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Polarization Fluctuations near a Ferroelectric Phase Transition

M. E. Lines
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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Critical polarization fluctuations in the nonpolar phase of a ferroelectric have been determined self-consistently using a correlated effective-field theory of ferroelectricity. Static correlations take the form of highly developed ferroelectric chains along an incipient polar direction, with interchain correlations being relatively very weak and of either sign. Neither interchain nor intrachain correlations exhibit an exponential decay at large distances and a unique definition of correlation length is correspondingly difficult to obtain. The new statistical theory is able to describe phase transitions of both displacement and order-disorder character and predicts a paraelectric susceptibility divergence as $t = T - T_C \to 0$ of the form $[\ln(1/t)]/t$ and a specific heat going as $A - [B'/\ln(1/t)]$, where A and B' are constants. These forms are to be compared with the Curie-Weiss susceptibility and the logarithmic divergence of specific heat which follow from the commonly used random-phase approximation.

I. INTRODUCTION

Statistical theories which discuss the critical properties of ferroelectric phase transitions, both for displacement and tunneling (order-disorder) models, still commonly make use of a random-phase approximation (RPA) to "close" the many-body problem. In general, theorists are much more satisfied with this rather crude statistical approximation in the ferroelectric context than, say, in magnetism. The reason is not difficult to find; it often gives the correct *temperature dependence* (as far as experiment can tell at present) for the limiting "critical" behavior of susceptibility, correlation function, soft-mode frequency, etc., for ferroelectric systems, but not for magnetic ones. The common explanation is that magnetic transitions are precipitated by short-range forces while most ferroelectric phase transitions are controlled by long-range forces (presumably largely dipolar in nature), and the RPA (and in particular the Bragg-Williams method for the zero wave-vector limit) becomes exact in the long-range limit.[1]

Although this last statement is true, it unfortunately has little relevance for dipolar forces and ferroelectricity since dipolar forces are not long range in the Bragg-Williams sense. Worse still, there are indications that the RPA does not give even approximately correct numerical predictions[2,3] and is, quite possibly, less quantitatively reliable in a ferroelectric context than in a magnetic one. The fact that it produces the correct temperature dependence for a number of thermodynamic quantities near a ferroelectric phase transition must, in some sense, be fortuitous. The present author, for example, feels that theorists understand less why the critical exponent for ferroelectric susceptibility should be unity (Curie-Weiss law) than why it should be ≈ 1.375 for the Heisenberg ferromagnet.[4] For the latter case, a well-developed high-temperature-series extrapolation technique has been defined to indicate the 1.375 exponent with some precision. An equivalent calculation for dipolar forces is completely lacking.

Random-phase theories, by neglecting correlations completely, are known to violate the fluctuation-dissipation theorem. One can progress beyond RPA by statistically approximating correlations in such a way that they can be determined self-consistently to be in accord with the fluctuation theorem. A lattice-dynamical theory of this type already exists (the self-consistent phonon approximation[5]) and in its simplest form has been used to discuss structural transitions[6,7] although it has not yet, it seems, been used to evaluate ferroelectric critical properties for a dominantly dipolar interaction potential. In lowest order, the self-consistent phonon theory statistically approximates correlation terms in the equations of motion to allow linearization in terms of collective (phonon) coordinates. The statistical correlations are then determined self-consistently to describe a temperature-dependent harmonic motion about statistical equilibrium.

The present paper also statistically approximates the lattice-dynamical equations of motion to preserve correlations, but in a manner which allows the self-consistent description of the ionic motion of individual lattice primitive cells. The procedure, however, does not include any linearizing of the equations of motion and therefore, unlike the self-consistent phonon scheme, is not built in lowest order on quasiharmonic dynamics, but is formally applicable both for displacement and order-disorder phase transitions right through to the Ising limit itself. This paper concentrates on static (time-independent) properties alone and, since the statistical principles behind the self-consistent phonon and present approximations are essentially the same, it seems likely that at least the qualitative form of the present critical findings would result also from the former.

The present theory develops a statistical procedure which goes a step beyond the RPA in allowing for the effect of intercell forces. Intercell correlations are defined in a simple way and are determined completely by requiring them to satisfy the fluctuation theorem of statistical mechanics. The theory can be set out in a rather general formalism embracing, in a single representation, models of both displacement and order-disorder ferroelectrics, as well as examples in a magnetic context. In the disordered phase, at least, the results for the Ising model are equivalent to those obtained by use of the Onsager-reaction field or the spherical approximation.[8,9] Whether this correspondence holds more generally has not been ascertained.

The resulting theory is pursued in detail for the case of dipolar interactions. We find that polarization fluctuations in the nonpolar phase are quite anisotropic with well-established short-range correlations in chains along the incipient polar axis. Correlations between chains are quite weak and may be of either sign. The concept of correlation length in such an anisotropic situation is discussed with particular reference to critical behavior. It is easy to see the manner in which very sizable numerical errors can be incurred by use of a random-phase effective-field approximation. In particular, the Lorentz-field concept may have little to do with the determination of a Curie temperature. On the other hand, the improvement of the statistical approximation removes the one great success of the random-phase theory, namely, the simple Landau critical behavior. However, the extent to which it does so is quite small (involving logarithmic terms) and it is instructive to compare the dipolar case with the more well-known magnetic situation (Heisenberg or Ising ferromagnetism) in the same approximation.

Results are presented for susceptibility, specific heat, and polarization fluctuations, all in a nonpolar phase. They are cast in a form which is equally applicable for displacement and order-disorder systems (or, indeed, any intermediate situation). Emphasis is placed on computation of static polarization correlations as a function of range and orientation, both for near neighbors and in the limit of infinite distance. Some general rules concerning polarization fluctuations near a ferroelectric phase transition can be conjectured for the nonpolar phase. The polar phase has not been pursued in this paper. It also appears to be much less simple to conjecture about fluctuations in antiferroelectrics, even those for which dipolar forces may be primarily responsible.

II. STATISTICAL APPROXIMATION

Consider the many-body Hamiltonian (or, more specifically, its potential energy part)

$$\mathcal{H}=\sum_{i}\left[V(\xi_i)-h_i\xi_i\right]-\sum_{i,j}v_{ij}\xi_i\xi_j\,, \qquad (2.1)$$

in which $V(\xi_i)$ is a potential energy involving an elementary polarization coordinate ξ_i, h_i is an applied field, and v_{ij} is an interaction potential. For the simplest conceivable model of a ferroelectric, ξ_i would define the polarization associated with an individual charged ion. In a more realistic model[10] ξ_i labels the normal-mode coordinate for motion of ions in the ith primitive cell, with the symmetry of the soft mode. Near to a phase transition in particular, ionic motion is dominated by the ferroelectric mode and the single-mode approximation is valid.

In the conventional RPA, an effective Hamiltonian $\mathcal{H}(i)$ for the ith cell is written by replacing all $\xi_j \neq \xi_i$ by their ensemble averages $\langle\xi_j\rangle$. Thus

$$\mathcal{H}(i)=V(\xi_i)-h_i\xi_i-\textstyle\sum_j v_{ij}\xi_i\langle\xi_j\rangle\,,\quad \text{RPA}\,. \qquad (2.2)$$

In this paper we shall go beyond RPA to allow for intercell correlations by including in (2. 2) an additional term proportional to the fully correlated motion,

$$\mathcal{H}(i)=V(\xi_i)-h_i\xi_i-\textstyle\sum_j v_{ij}\xi_i(\langle\xi_j\rangle+\alpha\Delta\xi_j)\,, \qquad (2.3)$$

where $\Delta\xi_j$ is an operator with expectation value at any instant of time equal to that of $\xi_i-\langle\xi_i\rangle$ at the same time (i. e., fully correlated to the motion of the ith coordinate) and where α is a dimensionless *temperature-dependent* parameter with value between zero and unity. Thus, the parameter α is a measure of intercell correlations; $\alpha=0$ represents the random-phase limit and $\alpha=1$ represents the fully correlated limit. We shall show that α can be determined completely from the fluctuation theorem of statistical mechanics.

The equation of motion for the ith cell can now be written using (2. 3); it is

$$-\dot{p}_i=\frac{\partial\mathcal{H}(i)}{\partial\xi_i}=\frac{\partial V(\xi_i)}{\partial\xi_i}-h_i-\textstyle\sum_j v_{ij}(\langle\xi_j\rangle+\alpha\Delta\xi_j)\,, \qquad (2.4)$$

where, by definition, $\Delta\xi_j$ can now be replaced by $\xi_i-\langle\xi_i\rangle$, and where p_i is the conjugate-momentum coordinate. We now note that this same equation of motion would result directly from (2. 3) if $\Delta\xi_j$ were replaced by $\frac{1}{2}\xi_i-\langle\xi_i\rangle$ in the effective Hamiltonian. In this way we obtain an effective Hamiltonian for ith-cell motion in terms of operator ξ_i and ensemble averages alone. Specifically,

$$\mathcal{H}(i)=V(\xi_i)-h_i\xi_i-\textstyle\sum_j v_{ij}\xi_i\langle\xi_j\rangle -\textstyle\sum_j \alpha v_{ij}\xi_i(\frac{1}{2}\xi_i-\langle\xi_i\rangle)\,. \qquad (2.5)$$

Mathematically, it is simplest to pursue the disordered phase, and the present paper will be devoted exclusively to temperatures at or above the

Curie point T_C. We should also bear in mind that the single-mode approximation itself may become less adequate for the description of ferroelectric phenomena if we venture too far away from T_C in either direction.

Let us calculate first the ensemble average

$$\langle \xi_i \rangle = \mathrm{Tr}(\xi_i \rho_i)/\mathrm{Tr}(\rho_i) , \tag{2.6}$$

where the density matrix ρ_i for the ith cell is $e^{-\mathcal{H}(i)/kT}$. In the limit of small applied field h_i we can expand the exponential to first order in small quantities to obtain

$$\langle \xi_i \rangle = (\langle \xi_i^2 \rangle / kT)\,[h_i + \textstyle\sum_j v_{ij}(\langle \xi_j \rangle - \alpha \langle \xi_i \rangle)] , \tag{2.7}$$

where

$$\langle \xi_i^2 \rangle = \mathrm{Tr}(\xi_i^2 e^{-V'(\xi_i)/kT})/\mathrm{Tr}(e^{-V'(\xi_i)/kT}) \tag{2.8}$$

and

$$V'(\xi_i) = V(\xi_i) - \alpha \textstyle\sum_j \frac{1}{2} v_{ij} \xi_i^2 . \tag{2.9}$$

Introducing Fourier transforms with respect to the spatial lattice assuming translational invariance, Eq. (2.7) becomes [since $\langle \xi_i^2 \rangle$ of (2.8) is independent of cell site i]

$$\langle \xi_K \rangle = (\langle \xi_i^2 \rangle / kT)\,[h_K + \langle \xi_K \rangle (v_K - \alpha v_0)] , \tag{2.10}$$

using an obvious notation in which $\vec{K}$ is a reciprocal-lattice wave vector (the vector notation being omitted in subscripts) and where, for example,

$$\xi_K = (N)^{-1/2} \sum_i \xi_i e^{i\vec{K}\cdot\vec{i}} \tag{2.11}$$

and

$$v_K = \sum_{j \neq i} v_{ij} e^{i\vec{K}\cdot(\vec{i}-\vec{j})} , \tag{2.12}$$

N being the number of cells in the macroscopic lattice.

The wave-vector-dependent susceptibility now follows immediately as

$$\chi_K = \langle \xi_K \rangle / h_K = (\tau + \alpha v_0 - v_K)^{-1} , \tag{2.13}$$

and, in particular,

$$\chi_0 = [\tau + (\alpha - 1) v_0]^{-1} , \tag{2.14}$$

where

$$\tau = kT/\langle \xi_i^2 \rangle \tag{2.15}$$

and we have taken α to be independent of h_K at least to first order. But χ_K can also be calculated directly as

$$\chi_K = \frac{\partial}{\partial h_K} \frac{\mathrm{Tr}(\xi_K \rho)}{\mathrm{Tr}(\rho)} , \tag{2.16}$$

with

$$\rho = \exp\{[-\sum_i V(\xi_i) + \sum_{i,j} v_{ij}\xi_i\xi_j + \sum_K h_K \xi_{-K}]/kT\} . \tag{2.17}$$

For $T \geqslant T_C$ we obtain

$$kT\chi_K = \langle \xi_K \xi_{-K} \rangle , \tag{2.18}$$

the well-known fluctuation theorem. Using (2.18) and (2.13) we find

$$\textstyle\sum_K (\tau + \alpha v_0 - v_K)^{-1} = \sum_K \langle \xi_K \xi_{-K} \rangle / kT = N \langle \xi_i^2 \rangle / kT = N/\tau . \tag{2.19}$$

Equations (2.19), (2.8), and (2.9) together now determine α completely as a function of temperature, and the formal statistical problem is closed.

Conventional RPA theory has $\alpha = 0$ at all temperatures and the above therefore implies that this approximation (and, in particular, the Bragg-Williams method) must violate the fluctuation theorem, a point which has been made before.[1] The violation is readily demonstrated. From the fluctuation result (2.18) we find

$$\chi_0 = \langle \xi_0^2 \rangle / kT = (1/kT)(\langle \xi_i^2 \rangle + \sum_{j \neq i} \langle \xi_i \xi_j \rangle) , \tag{2.20}$$

while the Bragg-Williams scheme [Eq. (2.14) with $\alpha = 0$] gives

$$\chi_0 = \langle \xi_i^2 \rangle / (kT - v_0 \langle \xi_i^2 \rangle) , \quad \text{RPA} . \tag{2.21}$$

The latter, in conjunction with (2.20), clearly implies nonzero correlations in direct violation of the initial basic assumption of RPA theory. We note, however, that α can be eliminated from (2.13) and (2.14) to give

$$\chi_K^{-1} = \chi_0^{-1} + v_0 - v_K , \tag{2.22}$$

an equation valid in both RPA and the present correlated scheme.

It is of particular interest to calculate the detailed correlations $\langle \xi_i \xi_{i+R} \rangle$ themselves. Using the fluctuation theorem to relate the correlations to wave-vector-dependent susceptibility, we have

$$\langle \xi_i \xi_{i+R} \rangle = (1/N) \textstyle\sum_K e^{i\vec{K}\cdot\vec{R}} \langle \xi_K \xi_{-K} \rangle = (kT/N) \sum_K \chi_K e^{i\vec{K}\cdot\vec{R}} , \tag{2.23}$$

from which using (2.22) we find

$$\langle \xi_i \xi_{i+R} \rangle = (kT/N) \textstyle\sum_K e^{i\vec{K}\cdot\vec{R}} / (\chi_0^{-1} + v_0 - v_K) . \tag{2.24}$$

In particular, the ratio of the correlations at distance R to the self-correlation at the same temperature follows immediately as a function of uniform susceptibility χ_0 *alone* and is valid for any potential function $V(\xi_i)$ no matter how complicated. This is a remarkably simple result in view of the usual complexity of $V(\xi_i)$ in real systems; we give it explicitly as

$$\langle \xi_i \xi_{i+R} \rangle / \langle \xi_i^2 \rangle = F(\vec{R})/F(0) , \tag{2.25}$$

where

$$F(\vec{R}) = \textstyle\sum_K e^{i\vec{K}\cdot\vec{R}} / (\chi_0^{-1} + v_0 - v_K) . \tag{2.26}$$

In the more general problem, Eq. (2.8) is the major stumbling block in the path of a numerical quantum-mechanical calculation since it necessitates obtaining eigenvalues of energy for motion in a temperature-dependent (through α) potential which can be, for ferroelectrics, anything between a quasiharmonic single well and an Ising-like double well but, unfortunately, appears very often to be somewhere in between. In $LiTaO_3$, for example,[10] $V'(\xi_i)$ for temperatures near T_C appears to have side minima of comparable depth to a central $\xi_i = 0$ minimum. This situation would seem to be impossibly complicated to treat quantum mechanically, although classically, of course, the problem is simpler in principle. The Ising limit with $\langle \xi_i^2 \rangle = \text{const}$ is the simplest hypothetical situation, in which case parameter α can be eliminated between (2.14) and (2.19) to give

$$\sum_K kT/(\chi_0^{-1} + v_0 - v_K) = N\langle \xi_i^2 \rangle , \qquad (2.27)$$

an equation which determines uniform susceptibility directly as a function of temperature without more ado. More generally, the right-hand side of (2.27) is still α dependent through (2.8) and (2.9) and one cannot escape the necessity of solving (2.8), (2.9), and (2.19) simultaneously for α in order to determine the temperature dependence of χ_0 quantitatively. It is this unpleasant facet of the general problem which makes Eqs. (2.25) and (2.26) for cell correlations look so attractive, and we shall pursue this aspect of the statistical problem in some detail.

Before going on to compute some numerical results for the case where interaction potential v_{ij}, at least at long range, is primarily of dipolar origin, one or two additional comments are pertinent. First, we have neglected throughout any complications arising from the presence of electronic contributions to polarization. The influence of the latter is not difficult to determine[2,10] but is not of direct concern in the present context. Second, in order to avoid the complexities arising from the dependence of v_K on specimen shape (when K is of order one over the sample dimensions) for dipolar forces, it is convenient to postulate a needle-shaped sample for which depolarizing effects are absent. The calculations, however, are also directly relevant for the conventional parallel-plate experimental setup (thin-wafer sample) if in this case h is construed as the internal Maxwell field rather than an external applied field.

Finally, we note that cell correlations of the form (2.3) were introduced earlier by the present author[2] to enable the understanding of experimental results for ferroelectric $LiTaO_3$ and $LiNbO_3$. In that paper, however, the correlations were simply determined by fitting (2.14), or its equivalent, to the experimentally measured χ_0. It was found that in spite of Curie-Weiss–like behavior, correlations, as measured by α, were very strong near T_C but with little if any temperature dependence. Thus the earlier theory was not of closed form, having α as a free parameter to be determined by fitting experimental data. The present paper removes that degree of arbitrariness enabling α to be determined theoretically from a knowledge of the form of the intercell interaction forces and hence, hopefully, eventually leading to some understanding of the empirical results obtained for $LiTaO_3$ and $LiNbO_3$.

III. DIPOLAR INTERACTIONS

For ferroelectric systems the intercell potential v_{ij} will be very largely of dipolar origin at long range although, of course, for nearest-neighbor cells in particular, contributions from other sources will be important. There is, however, another reason why v_{ij} will differ from classic dipolar form for near-neighbor cells. This results from the fact that ξ_i is a normal-mode coordinate defining the motion of all ions in cell i and hence describing a charge displacement which has a very considerable spatial extent. The familiar point-dipole expression for dipolar energy therefore becomes appropriate for v_{ij} only at long range.

Close enough to a phase transition, ionic motion is dominated by the ferroelectric soft mode by simple virtue of its low excitation energy. This mode is, in general, strongly polar and therefore defines elementary dipoles $\vec{\xi}_i$ per cell. As $T \to T_C^+$ the ionic motion is increasingly dominated by long-wavelength polar excitations which define a direction λ, the incipient polar axis. (This does not imply, of course, that the motion of all, or even any, individual ions is necessarily in this direction.) In many cases, λ is defined unambiguously simply by the symmetry of the soft mode (e.g., the A_1 soft mode in $LiTaO_3$ or $LiNbO_3$ with polar motion along the unique hexagonal axis).[11] In other cases λ may be degenerate to a finite degree. For cubic structures in particular soft-mode energy is isotropic in the $K \to 0$ limit,[12,13] but this infinite degeneracy is quickly lifted for nonzero K, allowing us, even here, to think of polar motion as becoming increasingly restricted to the incipient polar axis (e.g., a cubic axis in $BaTiO_3$) as $T \to T_C^+$.

In the analysis below of the approach to the phase transition from a nonpolar phase we shall therefore effect the enormous simplification of restricting polar motion to a direction λ, thereby justifying the use of a scalar formalism in Sec. II. The approximation is best for systems of low crystallographic symmetry, but it should have some relevance, at least qualitatively, in a more general context. The long-range dipolar nature of v_{ij} controls the long-wavelength form of v_K which may now, by virtue of the above restriction, be identified with the single matrix element $v_K^{\lambda\lambda}$. The well-known form for the continuum limit[14,15] is

$$(1/N)\,(v_0 - v_K) = 4\pi K_\lambda^2/K^2\ , \tag{3.1}$$

where K_λ is the component of wave vector $\vec{K}$ in direction λ. For a discrete lattice it is necessary to add structure-dependent terms. For mathematical simplicity we retain only a lowest-order lattice-dependent term, in the form

$$(1/N)\lim_{K\to 0}(v_0 - v_K) = 4\pi\,(K_\lambda^2/K^2) + \beta K^2 a^2\ , \tag{3.2}$$

where β is a structure-dependent dimensionless parameter and a is a primitive cell dimension.

It is now possible to use (3.2) in conjunction with the theory of Sec. II to investigate critical properties, to the extent that they are dominated by the long-wavelength excitations.

IV. SUSCEPTIBILITY

Substituting (3.2) in (2.27) one readily verifies that

$$(N\langle\xi_i^2\rangle_{T_C}/kT_C) - (N\langle\xi_i^2\rangle_T/kT) = \textstyle\sum_K\left[(v_0 - v_K)^{-1} - (\chi_0^{-1} + v_0 - v_K)^{-1}\right] \tag{4.1}$$

is dominated by long-wavelength contributions and may therefore be evaluated explicitly from the knowledge (3.2) to give

$$(N\langle\xi_i^2\rangle_{T_C}/kT_C) - (N\langle\xi_i^2\rangle_T/kT) = \tfrac{1}{4}\chi^{-1}(4\pi\beta)^{-3/2}\ln(\beta\chi)\ , \tag{4.2}$$

in the limit $T\to T_C$, $\chi\to\infty$, where $\chi = N\chi_0$ is the uniform dielectric susceptibility *per unit volume*, and where $\langle\xi_i^2\rangle_T$ refers to an ensemble average at temperature T.

For the case of an Ising potential function $V(\xi_i)$, the ensemble average $\langle\xi_i^2\rangle_T$ is independent of temperature T and can therefore be set equal to a constant, say, $\Xi.^2$ For this case the left-hand side of (4.2) becomes equal to $N\Xi^2 t/kT_C^2$, where $t = T - T_C$, and the equation has a solution for the temperature dependence of susceptibility of the form

$$\chi^{-1}\sim t/\ln(1/t)\ , \qquad t\to 0 \tag{4.3}$$

to lowest order $\{$neglecting terms smaller by a factor $\ln[\ln(1/t)]/\ln(1/t)\}$. More generally, $\langle\xi_i^2\rangle$ is both temperature and α dependent via (2.8) and (2.9). For the more general case of arbitrary $V(\xi_i)$ we find

$$\chi^{-1}\ln\chi\sim At + Bt\,\frac{d\alpha}{dT}\ , \qquad t\to 0 \tag{4.4}$$

where the derivative is taken at $T = T_C$, and where A and B are constants. Using (2.14) it is possible to rewrite this as

$$\chi^{-1}\ln\chi = Ct + Dt\,\frac{d\chi^{-1}}{dT}\ , \qquad t\to 0 \tag{4.5}$$

where again C and D are constants. This equation also has the solution (4.3) to lowest order since the derivative of χ^{-1} from (4.3) goes to zero as $T\to T_C$. The relationship (4.3) is therefore valid in the present approximation for arbitrary $V(\xi_i)$; that is, for displacement and order-disorder ferroelectrics.

We note in passing that the Curie temperature T_C is given by

$$N\langle\xi_i^2\rangle_{T_C}/kT_C = \textstyle\sum_K (v_0 - v_K)^{-1}\ , \tag{4.6}$$

which is not determined by the long-range form of v_K alone but requires explicit knowledge of v_K throughout the Brillouin zone. In the Ising limit, for which $\langle\xi_i^2\rangle_{T_C}$ is independent of the correlation parameter α, we can compare T_C from (4.6) with the equivalent RPA (or Bragg-Williams) Curie temperature T_C^{BW} to obtain

$$T_C^{\mathrm{BW}}/T_C = \frac{1}{N}\sum_K\left[1 - (v_K/v_0)\right]^{-1}\ , \tag{4.7}$$

which is, in general, greater than unity. We have evaluated this ratio for the case of an fcc lattice of interacting dipoles constrained to a z direction. Using values of $v_K \equiv v_K^{zz}$ calculated by Cohen and Keffer[14] for representative points throughout the first Brillouin zone (with $v_0 = 4\pi N/3$) we compute $T_C^{\mathrm{BW}}/T_C = 1.40$ for this case. In other words, simple random-phase theory overestimates T_C by 40% in this instance. Moreover, this deviation may well be relatively small compared to other possible situations. The fcc lattice has β of Eq. (3.2) of order 0.5 and has no antiferroelectric dipolar arrangements close in energy to that of the ferroelectric array. It is well known that for some lattice structures (the simple-cubic lattice is one example) dipolar forces favor an antiferroelectric array. It is therefore quite conceivable that for other ferroelectric lattices $v_0 - v_K$ might well approach small values at a number of other points (related by symmetry) in the Brillouin zone as well as at $K\to 0$. This situation (or, perhaps, a smaller value β) would produce very much larger discrepancies than the 40% of the fcc lattice between the random-phase and the self-consistent correlation theories. As a result, it would seem unwise to associate the Lorentz-field concept too closely with Curie temperature.

V. SPECIFIC HEAT

Once again, close enough to the critical point, we can obtain information concerning the (critical) behavior of specific heat from a knowledge of the limiting behavior (3.2) of v_K alone. Consider the internal energy $\langle\mathcal{H}\rangle$ of the many-body system. It is, in the limit of zero applied field,

$$\langle\mathcal{H}\rangle = N\langle V(\xi_i)\rangle - \tfrac{1}{2}N\textstyle\sum_j v_{ij}\langle\xi_i\xi_j\rangle\ , \tag{5.1}$$

and, using Eq. (2.24), this can be rewritten as

$$\langle\mathcal{H}\rangle = N\langle V(\xi_i)\rangle - \frac{1}{2}\,\frac{kT}{8\pi^3}\int\frac{v_K}{\chi^{-1} + N^{-1}(v_0 - v_K)}\ , \tag{5.2}$$

where the integral is over the first Brillouin zone. This equation, in turn, can be rearranged as

$$\langle \mathcal{H} \rangle = N \langle V(\xi_i) \rangle + \tfrac{1}{2} NkT - \tfrac{1}{2} \frac{NkT}{8\pi^3} (\chi^{-1} + N^{-1} v_0) I \; , \tag{5.3}$$

where I is the Brillouin-zone integral

$$I = \int \frac{1}{\chi^{-1} + N^{-1}(v_0 - v_K)} \; , \tag{5.4}$$

which, using (2.27), transforms to $I = 8\pi^3 N \langle \xi_i^2 \rangle / kT$ to give

$$\langle \mathcal{H} \rangle = N \langle V(\xi_i) \rangle + \tfrac{1}{2} NkT - \tfrac{1}{2} N^2 \langle \xi_i^2 \rangle (\chi^{-1} + N^{-1} v_0) \; . \tag{5.5}$$

The specific heat is now obtained as the first derivative with respect to the temperature of $\langle \mathcal{H} \rangle$. Assuming that $\langle V(\xi_i) \rangle$ and $\langle \xi_i^2 \rangle$ can be expanded in a Taylor series about T_C (this assumption is, of course, not necessary for the Ising limit in which case these quantities are both temperature independent), we find a specific heat C_t with leading terms of the form

$$C_t = A - B \frac{d\chi^{-1}}{dt} - C\chi^{-1} + Dt \; , \qquad t \to 0 \tag{5.6}$$

where A, B, C, and D are constants and in the Ising limit $C = D = 0$, $A = \frac{1}{2} Nk$, and $B = \frac{1}{2} N^2 \langle \xi_i^2 \rangle$. With the knowledge (4.3) of the limiting behavior of reciprocal susceptibility we derive, for arbitrary potential function $V(\xi_i)$, a critical form

$$C_t = A - [B' / \ln(1/t)] \; , \qquad t \to 0 \; . \tag{5.7}$$

This represents a logarithmic approach to a finite value at T_C and is to be compared with the RPA result[16] of a logarithmic *divergence* of C_t as $t \to 0$.

It is of interest to note the equivalent results for an isotropic (e.g., exchange) interaction potential v_K for which $v_0 - v_K \sim K^2$ as $K \to 0$. For this case RPA predicts $\chi^{-1} \propto t$ and a divergence of specific heat at T_C as $t^{-1/2}$ (see, for example, Brout[1]). The self-consistent correlation theory for this case shows $\chi^{-1} \propto t^2$ (the spherical result) and a linear approach $A - B't$ of specific heat to a finite value at the Curie temperature. For magnetism, experimental results prefer a behavior between these two extremes for both χ^{-1} and C_t, with a possible logarithmic divergence of specific heat as $t \to 0$ and a critical index between 1 and 2 (of order 1.3) for susceptibility.

VI. CORRELATION PARAMETER α

Combining Eqs. (2.14), (2.15), and (2.27) it is possible to relate the correlation parameter α directly to susceptibility in the form

$$\sum_K \frac{1}{\chi^{-1} + N^{-1}(v_0 - v_K)} = \frac{N}{\chi^{-1} + N^{-1} v_0 (1 - \alpha)} \; , \tag{6.1}$$

where $\chi = N\chi_0$ is the susceptibility per unit volume. This relationship (6.1) is valid for arbitrary $V(\xi_i)$. We notice in particular that the correlation α_C *at* the Curie temperature follows from

$$\sum_K (v_0 - v_K)^{-1} = \frac{N}{v_0 (1 - \alpha_C)} \; , \tag{6.2}$$

and is therefore $\alpha_C = 0.28$ for the fcc example cited in Sec. IV. There is evidence that values of α_C larger than 0.9 can be found in some more realistic situations.[2]

It is simple to verify from Sec. II that a temperature-independent α in a paraelectric phase leads to a Curie-Weiss uniform susceptibility. Since (experimentally) quasi-Curie-Weiss behavior is often found near ferroelectric phase transitions, this would indicate, at most, a very slowly temperature-dependent α. This has already been stressed in Ref. 2. Nevertheless, from (6.1) and (3.2) we can show that α cannot be truly temperature independent in the self-consistent theory.

Writing (6.1) for $T = T_C + t$, then again for $T = T_C$, and substracting one equation from the other leads directly to

$$(\alpha_C - \alpha) = \tfrac{1}{4} (v_0/N)(1 - \alpha_C)^2 (4\pi\beta)^{-3/2} \chi^{-1} \ln(\beta\chi) \; , \tag{6.3}$$

in the limit $\chi \to \infty$ (i.e., $t \to 0$). In conjunction with (4.3), this implies

$$\alpha_C - \alpha \sim t \; , \qquad t \to 0 \; . \tag{6.4}$$

An equivalent result is easily established for an isotropic (exchange) form of interaction potential with

$$\lim_{K \to 0} (v_0 - v_K) \propto K^2 \; .$$

It is

$$\alpha_C - \alpha \sim \chi^{-1/2} \; , \qquad t \to 0 \tag{6.5}$$

from which, using the fact that $\chi^{-1} \propto t^2$ for this case, we again find a linear relationship between $\alpha_C - \alpha$ and t in the limit $T \to T_C$.

Thus, using α as a measure of correlations, we are struck by the similarity in qualitative behavior between the two systems (exchange and dipolar) rather than the differences. However, there are other more informative scalar measures of correlation (usually a correlation length in units of cell dimension) and they shall be discussed below. Since a single scalar correlation parameter can indicate only a single gross aspect of the detailed correlations $\langle \xi_i \xi_{i+R} \rangle$, different definitions can lead to seemingly conflicting statements concerning critical behavior. Such confusion already exists in the literature on ferroelectrics[17,18] where, as we shall see below, it is difficult to define a critical correlation length in an unambiguous manner.

VII. CORRELATIONS $\langle \xi_i \xi_{i+R} \rangle$

In the theory of Sec. II detailed intercell correlations $\langle \xi_i \xi_{i+R} \rangle$ are expressed explicitly as a function of $v_0 - v_K$ and χ_0 by (2.25) and (2.26). A knowledge of the limiting long-wavelength form of $v_0 - v_K$ [Eq. (3.2)] then dictates the form of the correlations as $R \rightarrow \infty$. A mere glance at the equations and the symmetry of $v_0 - v_K$ in (3.2) tells us that these detailed correlations are extremely anisotropic. We shall investigate the limiting form of $\langle \xi_i \xi_{i+R} \rangle$ as $R \rightarrow \infty$ along the λ (or z) axis (longitudinal correlations) and also for R perpendicular to λ (the x or y axis; transverse correlations).

Using (3.2) and (2.24) we can write

$$N\langle \xi_i \xi_{i+R} \rangle = (kT/N) \sum_K e^{i\vec{K}\cdot\vec{R}} \times [\chi^{-1} + 4\pi(K_z^2/K^2) + \beta K^2 a^2]^{-1} \qquad (7.1)$$

to the extent that the summation is dominated by the limiting long-wavelength contributions (i.e., for $R \rightarrow \infty$). Replacing the summation by an equivalent integral, the mathematical problem for longitudinal correlations at quasi-infinite range becomes formally an evaluation of

$$N\langle \xi_i \xi_{i+R} \rangle = \frac{kT}{8\pi^3} \iiint \frac{e^{iRz}\, dx\, dy\, dz}{\chi^{-1} + 4\pi(z/r)^2 + \beta r^2} \;, \qquad (7.2)$$

where $r^2 = x^2 = y^2 + z^2$, where R is here and henceforth measured in units of "cell dimension," and where the integral can be taken over all r space. The equivalent expression for transverse correlations is obtained by replacing e^{iRz} by e^{iRx} on the right-hand side of (7.2). These integrals are discussed in Appendix A.

From (7.2) we find that when χ^{-1} is nonzero but approaching small values

$$\lim_{R\rightarrow\infty} \langle \xi_i \xi_{i+R} \rangle \sim kT\chi^2/(R^3 N) \quad \text{(longitudinal)} \;, \qquad (7.3)$$

which is to be contrasted with the familiar Ornstein-Zernike form $(1/R)\exp(-R\chi^{-1/2})$ for isotropic (exchange) interactions. The equivalent result for transverse correlations is (Appendix A)

$$\lim_{R\rightarrow\infty} \langle \xi_i \xi_{i+R} \rangle \sim -kT\chi^{1/2}/(R^3 N) \quad \text{(transverse)} \;, \qquad (7.4)$$

which is again to be compared with $(1/R)\exp \times (R\chi^{-1/2})$ for isotropic interactions. Thus the ratio of longitudinal to transverse correlations as $T \rightarrow T_C^+$ goes as $\chi^{3/2}$, indicating that the polarization correlations are enormously concentrated in the incipient polar direction. For cubic systems the incipient polar direction will be degenerate by symmetry and the corresponding correlations will be along several equivalent directions (e.g., the cubic axes in $BaTiO_3$). This type of behavior has already been observed in the nonpolar phase of some perovskites,[19-21] although our interpretation of the phenomenon differs from the static disorder picture envisaged by Comès *et al.*[19-21] and involves only dynamic disorder with both charge motion (fluctuations) and correlations being dominantly along the same incipient polar direction.

For transverse correlations, the negative sign in (7.4) is noteworthy. It is quite unusual for negative correlations to be found in a system which orders positively. It is true (see Appendix A) that additional positive transverse correlations going as $\exp(-R\chi^{-1/2})$ are also present, but these cannot compete favorably with (7.4) except possibly in the limit $\chi^{-1} \rightarrow 0$ itself. From the numerical computations below it would appear that some transverse correlations do actually retain a negative sign right into the phase transition. The limiting situation as $R \rightarrow \infty$, $\chi \rightarrow \infty$, has not been resolved for transverse correlations.

The critical behavior for the dominant longitudinal correlations is easier to assess. The relationship (7.3) holds for nonzero χ^{-1}. At the Curie point itself (see Appendix A) the correlations go over to

$$\lim_{R\rightarrow\infty} \langle \xi_i \xi_{i+R} \rangle \sim kT/R\beta N \quad (\text{longitudinal}\;,\; T = T_C) \;, \qquad (7.5)$$

indicating, in particular, a divergence as $\beta \rightarrow 0$ (for which case $T_C \rightarrow 0$ corresponding to the dipolar continuum).

To get some feel for near-neighbor correlations we have evaluated (7.1) numerically by computer assuming a simple-cubic-lattice geometry, $\beta = \frac{1}{2}$ (a value typical for the ferroelectrically stable cubic lattices), and taking the long-wavelength form of $v_0 - v_K$ to be valid over the entire Brillouin zone. Numerical results for $\langle \xi_i \xi_{i+R} \rangle / \langle \xi_i^2 \rangle$ as a function of uniform static susceptibility alone are computed for near-neighbor R in both the longitudinal and transverse directions. Results are displayed in Figs. 1–3. Since for any real ferroelectric system $v_0 - v_K$ will almost certainly differ markedly from its long-wavelength form away from the zone center, the figures are only meant to indicate a very qualitative picture. Nevertheless, some gross features are obviously worthy of comment.

First, the longitudinal correlations are well behaved in the sense that they are uniformly positive, decrease monotonically with increasing R and with increasing temperature $T - T_C$, and extrapolate smoothly to the limiting $1/R^3$ behavior of (7.3). The transverse correlations are quite a different story. They are almost nonexistent (less than of order 2%) except for nearest neighbors. They are also, in general, not a monotonically decreasing function of R or $T - T_C$, and they show a tendency to oscillate in sign, with second-, fourth-, sixth-, etc., neighbor correlations being of negative sign.

We are now in a position to discuss the concept of correlation length L_c. For correlations with a limiting exponential decay, an unambiguous definition (in the sense of static-scaling theory) can be made by writing the decay as e^{-R/L_c}. Thus, in the exchange force context, $L_c \sim \chi^{1/2}$ and for an isotropic system this enables us to write

$$\chi_K \sim 1/(L_c^{-2} + K^2) \text{ (exchange forces) }, \qquad (7.6)$$

in the long-wavelength limit.

For dipolar interactions (3. 2), χ_K reduces to the form (7. 6) only for wave vectors perpendicular to the $z(\lambda)$ axis. Since these perpendicular (x and y) directions dominate the quasielastic neutron scattering at long wavelengths, Yamada *et al.*[18] have defined a correlation length for $BaTiO_3$ using (7. 6) and hence quote an $L_c \sim \chi^{1/2} \sim (T - T_C)^{1/2}$ for the dipolar system. It is difficult to see the physical significance of such a correlation length. It is obviously associated with the $\exp(-R\chi^{-1/2})$ contributions to transverse correlations referred to above but can have little relevance as far as the dominant longitudinal correlations are concerned. For the latter, a valid concept would be to define a (longitudinal) correlation length L_c as the distance for which (as R and χ become large) correlations (7. 3) and (7. 5) become of comparable magnitude. That is,

$$kT/L_c \sim kT\chi^2/L_c^3 , \qquad (7.7)$$

or $L_c \sim \chi$. However, a case can also be made for defining L_c from

$$\lim_{R\to\infty} \langle \xi_i \xi_{i+R} \rangle / \langle \xi_i^2 \rangle \sim (L_c/R)^p , \qquad (7.8)$$

which, from (7. 3), leads to $p = 3$ and $L_c \sim \chi^{2/3}$ for the dominant correlations. Yet again, from (2. 20) one might conceive of a correlation volume V_c defined by

$$kT\chi_0 = \textstyle\sum_j \langle \xi_i \xi_j \rangle = (V_c/v) \langle \xi_i^2 \rangle , \qquad (7.9)$$

where v is the volume of a primitive lattice cell. In terms of macroscopic units, defining $P_i = \xi_i / v$, Eq. (7. 9) becomes

$$kT\chi = V_c \langle P_i^2 \rangle . \qquad (7.10)$$

Since $\langle \xi_i^2 \rangle$ (or $\langle P_i^2 \rangle$) remains finite as $T \to T_C^+$, this leads to $V_c \sim \chi$. In short, in the absence of an exponential correlation decay, a unique definition of correlation length is difficult, if not impossible, to find.

A rather practical definition of a correlation volume has been made by Wemple and co-workers[22–24] which bears outwardly a strong resemblance to (7. 10). They write, for a disorder phase,

$$kT\epsilon = V_c' \langle P_\Delta^2 \rangle , \qquad (7.11)$$

where ϵ is the dielectric constant. Equivalently, we can express this as

$$kT\chi = (V_c'/4\pi) \langle P_\Delta^2 \rangle . \qquad (7.12)$$

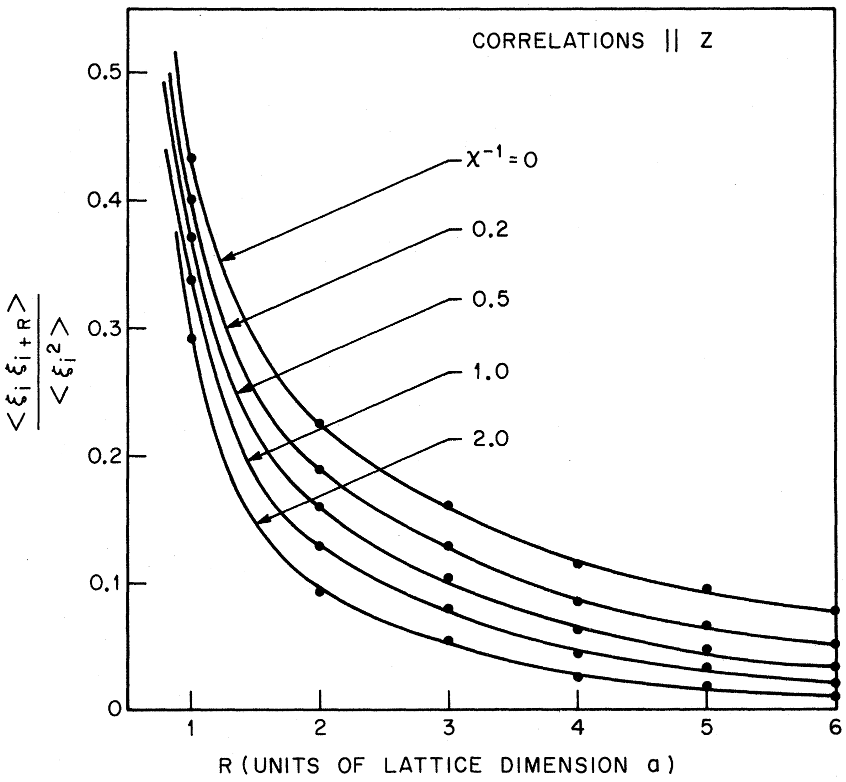

FIG. 1. Paraelectric polarization correlations $\langle \xi_i \xi_{i+R} \rangle$ for near neighbors $R = na$ along the z axis of a simple-cubic lattice, computed from Eqs. (2. 25) and (2. 26) for the interaction potential $(1/N)(v_0 - v_K) = 4\pi(K_z^2/K^2) + \frac{1}{2}K^2a^2$ and for several values of reciprocal susceptibility. The curves are valid for arbitrary local single-cell potential $V(\xi_i)$ of Eq. (2. 1). The continuous curves interpolating between the physical (integer n) values of the abscissa are merely guides to the eye.

In these equations, $\langle P_\Delta^2\rangle$ is that mean-square polarization which controls the shift ΔE in energy (as one approaches the critical region) of interband electronic oscillators through the equation

$$\Delta E=\beta'\langle P_\Delta^2\rangle\,, \qquad (7.13)$$

where β' is an interband polarization potential[25] measured by probing with a uniform applied field. Since ΔE controls the critical temperature variation of many measurable electronic properties, their anomalous behavior as $T\to T_C$ can be cast, through Eqs. (7.12) and (7.13), in terms of V_c', which proves to be rather insensitive to temperature $T-T_C$[22–24] and of order 10^4–10^5 Å^3 in the perovskite-oxide ferroelectrics.

It is evident that V_c' (or more truly $V_c'/4\pi$) is a volume over which fluctuations are closely correlated in some sense, and that $\langle P_\Delta^2\rangle$ (differing from $\langle P_i^2\rangle$) is some fluctuation average over this volume. However, the precise mathematical form for $\langle P_\Delta^2\rangle$ in terms of microscopic correlations must await a careful analysis of the statistical mechanism by which the band edge reacts to polarization fluctuations. At this time we note only from Fig. 3 that it is difficult to conceive of any transverse dimension L_t for such a correlation volume differing substantially from ~ $2a$. It is now difficult not to comment (whether it is relevant or not) that an obvious

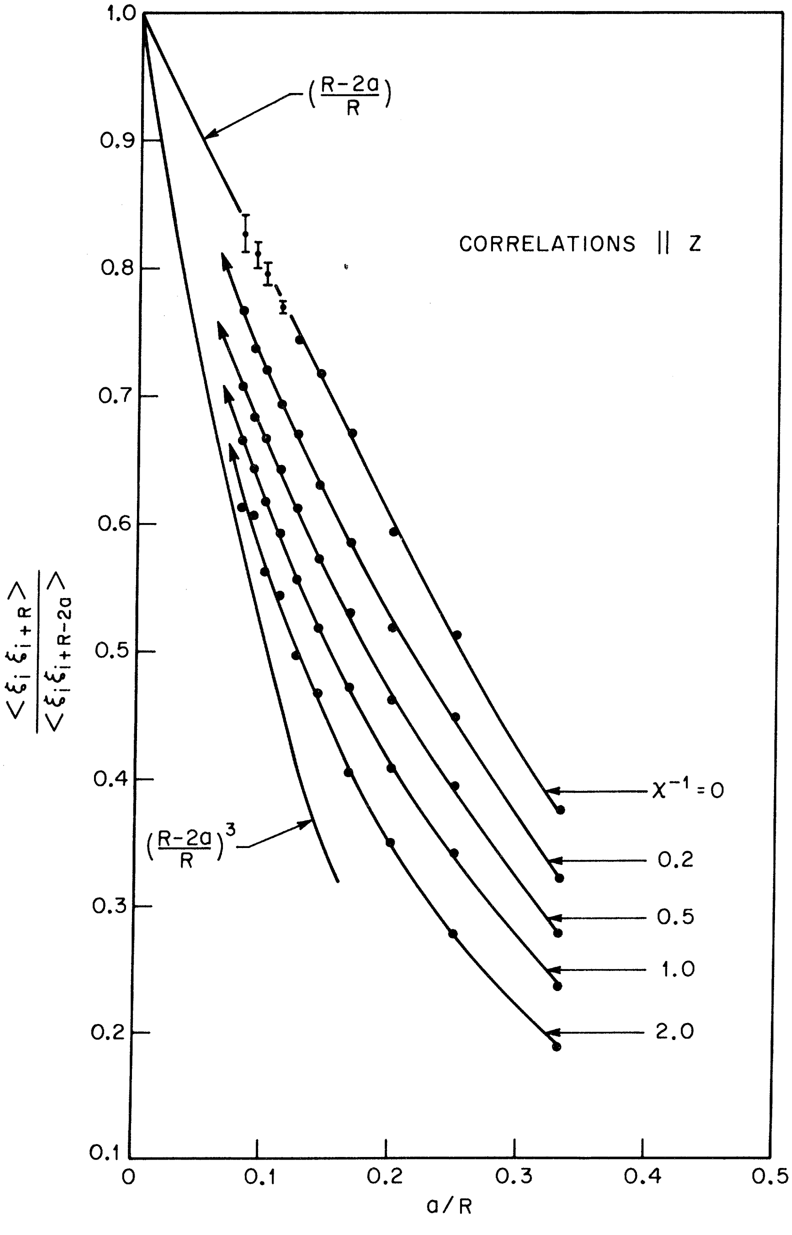

FIG. 2. Computed near-neighbor data of Fig. 1 (extended out to $n=12$) are replotted in a manner demonstrating their smooth approach to the limiting $(1/R^3)$ form of (7.3) as $R\to\infty$.

linear measure of longitudinal correlations, namely,

$$\frac{L_l}{a} = \sum_{-\infty}^{\infty} \frac{\langle \xi_i \xi_{i+R} \rangle}{\langle \xi_i^2 \rangle} \approx 3.4 + 0.9 \ln\chi \, , \qquad (7.14)$$

(see Appendix B) combines with $L_t = 2a$ to describe a volume $L_l L_t^2$ which, if associated with $V_c'/4\pi$, gives for the range $\chi \sim 10^2$–10^3 and for perovskite oxides ($a^3 \approx 64$ Å^3) the result $V_c' \sim (2.5$–$3) \times 10^4$ Å^3 in order-of-magnitude agreement with the findings of Refs. 22–24.

VIII. SUMMARY

Polarization fluctuations have been determined self-consistently using a correlated effective-field theory of ferroelectricity. Assuming an interaction potential between primitive cell polar displacements ξ_i which goes over to a classical dipolar form at large intercell distance, the critical behavior of dielectric susceptibility χ, specific heat C_t, and polarization correlations $\langle \xi_i \xi_{i+R} \rangle$ have been calculated for a paraelectric phase as $t = T - T_C \to 0$. We find $\chi \sim [\ln(1/t)]/t$ and $C_t \sim A - [B'/\ln(1/t)]$, where A and B' are constants. Polarization correlations take the form of well-developed ferroelectric linear chains in an incipient polar direction with a decay along the length going as $\langle \xi_i \xi_{i+R} \rangle \sim \chi^2/R^3$ in the limit of large R. Correlations between chains are extremely small by comparison and can be of either sign. The lack of an exponential decay for correlations makes a unique definition of correlation length or volume very difficult and has led to conflicting statements in the literature concerning the presence or absence of "critical behavior" for such a concept.

The critical behavior found for χ and C_t differs only slightly in functional form from the Curie-Weiss χ and logarithmically diverging C_t predicted by conventional RPA theory. However, numerical predictions of relevant amplitudes, Curie temperature, etc., can differ very markedly between the two theories. The form calculated for the polarization correlations is in qualitative agreement with x-ray and neutron-diffuse-scattering findings for the ferroelectric perovskites.

The theory of the present paper would suggest that highly developed linear correlations in an incipient polar direction should be a general property of a wide class of ferroelectrics in a nonpolar phase as $T \to T_C^+$. The equivalent situation for an antiferroelectric is more difficult to ascertain since the lattice instability occurs away from the center of the Brillouin zone and we have, at present, little *a priori* knowledge of the form of the interaction

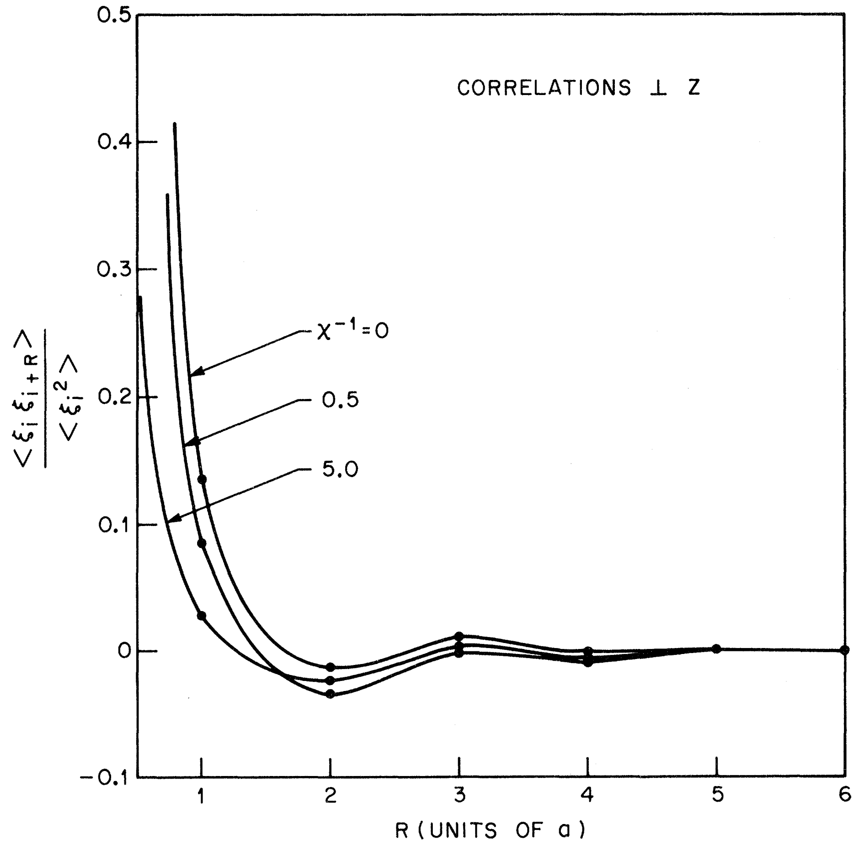

FIG. 3. As Fig. 1, but computed for near neighbors along an x (or y) axis. Again, the continuous curves are merely guides to the eye, and the data are again valid for arbitrary $V(\xi_i)$ of (2.1).

potential Fourier transform v_K except as $K \rightarrow 0$. It seems reasonable to surmise, however, that for crystal structures which tend to exhibit ferroelectricity (e.g., perovskites) there will be a fairly low-lying strongly polar mode even in those examples which actually become antiferroelectric. In such a case the characteristic chainlike correlations of the incipient ferroelectric will still be present (now in addition to the critical correlations associated with the antiferroelectric transition itself), although they will not exhibit any critical behavior as the temperature is lowered towards the antiferroelectric instability. Evidence for the coexistence of two quite distinct types of correlation in an incipient antiferroelectric ($NaNbO_3$) has already been found[26,27] using x-ray diffuse-scattering techniques. One type of correlation is indeed chainlike and noncritical and presumably results from the form $v_0 - v_K$ of Eq. (3.2) for a low-lying strongly polar mode which, in $NaNbO_3$, does not trigger the phase transition. The other type of correlations is observed[26,27] to be planar and critical. These are therefore probably associated with a different optic mode of vibration which is going soft at a point away from the zone center. Since, at present, we know nothing of the form of v_K for this soft mode in the neighborhood of its condensation, it is not possible to comment on the planar form found experimentally for the associated critical correlations.

ACKNOWLEDGMENT

It is a pleasure to acknowledge discussions with P. C. Hohenberg concerning the concept of correlation length in the absence of an exponential correlation decay.

APPENDIX A

Longitudinal Correlations

Consider the integral

$$I_z = \frac{kT}{8\pi^3} \iiint e^{iRz} [\chi^{-1} + 4\pi(z^2/r^2) + \beta r^2]^{-1} \, dx\, dy\, dz \tag{A1}$$

of Eq. (7.2), in which $R \rightarrow \infty$, $r^2 = x^2 + y^2 + z^2$, and the integral is over all space. Transforming to cylindrical coordinates ρ, z, θ, it becomes

$$I_z = \frac{kT}{4\pi^2} \int_0^\infty \rho\, d\rho \int_{-\infty}^{\infty} \frac{e^{iRz}(\rho^2 + z^2)\, dz}{\beta(\rho^2 + z^2)^2 + 4\pi z^2 + \chi^{-1}(\rho^2 + z^2)} . \tag{A2}$$

Consider first the integral over z. It can be replaced (to the extent that I_z is an analytic function of R) by the integral taken for complex z from $-\infty$ to ∞ along the real axis and then around the semicircle at infinity in the positive half-plane. The integrand in (A2) has poles at

$$z^2 = -\rho^2 - (c/2\beta)\, \{1 \mp [1 + (16\,\pi\beta\rho^2/c^2)]^{1/2}\} , \tag{A3}$$

in which $c = 4\pi + \chi^{-1}$.

The dominant contributions to I_z (as $R \rightarrow \infty$) are, in general, those for which $z \rightarrow 0$; i.e., from solutions to (A3) for which $z \rightarrow 0$. Now Eq. (A3) has solutions as $z \rightarrow 0$ only for the upper sign and for $\rho \rightarrow 0$. Expanding the root in (A3) for $\rho \ll 1$, the upper solution is

$$z = i\,[(\chi^{-1}\rho^2/c) + (16\pi^2\beta\rho^4/c^3)]^{1/2} , \tag{A4}$$

to terms in ρ^4 inside the root. Now, from the theory of residues, (A2) can be directly reduced to

$$I_z = (kT/c^2) \int_0^\infty \rho^2 e^{-R\rho q^{1/2}} d\rho / q^{1/2} , \tag{A5}$$

where

$$q = (\chi^{-1}/c) + (16\pi^2\beta\rho^2/c^3) \tag{A6}$$

and we have neglected terms $\rho^4 \exp(-R\rho q^{1/2})$ in the numerator because (A5) is dominated by contributions as $\rho \rightarrow 0$.

If χ^{-1} is nonzero, (A5) reduces in lowest order to

$$\begin{aligned} I_z &= \frac{kT}{c^{3/2}} \int_0^\infty \rho^2 \chi^{1/2} \exp(-R\rho/c^{1/2}\chi^{1/2})\, d\rho \\ &= \frac{2kT\chi^2}{R^3} \qquad (\chi^{-1} \neq 0,\ R \rightarrow \infty) . \end{aligned} \tag{A7}$$

If, on the other hand, χ^{-1} is zero ($T = T_C$), then (A5) becomes

$$I_z = \frac{kT}{8\pi^{3/2}\beta^{1/2}} \int_0^\infty \rho \exp[-R\rho^2(\beta/4\pi)^{1/2}]\, d\rho = \frac{kT}{8\pi R\beta} \qquad (\chi^{-1} = 0,\ R \rightarrow \infty) . \tag{A8}$$

Transverse Correlations

Consider now the integral

$$I_x = \frac{kT}{8\pi^3} \iiint e^{iRx} [\chi^{-1} + 4\pi(z^2/r^2) + \beta r^2]^{-1} \, dx\, dy\, dz , \tag{A9}$$

again taken over all space, where $r^2 = x^2 + y^2 + z^2$. We perform first the integral over x, replacing it by an integral taken for complex x from $-\infty$ to ∞ along the real axis and around the semicircle at infinity in the positive half-plane. The integrand has poles at

$$x^2 = -[y^2 + z^2 + (\chi^{-1}/2\beta)] \pm [(\chi^{-1}/2\beta)^2 - (4\pi z^2/\beta)]^{1/2} . \tag{A10}$$

The dominant contribution to (A9) as $R \rightarrow \infty$ comes from $x \rightarrow 0$. Equation (A10) has solutions at arbitrarily small x when χ^{-1} is nonzero, only from the upper sign and for $y \rightarrow 0$, $z \rightarrow 0$, in which case

$$x^2 = -y^2 - z^2 - (4\pi z^2/\chi^{-1}) + O(z^4) . \tag{A11}$$

However, unlike the case for longitudinal correlations, the lower-sign solution can also take on arbitrarily small values as $\chi^{-1} \rightarrow 0$ since for $y = 0$, $z = 0$ the pertinent solution of (A10) goes as $x \sim i$

$\times(\chi^{-1})^{1/2}$ and therefore gives rise to correlations (contributions to I_x) going as $\exp(-R\chi^{-1/2})$. These correlations are small compared to those arising from (A11) (which, below, will be shown to go as $1/R^3$) for any finite χ^{-1} as $R\to\infty$, but may eventually become the dominant transverse contributions in the limit $\chi^{-1}\to 0$, $T\to T_C^+$.

For nonzero χ^{-1}, using (A11) and the theory of residues, I_x reduces in lowest order to

$$I_x = -\frac{kT\chi^2}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{z^2\exp[-R(y^2+gz^2)^{1/2}]\,dy\,dz}{(y^2+gz^2)^{1/2}} \;, \tag{A12}$$

where $g = 1+4\pi\chi$. Equation (A12) is a form which can be integrated directly using coordinates $r^2 = y^2 + gz^2$, $\theta = \tan^{-1}(g^{1/2}z/y)$ to give

$$I_x = -\frac{kT\chi^2}{2g^{3/2}}\int_0^{\infty} r^2 e^{-Rr}\,dr = -\frac{kT\chi^2}{R^3 g^{3/2}} \;. \tag{A13}$$

In particular, for $4\pi\chi \gg 1$, we find I_x goes as $-kT\chi^{1/2}/R^3$ and therefore that the ratio I_z/I_x of longitudinal to transverse correlations at infinity is proportional to $\chi^{3/2}$, exhibiting the very marked anisotropy of the dielectric correlations in the vicinity of a phase transition.

APPENDIX B

Longitudinal correlations $\langle \xi_i \xi_{i+R}\rangle$ for near neighbors $R = na$ along the z axis of a simple-cubic lattice can be calculated directly from (2.25) and (2.26) using a computer for the approximate numerical integrations required. We have taken an interaction potential $(1/N)(v_0 - v_K) = 4\pi(K_z^2/K^2) + \beta K^2 a^2$, with $\beta = \frac{1}{2}$, to be valid over the entire Brillouin zone and have computed directly out to $n = 12$, beyond which the increasingly rapid oscillation of the integrand makes numerical accuracy increasingly difficult to obtain. Results for longitudinal $\langle \xi_i \xi_{i+R}\rangle/\langle \xi_i^2\rangle$, $R = na$, $n = 1, 2, \ldots, 12$, are as follows for $T = T_C$ ($\chi^{-1} = 0$): 0.432, 0.226, 0.162, 0.116, 0.096, 0.078, 0.069, 0.058, 0.053, 0.046, 0.043, and 0.038. These are plotted in Fig. 2, from which we see that the series is tending to go as $1/R$, in agreement with (A8).

For values of χ^{-1} approaching zero, but finite, these near-neighbor values are essentially unchanged. However, from (A7) we know that the correlations for $T \neq T_C$ must eventually go as $1/R^3$ as $R\to\infty$. Let us define a correlation length N_c (in units of cell dimension a) for which, as $R\to\infty$ and $\chi^{-1}\to 0$, correlations (A7) and (A8) become equal. Thus

$$2kT\chi^2/N_c^3 = kT/8\pi\beta N_c \;, \tag{B1}$$

which is $N_c^2 = 16\pi\beta\chi^2$. We now consider the sum

$$S = \sum_{n=1}^{\infty}\langle \xi_i \xi_{i+na}\rangle/\langle \xi_i^2\rangle \quad \text{(longitudinal)} \;, \tag{B2}$$

and we shall sum it using the following approximations. For $n = 1-12$ we use the computed values given above; for $n = 13$ to N_c we continue in a series going as $1/n$; and finally, from $n = N_c$ to ∞ we continue in a series going as $1/n^3$. Thus, writing $\langle \xi_i \xi_{i+na}\rangle/\langle \xi_i^2\rangle \equiv T_n$, we have

$$S = T_1 + \cdots + T_{11} + T_{12}\sum_{n=12}^{N_c}\frac{12}{n} + T_{N_c}\sum_{n=N_c}^{\infty}\left(\frac{N_c}{n}\right)^3 \;, \tag{B3}$$

which sums to

$$S \approx 1.38 + 12T_{12}\ln(N_c/12) + 6T_{12} \;. \tag{B4}$$

Noting from above that $T_{12} = 0.038$ and that, for $\beta = \frac{1}{2}$, $N_c \approx 5\chi$, we calculate

$$S \approx 1.21 + 0.46\ln\chi \;. \tag{B5}$$

It follows immediately that

$$\sum_{n=-\infty}^{\infty}\frac{\langle \xi_i \xi_{i+na}\rangle}{\langle \xi_i^2\rangle} = 2S + 1 \approx 3.4 + 0.9\ln\chi \;. \tag{B6}$$

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Acoustic Attenuation and Frequency Shift in Ferromagnetic Insulators at Low Temperature

S. K. Ghatak
Saha Institute of Nuclear Physics, Calcutta-9, India

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The propagation of an acoustic wave in a ferromagnetic insulator at low temperatures has been investigated theoretically. Two models describing the interaction of the spin system with the acoustic wave have been considered, namely, (i) the modulation of exchange interaction and (ii) the modulation of single-ion magnetostriction, due to lattice vibrations. The attenuation and frequency shift of acoustic waves in a simple cubic system have been considered for two-magnon–one-phonon processes arising from these interaction mechanisms. It is found that because of the magnon-phonon interaction the phonon frequency is renormalized even at absolute zero for the process in which either the two magnons fuse to produce a phonon, or a phonon is destroyed to produce two magnons. In addition, for a single-ion magnetostrictive interaction, the above process exhibits the result that the first derivative of the renormalized part of the frequency with respect to wave vector $\vec{q}$ has a logarithmic singularity at $|\vec{q} \pm \vec{L}| = 2k_m$, where k_m is the magnitude of the maximum wave vector for the magnons, and $\vec{L}$ is a reciprocal-lattice vector. The results obtained have been compared with those of other workers.

I. INTRODUCTION

The spin-phonon interaction in ferromagnetic insulators and its effect on acoustic propagation through these materials at low temperatures have been of considerable interest for a long time.[1-7] A variety of models for the interaction and also a number of theoretical methods have been used in this connection.

The spin-phonon coupling in ferromagnetic insulators can be described in terms of two types of interaction,[8] namely, (a) the volume magnetostrictive interaction and (b) the single-ion magnetostrictive interaction. At low temperatures both these interactions can be described in terms of scattering and absorption processes involving different numbers of magnons and phonons. The one-magnon-one-phonon process in these was considered by Kittel,[1] Schlömann,[2] and Akhiezer *et al.*[3] The two-magnon–one-phonon process occurs in the next higher order, which is composed of two parts: (i) the scattering of a magnon with the annihilation or the creation of a phonon and (ii) the annihilation of a phonon with the simultaneous creation of two magnons, and the reverse process.

For the volume magnetostrictive interaction, the process (i) was considered by Tani,[4] Pytte,[5] and Kaganov and Chikvashvili.[6] Process (ii) was investigated by Silberglitt.[7] Silberglitt's results, however, are valid only at $T = 0$ °K, since the irreducible self-energy diagram considered by him is of the lowest order in both the spin-phonon interaction and the density of spin waves. For single-ion magnetostrictive interaction, process (ii) was studied by Kaganov and Chikvashvili. They started with a phenomenological interaction Hamiltonian and calculated the phonon damping using the rate-equation approach. Process (i) for this particular mechanism has not been considered so far.

Here we study processes (i) and (ii) for each of the two mechanisms (a) and (b), but we present the details only for the single-ion magnetostrictive interaction. The reason is that the recent experimental data[8] on acoustic wave attenuation suggest single-ion magnetostrictive interaction to be as important as the other one, which has been previously treated only in part. The results of the volume magnetostrictive interaction are also given to facilitate a comparison of the relative importance of the two mechanisms. We also note that our results are valid for $T \neq 0$ °K.

The functional-derivative technique[9-11] has been used to calculate the phonon Green's function in the presence of the magnon-phonon interaction. The real part of the self-energy gives the frequency shift (or velocity shift), and the phonon lifetime is obtained from the imaginary part. The acoustic attenuation is obtained in the lowest order of the magnon-phonon interaction from the phonon lifetime. Section II contains a description of the