Statistical Mechanics of a Simple Model of a Displacive Ferroelectric*

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A displacive ferroelectric is represented by a model in which there is only one species of movable ion. The potential energy is taken to be an arbitrary unstable quadratic form in the ionic displacements, plus a quartic term $\gamma \Sigma (\vec{r}_i \cdot \vec{r}_j)^2$, $(\gamma > 0)$. The statistical mechanics is done variationally by means of approximate distribution functions containing parameters which are chosen so as to minimize the free energy. The mean-field approximation uses a distribution function of the form $\Pi g(\vec{r}_i)$ and the self-consistent phonon approximation (SPA) uses a Gaussian in the quadratic normal coordinates, the coefficients in the Gaussian being identified with the squares of the temperature-dependent frequencies. In both approximations it is found that the ferroelectric phase transition can be either first or second order, depending on the quadratic potential. The SPA shows "softening" of the $\vec{q}=0$ mode in the paraelectric phase. The frequency of this mode vanishes when $T=T_c$, where T_c is the lowest temperature at which the paraelectric phase exists either stably or metastably. The SPA leads to a Curie-law susceptibility in the paraelectric phase only when the quadratic forces are of sufficiently long range.

I. INTRODUCTION

The value of simple models has been well established in solid-state physics and statistical mechanics. Analysis of the Ising and Heisenberg Hamiltonians has greatly enhanced our understanding of ferromagnets. In the same spirit we have studied the simplest Hamiltonian which appears to us to embody the essential features of a displacive ferroelectric. Our tool for analyzing the system is a powerful variational principle discussed in Sec. II.

The Ising and Heisenberg models study the orientational ordering of a collection of objects with permanent magnetic (or electric) moments, of fixed magnitude, each attached to a definite lattice site. The essentially new feature of the displacive ferroelectrics is that the magnitude of the moments is also variable, and in fact the same interactions which align the moments also create them.

We consider a model crystal in which there is only one kind of movable ion. Other ions may be present, but are assumed not to move. Only the movable ions appear explicitly in the Hamiltonian. Furthermore, we assume that at sufficiently high temperature the system has no spontaneous polarization. Let $\vec{R}_i$ be the mean position of the ith ion at high temperature. We assume that the vectors $\vec{R}_i$ form some kind of lattice. Let $\vec{r}_i$ be the vector from $\vec{R}_i$ to the instantaneous position of the ith ion. The interactions between the ions are assumed to be such that a simultaneous displacement of all the movable ions (by the same small amount) away from the sites $\vec{R}_i$ will lower the energy. However, the thermal chaos (entropy) prevails at high temperature, so that there is no spontaneous polarization.

The instability of the lattice against simultaneous displacement of all the (movable) ions is put into the Hamiltonian via a term

$$\frac{1}{2}\sum_{ij} V_{ij}\vec{r}_i \cdot \vec{r}_j$$

in the potential energy, where the quadratic form is *not* positive definite. In particular, in order that the energy be negative when all the $\vec{r}_i$ are equal, we require that $\sum V_{ij}$ be negative. We note that the configuration defined by making all the $\vec{r}_i$ equal does *not* correspond to a translation of the entire crystal (which, of course, could not change the potential energy), but rather to a translation of the ions represented in the Hamiltonian *relative* to the ions not represented in the Hamiltonian. In this model the acoustical degrees of freedom have been "frozen out," so that all normal modes should be thought of as optical. The negativity of $\sum V_{ij}$ will be seen to correspond to "soft" behavior of a $\vec{q}=0$ optical mode, such as occurs in $BaTiO_3$ as the phase transition at 120 °C is approached from above. We could have used a more general quadratic form

$$\frac{1}{2}\sum_{ij,\lambda\mu} V_{ij}^{\lambda\mu} r_i^{\lambda} r_j^{\mu}, \tag{1.1}$$

where λ and μ take on the values 1, 2, and 3 corresponding to the x, y, and z components of $\vec{r}_i$ and $\vec{r}_j$. Since $\vec{r}_i$ is proportional to the dipole moment associated with the ith ion, it is easily seen that the conventional dipole-dipole interaction is of this form with

$$V_{ij}^{\lambda\mu} \propto \frac{3R_{ij}^{\lambda}R_{ij}^{\mu} - R_{ij}^2\delta^{\lambda\mu}}{R_{ij}^5}. \tag{1.2}$$

However, the important predictions of our model are unaltered by this extra generality, and we

therefore use the simpler form involving only $\vec{r}_i \cdot \vec{r}_j$, eliminating the need for careful consideration of principal axes and polarizations. If we stop with the quadratic term in the potential energy, there is no statistical mechanics, since all the ions will simultaneously displace to infinity; i.e., the classical coordinate space partition function

$$\int \exp[-\beta U(\vec{r}_1 \cdots \vec{r}_N) d\vec{r}_1 \cdots d\vec{r}_N]$$

will not exist. There must be an anharmonic restoring force which ultimately stabilizes the lattice. We take this to be of the simplest possible form, namely, $\gamma \sum r_i^4$ (with $\gamma > 0$), a quartic potential attracting each ion back to its own site. Our potential energy function is thus

$$U = \frac{1}{2} \sum_{ij} V_{ij} \vec{r}_i \cdot \vec{r}_j + \gamma \sum_i (\vec{r}_i \cdot \vec{r}_1)^2 . \qquad (1.3)$$

Note that the sum includes terms with $i = j$ and includes both (ij) and (ji). If there is an external field, we add $-Q\vec{E} \cdot \sum \vec{r}_i$, where Q is the ionic charge. The kinetic energy is $\sum p_i^2/2M$, and plays no role if the temperature is high enough for classical statistical mechanics to be valid.

Models closely related to the one defined by (1.3) have recently been studied by Lines,[1] Onodera,[2] Pytte,[3,4] and Gillis and Koehler.[5] The analyses have employed either the mean-field approximation (MFA) or the self-consistent phonon approximation (SPA). Gillis and Koehler have found that the SPA predicts a first-order phase transition for their model. The question of whether this prediction is correct, or merely a consequence of the inaccuracy of the SPA in the critical region, has been discussed in two Letters.[3,6]

The present work was done independently of the above-mentioned studies, and leads to the conclusion that both MFA and SPA can yield either a first- or second-order transition, depending on the nature of the quadratic coupling V_{ij}. The condition on V_{ij} which determines the order of the transition is different in the two approximations. We make no contribution to the discussion of which approximation is more credible, but believe that this discussion should be carried out within the framework of the simplest possible model. We shall see that the essential features of Gillis and Koehler's analysis emerge when we apply the SPA to our somewhat simpler Hamiltonian.

The model considered by Gillis and Koehler is a lattice of positive and negative ions arranged in a NaCl structure at high temperature and deforming via a first-order transition, to a rhombohedral structure. Their potential is translationally invariant, consisting of a quadratic form in the ionic displacements plus an anharmonic part which is fourth order in the relative displacement of nearest neighbors. They have explored the phase diagram of their model in the SPA, by means of extensive computer studies, in both the paraelectric and ferroelectric phases. Using the SPA to analyze our model, we obtain essentially the same phase diagram as Gillis and Koehler by analytical and graphical methods, with the exception of the discussion of the fate of the paraelectric phase as the temperature is lowered. Gillis and Koehler find that the phase exists, at least metastably, all the way down to $T = 0$, with the frequency of the zone-center optic mode never going strictly to zero. We find that the frequency of the zone-center optic mode vanishes at a finite temperature, below which the paraelectric phase ceases to exist even metastably.

II. VARIATIONAL PRINCIPLE

The basis for our calculation is the inequality

$$\int e^{-\beta U(R)} d^N R \geq \exp[-\beta \int U(R)\rho(R) d^N R - \int \rho(R) \ln \rho(R) d^N R] , \qquad (2.1)$$

where $\beta = (kT)^{-1}$, $d^N R$ is the volume element in N-dimensional coordinate space, and $\rho(R)$ is any probability distribution [$\rho(R) \geq 0$ and $\int \rho(R) d^N R = 1$]. This inequality was first stated by Gibbs.[7] If we take ρ to be the correct classical distribution, i.e.,

$$\rho(R) = \frac{\exp[-\beta U(R)]}{\int \exp[-\beta U(R)] d^N R} ,$$

then (2.1) becomes an equality, but is of course useless. The idea is to choose a trial $\rho(R)$ simple enough so that the right-hand side of (2.1) is calculable, but complicated enough to contain some physics.

The quantum-mechanical generalization of (2.1) is[8]

$$\mathrm{Tr}(e^{-\beta H}) \geq \exp \mathrm{Tr}(-\beta \rho H - \rho \ln \rho) , \qquad (2.1a)$$

where ρ is any density matrix. Once again, equality can be obtained by the choice

$$\rho = e^{-\beta H}/\mathrm{Tr}(e^{-\beta H}) .$$

Recognizing the left-hand side of (2.1a) as $e^{-\beta F}$, where F is the Helmholtz free energy, and calling the right-hand side $e^{-\beta \mathcal{F}}$, we obtain

$$F \leq \mathcal{F} = \mathrm{Tr}(\rho H) + (1/\beta)\,\mathrm{Tr}(\rho \ln \rho) , \qquad (2.2)$$

which simply states that the free energy arising from an approximate density matrix is higher than the true free energy. The two terms on the right-hand side of (2.2) are the approximate U (internal energy) and $-TS$ (entropy).

III. MEAN-FIELD APPROXIMATION

We shall use classical statistical mechanics to treat the model defined by (1.1). As our first trial

distribution function we use

$$\rho = \prod_i g(\vec{r}_i) \,. \tag{3.1}$$

It is easy to find the optimal form of g (Appendix A), but the actual determination of the parameters in g requires a full understanding and tabulation of a transcendental function of two variables. Instead, we choose an analytically tractable g which contains enough physics to lead to an interesting and readily understandable phase diagram, i.e.,

$$g(\vec{r}_i) = (A/\pi)^{3/2} \exp[-A\,(\vec{r}_i - \vec{\Delta})^2] \,, \tag{3.2}$$

where A and $\vec{\Delta}$ are variational parameters which will be chosen so as to maximize the right-hand side of (2.1) (i.e., minimize the approximate free energy $\mathcal{F}$). The normalization of (3.2) is appropriate to three dimensions.

The use of a distribution of the form (3.1), which states that the ions move independently in some kind of potential which is self-consistently determined, is usually called the mean-field approximation (MFA). It should be emphasized that in this paper we use the terminology MFA to refer to the distribution given by (3.1) and (3.2) rather than by (3.1) with the optimal g. Onodera[2] has studied some of the consequences of using the optimal g. The distribution (3.2) would be exact for a system of independent ions, each bound harmonically to its own (possibly displaced) force center, with the oscillator frequency related to A by the equation $A = \frac{1}{2}M\omega^2\beta$. This is essentially the Einstein model of a solid, and by optimizing with respect to A and $\vec{\Delta}$ we shall find the best Einstein model at each temperature.

Initially, we will calculate in the absence of an external electric field. At a given temperature, if the best $\vec{\Delta}$ turns out to be nonzero, then the system is ferroelectric, the polarization per ion being $Q\vec{\Delta}$. Insertion of (3.1) and (3.2) into (2.1) yields, in a completely straightforward manner,

$$\frac{\mathcal{F}}{N} = \frac{3V_{00}}{4A} + \frac{\Delta^2}{2}\sum_j V_{0j} + \gamma\left(\frac{15}{4A^2} + \frac{5\Delta^2}{A} + \Delta^4\right) + \frac{3}{2\beta}\ln A + \text{const} \,. \tag{3.3}$$

The constant is independent of A and $\vec{\Delta}$, and will henceforth be omitted. The first two terms on the right-hand side are the expectation value of the harmonic part of the potential energy, the third term is the anharmonic potential energy, and the last term in the entropy term $-TS$. The number of ions is N, and we have made use of translation invariance to replace V_{ii} by V_{00} and $\sum_j V_{ij}$ by $\sum_j V_{0j}$, where 0 refers to some particular ion. In $\sum_j V_{0j}$, the sum includes a term $j = 0$.

The free energy (3.3) depends only on the magnitude of $\vec{\Delta}$ and not on its direction, as a result of the invariance of (1.3) under simultaneous rotation of all the $\vec{r}_i$. We shall imagine that the degeneracy with respect to the direction of $\vec{\Delta}$ is broken by a weak external field in the x direction, which we therefore choose as the direction of $\vec{\Delta}$. The coefficient of Δ^4 in (3.3) is positive, and thus the value of Δ^2 which minimizes $\mathcal{F}/N$ will be zero unless the coefficient of Δ^2 is negative. In order that the distribution function be normalizable, A must be positive; therefore, a necessary (but not sufficient) condition for the existence of a ferroelectric phase is $\sum_j V_{0j} < 0$. This is identical with the condition which we imposed in Sec. I, and we define

$$W \equiv -\sum_j V_{0j} > 0 \,. \tag{3.4}$$

Varying $\mathcal{F}/N$ with respect to Δ^2, we find

$$\Delta^2 = W/4\gamma - 5/2A \tag{3.5a}$$

or

$$\Delta^2 = 0 \,, \tag{3.5b}$$

with (3.5b) holding when the right-hand side of (3.5a) is negative. Considered as a function of A, (3.3) always has a true minimum for some positive value of A. Differentiation and solution of a quadratic yields the optimal A as

$$A = \tfrac{1}{3}\beta\{\tfrac{3}{4}V_{00} + 5\gamma\Delta^2 + [(\tfrac{3}{4}V_{00} + 5\gamma\Delta^2)^2 + 45\gamma/\beta]^{1/2}\} \,. \tag{3.6}$$

For a given inverse temperature β, one must solve (3.6) simultaneously with (3.5a) and also with (3.5b). The free energies of the two solutions must then be compared to see which is lower. This program appears quite tedious, since it must be carried out at all temperatures, and for all values of V_{00}, W, and γ. However, a little dimensional analysis indicates that the situation is much simpler than it would first appear to be. Equation (3.3) gives the free energy as a function of the parameters A and Δ^2, the inverse temperature β, and the quantities V_{00}, W, and γ which are properties of the Hamiltonian. If the minimization with respect to A and Δ^2 is performed, and the nature of the solution is studied as β varies over its full range, it will be found that either there is no phase transition ($\Delta^2 = 0$ for all β), or there is a first-order phase transition ($\Delta^2 = 0$ at high temperature and jumps discontinuously to a finite value at some lower temperature), or there is a second-order phase transition ($\Delta^2 = 0$ at high temperatures and moves continuously away from zero as the temperature is lowered through the transition temperature). The answer to the question "Which of these three cases occurs?" can only depend on the dimensionless numbers which can be formed from V_{00}, W, and γ. The only such number is

$$x \equiv V_{00}/W \,, \tag{3.7}$$

and therefore the nature of the phase transition, if any, can depend only on this ratio and not at all on γ (as long as γ is not zero).

The above line of reasoning suggests the introduction of dimensionless variables, namely,

$$\delta^2 = \gamma\Delta^2/W\,, \quad a = AW/\gamma\,, \quad \beta^* = \beta W^2/\gamma\,, \tag{3.8}$$

and the dimensionless free energy

$$f = \frac{\mathcal{F}}{N}\,\frac{\gamma}{W^2}\,,$$

which leads to the dimensionless forms of (3.3), (3.5), and (3.6)

$$f = \frac{3x}{4a} - \tfrac{1}{2}\delta^2 + \frac{15}{4a^2} + \frac{5\delta^2}{a} + \delta^4 + \frac{3}{2\beta^*}\ln a + \text{const.} \tag{3.9}$$

$$a = 10/(1-4\delta^2)\,, \tag{3.10a}$$

or

$$\delta^2 = 0\,, \tag{3.10b}$$

$$a = \frac{\beta^*}{3}\left\{\frac{3x}{4} + 5\delta^2 + \left[\left(\frac{3x}{4} + 5\delta^2\right)^2 + \frac{45}{\beta^*}\right]^{1/2}\right\}. \tag{3.11}$$

The only memory of the Hamiltonian is in x, and the simple additive form in which x occurs in (3.11) leads to an easy visualization of the phase diagram for all values of x. With the introduction of

$$z = 3x/20 + \delta^2\,,$$

Eq. (3.11) becomes

$$a = \tfrac{1}{3}\beta^*\{5z + [(5z)^2 + 45/\beta^*]^{1/2}\}\,. \tag{3.12}$$

This family of curves in the z-a plane is shown graphically in Fig. 1.

For any finite β^* the limiting form of (3.12) for large positive z is $a = \frac{10}{3}\beta^* z$, and for large negative z is $a = -3/2z$, the latter being independent of β^*. A curve corresponding to larger β^* is everywhere above a curve corresponding to smaller β^*. The limiting curve, for $\beta^* = \infty$, has the form $a = -3/2z$ and exists only for $z < 0$. Minimization of f with respect to δ^2 always yields a value $0 \le \delta^2 < \frac{1}{4}$, the upper limit (which implies $a \to \infty$) being associated with a distribution which sharply localizes all the ions at the value of $\vec{\Delta}$ which minimizes the internal energy. To solve (3.12) and (3.10a) simultaneously, we superimpose the graph of (3.10a) (the dashed curve in Figs. 2–4) on Fig. 1, placing the left end of the dashed curve at the point ($z = 3x/20$, $a = 10$). To increase x, we merely slide the dashed curve to the right. For a given x and β^*, the dashed curve may have zero, one, or two intersections with the appropriate curve on Fig. 1. The paraelectric phase (3.10b) is represented by the point on the temperature-dependent curve (Fig. 1) for which $z = 3x/20$ (i.e., $\delta^2 = 0$). Thus, the free energies of as many as three points may have to be compared in order to find out which is the thermodynamically stable phase. Fortunately, this proves to be easy.

When $x < -\frac{5}{3}$, there is no intersection of (3.11) with (3.10a), no matter what the temperature. Therefore the system chooses the paraelectric state $\delta^2 = 0$. When $x = -\frac{5}{3}$ (Fig. 2), the dashed curve has its first intersection with the family of solid curves [which represent (3.12)], the intersection occurring with the $\beta^* = \infty$ ($T = 0$) curve at $\delta^2 = \frac{1}{4}$, $a = \infty$. As x increases beyond $-\frac{5}{3}$ (Fig. 3) the dashed curve intersects all solid curves corresponding to values of β^* greater than a certain critical value, which we call $\beta_0^*(x)$. For $\beta^* < \beta_0^*(x)$ [i.e., $kT > W^2/\gamma\beta_0^*(x)$], there is no intersection and the system lives at the left end of the solid curve (paraelectric state). As β^* increases (decreasing T) the first intersection is a tangency (labeled C in Fig. 3), with two intersections (A and B) occurring for β^* slightly greater than $\beta_0^*(x)$. The intersection A may (depending on the value of x) disappear as β^* increases further, but this is unimportant because the system never elects to live in A, even as a metastable state. To see this, note that

$$f(B) - f(A) = \int_A^B \nabla f \cdot d\vec{l}\,, \tag{3.13}$$

where the gradient and $d\vec{l}$ are in the plane of the two variables a and δ^2.

We can take any path of integration, for example, the dashed curve ACB. Since $\partial f/\partial(\delta^2) = 0$ on this curve, (3.13) becomes

$$f(B) - f(A) = \int_{ACB} \frac{\partial f}{\partial a}\,da\,.$$

But as a is varied on a line of constant δ^2, f goes through a true minimum on the solid curve AB, and therefore $\partial f/\partial a$ is a negative on the dashed curve ACB. Since ACB is a rising curve, da is positive and thus $f(B) - f(A) < 0$, i.e., $f(B) < f(A)$. The argument is equally simple if the solid curve AB is taken as the integration path. In fact, the arguments are readily extended (Appendix B) without any algebra to show that B is a local minimum of the free energy and A is a saddle point.

The free energy of B must be compared with that of the paraelectric state E, in order to see whether the ferroelectric state is thermodynamically stable (i.e., the free energy has its global minimum at B) or only metastable. When $\beta^* = \beta_0^*(x)$, the free energy of the paraelectric phase D is strictly less than that of the incipient ferroelectric phase C. This follows from the equation

$$f(C) - f(D) = \int_D^C \nabla f \cdot d\vec{l} = \int_D^C \frac{\partial f}{\partial(\delta^2)}\,d(\delta^2)\,, \tag{3.14}$$

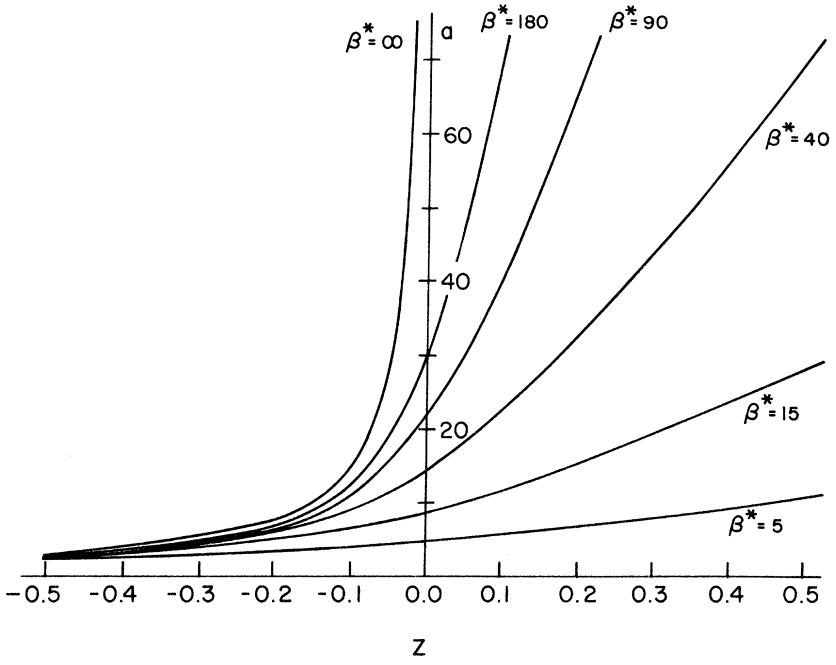

FIG. 1. Curves on which $\partial\mathcal{F}/\partial a = 0$. The abscissa z is the square of the dimensionless polarization, translated by an amount depending on the form of the quadratic potential. The ordinate a is proportional to the square of the effective frequency in the mean-field approximation.

where the last integral is taken along the solid curve from D to C. But

$$\frac{\partial f}{\partial(\delta^2)} = 2\delta^2 + \frac{5}{a} - \frac{1}{2} , \tag{3.15}$$

which is a decreasing function of a for fixed δ^2; since DC lies below the dashed curve, on which $\partial f/\partial(\delta^2) = 0$, it follows that $\partial f/\partial(\delta^2) > 0$ on DC and the right-hand side of (3.14) is positive, since $d(\delta^2) > 0$. By a continuity argument, it follows that E has lower free energy than B for some range of β^* greater than $\beta_0^*(x)$.

To find out whether the free energy of the ferroelectric phase B ever becomes less than that of E as β^* is increased (T is lowered), we first note that $f(B) - f(E)$ decreases as β^* increases. This follows from

$$f(B) - f(E) = \int_E^B \frac{\partial f}{\partial(\delta^2)}\, d(\delta^2) , \tag{3.16}$$

where the path of integration is the solid curve. If we write the same equation for a larger value of β^*, then the solid curve $E'B'$ is everywhere above EB (E' and B' represent the nonferroelectric and ferroelectric phases for the larger β^*). Equation (3.15) implies that $\partial f/\partial(\delta^2)$ at a point on $E'B'$ is less than $\partial f/\partial(\delta^2)$ at the corresponding point (i.e., the point with the same value of δ^2) on EB. Points on $E'B'$ which are to the right of B do not correspond to any point on EB. However, such points lie to the left of the dashed curve and thus $\partial f/\partial(\delta^2) < 0$ at such points. Since $d(\delta^2) > 0$ in (3.16), it follows that $f(B) - f(E)$ decreases with increasing β^*. This simply says that if the ferroelectric phase is not stable at zero temperature, it will not be stable at any finite temperature; the basic point is that the internal energy favors the ferroelectric phase, while the entropy term $-TS$ favors the paraelectric phase, but the entropy term becomes less important as T is decreased. It follows that for a given value of x, a stable ferroelectric phase will exist for sufficiently low temperature if and only if $f(B) - f(E) < 0$ when $T = 0$ ($\beta^* = \infty$). If $x > 0$, (3.11) implies that as $\beta^* \to \infty$, the values of a at points E and B tend to infinity linearly in β^*. Since $\delta^2 = 0$ at E and $\delta^2 = \frac{1}{4}$ at B in the limit $\beta^* = \infty$, (3.9) yields

$$f(B) - f(E) = -\tfrac{1}{16} ,$$

when $x > 0$ and $\beta^* \to \infty$. Therefore, a stable ferroelectric phase exists for sufficiently low T when $x > 0$. In the range $-\frac{5}{3} < x < 0$, the value of a at the point B still grows linearly with β^* for large β^*, but the value of a at point E becomes $-10/x$ as $\beta^* \to \infty$. Thus, as $\beta^* \to \infty$, $f(B) \to -\frac{1}{16}$ and

$$f(E) \to -\frac{3}{40}x^2 + \frac{3}{80}x^2 = -\frac{3x^2}{80}$$

so that

$$f(B) - f(E) \lesseqgtr 0 \quad \text{for} \quad x \gtreqless -\sqrt{\tfrac{5}{3}} .$$

We conclude that for $-\frac{5}{3} < x < -\sqrt{\frac{5}{3}}$ the ferroelectric phase is at best metastable, and the thermodynamically stable phase is paraelectric at all temperatures. For $x > -\sqrt{\frac{5}{3}}$, the ferroelectric phase becomes stable for $\beta^* > \beta_1^*(x)$ (i.e., suffi-

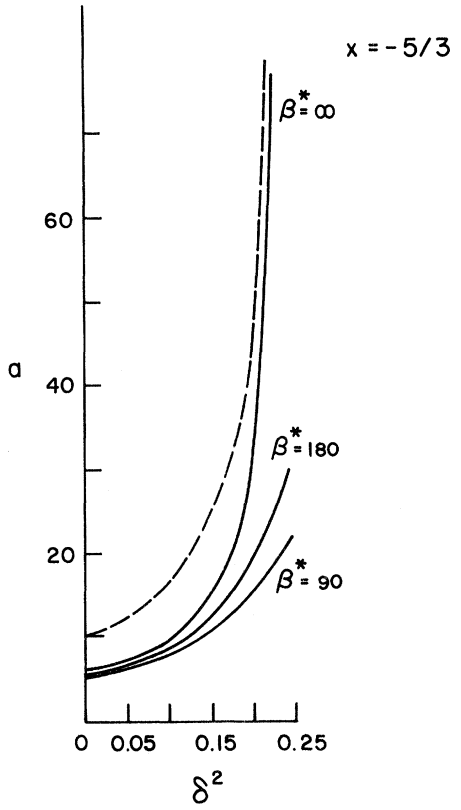

FIG. 2. Solution of (3.10a) (dashed curve) and (3.11) (solid curves) when $x=-\frac{5}{3}$. A metastable ferroelectric phase first appears at $\beta^*=\infty$ ($T=0$), $\delta^2=\frac{1}{4}$, $a=\infty$.

ciently low T), where

$$\beta_1^*(-\sqrt{\tfrac{5}{3}})=\infty$$

and the function $\beta_1^*(x)$ decreases with increasing x (i.e., the temperature below which the ferroelectric phase is stable increases as x increases).

For x slightly greater than $-\sqrt{\frac{5}{3}}$ the transition from the paraelectric to ferroelectric phases is first order; i.e., as T decreases, the value of δ^2 jumps discontinuously from 0 to a finite value. For x sufficiently large, the picture changes (Fig. 4). For small β^* (high T) the system is paraelectric, but as β^* increases beyond a critical value $\beta_2^*(x)$, the value of δ^2 (square of the dimensionless polarization) associated with the ferroelectric phase B moves continuously away from zero. B is the thermodynamically stable phase, as one can see by writing

$$f(B)-f(E)=\int_E^B \frac{\partial f}{\partial(\delta^2)}\,d(\delta^2)\,, \qquad (3.17)$$

where the path of integration is the solid curve, and the integrand is negative because $\partial f/\partial(\delta^2)$ is a decreasing function of a [see (3.15)] and the solid curve EB is above the dashed curve on which $\partial f/\partial(\delta^2)=0$. Therefore the system actually follows the state B for $\beta^* > \beta_2^*(x)$, and we have a second-order phase transition. The critical value of x at which the transition becomes second order is found by requiring the slope of the dashed curve at its left end to be equal to the slope of the solid curve which meets it there. With a little algebra we find the critical value of x to be $-\frac{1}{3}$. Furthermore, we find

$$\beta_2^*(x) = 20/(1+x)\,.$$

To summarize: If $x<-\frac{5}{3}$, no ferroelectric phase exists; if $-\frac{5}{3}<x<-\sqrt{\frac{5}{3}}$, a metastable ferroelectric phase exists at sufficiently low T but is never stable; if $-\sqrt{\frac{5}{3}}<x<-\frac{1}{3}$, there is a first-order transition to the ferroelectric phase; if $-\frac{1}{3}<x$, there is a second-order transition. The fact that the MFA can yield either a first- or second-order transition, depending on the parameters in the Hamiltonian, has also been noted by Gillis and Koehler.[6]

The most obvious error[9] in these predictions occurs when the interactions between distinct ions

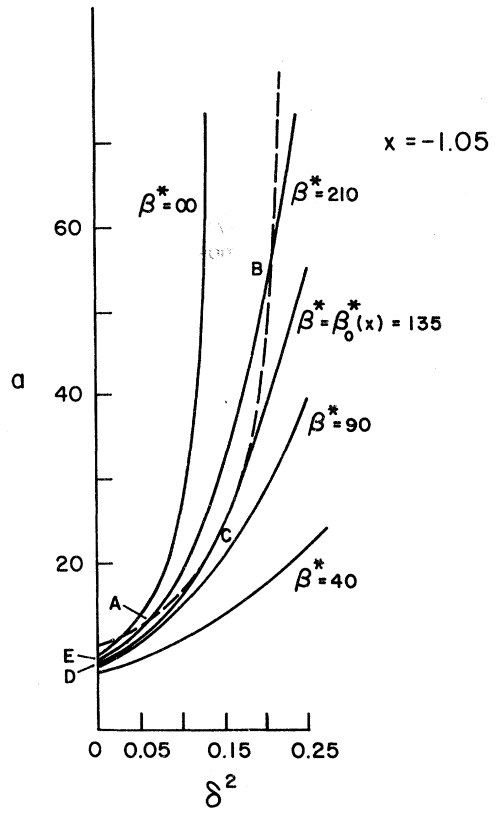

FIG. 3. When $x=-1.05$, the dashed curve intersects the solid curve twice, in an appropriate temperature range. The intersection B, corresponding to larger polarization than intersection A, represents a stable ferroelectric phase at sufficiently low temperature.

are turned off, i.e., $V_{ij}=0$ for $i\neq j$. In this case the exact solution certainly exhibits no phase transition, while the present approximation gives a first-order transition since $x=-1$. This defect would be remedied if the best g were used in (3.1). The Gaussian approximation underestimates the entropy of the unpolarized phase; for example, in one dimension our distribution is peaked at the origin, while the exact distribution has two peaks, one to the right of the origin and one to the left. Since we are most interested in situations in which there is substantial interaction among distinct ions, the failure of our scheme in the noninteracting limit causes us only mild alarm.

An approximate distribution function in the absence of an electric field does not unambiguously define a method for calculating the static electric susceptibility. If the distribution function adopted in the absence of a field is $\rho_0(R)$, and if we adopt the distribution

$$\rho(R)=C\rho_0(R)\,e^{\beta QE\sum_i x_i} \tag{3.18}$$

to describe the system in an external field in the x direction (C is a normalization constant), then the mean polarization is in the x direction, with magnitude

$$Q\left\langle\sum_i x_i\right\rangle=\frac{Q\int\rho_0(R)e^{\beta QE\sum_i x_i}\sum_i x_i\,d^NR}{\int\rho_0(R)e^{\beta QE\sum_i x_i}\,d^NR}\,, \tag{3.19}$$

which reduces, for small E, to

$$Q\left\langle\sum_i x_i\right\rangle=\beta Q^2E\left\langle\left(\sum_i x_i\right)^2\right\rangle_0\,, \tag{3.20}$$

giving an electric susceptibility

$$\chi=\beta Q^2\left\langle\left(\sum_i x_i\right)^2\right\rangle_0\,, \tag{3.21}$$

where $\langle\ \rangle_0$ means that the average is taken using the distribution $\rho_0(R)$, and it is assumed that $\rho_0(R)$ refers to an unpolarized phase, so that $\langle\sum_i x_i\rangle_0=0$ and the expansion in powers of E is meaningful. It has also been assumed that off-diagonal terms like $\langle\sum_i x_i\sum_j y_j\rangle_0$ vanish; we shall also assume cubic symmetry, so that the diagonal components of the susceptibility tensor are equal. If $\rho_0(R)$ is the exact distribution in zero field, then (3.18) and (3.21) are also exact. However, if $\rho_0(R)$ is only approximate, we are not necessarily constrained to use (3.18) in the presence of a field, and usually we can find another $\rho(R)$ which gives a lower free energy. We are primarily interested in the susceptibility in the region of second-order phase transition ($x>-\frac{1}{3}$) at temperatures above T_c, and therefore use the ρ_0 given by (3.2), with $\vec{\Delta}=0$. At finite field, we again use a distribution of the form (3.2), but with $\vec{\Delta}\neq 0$ and presumably proportional to $\vec{E}$, and with possibly a different value of A. Note that this distribution includes (3.18) as a special case (with A equal to its zero-field value, and $\Delta=\beta QE/2A$).

Including the term $-QE\sum x_i$ in the energy, we obtain for the trial free energy

$$\mathcal{F}/N=\mathcal{F}_0/N-QE\Delta\,, \tag{3.22}$$

where $\mathcal{F}_0$ is given by (3.3). The minimum of $\mathcal{F}_0/N$ occurs when $A=A_0$, $\Delta=0$. Minimization of (3.22) will repect to Δ yields, in the limit of small E,

$$\Delta=\frac{QE}{(10\gamma/A_0)-W}\,. \tag{3.23}$$

For $T>T_c$ the denominator is positive, being just

$$2\,\frac{\partial}{\partial\Delta^2}\left(\frac{\mathcal{F}_0}{N}\right)\Big|_{\substack{A=A_0\\ \Delta^2=0}}\,,$$

and the replacement of A by A_0 in (3.23) is accurate for small E, since $A-A_0$ is proportional to E and the more accurate treatment would change Δ by a second-order quantity in E. The susceptibility is given by

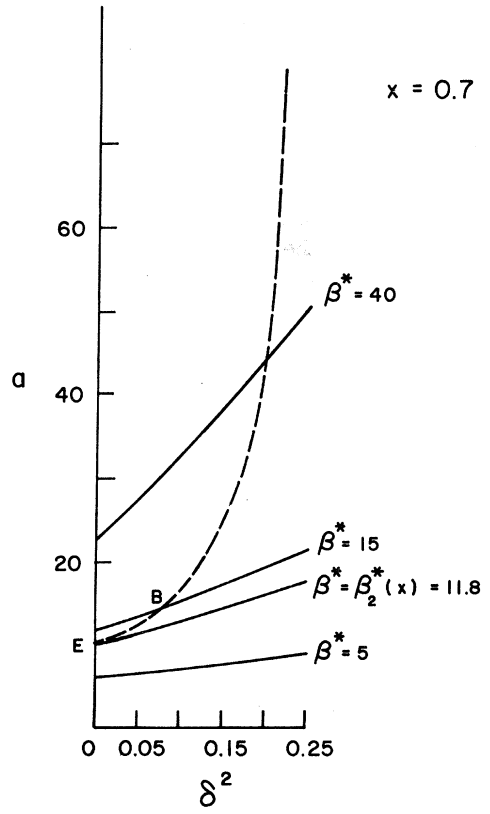

FIG. 4. When $x=0.7$ the mean-field approximation predicts a second-order transition from the paraelectric to ferroelectric phases. The transition is second order if the slope of the dashed curve at its left end is greater than that of the solid curve at the same point.

$$\frac{\chi}{N} = \frac{Q^2}{10\gamma/A_0 - W} \ . \tag{3.24}$$

The denominator vanishes when $T = T_c$ (where $kT_c = W^2/\gamma\beta_2^*$) and is proportional to $T - T_c$ for T slightly greater than T_c. Thus we have a Curie-law susceptibility, exactly as in the Landau theory, for temperatures slightly above the second-order transition temperature. This result is to be contrasted with (3.18); with our choice of ρ_0 the latter gives

$$\chi/N = \beta Q^2/2A_0 \ ,$$

which exhibits no singular behavior as T approaches T_c.

IV. SELF-CONSISTENT PHONON APPROXIMATION

The obvious improvement over (3.2) would be to make a Debye or Born–von Karman model of the solid, i.e., to use a distribution function appropriate to a system in which all the forces are harmonic but not all the normal frequencies are equal. The dimensionality of the system should then begin to enter in a significant way—a feature which is absent in the previous approximation.

In order to carry out this program, it is convenient to specify the configuration of the system through the values of the normal coordinates $\alpha_{q\lambda}$ instead of the "actual" coordinates $\vec{r}_i$. The $\alpha_{q\lambda}$ are the linear combinations of the displacements which diagonalize the quadratic part of the potential, i.e.,

$$\alpha_{q\lambda} \equiv \hat{e}_\lambda(\vec{q}) \cdot \frac{1}{\sqrt{N}} \sum_j \vec{r}_j \, e^{-i\vec{q}\cdot\vec{R}_j} \ . \tag{4.1}$$

The form of the $\alpha_{q\lambda}$ [except for the choice of the polarization unit vectors $\hat{e}_\lambda(\vec{q})$] follows from the translational invariance of the lattice. If we had assumed the most general quadratic form (1.1), then the polarization vectors $\hat{e}_\lambda(\vec{q})$ would be the eigenvectors of the "Fourier matrix"

$$\tilde{V}(\vec{q}) \equiv \sum_j \tilde{V}_{0j} \, e^{i\vec{q}\cdot(\vec{R}_j - \vec{R}_0)} \ , \tag{4.2}$$

where $\tilde{V}_{0j}$ is the matrix whose elements are $V_{0j}^{\lambda\mu}$. Since we have taken $\tilde{V}_{0j}$ as a multiple of the unit matrix, any vector is an eigenvector of $\tilde{V}(\vec{q})$ and we choose the polarization vectors $\hat{e}_\lambda$ along the x, y, and z axes, independent of $\vec{q}$. In the general case, $\tilde{V}(\vec{q})$ would have three distinct eigenvalues corresponding to the different polarizations, but in our case they are all equal, having the value

$$V(\vec{q}) = \sum_j V_{0j} e^{i\vec{q}\cdot(\vec{R}_j - \vec{R}_0)} \ . \tag{4.3}$$

Let the $\vec{R}_i$ form a cubic lattice, the edge of the crystal having length na, where a^3 is the volume of the unit cell and $n^3 = N$. Then the values of $\vec{q}$ are

$$\vec{q} = \left(\frac{2\pi}{na} m_1, \frac{2\pi}{na} m_2, \frac{2\pi}{na} m_3\right), \tag{4.4}$$

where m_1, m_2, and m_3 are integers in the range $-\frac{1}{2}(n-1)$ to $\frac{1}{2}(n-1)$. Any n consecutive values of m_1, m_2, and m_3 define all the independent $\alpha_{q\lambda}$, but it is convenient to make the range symmetric about zero (assume n odd).

Using the inverse of (4.1),

$$\vec{r}_j = \frac{1}{\sqrt{N}} \sum_{q\lambda} \alpha_{q\lambda} \hat{e}_\lambda(\vec{q}) e^{i\vec{q}\cdot\vec{R}_j} \ , \tag{4.5}$$

we can rewrite the energy as

$$U = \frac{1}{2} \sum_{q\lambda} V(\vec{q}) \, \alpha_{q\lambda} \alpha_{-q\lambda} + \frac{\gamma}{N} \sum_{q,q',q'',\lambda,\lambda'} \alpha_{q\lambda} \alpha_{q'\lambda} \alpha_{q''\lambda'} \alpha_{-(q+q'+q'')\lambda'} \ . \tag{4.6}$$

The $\alpha_{q\lambda}$ are complex and satisfy $\alpha_{-q\lambda} = (\alpha_{q\lambda})^*$ because of the reality of the $\vec{r}_i$. Writing $\alpha_{q\lambda} = c_{q\lambda} + i s_{q\lambda}$ where c and s are the cosine and sine transforms and are real, we have $c_{-q\lambda} = c_{q\lambda}$ and $s_{-q\lambda} = -s_{q\lambda}$. The $c_{q\lambda}$ and $s_{q\lambda}$ with $m_1 \geq 0$ (excluding $s_{0\lambda}$, which is identically zero) can be used as coordinates for the system.

Since $\alpha_{q\lambda}\alpha_{-q\lambda} = c_{q\lambda}^2 + s_{q\lambda}^2$, the distribution function would be a pure Gaussian in the $c_{q\lambda}$ and $s_{q\lambda}$ if the potential were purely harmonic. We shall use a trial distribution function which is Gaussian in the $c_{q\lambda}$ and $s_{q\lambda}$, but with coefficients which will be chosen so as to minimize $\mathcal{F}$. From (4.1) it is evident that displacement of all the $\vec{r}_j$ by the same amount $\vec{\Delta}$ will leave the value of $\alpha_{q\lambda}$ unaltered except when $\vec{q} = 0$. If $\vec{\Delta}$ is in the x direction ($\lambda = 1$), then α_{01} is shifted by $\Delta\sqrt{N}$. Thus we incorporate the possibility of a polarized phase by allowing for a shift in the center of the distribution of c_{01}. Our trial distribution, then, is

$$\rho = \eta \exp\left[-\left(\frac{1}{2} \sum_\lambda A_{0\lambda} (c_{0\lambda} - \delta_{\lambda 1} \Delta\sqrt{N})^2 + \sum_{q\lambda}{}' A_{q\lambda}(c_{q\lambda}^2 + s_{q\lambda}^2) \right) \right] \ , \tag{4.7}$$

where the $A_{q\lambda}$ and Δ are variational parameters and $\sum'$ means a sum over $\vec{q}$ vectors with $m_1 \geq 0$, excluding $\vec{q} = 0$. The normalization factor η is given by

$$\eta = \prod_{q\lambda}{}' \left(\frac{A_{q\lambda}}{\pi}\right)^{1/2} \prod \left(\frac{A_{0\lambda}}{2\pi}\right)^{1/2} \ . \tag{4.8}$$

Because of the complete symmetry of the $c_{q\lambda}$ and $s_{q\lambda}$ for $\vec{q} \neq 0$, nothing would be gained by introducing separate coefficients for $c_{q\lambda}$ and $s_{q\lambda}$. The $A_{q\lambda}$ are necessarily positive, in order that (4.7) be normalizable, and we can define "quasiharmonic"

frequencies by

$$M\Omega_{q\lambda}^2 = A_{q\lambda}/\beta \ . \tag{4.9}$$

The $\Omega_{q\lambda}$ are the frequencies of the normal modes in a fictional harmonic system, for which (4.7) would be the exact distribution function. By contrast, the normal frequencies of the quadratic potential

$$\frac{1}{2}\sum_{ij} V_{ij}\vec{r}_i\cdot\vec{r}_j$$

are given by

$$M\omega_{q\lambda}^2 = V(\vec{q}) \ . \tag{4.10}$$

From (4.3) we see that

$$V(0) = -W < 0 \ , \tag{4.11}$$

so that $\omega_{q\lambda}$ is imaginary for small $\vec{q}$, indicating the instability of the lattice. If all the $A_{q\lambda}$ in (4.7) are taken as equal, having the common value $2A$, then (4.7) becomes identical with the distribution (3.1), (3.2) used in our mean-field approximation. Thus the present scheme is guaranteed to yield a lower Helmholtz free energy. We call (4.7) the "self-consistent phonon approximation" (SPA). This approximation, as well as possible generalizations, has been discussed by Werthamer and others.[10] In Appendix E we discuss the quantum-mechanical version of the SPA, which leads to essentially the same results as the classical treatment.

Equation (4.6) expresses the Hamiltonian in terms of the $c_{q\lambda}$ and $s_{q\lambda}$. In evaluating the right-hand side of (2.1) with ρ given by (4.7), the $c_{q\lambda}$ and $s_{q\lambda}$ can be used as the basic integration variables instead of the $\vec{r}_i$. The transformation is orthogonal, so the Jacobian is unity. The resultant Helmholtz free energy is

$$\frac{\mathfrak{F}}{N} = \frac{1}{N}{\sum_{q\lambda}}' \frac{V(\vec{q})}{A_{q\lambda}} + \Delta^2\left(-\frac{W}{2} + \frac{4\gamma}{N}{\sum_{q\lambda}}' \frac{1+2\delta_{\lambda 1}}{A_{q\lambda}}\right) + \gamma\Delta^4 + \frac{4\gamma}{N^2}{\sum_{q\lambda}}'{\sum_{q'\lambda'}}' \frac{1+2\delta_{\lambda\lambda'}}{A_{q\lambda}A_{q'\lambda'}} + \frac{1}{N\beta}{\sum_{q\lambda}}' \ln A_{q\lambda} + O\left(\frac{1}{N}\right) \ . \tag{4.12}$$

In the above, the primed summations are over *half* of $\vec{q}$ space; since terms of order $1/N$ are omitted, it does not matter whether $\vec{q}=0$ is included or excluded. We have looked very carefully into the question of whether, under some circumstances, one of the $A_{q\lambda}$ (most likely A_{01}) becomes of order $1/N$, so that a single term in the sums can be important. This phenomenon, which occurs in the theory of Bose–Einstein condensation, does not occur in the present model.

It is evident that a necessary condition for $\mathfrak{F}$ to be minimized by a nonzero value of Δ is $W>0$, i.e., $V(0)<0$. This verifies the physical idea which was built into the model. Varying $\mathfrak{F}$ with respect to $A_{q\lambda}$, we obtain

$$A_{q\lambda}/\beta = V(\vec{q}) + F_\lambda \ , \tag{4.13}$$

where

$$F_\lambda \equiv 4\gamma\Delta^2(1+2\delta_{\lambda 1}) + 8\gamma K_\lambda \tag{4.14}$$

and

$$K_\lambda \equiv \frac{1}{N}{\sum_{q'\lambda'}}' \frac{1+2\delta_{\lambda\lambda'}}{A_{q'\lambda'}} \ . \tag{4.15}$$

Passing to the limit $N\to\infty$, it is useful to define

$$G(F) \equiv \left(\frac{a}{2\pi}\right)^\nu \int d^\nu q \ \frac{1}{V(q)+F} \ , \tag{4.16}$$

where ν is the dimensionality of the system, a is the lattice constant, and the integral is over the interior of the cube $-\pi/a \le q_x, q_y, q_z \le \pi/a$ rather than just a half-cube, as in the summation. We can express K_λ in terms of this function; making use of the complete symmetry between $\lambda=2$ and $\lambda=3$, we obtain

$$K_1 = \frac{3}{2\beta}G(F_1) + \frac{\nu-1}{2\beta}G(F_2) \quad (\nu=1,\ 2,\ 3), \tag{4.17a}$$

$$K_3 = K_2 = \frac{1}{2\beta}G(F_1) + \frac{\nu+1}{2\beta}G(F_2) \quad (\nu=2,\ 3) \ . \tag{4.17b}$$

Minimization of $\mathfrak{F}$ with respect to Δ^2 yields

$$\Delta^2 = W/4\gamma - 2K_1 \ , \tag{4.18}$$

or, if the right-hand side of (4.18) is negative,

$$\Delta^2 = 0 \ . \tag{4.19}$$

V. PARAELECTRIC PHASE IN SELF-CONSISTENT PHONON APPROXIMATION

Let us first examine the unpolarized solution $\Delta^2 = 0$, which is indeed the correct solution at high temperature. In this case, all polarizations are equivalent ($F_1 = F_2 \equiv F$). The value of F is determined by solving the transcendental equation which results from combining (4.13), (4.14), and (4.17a):

$$\frac{G(F)}{F} = \frac{\beta}{4(\nu+2)\gamma} \ . \tag{5.1}$$

To understand the properties of this equation, one must make further assumptions about $V(\vec{q})$. We assume that $V(\vec{q})$ attains its minimum value at $\vec{q}=0$. Furthermore, we start by assuming that V_{ij} decreases fast enough for large $|\vec{R}_i - \vec{R}_j|$ to permit a moment expansion of (4.3), i.e.,

$$V(\vec{q}) = \sum_j V_{0j}\{1 + i\vec{q}\cdot(\vec{R}_j - \vec{R}_0) - \tfrac{1}{2}[\vec{q}\cdot(\vec{R}_j - \vec{R}_0)]^2 + \cdots\} \ . \tag{5.2}$$

In (1.3), V_{ij} is symmetric by definition; therefore

all odd terms in (4.21) vanish, and for small q we have

$$V(\vec{q}) = -W + \alpha q^2 + \cdots , \tag{5.3}$$

where

$$\alpha = -\frac{1}{6}\sum_j V_{0j}|\vec{R}_j - \vec{R}_0|^2 > 0 . \tag{5.4}$$

In three dimensions α will be finite and (5.3) valid if V_{ij} falls off faster than the inverse fifth power of $|\vec{R}_i - \vec{R}_j|$ at large separations. If this condition is satisfied, we say that the quadratic forces are of "short range." The case in which the moment expansion (5.3) is not valid is also interesting and will be discussed later. In writing (5.3) and (5.4) we have assumed cubic symmetry; more generally, αq^2 would be replaced by $\alpha_1 q_1^2 + \alpha_2 q_2^2 + \alpha_3 q_3^2$, without significant changes in the sequel.

From (4.13) it follows that F must be greater than W in order that all the $A_{q\lambda}$ be positive and the distribution function normalizable. For $F > W$ the function $G(F)$ is a decreasing function of F, tending to F^{-1} for large F. $G(F)/F$ is also a decreasing function. Equation (5.1) will be soluble for arbitrarily large β (i.e., arbitrarily low temperature) if and only if $G(W) = \infty$. For short-range quadratic forces, the denominator of (4.16), with $F = W$, is αq^2 for small q. Thus $G(W)$ behaves like

$$\int \frac{d^\nu q}{q^2} ,$$

which diverges in one and two dimensions as

$$\int \frac{dq}{q^2} \quad \text{and} \quad \int \frac{q\,dq}{q^2} \quad ,$$

respectively, but converges in three dimensions as

$$\int \frac{q^2\,dq}{q^2} \quad .$$

The left-hand side of (5.1) is shown in Fig. 5. In one and two dimensions (upper curve) a solution of (5.1) exists for all β. In three dimensions a solution fails to exist for $\beta > \beta_c$, where

$$\frac{G(W)}{W} = \frac{\beta_c}{20\gamma} . \tag{5.5}$$

If we had not cavalierly replaced sums by integrals and had treated the $\vec{q} = 0$ term more carefully, we would find that in three dimensions a solution for F exists even for $\beta > \beta_c$, with F differing from W by an amount proportional to N^{-1}, all in close analogy with the situation in the condensed ideal Bose gas. We presently believe that the paraelectric solution which Gillis and Koehler have found by numerical methods even at arbitrarily low temperatures is the one which we lose by taking the infinite-volume limit (i.e., replacing a sum by an integral). Since the effective frequency of the $\vec{q} = 0$ "soft mode" is [see (4.9)]

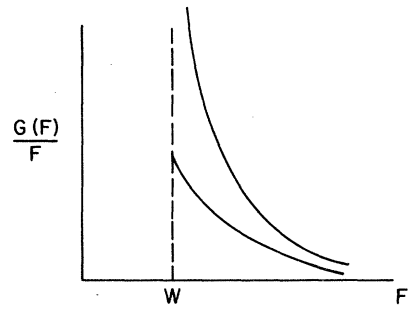

FIG. 5. Graphical solution of Eq. (5.1), which determines the parameter F and thus the self-consistent phonon dispersion relation in the paraelectric phase. In one and two dimensions (upper curve) a solution exists for all β. In three dimensions a solution exists only when $\beta < \beta_c$; the paraelectric phase ceases to exist even metastably when $\beta > \beta_c$. Short-range quadratic forces have been assumed.

$$\Omega_0^2 = (1/M)(F - W) , \tag{5.5a}$$

we believe that their soft-mode frequency would become strictly zero below a certain temperature if the mesh used in their $\vec{q}$ sums were made infinitely fine (which is equivalent to going to an infinitely large system). Addition of acoustic phonons (translational invariance) does not alter the predictions of our model in an essential way. At any rate, there is no need to study the paraelectric solution for $\beta > \beta_c$, because, as will shortly be seen, the system makes a transition to the polarized phase at some value of β less than β_c, i.e., at some temperature higher than T_c.

It is gratifying to see that the SPA, in contrast with the MFA, discriminates between a three-dimensional system and one- and two-dimensional systems. However, although the solution of (5.1) representing an unpolarized phase exists all the way down to $T = 0$ in one and two dimensions, it will be seen (Appendix D) that even in these cases our analysis predicts that the system will eventually jump to another (polarized) solution. Our predictions for the three-dimensional case bear some resemblance to what is seen in $BaTiO_3$, though our model is obviously much too simple. If Ω_q is identified with the frequency of the soft transverse-optical mode as measured in neutron scattering from the paraelectric phase, the data of Harada, Axe, and Shirane[11] indicate that Ω_0 is very small at 150 °C. Very heavy damping of the mode, and interactions with acoustical modes, makes it difficult to extract a value for Ω_0 from the data. Barker[12] uses the infrared reflectivity data of Ballantyne[13] to infer $\Omega_0^2 \propto T - T_c$, where $T_c = 105$ °C. The system makes a first-order transition to a ferroelectric phase at $T = 120$ °C, before the TO mode becomes completely soft. Similarly, the static

electric susceptibility in the paraelectric phase shows a Curie-law behavior[14] $\chi \propto (T - T_c)^{-1}$, but does not become truly infinite, owing to the intervention of the first-order transition. With appropriate assumptions about the character of the quadratic forces, our model can explain both the first-order transition and the temperature dependence of Ω_0 and χ. We shall see that it is necessary to abandon the assumption that the quadratic forces are of short range.

To calculate the susceptibility, we add the term $-QE\sum_i x_i$ to the Hamiltonian and still use a distribution of the form (4.7). Note that $\sum_i x_i = N^{1/2} c_{01}$, so that it is reasonable to expect the field only to shift the center of the distribution of c_{01}. If we took

$$\rho = \rho_0 e^{\beta QE \sum x_i} ,$$

where ρ_0 is the zero-field unpolarized ($\Delta = 0$) distribution given by (4.7), this would correspond to choosing

$$\Delta = QE\beta/2A_{01} .$$

However, just as in the molecular-field case, we can do better by optimizing with respect to Δ. The free energy is

$$\mathfrak{F}/N = \mathfrak{F}_0/N - QE\Delta ,$$

where $\mathfrak{F}_0/N$ is the zero-field energy (4.12). We are studying the solution which has $\Delta = 0$ in the absence of a field. It is clear that Δ will be proportional to E for small E, and thus the $A_{q\lambda}$ will differ from their zero-field values by terms proportional to E^2. Minimization of $\mathfrak{F}/N$ with respect to Δ gives

$$\Delta = \frac{QE}{-W + [4\gamma(\nu+2)/\beta]G(F)} = \frac{QE}{F - W} , \qquad (5.6)$$

where (5.1) has been used to simplify the denominator. If (5.3) holds for small q (short-range forces), then it is easily shown that in three dimensions $G(F)$ has a square-root singularity at $F = W$, i.e.,

$$G(F) = G(W) - \frac{a^3}{4\pi} \frac{(F - W)^{1/2}}{\alpha^{3/2}} + \cdots . \qquad (5.7)$$

It follows from (5.1) and (5.5) that $F - W$ is proportional to $(T - T_c)^2$, so that the susceptibility $Q\Delta/E$ is proportional to $(T - T_c)^{-2}$. From (5.5a) we find $\Omega_0^2 \propto (T - T_c)^2$. The relation between the static susceptibility and the frequency of the soft mode is a special case of the Sachs–Lyddane–Teller theorem.[15]

In order to obtain a Curie-law susceptibility, we must modify the assumption (5.3). If, for small $\vec{q}$, (5.3) is replaced by

$$V(\vec{q}) = -W + \epsilon|\vec{q}| + \cdots , \qquad (5.8)$$

then from (4.16) we see that in three dimensions

$$G'(W) \propto \int \frac{q^2 dq}{q^2}$$

is finite. Then (5.7) is replaced by

$$G(F) = G(W) - |G'(W)|(F - W) + \cdots . \qquad (5.9)$$

From (5.1) and (5.5) we now find that $F - W$ is proportional to $T - T_c$, so that (4.25) leads to a Curie-law susceptibility, and the frequency Ω_0 of the $q = 0$ "soft mode" is proportional to $(T - T_c)^{1/2}$. The assumption (5.8) also leads [via (4.9) and (4.13)] to the dispersion relation for small q

$$\Omega_q^2 = \Omega_0^2 + \text{const.} \times |\vec{q}| . \qquad (5.10)$$

In neutron scattering studies of the soft transverse-optical branch[11] the data are generally fitted with a curve of the form

$$\Omega_q^2 = \Omega_0^2 + \text{const.} \times q^2 . \qquad (5.11)$$

However, linewidths become very large as the mode softens, and it is not clear what experimental quantity should be identified with Ω_q in this case. For small $\vec{q}$ and T near T_c the widths become large compared with Ω_0^2 and it is not really possible to distinguish between (5.10) and (5.11).

More generally, if

$$V(\vec{q}) = -W + \epsilon|\vec{q}|^m \quad (m < \tfrac{3}{2}) , \qquad (5.12)$$

then $G'(W)$ will be finite and the susceptibility will follow the Curie law. For example, if $V_{ij} \propto |\vec{R}_i - \vec{R}_j|^{-4}$ at large distances, we will have $m = 1$. The dipole-dipole interaction (1.2) is not spherically symmetric, but falls off like $|\vec{R}_i - \vec{R}_j|^{-3}$. We have studied the eigenvalues of the matrix $\tilde{V}(\vec{q})$ for this interaction and find that the lowest eigenvalue (corresponding to a doubly degenerate TO mode) has a q^2 dependence despite the breakdown of the moment expansion. The situation is further complicated by the fact that when $|\vec{q}|$ becomes very small (such as the reciprocal of the sample size), the matrix becomes shape dependent. An adequate treatment of this interaction would require taking account of domain formation, which can be described by a modification of the distribution function but seems hardly worthwhile in the context of our highly idealized model.

At any rate, to bring our model into reasonable agreement with the real world we must assume that (5.12) is true.

VI. FERROELECTRIC PHASE IN SELF-CONSISTENT PHONON APPROXIMATION

In the ferroelectric phase ($\Delta^2 \neq 0$) the spectrum of quasiharmonic frequencies will have two branches, one representing displacements parallel to the polarization ($\lambda = 1$) and one representing displacements perpendicular to the polarization ($\lambda = 2, 3$). We concern ourselves now with the three-dimen-

sional case ($\nu = 3$) and shall discuss lower dimensionalities later (see Appendix D).

In the paraelectric phase the parameter F, and thus the quasiharmonic spectrum, was determined self-consistently by the transcendental equation (5.1). Now we must deal with a pair of coupled transcendental equations, whose solutions can be easily understood graphically. From (4.14) and (4.17) we find

$$F_1 = 12\gamma\Delta^2 + 8\gamma K_1 \,, \tag{6.1a}$$

$$F_3 = F_2 = 4\gamma\Delta^2 + 8\gamma K_2 \tag{6.1b}$$

and

$$K_1 = \frac{3}{2\beta}\, G(F_1) + \frac{1}{\beta}\, G(F_2) \,, \tag{6.2a}$$

$$K_3 = K_2 = \frac{1}{2\beta}\, G(F_1) + \frac{2}{\beta}\, G(F_2) \,. \tag{6.2b}$$

Equations (4.18) and (6.1a) yield

$$\Delta^2 = (F_1 - W)/8\gamma \,, \tag{6.3}$$

which can be substituted into (6.1a) and (6.1b). Then (6.1a)–(6.2b) are four equations in the four unknowns F_1, F_2, K_1, and K_2. Eliminating K_1 and K_2, we have

$$-\frac{F_1}{16\gamma} + \frac{3W}{16\gamma} = \frac{3}{2\beta}\, G(F_1) + \frac{1}{\beta}\, G(F_2) \,,$$

$$\frac{F_2}{8\gamma} - \frac{F_1}{8\gamma} + \frac{W}{16\gamma} = \frac{1}{2\beta}\, G(F_1) + \frac{2}{\beta}\, G(F_2) \,.$$

To expedite graphical solution, we replace this pair of equations by the equivalent pair

$$F_1 = 3F_2 - \frac{40\gamma}{\beta}\, G(F_2) \,, \tag{6.4a}$$

$$F_2 = -\tfrac{1}{2}F_1 + \tfrac{5}{2}W - \frac{20}{\beta}\, G(F_1) \,. \tag{6.4b}$$

Figure 6 shows the graphical solution of these equations. In each case the curve labeled A represents (6.4a), and B represents (6.4b). The curves are drawn under the assumption of short-range quadratic forces [i.e., Eq. (5.3)], which implies $G'(W) = -\infty$. Then we shall discuss the changes produced by assuming long-range quadratic forces [Eq. (5.8)].

Both F_1 and F_2 must be greater than W, in order that the $A_{q\lambda}$ be positive [see (4.13)] and the distribution function normalizable. In Fig. 6(a), which is drawn at the inverse temperature β_c defined by (5.5), curve A starts horizontally and B vertically because $G'(W) = -\infty$. Since $G(F) \sim 1/F$ for large F, it is clear that curve A ultimately has a slope of $+\frac{1}{3}$, and curve B ultimately has a slope of $-\frac{1}{2}$, so that there must be an intersection in addition to the one at (W, W). For $\beta > \beta_c$ ($T < T_c$) the intersection near (W, W) disappears [Fig. 6(b)]. For β a little less than β_c (T a little greater than T_c) there are

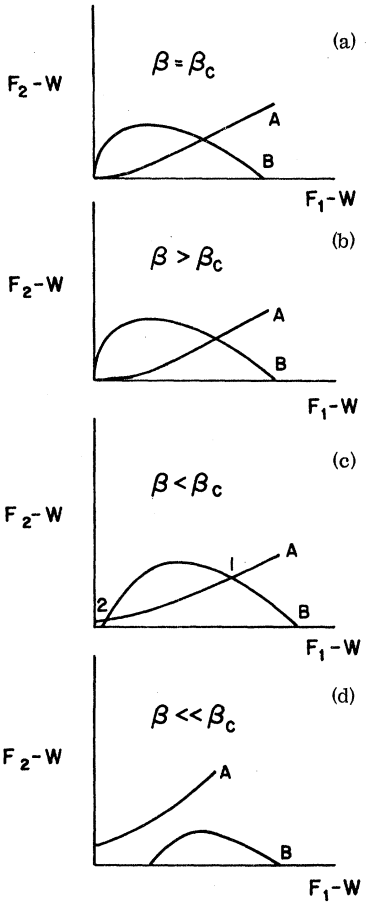

FIG. 6. Graphical determination of the parameters F_1 and F_2, which determine the self-consistent phonon dispersion relation in the ferroelectric phase. Curves A and B represent (6.4a) and (6.4b), respectively. At high temperature there are no intersections [(d)] and the system is paraelectric. At somewhat lower temperatures [(c)] there are two intersections, the state of larger polarization (labeled 1) having the lower free energy. For $T < T_c$ [(b)] the intersection 2 disappears. The system makes a first-order transition from the paraelectric state to the ferroelectric state 1. The graphs are drawn for the three-dimensional case, under the assumption of short-range quadratic forces.

two intersections, one [labeled 2 in Fig. 6(c)] near (W, W). For $\beta \ll \beta_c$ ($T \gg T_c$) there are no intersections and the ferroelectric phase does not exist.

At sufficiently high temperature the system must live in the paraelectric phase, represented by a point on the 45° line ($F_1 = F_2$) in the $F_1 - F_2$ plane. A second-order transition would be one in which the system follows the 45° line down to (W, W) at T_c and then moves continuously away from (W, W) as T is lowered below T_c. But from Fig. 6(b) we see that this is not possible, since there is no intersection near (W, W) as T is lowered below T_c. The two ferroelectric states labeled 1 and 2 in

Fig. 6(c) come into existence at some temperature T_0 which is greater than T_c. T_0 is the temperature at which curves A and B are tangent at one point. In Appendix C we show that the state 1 (which has the larger polarization) has lower free energy than 2. Since 2 coincides with the paraelectric state when $T = T_c$, it is clear that the system must have made a *first-order transition* from the paraelectric state to state 1 at some temperature T_1 which is in the range $T_c < T_1 < T_0$.

If the assumption of short-range quadratic forces is abandoned in favor of (5.8), then $G'(W)$ will be finite and the topology of the curves may change, permitting in some cases a second-order transition. We define

$$\mu \equiv - G'(W) \tag{6.5}$$

and

$$\alpha = \frac{dF_2/dF_1|_{F_1=W,\beta=\beta_c} \text{ on } B}{dF_2/dF_1|_{F_1=W,\beta=\beta_c} \text{ on } A} = \left(-\frac{1}{2} + \frac{20\gamma\mu}{\beta_c}\right)\left(3 + \frac{40\gamma\mu}{\beta_c}\right) . \tag{6.6}$$

If $\alpha > 1$, the curves still look like those in Fig. 6, except that A now has a positive slope at the origin and B has a finite slope. As in Fig. 6(b), no intersection near (W, W) exists for $\beta > \beta_c$ and the transition is first order, but "almost" second order in the sense that the susceptibility in the paraelectric phase obeys a Curie law $\chi \propto (T - T_c)^{-1}$, where T_c is below the temperature T_1 at which the transition occurs. If $\alpha < 1$, curves A and B do not intersect for $T > T_c$ [Fig. 7(c)], and the system therefore is in the paraelectric phase for all $T > T_c$. For $T < T_c$ there is an intersection which moves continuously away from (W, W) as T is lowered [Fig. 7(b)]. If we define $\delta = 1 - T/T_c$ and $y = 20\gamma\mu/\beta_c$, then for small δ the intersection of the two curves in Fig. 7(b) occurs at

$$F_2 - W = \frac{2W\delta y}{1-\alpha} ,$$

$$F_1 - W = 2W\delta\left(1 + \frac{y(3+2y)}{1-\alpha}\right) .$$

The critical value of y for which $\alpha = 1$ is

$$y_{\text{crit}} = \tfrac{1}{2}(\sqrt{6} - 1) \approx 0.72 .$$

We have a first-order transition for $y > 0.72$ and second-order transition for $y < 0.72$. Finally, (5.5) allows y to be expressed purely in terms of the frequency distribution of the harmonic part of the potential:

$$y = \frac{-V(0)\int[V(\vec{q}) - V(0)]^{-2}\, d^3q}{\int[V(\vec{q}) - V(0)]^{-1} d^3q} = \frac{-\omega_0^2 \int[\omega^2(\vec{q}) - \omega_0^2]^{-2} d^3q}{\int[\omega^2(\vec{q}) - \omega_0^2]^{-1} d^3q} . \tag{6.7}$$

For short-range quadratic forces we have $y = \infty$. For a first-order transition, with a Curie-law susceptibility in the paraelectric phase, we require $0.72 < y < \infty$.

ACKNOWLEDGMENTS

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APPENDIX A: BEST MEAN-FIELD APPROXIMATION

If we use a distribution of the form (3.1) with arbitrary f, the approximate free energy is

$$\frac{\mathfrak{F}}{N} = \frac{1}{2}\langle\vec{r}\rangle \cdot \langle\vec{r}\rangle \sum_{j\neq 0} V_{0j} + \tfrac{1}{2} V_{00}\langle r^2\rangle + \gamma\langle r^4\rangle + \frac{1}{\beta}\int g(r)\ln g(r)\, d^3r , \tag{A1}$$

where

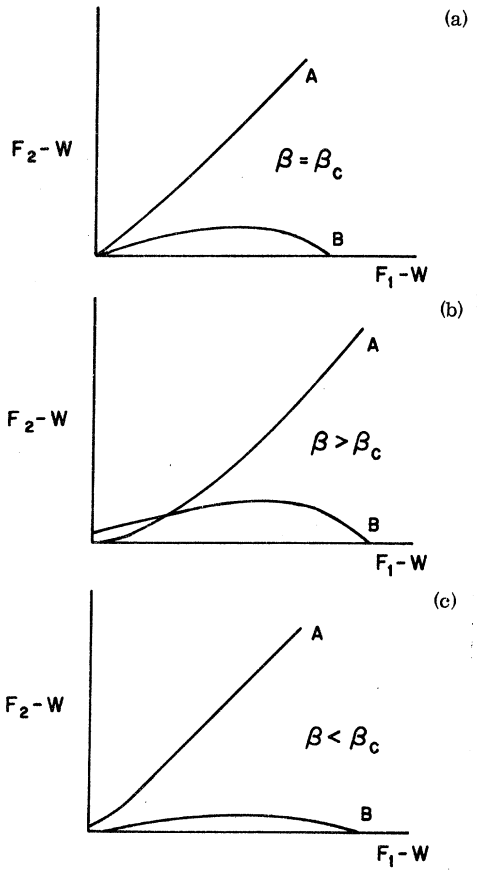

FIG. 7. Graphical determination of F_1 and F_2 when the quadratic forces are of long range and $\alpha < 1$ [see Eq. (6.6)]. In this case a unique solution, representing a ferroelectric phase, exists for $T < T_c$ [(b)]. The solution joins the paraelectric phase continuously when $T = T_c$, so the transition is second order. The F_2–W scale has been expanded for clarity.

$$\langle\vec{r}\rangle = \int \vec{r} g(\vec{r}) d^3r \,, \quad \langle\vec{r}^2\rangle = \int r^2 g(\vec{r}) d^3r \,,$$
$$\langle\vec{r}^4\rangle = \int r^4 g(\vec{r}) d^3r \,.$$

Dimensional analysis tells us, as before, that the character of the transition can depend only on the dimensionless number x [see (3.7)]. Minimization of $\mathcal{F}$ subject to the normalization condition $\int g(\vec{r}) d^3r = 1$ yields

$$g = C \exp[-\beta(\gamma r^4 + \tfrac{1}{2} V_{00} r^2 + \vec{A}\cdot\vec{r})] \,, \tag{A2}$$

where C and $\vec{A}$ are determined by the conditions

$$\int g(\vec{r}) d^3r = 1 \quad \text{and} \quad \vec{A} = \langle\vec{r}\rangle \sum_{j\neq 0} V_{0j} \,. \tag{A3}$$

In the paraelectric phase $A = 0$. Complete exploration of the phase diagram would clearly require an understanding of a transcendental function of two variables. We are not convinced that the effort involved is worthwhile.

APPENDIX B: CHARACTER OF STATIONARY POINTS OF FREE ENERGY IN MEAN-FIELD APPROXIMATION

The points A and B in Fig. 3 are the intersections of the solid curve $\partial f/\partial a = 0$ and the dashed curve $\partial f/\partial(\delta^2) = 0$. From (3.9) the following statements are evident: (i) $\partial f/\partial a$ is positive above the solid curve and negative below the solid curve; (ii) $\partial f/\partial a$ is negative to the right of the solid curve and positive to the left of the solid curve; (iii) $\partial f/\partial(\delta^2)$ is negative above the dashed curve and positive below the dashed curve; and (iv) $\partial f/\partial(\delta^2)$ is positive to the right of the dashed curve and negative to the left of the dashed curve.

Any point P in the neighborhood of B can be reached from B by traveling along the dashed curve and then horizontally. We write

$$f(P) - f(B) = \int_B^P \nabla f \cdot d\vec{l} = \int \frac{\partial f}{\partial a} da + \int \frac{\partial f}{\partial(\delta^2)} d(\delta^2) \,, \tag{B1}$$

where the first integral is evaluated along the dashed curve and the second integral is evaluated along the horizontal line. If $a(P) > a(B)$, then the relevant position of the dashed curve is above the solid curve, and both da and $\partial f/\partial a$ are positive, and thus $(\partial f/\partial a)da$ is positive. If $a(P) < a(B)$, then the relevant position of the dashed curve is below the solid curve, and both $\partial f/\partial a$ and da are negative so $(\partial f/\partial a)da$ is again positive. Similarly, on the horizontal part of the path both $\partial f/\partial(\delta^2)$ and $d(\delta^2)$ have the same sign. Thus $f(P) - f(B)$ is positive, so B is a minimum.

The situation is different near A because the dashed curve has a smaller slope than the solid curve at A. In particular, if P is on the dashed curve or solid curve, we have $f(P) - f(A) < 0$. On the other hand, if P is on the same horizontal or vertical line as A, we have $f(P) - f(A) > 0$. Thus A is a saddle point.

APPENDIX C: CHARACTER OF STATIONARY POINTS OF FREE ENERGY IN SELF-CONSISTENT PHONON APPROXIMATION

The curves A and B [representing (6.4a) and (6.4b) of Fig. 6(c)] intersect twice if the temperature is in the range $T_c < T < T_0$, where T_0 is the temperature at which tangency occurs. We shall show that the intersection 1, corresponding to larger polarization than the intersection 2 [see (6.3)], has the lower free energy, and that 2 is only a saddle point and therefore not even metastable. Since 2 coincides with the paraelectric phase when $T = T_c$, it follows that the system must make a first-order transition from the paraelectric phase to 1 at some temperature T_1 in the range $T_c < T_1 < T_0$. Gillis and Koehler[5] have reached identical conclusions in analyzing their model.

In Appendix B we have proved the same proposition in the MFA. As in the MFA, direct comparison of the free energies of 1 and 2 is inelegant, and instead we look for a path from 2 to 1 such that the free energy is obviously monotonically decreasing along the path. First it is necessary to define the free energy at an arbitrary point in the $F_1 - F_2$ plane (where $F_1 \geq W$, $F_2 \geq W$). This can be done in many different ways, all of which agree at the point 1, and all of which agree at the point 2, but which may not agree at other points. The most convenient definition proves to be the following: evaluate (4.12) with $A_{q1} = \beta[V(\vec{q}) + F_1]$ and $A_{q2} = A_{q3} = \beta[V(\vec{q}) + F_2]$ and then formally minimize the resulting function with respect to Δ^2, taking no note of the restriction $\Delta^2 \geq 0$. The resulting free energy is

$$\begin{aligned}\frac{\mathcal{F}(F_1, F_2)}{N} = &-\frac{1}{2\beta}[F_1 G(F_1) + 2F_2 G(F_2)] \\ &- \frac{1}{4\gamma}\left(-\frac{W}{2} + \frac{6\gamma}{\beta} G(F_1) + \frac{4\gamma}{\beta} G(F_2)\right)^2 \\ &+ \frac{\gamma}{\beta^2}[3G(F_1)^2 + 8G(F_2)^2 + 4G(F_1)G(F_2)] \\ &+ \frac{1}{2\beta}[H(F_1) + 2H(F_2)] + \text{const.} \,,\end{aligned} \tag{C1}$$

where the additive constant does not depend on F_1 and F_2 and $H(F) \equiv \int G(F) dF$. [An inconvenient definition, which did not lead us to a proof of the desired result, is to evaluate (4.12) with the above choice of $A_{q\lambda}$, using (6.3) to eliminate Δ^2.]

The partial derivatives of $\mathcal{F}$ are

$$\phi_1 \equiv \frac{1}{N}\frac{\partial \mathcal{F}}{\partial F_1} = -\frac{G'(F_1)}{\beta} \times\left(\frac{12\gamma}{\beta} G(F_1) + \frac{8\gamma}{\beta} G(F_2) + \frac{F_1}{2} - \frac{3}{2} W\right), \tag{C2a}$$

$$\phi_2 \equiv \frac{1}{N}\frac{\partial \mathfrak{F}}{\partial F_2} = -\frac{G'(F_2)}{\beta}$$

$$\times\left(\frac{8\gamma}{\beta}G(F_2) - \frac{8\gamma}{\beta}G(F_1) - F_2 + W\right) . \quad \text{(C2b)}$$

The pair of equations $\phi_1 = 0$ and $\phi_2 = 0$ are equivalent to the system (6.4a) and (6.4b). Graphs of $\phi_1 = 0$ and $\phi_2 = 0$ are shown in Fig. 8. Since $(8\gamma/\beta)G(F_2) - F_2$ is a decreasing function of F_2 and $(8\gamma/\beta)G(F_1)$ is a decreasing function of F_1, the curve $\phi_2 = 0$ is monotone increasing and always passes through (W, W). The curve $\phi_1 = 0$ has a negative slope when $F_1 = W$ and becomes asymptotically vertical when $(12\gamma/\beta)G(F_1) + \frac{1}{2}F_1 = \frac{3}{2}W$. The curves $\phi_1 = 0$ and $\phi_2 = 0$ intersect twice if $T_c < T < T_0$ [Figs. 8(b) and 8(c)]. If we choose the curve $\phi_2 = 0$ as our path of integration from 2 to 1, we can write

$$(1/N)[\mathfrak{F}(1) - \mathfrak{F}(2)] = \int_2^1 \phi_1 \, dF_1 . \quad \text{(C3)}$$

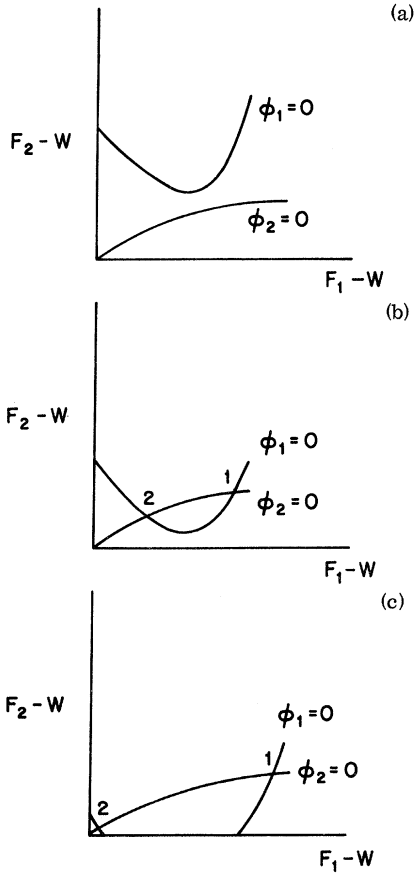

FIG. 8. Curves in the F_1-F_2 plane on which $\phi_1 = \partial(\mathfrak{F}/N)/\partial F_1 = 0$ and $\phi_2 = \partial(\mathfrak{F}/N)/\partial F_2 = 0$. By going from 2 to 1 along the curve $\phi_2 = 0$ we prove that $\mathfrak{F}(1) < \mathfrak{F}(2)$. (a) $T > T_0$, (b) T slightly less than T_0, (c) T slightly greater than T_c.

From the above expression for ϕ_1 it is evident that ϕ_1 is negative at all points in the $F_1 - F_2$ plane which are above the curve $\phi_1 = 0$ [since $-G'(F_1)$ is positive and $G(F_2)$ decreases with increasing F_2]. Since the curve $\phi_2 = 0$ lies above $\phi_1 = 0$ between 1 and 2, it follows that $\phi_1 < 0$ on this path and thus $\mathfrak{F}(1) < \mathfrak{F}(2)$. More generally, since $\mathfrak{F}$ decreases as we move away from 2 along the curve $\phi_2 = 0$ but increases as we move away from 2 on a vertical line (consider the sign of ϕ_2 as F_2 is varied), we can see that 2 is a saddle point. Similarly, since any point near 1 can be reached by traveling along the curve $\phi_2 = 0$ and then vertically, we can see that 1 is a true minimum.

APPENDIX D: FERROELECTRIC PHASE IN ONE AND TWO DIMENSIONS, IN SELF-CONSISTENT PHONON APPROXIMATION

In one and two dimensions we confine ourselves to discussion of quadratic forces for which $G(W) = \infty$. We call such forces "short range." This definition includes the case $V_{ij} \propto \delta_{ij}$, for which $G(F) = (F - W)^{-1}$. We shall see that the SPA predicts a first-order transition to a ferroelectric phase in one and two dimensions with short-range quadratic forces. The prediction is evidently wrong, at least in the limiting case $V_{ij} \propto \delta_{ij}$.

In one dimension (4.13)–(4.18) yield

$$(12\gamma/\beta)G(F) = \tfrac{3}{2}W - \tfrac{1}{2}F \quad \text{(D1)}$$

and

$$\Delta^2 = (F_1 - W)/8\gamma , \quad \text{(D2)}$$

the latter being true independently of dimensionality. Graphical solution of (D1) is shown in Fig. 9, the right-hand side being represented by the straight line and the left-hand side by the two curves labeled "high T" and "low T." The high-T curve does not intersect the straight line, so the system must use the paraelectric solution. The low-T curve intersects the straight line twice. The intersection labeled 1 corresponds to greater polarization and can be shown, by a proof similar to that in Appendix C, to represent a state of lower free energy than intersection 2. As $T \to 0$, the value of F at intersection 2 approaches W, so 2 becomes identical with the paraelectric state. Thus, according to the SPA, the system must make a first-order transition from the paraelectric state to 1 at some finite temperature.

Analysis of the two-dimensional case is identical with the three-dimensional case, taking note of changes in the coefficients in (4.17). The parameters F_1 and F_2 are found by solving the system

$$F_1 = 3F_2 - (32\gamma/\beta)G(F_2) , \quad \text{(D3a)}$$

$$F_2 = 4W - F_1 - (32\gamma/\beta)G(F_1) , \quad \text{(D3b)}$$

which replaces (6.4a) and (6.4b). Graphical solu-

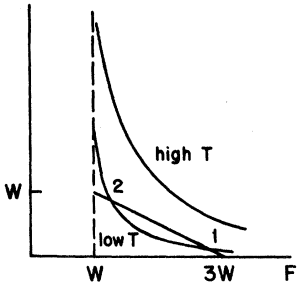

FIG. 9. Graphical determination of F in the ferroelectric phase in one dimension, with short-range quadratic forces. The straight line represents the right-hand side of Eq. (D1), and the curves represent the left-hand side of (D1) at high T and low T, respectively. At high T there are no intersections, and the system is paraelectric. At low T there are two intersections, the state of greater polarization (labeled 1) having lower free energy. The SPA predicts a first-order transition from the paraelectric phase to 1.

tion is shown at high T [Fig. 10(a)] and low T [Fig. 10(b)], with (D3a) and (D3b) labeled by A and B respectively. At high T there is no intersection, and the system must be paraelectric. At low T there are two intersections. Intersection 1 can again be shown to represent a state of lower free energy than 2. As $T \to 0$, the point 2 approaches (W, W), the low-temperature limit of the paraelectric solution. Therefore the SPA predicts a first-order transition from the paraelectric state to 1 at a finite temperature.

APPENDIX E: QUANTUM-MECHANICAL SELF-CONSISTENT PHONON APPROXIMATION

A quantum-mechanical analysis of our model in the SPA does not alter the predictions of the classical investigation, but merely revises the critical numbers. In this Appendix we will exhibit the straightforward generalization to quantum mechanics and verify that the key classical quantities have close quantum analogs. In particular, we shall see that the basic equations (4.12)–(4.18) remain essentially unchanged.

Our quantum-mechanical analysis proceeds similarly to that of Pytte and Feder.[16] Boson creation and annihilation operators are defined in terms of $c_{q\lambda}$ and the conjugate momentum $p_{q\lambda}$ by

$$c_{q\lambda} = \hbar(4M\epsilon_{q\lambda})^{-1/2}(a^\dagger_{q\lambda} + a_{q\lambda}) ,$$
$$p_{q\lambda} = i\,(M\epsilon_{q\lambda})^{1/2}\,(a^\dagger_{q\lambda} - a_{q\lambda}) , \tag{E1}$$

where λ can assume six values (three when $\vec{q}=0$) corresponding to the three polarizations and the sine or cosine normal coordinate. As a trial density matrix we choose

$$\rho = \eta \prod_{q\lambda}{}' \exp(-\beta\epsilon_{q\lambda}a^\dagger_{q\lambda}a_{q\lambda}) \prod_{\lambda} \exp(-\beta\epsilon_{0\lambda}a^\dagger_{0\lambda}a_{0\lambda}) , \tag{E2}$$

where the normalization factor η is

$$\eta = \prod_{q\lambda}{}' (1-e^{-\beta\epsilon_{q\lambda}}) \prod_{\lambda} (1-e^{-\beta\epsilon_{0\lambda}}) . \tag{E3}$$

The prime in a product or sum indicates that the range is half of $\vec{q}$ space, excluding $\vec{q}=0$. The $\epsilon_{q\lambda}$ are variational parameters. If the parameters in (E1) are not initially taken to be identical with those in (E2), minimization of the free energy leads to the conclusion that they are identical. The Δ dependence has been excluded from (E3), since it is easily put into the free energy by hand. The alternative is to define $a^\dagger_{01}$ and a_{01} based on $c_{01} - \Delta\sqrt{N}$ and to add a compensating term to the effective Hamiltonian in the density matrix. We can remove the constants $\hbar$ and M from the calculation with the following definitions:

$$\mathfrak{D} = (M/\hbar^2)^{1/2}\Delta, \quad \Gamma = \gamma\hbar^4/M^2, \quad v_q = \hbar^2 V(\vec{q})/M . \tag{E4}$$

As in the classical equations, the mass need not appear in quantum mechanics; it merely serves to scale spring constants. For small q, v_q, which corresponds to the square of the unrenormalized vibration frequency, is negative.

Introducing the kinetic-energy term into the Hamiltonian

$$H_{KE} = (2M)^{-1}\left(\frac{1}{2}\sum_{q\lambda}{}' p^2_{q\lambda} + \sum_{\lambda} p^2_{0\lambda}\right) ,$$

we find the quantum-mechanical free energy to be

$$\frac{\mathfrak{F}}{N} = \Gamma\mathfrak{D}^4 + \mathfrak{D}^2\left(\frac{1}{2}v_0 + \frac{4\Gamma}{N}\sum_{q\lambda}{}'(1+2\delta_{\lambda 1})\frac{n_{q\lambda}+\frac{1}{2}}{\epsilon_{q\lambda}}\right) + \frac{1}{N}\sum_{q\lambda}{}'\left(\epsilon_{q\lambda} + \frac{v_q}{\epsilon_{q\lambda}}\right)(n_{q\lambda}+\tfrac{1}{2})$$
$$+ \frac{4\Gamma}{N^2}\sum_{q\lambda}{}'\sum_{q'\lambda'}{}'(1+2\delta_{\lambda\lambda'})\frac{n_{q\lambda}+\frac{1}{2}}{\epsilon_{q\lambda}}\,\frac{n_{q'\lambda'}+\frac{1}{2}}{\epsilon_{q'\lambda'}} - \frac{2}{\beta N}\sum_{q\lambda}{}'[\beta\epsilon_{q\lambda}(n_{q\lambda}+1)+\ln n_{q\lambda}] + O\left(\frac{1}{N}\right) . \tag{E5}$$

As in (4.12), the neglect of terms of order $1/N$ eliminates the need for careful consideration of the $\vec{q}=0$ mode. In (E5), $\lambda = 1, 2, 3$ and account has been taken of the complete symmetry between the sine and cosine normal coordinates, and $n_{q\lambda} = (e^{\beta\epsilon_{q\lambda}}-1)^{-1}$.

As in (4.15), we define

$$\mathcal{K}_\lambda = \sum_{q'\lambda'}{}'(1+2\delta_{\lambda\lambda'})(n_{q'\lambda'}+\tfrac{1}{2})/\epsilon_{q'\lambda'} . \tag{E6}$$

Variation of the free energy with respect to $\epsilon_{q\lambda}$ and some manipulation yields, as in (4.13) and (4.14),

$$\epsilon_{q\lambda}^2 = v_q + f_\lambda , \tag{E7}$$

where now

$$f_\lambda = 8\Gamma\mathcal{K}_\lambda + 4\Gamma\mathfrak{D}^2(1+2\delta_{\lambda 1}) . \tag{E8}$$

Variation with respect to $\mathfrak{D}^2$ gives

$$\mathfrak{D}^2 = w/4\Gamma - 2\mathcal{K}_1 . \tag{E9}$$

If the right-hand side of (E9) is negative,

$$\mathfrak{D}^2 = 0 . \tag{E10}$$

In (E9), $w \equiv -\hbar^2 v_0/M \equiv \hbar^2 W/M$ is positive. We have thus produced the quantum generalizations of the key variational equations (4.13), (4.14), (4.18), and (4.19).

In order for the subsequent classical analysis of Secs. IV–VI to apply in quantum mechanics, we must verify that the quantum analog of $(1/\beta)G(F)$ of (4.16) has the same essential properties. With the aid of (E6) and (E7) we can see that the quantum function corresponding to $(1/\beta)G(F)$ is

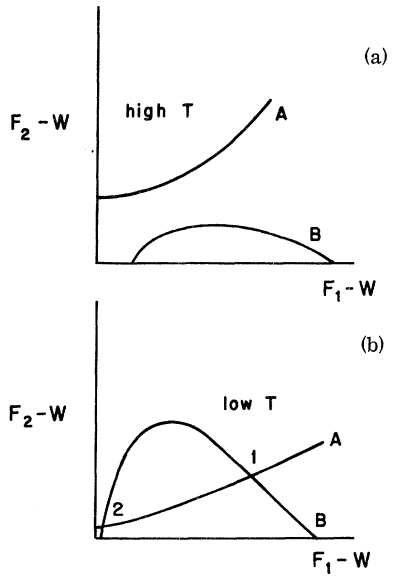

FIG. 10. Determination of F_1 and F_2 for the ferroelectric phase in two dimensions, with short-range quadratic forces. Curves A and B represent (D3a) and (D3b), respectively. At high T [(a)] no intersection exists, and the system is paraelectric. At low T [(b)] there are two intersections, the state of larger polarization (labeled 1) having lower free energy. The SPA predicts a first-order transition from the paraelectric phase to 1.

$$\mathcal{G}(f;\beta) = \left(\frac{a}{2\pi}\right)^\nu \int d^\nu q\,(v_q+f)^{-1/2}\left(\{\exp[\beta(v_q+f)^{1/2}]-1\}^{-1}+\tfrac{1}{2}\right) = \frac{1}{2}\left(\frac{a}{2\pi}\right)^\nu \int d^\nu q\,(v_q+f)^{-1/2}\coth\tfrac{1}{2}\beta(v_q+f)^{1/2} . \tag{E11}$$

The following are the properties of $(1/\beta)G(F)$ which were invoked in our analysis.

(i) $(1/\beta)G(F)$ is a monotonically decreasing function of F which approaches zero asymptotically for large F.

(ii) $(1/\beta)G(F)$ is monotonically decreasing as β increases.

(iii) As $F \to W$,

$$(1/\beta)G(F) \propto \int d^\nu q\,[V(q)+F]^{-1} \sim \int d^\nu q\,[(F-W)+\alpha q^n]^{-1} .$$

Quick inspection indicates that the first two properties hold for $\mathcal{G}(f;\beta)$. The third property is necessary to determine the order of the transition and the dependence on dimensionality. It concerns the domain of $F \gtrsim W$ and $|q| \gtrsim 0$. In this region $v_q + f$ is correspondingly small. Hence the hyperbolic cotangent can be replaced by the inverse of its argument. In this critical range, then, $\mathcal{G}(f;\beta)$ is identical in form with $(1/\beta)G(F)$, and hence it and its derivatives at $f = w$ have the same convergence properties as the classical function at $F = W$.

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Two-Time Spin-Pair Correlation Function of the Heisenberg Magnet at Infinite Temperature

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The two-time spin-pair autocorrelation function $\sigma(\vec{0},t)$ and the Fourier-space transform $I(\vec{k},t)$ of the two-time spin-pair correlation function $\sigma(\vec{R}_{if},t)$, are expressed in terms of the "friction function" occurring in the generalized Langevin equation for the spin operator s_i^z and its Fourier-space transform S_k^z, respectively. The friction function is determined in the form of a product of a Gaussian distribution function and a power series as a function of time t for the isotropic Heisenberg magnet and the XY magnet of spin $\frac{1}{2}$ at infinite temperature. By truncating the power series to the exactly known term, satisfactory results are obtained for $I(\vec{k},t)$ of the isotropic Heisenberg magnet of the linear chain and sc lattice. Satisfactory results for $\sigma(\vec{R}_{if},t)$ are achieved by taking an inverse Fourier-space transform of the thus determined $I(\vec{k},t)$.

I. INTRODUCTION

In a recent paper,[1] the short-time-expansion coefficients have been provided for the spin-pair correlation function $\sigma(\vec{R}_{if},t)$ of the Heisenberg magnet of spin $\frac{1}{2}$ at infinite temperature—up to terms of $O(t^{10})$ for the linear chain and up to $O(t^8)$ for the square and sc lattices. In another paper,[2] the short-time expansion of $\sigma(\vec{R}_{if},t)$ and its Fourier-space transform $I(\vec{k},t)$ are expressed as a product of the Gaussian distribution function and a power series in time t. The expressions obtained by truncating the power series to the exactly known coefficients are found to give very good values at short times $0\le\tau<2.0$, where $\tau=(2z)^{1/2}Jt$, z is the coordination number of the lattice, and J is the exchange integral. But at larger times, they decay to zero too fast. The Fourier-time transform of the truncated expression for $I(\vec{k},t)$ gives the Gram-Charlier expansion of the scattering function $S(\vec{k},\omega)$, which Collins and Marshall[3] suggested for the analysis of $S(\vec{k},\omega)$; $S(\vec{k},\omega)$ being the Fourier-time transform of $I(\vec{k},t)$. The above conclusion about the truncated expression for $I(\vec{k},t)$ indicates the limitation of that expansion. The expressions are valid for large $\vec{k}$ or not very small ω. Inadequacy of the Gram-Charlier expansion for small $\vec{k}$ is stated also by Tahir-Kheli and McFadden.[4]

When investigating the two-time correlation function, the equation of motion is often set up. The memory function or friction function occurring in the equation is considered to decay faster than the correlation function itself. The friction function is sometimes approximated by the Gaussian distribution function.[5] In the present paper, we take advantage of knowledge of the higher terms and express the friction function as a product of the Gaussian distribution function and a power series. The power series are truncated to the exactly known terms. Basic formulas for that calculation starting from the short-time expansion of the two-time correlation function are provided in Sec. II. We apply them to the two-time spin-pair autocorrelation function $\sigma(\vec{0},t)$ for the XY magnet and the isotropic Heisenberg magnet in Sec. III. Corresponding calculations for the Fourier-space transform $I(\vec{k},t)$ of $\sigma(\vec{R}_{if},t)$ are given in Sec. IV. The results are compared with the exact expression for the one-dimensional XY magnet (referred to as the XY model),[6] the results of the computer simulation calculation of Windsor,[7] an exact solution for the linear Heisenberg magnet of finite length,[8] Blume and Hubbard's solution[9] of an integro-differential equation, and the results obtained with the aid of the Gram-Charlier expansion.[2]

II. TWO-TIME CORRELATION FUNCTION AND THE FRICTION FUNCTION

In this section, we consider a two-time correlation function $(A(t), A^\dagger(0))$ of an arbitrary operator A and its Hermitian conjugate $A^\dagger$: for example,

$$(A(t), A^\dagger(0)) = \langle A(t)A^\dagger(0)\rangle \ , \qquad (2.1)$$

where the bracket $\langle\cdots\rangle$ denotes the canonical average and

$$A(t)=e^{iHt}Ae^{-iHt} \ .$$

Here H is the Hamiltonian of the system. The