Polarization fluctuations in ferroelectric models

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We consider the relation between the finite-wave-vector susceptibility $\chi(\vec{q})$ of the six-vertex model family and the macroscopic susceptibility. This is nontrivial because $\chi(\vec{q})$ is singular at $\vec{q}=0$. Using exact results for the macroscopic susceptibility, we infer the analytic form of the anisotropy parameter appearing in the pair-correlation function at large separation. Proceeding phenomenologically, we consider the effect of relaxing the ice rules, and the effect of short-ranged interactions other than the ice rules (e.g., polarization gradient energies).

I. INTRODUCTION

This paper is concerned with long-wavelength polar fluctuations in model ferroelectric systems which obey or which nearly obey ice-rule constraints. Much of the discussion concerns the six-vertex model in two spatial dimensions (2D). Many exact results have been obtained for this model family,[1] and there are real systems to which these results may usefully be applied.[2–5] We will see that many of the conclusions drawn about the 2D models apply as well to the 3D case.

The 2D six-vertex model consists of arrows (pseudospins) assigned to each bond in a square planar array, such that precisely two arrows point into and two arrows point away from each vertex (the ice rules). Each of the six allowed vertices (shown in Fig. 1) has a weight $\omega_i = \exp(-\beta E_i)$, where E_i is the vertex energy. In the absence of external fields, symmetry requires that $\omega_1=\omega_2$, $\omega_3=\omega_4$, and $\omega_5=\omega_6$. There are two important characteristic parameters for this model family. One,

$$\Delta = \frac{\omega_1^2+\omega_3^2-\omega_5^2}{2\omega_1\omega_3} \quad , \tag{1}$$

is a measure of ferro- or antiferroelectric tendencies, since a transformation to a ferroelectric (antiferroelectric) phase occurs for $\Delta = 1(-1)$. The anisotropy parameter,

$$\eta = (\omega_1/\omega_3) \quad , \tag{2}$$

measures the preference for (1,2) vertices over (3,4) vertices, and hence the $x-y$ anisotropy of the polar configurations. The intrinsic inversion symmetry is removed by a pseudoelectric field with components (h, v) which lie along the directions (x', y') of the arrows and couple linearly to them, so that

$$(\omega_1/\omega_2) = \exp 2\beta(h+v) \quad , \tag{3a}$$

$$(\omega_3/\omega_4) = \exp 2\beta(h-v) \quad . \tag{3b}$$

In this paper, we use a coordinate system which is rotated by $\frac{1}{4}\pi$ from the bond axes (see Fig. 1), which thus coincides with the natural twofold axes of the anisotropic ($\eta \neq 1$) model. For example, we use field components (E_x, E_y) related to (h, v) by

$$E_x = 2^{-1/2}(h+v); \quad E_y = 2^{-1/2}(-h+v) \quad . \tag{4}$$

In general, expressions are more simplified in this system.

Our goal is to describe the long-wavelength polarization fluctuations, i.e., the small-$\vec{q}$ behavior of the wave-vector-dependent susceptibility $\chi(\vec{q})$. A recent study[5] of polarization correlations at large $\vec{r}$ gave partial information about $\chi(\vec{q})$; but in that study, the functional form was incompletely specified, and the relation between the macroscopic fluctuations and the merely long-wavelength ones was left altogether unclear. Here, we complete the derivation of $\chi(\vec{q}\neq 0)$ at small $\vec{q}$, and consider its relation to $\chi(\vec{q}=0)$. In addition, we offer conclusions about the effect on χ of ice-rule violations, and we consider phenomenologically the leading finite-q corrections to χ due to Δ-dependent energies associated with polarization gradients.

Since we are concerned with a synthesis of thermodynamic and microscopic quantities, we begin by

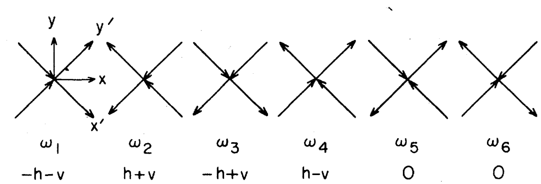

FIG. 1. Here we define the six vertices and their associated weights $\omega_i = \exp(-\beta\epsilon_i)$. The energy of each in the presence of horizontal and vertical fields (h and v) is also given. The primed coordinate system lies along the bond directions; the unprimed system faithfully reflects the symmetry properties of the $\{\omega_i\}$.

summarizing the relevant information currently available from each. Both developments are elaborations of Lieb's observation[6] that the transfer matrix for 2D ice has an eigenvector identical to that for the quantum 1D Heisenberg Ising ground state; this culminated in exact expressions for the free energy of the 2D six-vertex problem in an arbitrary external field by Sutherland, Yang, and Yang (SYY).[7] Their solution for the "disordered" region, $-1 \leq \Delta \leq 1$, can (with some rearrangement) be written in the form:

$$F - F_0 = \tfrac{1}{2}(\chi_x^{-1}P_x^2 + \chi_y^{-1}P_y^2) - \vec{P}\cdot\vec{E} + \cdots \quad ; \quad (5)$$

where the ellipsis represents higher-order terms in (P_x, P_y) and

$$\chi_x(\Delta,\eta) = 2\tilde{\lambda}\beta/(\pi-\mu) \quad , \quad (6a)$$

$$\chi_y(\Delta,\eta) = 2\beta/\tilde{\lambda}(\pi-\mu) \quad , \quad (6b)$$

$$\tilde{\lambda}(\Delta,\eta) = \frac{1+\sin z}{\cos z}; \quad z = \left(\frac{\pi\phi_0}{2\mu}\right) \quad , \quad (7)$$

and from SYY

$$\mu = \cos^{-1}(-\Delta) \ (0 > \mu > \pi) \quad ,$$
$$\exp(i\phi_0) = \left(\frac{1+\eta\exp(i\mu)}{\exp(i\mu)+\eta}\right) \quad . \quad (8)$$

Equations (5)–(8) are a straightforward transcription of SYY, in which we have: (i) supplied an omitted factor $\beta = (k_B T)^{-1}$; (ii) transformed from order parameter variables (P_h, P_v) which point along bonds in the six-vertex lattice to new variables rotated by $\frac{1}{4}\pi$,

$$P_x = (2)^{-1/2}(P_h + P_v); \quad P_y = (2)^{-1/2}(-P_h + P_v) \quad ; \quad (9)$$

and (iii) added a term $-\vec{P}\cdot\vec{E}$ to convert from a Helmholtz to a Gibbs free energy.

The other line of development involves pair-correlation functions. Sutherland[8] gave an exact result for the correlation function between vertical arrows at arbitrary $\vec{r}$, valid at $\Delta = 0$, where the problem simplifies to one of free fermions. Youngblood, Axe, and McCoy[5] (YAM) considered this problem further. They used: (i) Baxter's[9] correspondence between the six-vertex model and the dimer model; (ii) Fisher and Stephenson's[10] exact results for the dimer-model correlation functions; and (iii) a coarse-graining procedure to suppress antiferroelectric fluctuations.

Combining these things, they found explicit, asymptotically exact expressions for $g_{\alpha\beta}(\vec{R}) = \langle P_\alpha(\vec{r}\,')P_\beta(\vec{r})\rangle$ for large $\vec{R} = \vec{r} - \vec{r}\,'$. $\vec{P}(\vec{r})$ is the local generalization of the spatially homogeneous variable $\vec{P}$ of Eq. (5). $g_{\alpha\beta}(\vec{R})$ decays algebraically

$$g_{yy}(\vec{R}) \sim -A\frac{(x^2-\lambda^2y^2)}{(x^2+\lambda^2y^2)^2} \quad , \quad (10a)$$

$$g_{xy}(\vec{R}) \sim A\frac{2\lambda^2xy}{(x^2+\lambda^2y^2)^2} \quad , \quad (10b)$$

$$g_{xx}(\vec{R}) \sim A\lambda^2\frac{(x^2-\lambda^2y^2)}{(x^2+\lambda^2y^2)^2} \quad , \quad (10c)$$

where $\vec{R} = (x,y)$ measures the distance in units of the elementary six-vertex cell dimension, and $\sim$ denotes asymptotic equality as $R \to \infty$. These results were derived for $\Delta = 0$, but YAM were able to use the spin-spin correlation function[11–13] for the Heisenberg-Ising chain to establish that the form of Eq. (10) is generally valid for $-1 \leq \Delta \leq 1$, and further that

$$\pi A(\Delta) = (\pi-\mu)^{-1} = 1/\cos^{-1}(\Delta) \quad . \quad (11)$$

On the other hand, it was possible to evaluate λ only for the special case $\Delta = 0$,

$$\lambda(\Delta = 0, \eta) = \eta \quad . \quad (12)$$

II. WAVE-VECTOR-DEPENDENT SUSCEPTIBILITY

A. Long-wavelength response

Consider the linear response, $\vec{P}(\vec{r}) = \vec{P}(\vec{q}) \times \exp(i\vec{q}\cdot\vec{r})$, to a spatially inhomogeneous, long-wavelength perturbation, $\vec{E}(\vec{r}) = \vec{E}(\vec{q})\exp(i\vec{q}\cdot\vec{r})$:

$$\chi_{\alpha\beta}(\vec{q}) = \frac{P_\alpha(\vec{q})}{E_\beta(\vec{q})} = \beta\int d\vec{R}\exp(i\vec{q}\cdot\vec{R})g_{\alpha\beta}(\vec{R}) \quad , \quad (13)$$

where we have made use of the classical fluctuation dissipation theorem. Inserting the asymptotic expressions for $g_{\alpha\beta}(\vec{R})$, we find[5] the following expressions for $\chi_{\alpha\beta}(\vec{q})$:

$$\chi_{xx}(\vec{q}) = 2\pi A\beta\left(\frac{q_y^2}{\lambda q_x^2+\lambda^{-1}q_y^2}\right) \quad , \quad (14a)$$

$$\chi_{xy}(\vec{q}) = \chi_{yx}(\vec{q}) = 2\pi A\beta\left(\frac{-q_xq_y}{\lambda q_x^2+\lambda^{-1}q_y^2}\right) \quad , \quad (14b)$$

$$\chi_{yy}(\vec{q}) = 2\pi A\beta\left(\frac{q_x^2}{\lambda q_x^2+\lambda^{-1}q_y^2}\right) \quad . \quad (14c)$$

Note that $\chi(\vec{q})$ is singular: it tends to no unique value as $\vec{q} \to 0$, but rather depends upon the direction along which $\vec{q} = 0$ is approached. This behavior is familiar in certain electrostatics problems[14]; the clearest insight into its cause in the present case comes by transforming Eqs. (14) into a rotated coordinate system, whose axes are parallel and perpendicular to $\vec{q}$. In this system the tensor $\chi_{\alpha\beta}(\vec{q})$ is diagonal. Its diagonal elements are given by

$$\chi_{\parallel}(\vec{q}) = 0 \tag{15a}$$

and

$$\chi_{\perp}(\vec{q}) = 2\pi A\beta\left(\frac{q_x^2+q_y^2}{\lambda q_x^2+\lambda^{-1}q_y^2}\right) , \tag{15b}$$

so that the response is entirely transverse to $\vec{q}$. The explanation of the complete suppression of the longitudinal response is evident. The ice rules guarantee that polarization is locally conserved, so that

$$\vec{\nabla}\cdot\vec{P}(\vec{r}) = i\vec{q}\cdot\vec{P}(\vec{q})\exp(i\vec{q}\cdot\vec{r}) = 0 \tag{16}$$

for all $\vec{r}$. Thus, the ice rules alone force $\vec{P}(\vec{q})$ to be transverse, and this is in turn directly reflected in the singularity of $\chi(\vec{q})$.

One may inquire as to the effect on $\chi_{\alpha\beta}(\vec{q})$ of the shorter-ranged contributions to $g_{\alpha\beta}(\vec{R})$ omitted from Eq. (10). Since the neglected terms are shorter ranged, and because the singular behavior of $\chi_{\alpha\beta}(\vec{q})$ is associated with the range of the correlations, we expect (but have not proven) that the contribution of the neglected terms to the susceptibility, call it $\chi'(\vec{q})$, is nonsingular as $\vec{q}\to 0$. We know that the exact longitudinal susceptibility vanishes because of the ice rules, so that Eq. (15a), $\chi_{\parallel}(\vec{q})=0$, is exact. Therefore, if $\chi'(\vec{q})$ is indeed nonsingular, it must also tend to zero as $\vec{q}\to 0$ along every direction. This implies that Eq. (15b) for $\chi_{\perp}(\vec{q})$ is asymptotically exact as well.

B. $\vec{q}=0$ versus $\vec{q}\neq 0$ response

We saw from the preceding paragraphs that the ice rule, $\vec{\nabla}\cdot\vec{P}=0$, constitutes an important constraint on $\chi_{\alpha\beta}(\vec{q})$ near $\vec{q}=0$, and determines uniquely its singular form. We argue now that $\chi_{\alpha\beta}(\vec{q})$ can, in the $\vec{q}\to 0$ limit, be obtained directly from the homogeneous free energy [Eq. (5)] subject *only* to the additional constraint $\vec{\nabla}\cdot\vec{P}=0$. This hypothesis can be checked: it must give not only the proper form for $\chi_{\alpha\beta}(\vec{q})$, but also an expression for $A(\Delta)$ which can be compared with the correct one, Eq. (11). If correct, it will give new information in the form of $\lambda(\Delta,\eta)$, known until now only for $\Delta=0$.

For long-wavelength spatial fluctuations, the free energy is generalized by rewriting Eq. (5) as

$$F-F^0 = \sum_{\alpha,\vec{q}}\left[\frac{1}{2}\left(\frac{P_\alpha(\vec{q})P_\alpha(-\vec{q})}{\chi_\alpha}\right) - P_\alpha(\vec{q})E_\alpha(-q)\right] + \cdots , \tag{17}$$

where $\vec{E}(\vec{q})$ is the field conjugate to $\vec{P}(\vec{q})$, and $\chi_\alpha=(\chi_x,\chi_y)$ are given by Eqs. (14). However, at $\vec{q}\neq 0$, $P_x(\vec{q})$ and $P_y(\vec{q})$ are no longer independent, but are constrained by the ice rule

$$\vec{\nabla}\cdot\vec{P} = i\sum_\alpha q_\alpha P_\alpha(\vec{q}) = 0 . \tag{18}$$

The constraint can be introduced by a Lagrange multiplier, but in the present case it is simplest to use Eq. (18) to eliminate one component, e.g., $P_y(\vec{q})$, from Eq. (17) and then to minimize the resultant expression with respect to $P_x(\vec{q})$. By this means, one easily finds for $\chi_{\alpha\beta}(\vec{q})=P_\alpha(\vec{q})/E_\beta(\vec{q})$,

$$\chi_{xx}(\vec{q}) = \frac{q_y^2}{q_x^2\chi_y^{-1}+q_y^2\chi_x^{-1}} , \tag{19a}$$

$$\chi_{xy}(\vec{q}) = \chi_{yx}(\vec{q}) = \frac{-q_xq_y}{q_x^2\chi_y^{-1}+q_y^2\chi_x^{-1}} , \tag{19b}$$

$$\chi_{yy}(\vec{q}) = \frac{q_x^2}{q_x^2\chi_y^{-1}+q_y^2\chi_x^{-1}} . \tag{19c}$$

On comparison of Eqs. (14a)–(14c), with Eqs. (19a)–(19c) we find that they are indeed of the same form, and become equivalent if

$$\pi A(\Delta) = (\pi-\mu)^{-1} = [\cos^{-1}(\Delta)]^{-1} \tag{20}$$

and

$$\lambda(\Delta,\eta) = \tilde{\lambda} = \frac{1+\sin z}{\cos z} . \tag{21}$$

The value of A agrees with the independent evaluation[5] of Eq. (11) and confirms the correctness of the approach. In addition, $\lambda(\Delta=0,\eta)$ confirms previously known results[5] for $\Delta=0$, in which case $\mu=\pi/2$, $z=\phi_0$, and $\exp(i\phi_0)=(1+i\eta)/(i+\eta)$, so that

$$\cos z = \cos\phi_0 = \frac{2\eta}{\eta^2+1};\quad \sin z = \sin\phi_0 = \frac{\eta^2-1}{\eta^2+1}$$

and

$$\lambda(\Delta=0,\eta) = \frac{1+\sin\phi_0}{\cos\phi_0} = \eta . \tag{22}$$

Equation (21) for $\lambda(\Delta,\eta)$ represents the principal quantitative result of this paper. Equations (14), (20), and (21) completely characterize the behavior of long-wavelength polarization fluctuations in this model throughout the "disordered" regime, $-1<\Delta<1$. A plot of λ vs η for various values of Δ is shown in Fig. 2. We consider only the case $\eta>1$, since the choice of labeling of the x and y axis can be used to ensure this with no loss of generality. Note that for $\Delta<0$, λ is less than η, so that the basic vertex anisotropy is softened in the fluctuations, whereas for $\Delta>0$, λ is greater than η, and the anisotropy of the fluctuations is enhanced. This tendency culminates in singular behavior as one ap-

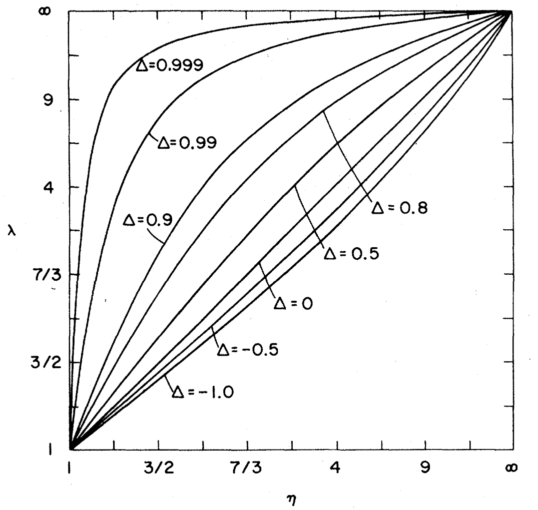

FIG. 2. Plots of $\lambda(\eta,\Delta=\text{const})$. As Δ approaches $+1$ (as T approaches T_0, the ferroelectric transition temperature), λ tends to infinity ($\lambda \propto T-T_0)^{-1/2}$. [See Eq. (7).] The axes are scaled so that the distance along the η axis is proportional to $(\eta-1)/(\eta+1)$, and similarly for the λ axis.

proaches the ferroelectric transformation at $\Delta(T=T_0)=1$. By expanding near $\Delta=1$, one can easily show that for small ϵ

$$\lambda\left(\Delta=1-\frac{\epsilon^2}{2},\eta\right)=\frac{2(\eta-1)}{\epsilon}\sim\frac{(\eta-1)}{(T-T_0)^{1/2}}\ , \tag{23}$$

since $\epsilon=[2(1-\Delta)]^{1/2}\sim(T-T_0)^{1/2}$.

In using $\vec{P}$ for the order-parameter variable, we invite a dielectric analogy; but we are doing a lattice statistics problem, not electrostatics, and the statistical mechanics is determined by the vertex-weighting scheme alone. In particular, while the vertex weights reflect the interaction of adjacent dipoles, nothing has been said here about long-ranged dipole-dipole interactions. Thus, at this point, we are not free to identify the susceptibility we calculate (which is the response to a field conjugate to the configurational polarization $\vec{P}$) with the physical dielectric susceptibility. According to at least one school of thought (which may be called the Onsager-Slater-Pauling approach), such an identification can be made in ice-rule systems. For a recent discussion of this point, see the review paper by Nagle.[15]

Another important aspect of dipolar interactions is that the wave-vector-dependent susceptibility of dipolar-coupled systems (including ferroelectrics) has a contribution which is singular[14] in the same way as is the susceptibility of ice-rule systems, since the long-ranged dipolar force tends to suppress longitudinal polarization fluctuations. In spite of having a similar effect on the susceptibility, this mechanism is, of course, quite distinct from the ice rules. Note that in the case of 2D bond networks, it is easy to distinguish the effects of ice rules (operating in 2D) from those of dipolar forces (which necessarily operate in 3D).

C. Gradient terms and ice-rule violations

In the previous section, we considered a generalization of the free energy of the six-vertex model to spatially varying external fields, and obtained the zero-field, small-q susceptibility. Now we wish to broaden the scope of our inquiry to take into account (a) ice-rule violations, and (b) the free-energy cost associated with a transverse polarization gradient.

In this section, we will proceed phenomenologically, by adding two terms to the free-energy expression developed so far, and then treating the resulting expression as if it were a Landau free-energy expansion. The first new term is $D[\vec{q}\cdot\vec{P}(\vec{q})]^2$, which is proportional to $(\vec{\nabla}\cdot\vec{P})^2$; this term expresses the free-energy cost of longitudinal $[\vec{q}\parallel\vec{P}(\vec{q})]$ polarization fluctuations, which violate the ice rules. The other new term is $C[\vec{q}\times\vec{P}(q)]^2$; this term expresses the free-energy cost of transverse $[\vec{q}\perp\vec{P}(\vec{q})]$ fluctuations (for example, the free-energy density at a vertical wall separating a region of "up" polarization from a region of "down" polarization). Rather than $(\vec{q}\times\vec{P})^2$, one might consider introducing separate terms for all distinct bilinear forms compatible with the twofold-symmetry axes of the model $[(\partial P_x/\partial x)^2$, $(\partial P_x/\partial y)\,(\partial P_y/\partial x)$, etc.], each with its own coefficient depending on Δ and η. Here, for simplicity, we have suppressed all but the rotationally invariant part. One could also consider generalizing the $(\vec{q}\cdot\vec{P})^2$ term in a similar way, but the $(\vec{q}\cdot\vec{P})^2$ form is special, in that it expresses the free-energy cost of ice-rule violations.

Minimizing the free energy, one obtains

$$\chi_{yy}(\vec{q})=\chi_y\frac{1+2\chi_x(Dq_x^2+Cq_y^2)}{1+2\chi_x(Dq_x^2+Cq_y^2)+2\chi_y(Dq_y^2+Cq_x^2)+4\chi_x\chi_yDCq^4}\ , \tag{24a}$$

$$\chi_{xy}(\vec{q})=\chi_x\chi_y\frac{-2(D-C)q_xq_y}{1+2\chi_x(Dq_x^2+Cq_y^2)+2\chi_y(Dq_y^2+Cq_x^2)+4\chi_x\chi_yDCq^4}\ , \tag{24b}$$

$$\chi_{xx}(\vec{q})=\chi_x\frac{1+2\chi_y(Dq_y^2+Cq_x^2)}{1+2\chi_y(Dq_y^2+Cq_x^2)+2\chi_x(Dq_x^2+Cq_y^2)+4\chi_x\chi_yDCq^4}\ . \tag{24c}$$

There are several limiting cases to consider.

(1) $C=0$, $D\rightarrow+\infty$. In this limit, we recover the previous (ice-rule) result. Longitudinal fluctuations are suppressed; the susceptibility is singular at $q=0$.

(2) $D=0$, $C\rightarrow+\infty$. This is the inverse situation; transverse fluctuations are suppressed. For example, in this limit

$$\chi_{yy}(\vec{q})=\chi_y\frac{q_y^2/\chi_y}{q_y^2/\chi_y+q_x^2/\chi_x} \; . \tag{25}$$

(3) $D=C>0$. There is no difference between transverse and longitudinal. We have

$$\chi_{yy}(\vec{q})=\frac{\chi_y}{1+2\chi_y Dq^2} \; , \tag{26}$$

etc., whose constant-intensity contours are simply circles. The anisotropy between divergence and curl is eliminated; the susceptibility resembles that characteristic of a scalar order parameter except, of course, that $\chi_{yy}\neq\chi_{xx}$.

A system which is incipiently ferroelectric ($\frac{1}{2}<\Delta<1$) and which is near to obeying the ice rules corresponds to $C>0$ and $D>>0$. When D and C are both finite, there is no singularity at the origin; the macroscopic susceptibilities are given by χ_x and χ_y, and these values are approached by $\chi(\vec{q})$ as $\vec{q}$ tends to zero along any direction. For example,

$$\chi_{yy}(q_x=0,q_y)=\chi_y\frac{1}{1+2\chi_y Dq_y^2} \tag{27}$$

and

$$\chi_{yy}(q_x,q_y=0)=\chi_y\frac{1}{1+2\chi_y Cq_x^2} \; . \tag{28}$$

We see that there are characteristic lengths $\xi_{\parallel}^y=(2\chi_y D)^{1/2}$ and $\xi_{\perp}^y=(2\chi_y C)^{1/2}$ associated with the longitudinal and transverse directions. Similar quantities can be defined for the x direction.

When $D=\infty$ and $C>0$ (an incipient ferroelectric obeying the ice rules), we have

$$\chi_{yy}(\vec{q})=\chi_y\frac{q_x^2}{q_x^2+(\chi_y/\chi_x)q_y^2+2\chi_y Cq^4} \; . \tag{29}$$

When the product $\chi_y C$ is small, the q^4 term in the denominator is significant only at relatively large q. But as the ferroelectric transition is approached, $\chi_y\rightarrow\infty$, and this term becomes progressively more important at ever smaller q, unless C also tends to zero in a suitable way. (C is, by construction, an unspecified function of Δ and η alone.) Equation (29) shows that the regime of $\vec{q}$ space inside which Eqs. (19a)–(19c) are valid diminishes as the ferroelectric transformation is approached. The corresponding real-space argument is that the large parameter in the asymptotic expansion of the correlation function is proportional to[5] $(x^2+\lambda^2y^2)^{1/2}$; the definition of

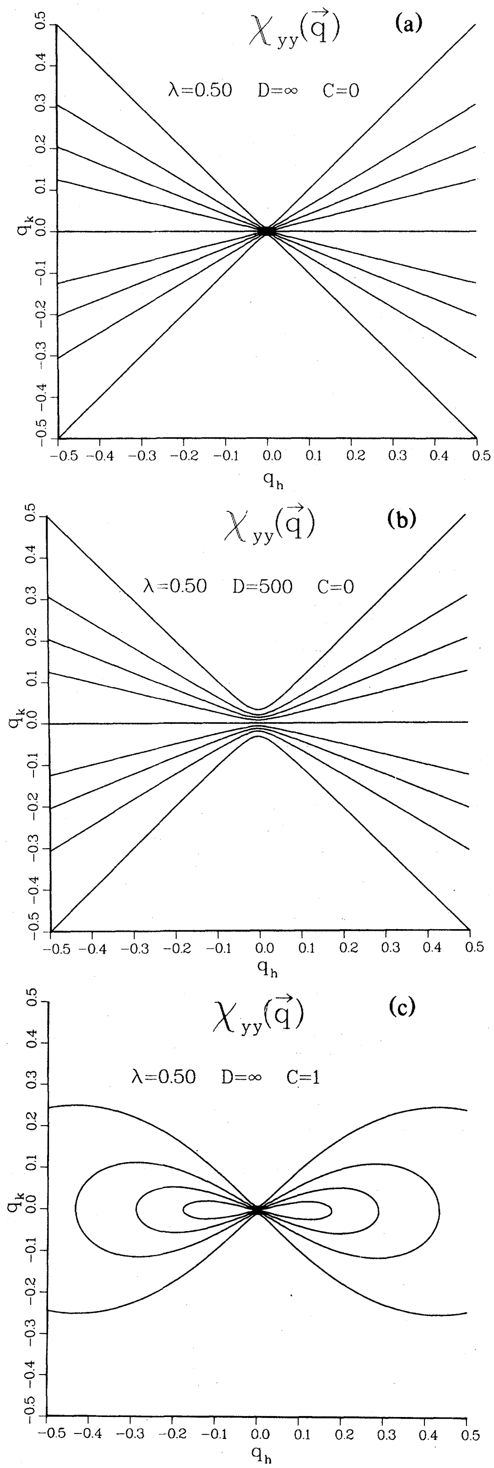

FIG. 3. Contours of constant $\lambda_{yy}(\vec{q})$ for three cases: (a) $D=\infty$, $C=0$, which corresponds to the ice-rule case at $\Delta=0$ [Eq. (14c)]; (b) D finite, showing that χ is no longer singular when the ice rules are relaxed; (c) $D=\infty$, $C=1$, showing that $\chi(q_x,q_y=0)$ peaks at $q_x=0$ when the system is incipiently ferroelectric ($\Delta>0$). In cases b and c, the susceptibility depends on $|q|$, as well as on $\hat{q}$.

"large separation" changes as the ferroelectric transition is approached.

Contour plots illustrating some of these cases are shown in Figs. 3(a)–3(c). First [Fig. 3(a)], we show the case $D=\infty$ and $C=0$; all the contours are straight lines meeting at $q=0$. If we relax the ice rules, this singularity is no longer present; this is illustrated in Fig. 3(b). There is not much difference in these two cases, except very near the origin. The explicit detection of the singularity by a measurement of $\chi(q)$ by a scattering experiment with finite q resolution is clearly a logical impossibility; the best one can do is set limits on how far χ is from being singular. Finally [Fig. 3(c)], when $D=\infty$, $C>0$, the singularity is present, but χ_{yy} is no longer flat along the q_x axis; it falls off with increasing q_x, reflecting the free-energy cost C of polarization gradients.

We have shown that in the large-D limit, the form of the singularity in $\chi(\vec{q})$ is correct. However, it is not clear how accurately χ is given for D infinite, $C\neq 0$. Consider a similar calculation for the Ising model. We write an equation like Eq. (17) involving the Ising pseudospin polarization and the exact bulk Ising susceptibility, and then we phenomenologically add a gradient term. (There is no distinction between longitudinal and transverse.) This will lead to a Lorentzian form for $\chi(q)$, which is an excellent approximation for many purposes.[16] However, $\chi(q)$ is not strictly Lorentzian; the deviation from Lorentzian behavior is expressed by the critical exponent η.[16] Thus, by analogy, we expect Eq. (24) to be a useful approximation, but we anticipate that the form of χ may differ when $C\neq 0$ or D is finite.

D. 3D ice-rule models

We have seen that, in 2D, the form $\chi(\vec{q})$ is determined by the ice rule, $\vec{\nabla}\cdot\vec{P}=0$. This suggests that the analysis of Sec. II B can be carried over to 3D ice-rule models as well. Consider, for example, a material with uniaxial symmetry [hexagonal ice or KDP (potassium dihydrogen phosphate) would serve as physical examples]. Then, in place of Eq. (17), we write

$$F-F_0=\frac{1}{2}\sum_{\vec{q}}\left[\frac{P_x^2(\vec{q})+P_y^2(\vec{q})}{\chi_a}+\frac{P_z^2(\vec{q})}{\chi_c}\right]-\vec{P}(\vec{q})\cdot\vec{E}(\vec{q})+\cdots \tag{30}$$

and once again solve for $\chi_{\alpha\beta}(\vec{q})$, $\alpha,\beta=(x,y,z)$, subject to the constraint $\vec{\nabla}\cdot\vec{P}=i\vec{q}\cdot\vec{P}(\vec{q})=0$. After some simple algebra, one finds that $\vec{\chi}(\vec{q})$ is diagonal in a system with basis vectors $(\vec{e}_{\parallel},\vec{e}_{\perp},\vec{e}_t)$, where $\vec{e}_{\parallel}$ is along $\vec{q}$, $\vec{e}_t$ is perpendicular to $\vec{q}$ and to the unique c axis, and $\vec{e}_{\perp}(q)$ is perpendicular to $\vec{q}$, but in the plane defined by $\vec{q}$ and the c axis. In this system, the equations analogous to Eqs. (15a)–(15c) are

$$\chi_{\parallel}(\vec{q})=0\ , \tag{31a}$$

$$\chi_{\perp}(\vec{q})=\frac{1}{\chi_c^{-1}\sin^2\Theta+\chi_a^{1}\cos^2\Theta}\ , \tag{31b}$$

$$\chi_t(\vec{q})=\chi_a\ , \tag{31c}$$

where Θ is the angle between $\vec{q}$ and $\vec{c}$. That is, the components of $\vec{\chi}(\vec{q})$ lying in the $\vec{q}$-$\vec{c}$ plane behave as for the 2D case, while the third component, $\chi_t(\vec{q})$, is not singular. In terms of Cartesian coordinates along principal crystal axes, we have, for example,

$$\chi_{zz}(\vec{q})=\frac{q_x^2+q_y^2}{(q_x^2+q_y^2)\chi_c^{-1}+q_z^2\chi_a^{-1}}\ . \tag{32}$$

Obviously, it is also possible to extend the discussion in 3D to include ice-rule violations as in Sec. III C, with similar results. In particular, $\chi(\vec{q})$ is no longer singular at $\vec{q}=0$ when D is finite.

Villain,[17] by summing diagrammatic expansions of the correlation function, predicted a singularity of this kind in 3D ice, and neutron scattering measurements were consistent with that prediction.[18] Scattering having this dipolar form was also observed in KDP.[19] Originally, this was attributed to long-ranged electrostatic dipolar interactions; but more recently, Havlin *et al.*[20] suggested that the anisotropic short-ranged interactions between the hydrogen bonds could be responsible. Equations (24a)–(24c) and Fig. 3 confirm this in a direct way. For finite D, one calculates scattering which resembles a dipolar pattern in its anisotropy, in qualitative agreement with observations.

III. SUMMARY

We have shown by direct Fourier transformation of the polarization correlation function that the wave-vector-dependent susceptibility tensor of 2D six-vertex systems in the paraelectric regime $(-1<\Delta<1)$ at small $\vec{q}$ has a single nonvanishing component

$$\chi_{\perp}(\vec{q})=2\pi\beta A\frac{q_x^2+q_y^2}{\lambda q_x^2+\lambda^{-1}q_y^2}\ .$$

The fluctuating component of $\vec{P}(\vec{q})$ is strictly transverse to $\vec{q}$. This follows directly from the ice-rule conservation law $\vec{\nabla}\cdot\vec{P}=0$. The dependences of A and λ on the vertex weights have been deduced by establishing the relation between $\chi(q\neq 0)$ and the macroscopic uniform susceptibility, which was nontrivial because of the singularity. The results are

$$A(\Delta)=(\pi\cos^{-1}\Delta)^{-1}\ ,$$

$$\lambda(\Delta,\eta)=\frac{1+\sin z}{\cos z}\ ,$$

with z defined in Eq. (7).

We have phenomenologically considered coupling terms corresponding to ice-rule violations and short-ranged forces. There is a characteristic length associated with each of these coupling constants. When ice-rule violations are allowed, the singular behavior of $\vec{q}=0$ is relaxed, and $\chi(\vec{q})$ is then well defined at $\vec{q}=0$. 3D ice-rule systems can be discussed in a similar way.

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