Council of the United Kingdom. The other (D.B.) is grateful to the Bantrell Foundation for financial support.

APPENDIX A

The d-dimensional integrations over $\mathbf{Q}$ space in Sec. III C involve expressions of the form

$$I=\int_{\mathbf{Q}} f(\mathbf{q},\mathbf{k})=\int \frac{d^dQ}{(2\pi)^d} f(\mathbf{q},\mathbf{k}) = \int\int \frac{d^nq}{(2\pi)^n}\frac{d^{d-n}k}{(2\pi)^{d-n}} f(\mathbf{q},\mathbf{k})\ , \tag{A1}$$

with $\mathbf{Q}=\mathbf{q}+\mathbf{k}$. Here $\mathbf{q}$ and $\mathbf{k}$ have n and $(d-n)$ components, respectively. It is useful (see below) to use spherical coordinates in the $\mathbf{q}$ and $\mathbf{k}$ subspaces separately, so that

$$f(\mathbf{q},\mathbf{k})=f(q,\theta_q,\varphi_q,\psi_q,\ldots;k,\theta_k,\varphi_k,\psi_k,\ldots)\ , \tag{A2}$$

and I becomes[20]

$$I=\left[K_nK_{d-n}\int q^{n-1}dq\int k^{d-n-1}dk\int_0^\pi \sin^{n-2}\theta_q\,d\theta_q\int_0^\pi \sin^{n-3}\varphi_q d\varphi_q\times\cdots\right.$$
$$\left.\times\int_0^\pi \sin^{d-n-2}\theta_k\,d\theta_k\int_0^\pi \sin^{d-n-3}\varphi_k\,d\varphi_k\times\cdots\times f(\mathbf{q},\mathbf{k})\right]$$
$$\times\left[\int_0^\pi \sin^{n-2}\theta_q d\theta_q\int_0^\pi \sin^{n-3}\varphi_q\,d\varphi_q\times\cdots\times\int_0^\pi \sin^{d-n-2}\theta_k\,d\theta_k\int_0^\pi \sin^{d-n-3}\varphi_k d\varphi_k\times\cdots\right]^{-1}, \tag{A3}$$

where

$$K_d^{-1}=2^{d-1}\pi^{d/2}\Gamma(d/2)\ . \tag{A4}$$

We are specifically interested in functions which involve products of Cartesian components of $\mathbf{q}$ and $\mathbf{k}$, such as

$$f(\mathbf{q},\mathbf{k})=F(q,k)(q^\alpha/q)^m(q^\beta/q)^n\cdots(k^\gamma/k)^{m_1}(k^\delta/k)^{n_1}\cdots\ . \tag{A5}$$

From symmetry arguments, it is clear that the integral I will vanish unless all the exponents in (A5) are *even*. In all such cases, the angular integrations can be carried out separately in the $\mathbf{q}$ and $\mathbf{k}$ subspaces with the aid of the identity,

$$\int_0^\pi \sin^m\theta\cos^n\theta\,d\theta=B((m+1)/2,(n+1)/2)=\Gamma((m+1)/2)\Gamma((n+1)/2)/\Gamma((m+n+2)/2)\ . \tag{A6}$$

Denoting the angular part of the integral I by

$$\langle(q^\alpha/q)^m(q^\beta/q)^n\cdots(k^\gamma/k)^{m_1}(k^\delta/k)^{n_1}\cdots\rangle=\langle(q^\alpha/q)^m(q^\beta/q)^n\cdots\rangle\times\langle(k^\gamma/k)^{m_1}(k^\delta/k)^{n_1}\cdots\rangle\ ,$$

with

$$\langle(q^\alpha/q)^m(q^\beta/q)^m\cdots\rangle$$
$$=\left[\int_0^\pi \sin^{n-2}\theta_q d\theta_q\cdots\int_0^\pi \sin^{n-3}\varphi_q d\varphi_q\cdots(q^\alpha/q)^m(q^\beta/q)^n\cdots\right]\left[\int_0^\pi \sin^{n-2}\theta_q d\theta_q\int_0^\pi \sin^{n-3}\varphi_q d\varphi_q\cdots\right]^{-1}, \tag{A7a}$$

and

$$\langle(k^\gamma/k)^{m_1}(k^\delta/k)^{n_1}\cdots\rangle=\left[\int_0^\pi \sin^{d-n-2}\theta_k d\theta_k\int_0^\pi \sin^{d-n-3}\varphi_k d\varphi_k\cdots(k^\gamma/k)^{m_1}(k^\delta/k)^{n_1}\cdots\right]$$
$$\times\left[\int_0^\pi \sin^{d-n-2}\theta_k d\theta_k\int_0^\pi \sin^{d-n-3}\varphi_k d\varphi_k\cdots\right]^{-1}, \tag{A7b}$$

we find

$$\langle(q^\alpha q^\beta/q^2)\rangle=\delta_{\alpha\beta}\langle\cos^2\theta_q\rangle=\left[\int_0^\pi \sin^{n-2}\theta_q\cos^2\theta_q d\theta_q\right]\delta_{\alpha\beta}\left[\int_0^\pi \sin^{n-2}\theta_q\,d\theta_q\right]^{-1}=\frac{1}{n}\delta_{\alpha\beta}\ , \tag{A8}$$

$$\langle(q^\alpha q^\beta q^\gamma q^\delta/q^4)\rangle=\frac{1}{n(n+2)}(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\gamma\beta})\ . \tag{A9}$$

Similar results are obtained for $\langle(k^\alpha k^\beta/k^2)\rangle$ and $\langle(k^\alpha k^\beta k^\gamma k^\delta/k^4)\rangle$ with $d-n$ replacing n everywhere. After carrying out the angular integrals, there remain integrations which involve only the magnitudes of $\mathbf{q}$ and $\mathbf{k}$. In our calculations there are three basic integrals of this type, from which all other integrals can be obtained. Setting $d=4$, these are

$$I_3=K_nK_{4-n}\int\int_{\substack{b^{-1}\le q^2+k^2\le 1\\ k\ge 0,q\ge 0}} q^{n-1}k^{3-n}dq\,dk\frac{1}{[(\Delta_1-\Delta_2)q^2+\Delta_3k^2]^2}$$
$$=K_4\ln b(\Delta_1-\Delta_2)^{-n/2}\Delta_3^{-(4-n)/2}\ , \tag{A10}$$

$$I_2=K_nK_{4-n}\int\int_{\substack{b^{-1}\le q^2+k^2\le 1\\ k\ge 0,q\ge 0}} q^{n-1}k^{3-n}dq\,dk\frac{1}{[(\Delta_1+\Delta_2)q^2+\Delta_3k^2]^2}$$
$$=K_4\ln b(\Delta_1+\Delta_2)^{-n/2}\Delta_3^{-(4-n)/2}\ , \tag{A11}$$

$$I_1=K_nK_{4-n}\int\int_{\substack{b^{-1}\le q^2+k^2\le 1\\ k\ge 0,q\ge 0}} q^{n-1}k^{3-n}dq\,dk\frac{1}{[(\Delta_1+\Delta_2)q^2+\Delta_3k^2][(\Delta_1-\Delta_2)q^2+\Delta_3k^2]}$$
$$=\frac{K_4\ln b\,\Delta_3^{-(4-n)/2}}{\Delta_2(n-2)}[(\Delta_1-\Delta_2)^{(2-n)/2}-(\Delta_1+\Delta_2)^{(2-n)/2}]\ , \tag{A12}$$

where we have used the identity

$$K_4=\tfrac{1}{2}K_nK_{4-n}B(n/2,(4-n)/2)=1/8\pi^2 .$$

To evaluate (A10)—(A12), we transformed to spherical coordinates, i.e., $q=Q\sin\theta$ and $k=Q\cos\theta$, with Q and θ in the range $(1/b$ to 1) and (0 to $\pi/2$), respectively, and then used[21]

$$\int_0^{\pi/2}\frac{(\sin\theta)^{2\mu-1}(\cos\theta)^{2\nu-1}}{(\alpha^2\sin^2\theta+\beta^2\cos^2\theta)^{\mu+\nu}}=\frac{B(\mu,\nu)}{2\alpha^{2\mu}\beta^{2\nu}} ,$$

$$\mathrm{Re}(\mu)>0,\ \mathrm{Re}(\nu)>0 , \quad \text{(A13)}$$

with $B(\mu,\nu)=\Gamma(\mu)\Gamma(\nu)/\Gamma(\mu+\nu)$.

---

*Present and permanent address.

[1]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), Chap. 14.

[2]See, e.g., S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, 1976); K. G. Wilson and J. Kogut, Phys. Rep. **12C**, 75 (1974); M. E. Fisher, Rev. Mod. Phys. **46**, 597 (1974).

[3]L. D. Landau, Phys. Z. Sowjetunion **11**, 26, 545 (1937); *The Collected Papers of L. D. Landau,* edited by D. ter Haar (Gordon and Breach-Pergamon, New York, 1965), p. 193.

[4]G. Baym, H. A. Bethe, and C. J. Pethick, Nucl. Phys. A **175**, 225 (1971); S. Alexander and J. McTague, Phys. Rev. Lett. **41**, 702 (1978).

[5]See, e.g., A. Aharony, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 395.

[6]T. Nattermann, Ferroelectrics **29**, 75 (1980).

[7]See, e.g., P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), Chap. 2.

[8]A. Michelson, Ph.D. thesis, Technion—Israel Insitute of Technology, Haifa, Israel, 1977 (unpublished).

[9]T. A. Aslanyan and A. P. Levanyuk, Fiz. Tverd. Tela **20**, 804 (1978) [Sov. Phys. Solid State **20**, 466 (1978)].

[10]In quantum field theories in which charge conjugation is an allowed symmetry, (2) would be forbidden. This, of course, does not apply to condensed matter. We thank S. Alexander for this comment.

[11]S. Alexander, R. M. Hornreich, and S. Shtrikman, in *Symmetries and Broken Symmetries in Condensed Matter Physics,* edited by N. Boccara (IDSET, Paris, 1981), p. 379.

[12]A. L. Korzhenevskii, Zh. Eksp. Theor. Fiz. **81**, 1071 (1981) [Sov. Phys.—JETP **54**, 568 (1981)].

[13]D. Blankschtein, E. Domany, and R. M. Hornreich, Phys. Rev. Lett. **49**, 1716 (1982). Two entries in this letter's table are incorrect; the correct expressions are given in our Table I. The results in the physically relevant region ($n\geq 2$) are unaffected. We are grateful to R. G. Petschek for bringing this to our attention and for clarifying correspondence and discussions.

[14]S. Alexander, in *Symmetries and Broken Symmetries in Condensed Matter Physics,* Ref. 11, p. 141.

[15]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983); **28**, 3669(E) (1983); **30**, 3264 (1984).

[16]R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. **35**, 1678 (1975).

[17]P. Bak, S. Krinsky, and D. Mukamel, Phys. Rev. Lett. **36**, 52 (1976).

[18]G. A. Smolenskii, F. M. Salaev, L. S. Kamzina, N. N. Krainik, and S. N. Dorogovtsev, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 257 (1983) [JETP Lett. **37**, 303 (1983)].

[19]A. V. Gomonnai, A. A. Grabar, Yu. M. Vysochanskii, A. D. Belyaeu, V. F. Machulin, M. I. Gurzan, and V. Yu. Slivka, Fiz. Tverd. Tela (Leningrad) **23**, 3602 (1981) [Sov. Phys. Solid State **23**, 2093 (1981)].

[20]K. G. Wilson, Phys. Rev. Lett. **28**, 548 (1972); A. Aharony, Phys. Rev. B **8**, 3323 (1973).

[21]See, e.g., I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1980), p. 377, formula 3.642(1).