Proton model of ferroelectrics with tunneling in the static fluctuation approximation

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The transverse Ising model is considered in the *static fluctuation approximation*. This hinges on the replacement of the local field operator with its mean value; only the quadratic fluctuations of the local field are retained. The model is applied to ferroelectrics of the order-disorder type, such as monoaxial crystalline threeglycinsulfate. Analytic expressions are derived for the spontaneous polarization, the specific heat, the pair correlation function, and the static susceptibility of this ferroelectric. Its main characteristics are then determined numerically as functions of the temperature. In particular, its critical behavior is obtained *automatically* for a specific value of some ''control'' parameter. It is predicted that, with respect to this parameter, the specific heat exhibits a logarithmic behavior to the right of the critical point; this is interpreted as a consequence of the long range and axial anisotropy of the dipole-dipole interaction. In passing, the behavior of the lattice Green function for the anisotropic dipole-dipole potential near the critical point is thoroughly examined.

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I. INTRODUCTION

The proton model with tunneling was suggested by Blinc [1] in 1960 for describing the soft-mode behavior in ferroelectrics of the order-disorder type with hydrogen bonds where lower states predominate. The main success of this model was in explaining the substantial isotopic shift of the critical temperature T_c. The model hinges on the suggestion that each proton can tunnel between two equilibrium positions of the hydrogen-bond potential. If the local potential has two deep minima then, for statistical purposes, it is interesting to observe that there exist only two degenerate states, each state belonging to one local minimum. If we neglect the excited vibrational states and consider only a two-level system, then the process of tunneling can be described in terms of $\frac{1}{2}$ *pseudospin*. As a result of such a transformation in the pseudospin formalism, the tunneling Hamiltonian will coincide with the Hamiltonian of the Ising model in a *transverse field*:

$$H=-\Delta\sum_{f} S_f^x-\frac{1}{2}\sum_{ff'} U_{ff'}S_f^zS_{f'}^z. \tag{1}$$

Here Δ is the frequency of the tunneling and $U_{ff'}$ is an intercell interaction having for most ferroelectrics the anisotropic dipole-dipole form. This model can be used as a preliminary step for describing the structural transitions of the order-disorder-type ferroelectrics with tunneling. It has been suggested by Kobayashi [2] that the hydrogen phonon modes play an important role in $K_2H_2PO_4$.

On the other hand, Hamiltonians with spin-phonon interaction containing linear phonon operators can again be reduced, after suitable canonical (unitary) transformations, to a Hamiltonian of type (1), albeit with a modified interaction between pseudospins. Accordingly, it is useful to investigate thoroughly the thermodynamic properties of the systems described by Hamiltonian (1).

In the present paper, this is carried out within the framework of the *static fluctuation approximation* (SFA). This approach was suggested earlier by one of the authors (R.R.N.) and successfully used for calculating the thermodynamic properties of the Ising and Heisenberg models [3].

In fact, the SFA can be invoked for calculating thermodynamic properties and equilibrium correlation functions (CFs) of a variety of many-body systems with strong interparticle interactions. A small parameter is *not* used and the approach can be applied to various geometrical configurations and *different boundary conditions*, including the conventional periodic boundary conditions widely used in statistical mechanics.

The SFA hinges on the replacement of the local field operator with its mean value (a *c* number); only the quadratic fluctuations of the local field are retained. As a result, for lattice systems, the so-called *difference long-range equations* (DLREs) can be obtained. (This term was taken from Ref. [4], where such equations were used to obtain the exact solution for the ferromagnetic Ising chain.) In general, the exact DLREs for Hamiltonian (1) are nonlinear and analytic methods of solution of nonlinear difference equations are not known. However, the above replacement leads to the approximate linearization of the exact DLREs and transformation of the conserved nonlinearity into a system of self-consistent equations. Below (Sec. III) we show *how* this single and controllable replacement is sufficient to calculate all main thermodynamic characteristics of the system. Prior to this (Sec. II), we present the basic ingredients of the SFA, together with the linearized DLRE for the transverse Ising model. Our conclusions are summarized in Sec. IV and mathematical details are relegated to an appendix.

II. PRINCIPLES OF THE SFA: THE LINEARIZED DLRE FOR THE TRANSVERSE ISING MODEL

For the present purposes it is convenient to express the initial Hamiltonian (1) in the form

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$$H=-\sum_{f}(\Delta S_f^x+\sigma_f S_f^z), \tag{2}$$

where σ_f defines the local field operator:

$$\sigma_f\equiv h_f+\sum_{f'} U_{ff'}S_{f'}^z. \tag{3}$$

The Heisenberg equations of motion for the pseudospin components S_f^α ($\alpha=x,y,z$; f is a fixed node of a lattice) are

$$\frac{dS_f^x}{d\tau}=[H,S_f^x]=-i\sigma_f S_f^y, \tag{4a}$$

$$\frac{dS_f^y}{d\tau}=[H,S_f^y]=-i\Delta S_f^z+i\sigma_f S_f^x, \tag{4b}$$

$$\frac{dS_f^z}{d\tau}=[H,S_f^z]=i\Delta S_f^y. \tag{4c}$$

Here $\tau\equiv it$. According to the SFA,

$$(\sigma_f)^2\cong\langle(\sigma_f)^2\rangle. \tag{5}$$

The underlying *physical meaning* is the following. The true quantum-mechanical spectrum of the operator σ_f defined by Eq. (3) is replaced with a distribution. It is then attempted to incorporate into the picture the moments of this distribution. As a first step we retain the *quadratic fluctuations* of σ_f. This leads to the approximate but linearized DLREs which can be solved self-consistently by well-known mathematical methods. Approximation (5) allows us to increase the region of applicability of the SFA (in comparison with previous attempts [3]) and obtain the DLREs for a wide class of Hamiltonians.

With this approximation, the solutions of the Heisenberg equations of motion (4) can be obtained in the following closed form:

$$S_f^x(\tau)=S_f^x(0)+\frac{[S_f^x(0)\langle(\sigma_f)^2\rangle-S_f^z(0)\Delta\sigma_f]}{\Omega_f^2}\times[\cosh(\Omega_f\tau)-1]-i\frac{\sigma_f}{\Omega_f}\sinh(\Omega_f\tau)S_f^y(0), \tag{6a}$$

$$S_f^y(\tau)=\frac{[S_f^x(0)\sigma_f-S_f^z(0)\Delta]}{\Omega_f}\sinh(\Omega_f\tau)+\cosh(\Omega_f\tau)S_f^y(0), \tag{6b}$$

$$S_f^z(\tau)=S_f^z(0)+\frac{[S_f^z(0)\Delta^2-S_f^x(0)\Delta\sigma_f]}{\Omega_f^2}\times[\cosh(\Omega_f\tau)-1]+i\frac{S_f^y(0)\Delta}{\Omega_f}\sinh(\Omega_f\tau). \tag{6c}$$

Here $\Omega_f\equiv\sqrt{\Delta^2+\langle(\sigma_f)^2\rangle}$ is the fundamental frequency of the dipole moment induced by the quadratic fluctuations of the local field. These solutions allow us to find the CFs, $\langle S_f^zA\rangle,\langle S_f^xA\rangle,\langle\sigma_fA\rangle$, where A is an operator containing an arbitrary combination of pseudospin variables $S_{f'}^z$, with nodes *not coinciding* with the chosen node f $(f'\neq f)$. The equations for these average values can be obtained using the well-known relation

$$\langle B(\beta)C\rangle=\langle CB\rangle, \tag{7}$$

B,C, being any quantum mechanical operators. Putting instead of B the above solutions for the pseudospin components $S_f^\alpha(\tau)$ $(\alpha=x,y,z)$ and instead of C the operators $S_f^\gamma A$ $(\gamma=x,y,z)$, then using the commutation rules for pseudospin operators ($S=\frac{1}{2}$), one can obtain, after some algebraic manipulations, the following DLREs for the system:

$$\langle S_f^zA\rangle=\eta_f\langle\sigma_fA\rangle. \tag{8}$$

$$\langle S_f^xA\rangle=\Delta\cdot\eta_f\langle\sigma_fA\rangle, \tag{9}$$

where

$$\eta_f\equiv\frac{1}{2\Omega_f}\tanh\left(\frac{\beta\Omega_f}{2}\right). \tag{10}$$

For the one-dimensional Ising model of ferromagnetics, equations of this kind were obtained in Ref. [4]; these made it possible to determine the exact solution for various boundary conditions. In the SFA the DLREs are linear and self-consistent. The DLREs (8)–(10) define all thermodynamic properties of the Ising model in the transverse field.

We shall *assume* that (i) a homogeneous external field is applied, (ii) the lattice is translationally invariant, and (iii) the quantities h_f and Ω_f do not depend on the node index *f*; henceforth they will be denoted by h and Ω. Now, putting in Eq. (8) $A=1$, we obtain the following equation for the average dipole moment:

$$\langle S_f^z\rangle=h_f+\eta_fU(0)\langle S_f^z\rangle \tag{11}$$

or

$$\langle S^z\rangle=\frac{hp}{U(0)(1-p)}. \tag{12}$$

Here p is given by the dimensionless expression

$$p\equiv\eta\sum_{f'}U_{ff'}=\eta U(0), \tag{13}$$

$U(0)$ being the zero Fourier-component of the potential.

From Eq. (11), denoting $\Delta S_f^z\equiv S_f^z-\langle S_f^z\rangle$, we can rewrite Eq. (8) in a form more convenient for practical calculations, namely,

$$\langle\Delta S_f^zA\rangle=\eta\langle\Delta\sigma_fA\rangle. \tag{14}$$

From this last equation one can determine the pair CF. To this end we put in Eq. (14) $A=\Delta S_{f'}^z$; so that

$$\begin{aligned}\langle \Delta S_f^z \Delta S_{f'}^z\rangle_c &= \eta\langle \Delta\sigma_f \Delta S_{f'}^z\rangle\\ &= \eta U_{ff'}\langle(\Delta S_f^z)^2\rangle\\ &\quad + \eta\sum_{f''\neq f'} U_{ff''}\langle \Delta S_{f''}^z \Delta S_{f'}^z\rangle_c, \end{aligned} \qquad (15)$$

$\langle\cdots\rangle_c$ signifying the true correlators between pseudospins located at different nodes of a lattice. To find the pair CF from Eq. (15), we impose *periodic boundary conditions*. In this case, using the respective Fourier transforms of the pair CF and potential, we find

$$\langle \Delta S_k^z \Delta S_{-k}^z\rangle = \langle(\Delta S_f^z)^2\rangle\left[\frac{1}{1-\eta U(k)} - 1\right] \qquad (16)$$

or, in the node representation,

$$\begin{aligned}\langle \Delta S_f^z \Delta S_{f'}^z\rangle_c &= \frac{\langle(\Delta S_f^z)^2\rangle}{N}\sum_k \frac{\exp(i\mathbf{k}\cdot\mathbf{r}_{ff'})}{1-\eta U(\mathbf{k})}\\ &\equiv \langle(\Delta S_f^z)^2\rangle G(\eta,\mathbf{r}_{ff'}),\end{aligned} \qquad (17)$$

$G(\eta,\mathbf{r}_{ff'})$ being the lattice Green function.

From Eq. (12) it follows that $p=1$ is a singular point. If $p=1$, then, at $h\to 0$, $\langle S^z\rangle$ can assume any value. Thus, it is convenient to choose p as an *independent* parameter. The value $p=1$ defines a possible phase transition for the spontaneous polarization ($\sim\langle S^z\rangle$). To see this we first examine the local-field dispersion

$$\Omega = \sqrt{\Delta^2 + \langle\sigma_f\rangle^2 + \langle(\Delta\sigma_f)^2\rangle}. \qquad (18)$$

From Eqs. (16) and (17)

$$\begin{aligned}\langle(\Delta\sigma_f)^2\rangle &= \sum_{f'f''} U_{ff'}U_{ff''}\langle \Delta S_{f'}^z \Delta S_{f''}^z\rangle\\ &= \frac{\langle(\Delta S_f^z)^2\rangle}{N}\sum_k \frac{U(\mathbf{k})U(-\mathbf{k})}{1-\eta U(\mathbf{k})}\\ &\equiv \frac{U(0)^2\langle(\Delta S_f^z)^2\rangle}{p^2}[G(p)-1].\end{aligned} \qquad (19)$$

Here $G(p)\equiv G(p,0)$ defines the momentum-space lattice Green function

$$G(p) \equiv \frac{1}{N}\sum_k \frac{1}{1-pU(\mathbf{k})/U(0)}, \qquad (20)$$

which depends on the dimension, geometry of lattice and the form of the potential. Using Eqs. (3) and (19), we have ($h=0$)

$$\begin{aligned}&\Omega(p,\Delta,\langle S^z\rangle)\\ &= \sqrt{\Delta^2 + \langle S^z\rangle^2 U^2(0) + \left(\frac{1}{4} - \langle S^z\rangle^2\right)\frac{U^2(0)}{p^2}[G(p)-1]}.\end{aligned} \qquad (21)$$

Invoking Eq. (10), which itself represents a self-consistent equation that defines the temperature $T(p,\Delta,\langle S^z\rangle)$, together with Eq. (13), we obtain

$$T(p,\Delta,\langle S^z\rangle) = \frac{\Omega(p,\Delta,\langle S^z\rangle)}{2\tanh^{-1}\left(2p\,\dfrac{\Omega(p,\Delta,\langle S^z\rangle)}{U(0)}\right)}. \qquad (22)$$

Next, we determine the average energy. From Eq. (2),

$$\langle H\rangle = -\sum_f \langle(\Delta S_f^x + S_f^z\sigma_f^z)\rangle = -N(\Delta\langle S^x\rangle + \langle S_f^z\sigma_f^z\rangle). \qquad (23)$$

Putting in Eq. (8) $A=\sigma_f^z$ and in Eq. (9) $A=1$, and using our main approximation (5), we finally arrive at

$$\frac{1}{N}\langle H\rangle = -\frac{p}{U(0)}[\Omega^2(p,\Delta,\langle S^z\rangle)]. \qquad (24)$$

Now, above the transition temperature T_c, $\langle S^z\rangle = 0$ and

$$\langle S^x\rangle = \frac{\Delta}{2\Omega(p,\Delta,\langle S^z\rangle)}\tanh\left(\frac{\Omega(p,\Delta,\langle S^z\rangle)}{2T}\right) = \frac{\Delta}{U(0)}p. \qquad (25)$$

This equation describes the paraelectric phase *without* spontaneous polarization.

Below the transition temperature, we obtain the ordering effect by putting in Eq. (10) $p=1$. We then have

$$\frac{1}{U(0)} = \frac{1}{2\Omega(1,\Delta,\langle S^z\rangle)}\tanh\left(\frac{\Omega(1,\Delta,\langle S^z\rangle)}{2T}\right), \qquad (26)$$

where

$$\begin{aligned}&\Omega(1,\Delta,\langle S^z\rangle)\\ &\equiv \sqrt{\Delta^2 + \langle S^z\rangle^2 U^2(0) + (\tfrac{1}{4} - \langle S^z\rangle^2)U^2(0)[G(1)-1]}.\end{aligned} \qquad (27)$$

Equations (26) and (27) define the spontaneous polarization as a function of T. It follows that

$$0|_{T=T_c} \leqslant \langle S^z\rangle \leqslant \sqrt{\frac{1}{4} - \left(\frac{\Delta}{U(0)}\right)^2\frac{1}{2-G(1)}}\,\Bigg|_{T=0}. \qquad (28)$$

It should be stressed that at $T=0$ the upper value is less than the corresponding value obtained in the framework of the mean-field approximation [5,6] where, at $T=0$, $\langle S^z\rangle = \{\tfrac{1}{4}[\Delta/U(0)]^2\}^{1/2}$, since $1\leqslant G(1) < 2$.

The ordered phase $\langle S^x\rangle$ is temperature independent:

$$\langle S^x\rangle = \frac{\Delta}{U(0)}. \qquad (29)$$

This coincides with the result given by mean-field theory [6]. The critical temperature is defined from Eq. (22) at $p=1$ and $\langle S^z\rangle = 0$:

$$T_c = \frac{U(0)\sqrt{[2\Delta/U(0)]^2 + G(1) - 1}}{4\tanh^{-1}[\sqrt{[2\Delta/U(0)]^2 + G(1) - 1}]}. \tag{30}$$

This equation describes T_c as a function of the tunnel splitting Δ. This is different from the value corresponding to the ordinary Ising model in the SFA ($\Delta = 0$):

$$T_c = \frac{U(0)\sqrt{G(1)-1}}{4\tanh^{-1}[\sqrt{G(1)-1}]} \tag{31}$$

up to the value $T_c = 0$, where $\Delta \equiv [U(0)/2]\sqrt{2 - G(1)}$. If $\Delta > [U(0)/2]\sqrt{2 - G(1)}$, the ordering effect does not play a role.

The static susceptibility above the critical point $\chi(\mathbf{k})$ is calculated easily with the help of the fluctuation-dissipation theorem

$$k_B T \chi(\mathbf{k}) = \langle \Delta S_k^z \Delta S_{-k}^z \rangle. \tag{32}$$

Using Eq. (16), we finally obtain for $T \geqslant T_c$:

$$\chi(\mathbf{k}) = \frac{1}{4T(p,0)}\left[\frac{1}{1 - pU(\mathbf{k})/U(0)} - 1\right], \tag{33}$$

where $T(p,\Delta,\langle S^z \rangle)$ is defined by Eq. (22). In particular, the homogeneous part of the static susceptibility above T_c is defined by the expression

$$[\chi(0)]^{-1} = 4T(p,0)\,\frac{1-p}{p}. \tag{34}$$

Clearly, then, the static susceptibility has a singular point at $p = 1$—in conformity with the foregoing conclusion concerning the possibility of a phase transition in the system at this point.

Equations (10), (12), (17), (20), (21), (22), and (30) form a closed system that completely defines the thermodynamics of the transverse Ising model ($S = \frac{1}{2}$) for a regular lattice of *any* dimension and for an *arbitrary* interaction between spins.

It is worth noting that approximation (5) incorporates the higher-order fluctuations of the local field in the sense that

$$(\sigma_f)^{2n} \cong \langle (\sigma_f)^2 \rangle^n; \quad (\sigma_f)^{2n+1} \cong \sigma_f \langle (\sigma_f)^2 \rangle^n. \tag{35}$$

The main difference of the SFA from the exact solution is that the true quantum-mechanical spectrum of the operator σ_f is defined by finite or infinite eigenvalues and all calculations are finally reduced to the consideration of nonlinear DLREs which at present *cannot be solved analytically*. To avoid this principal difficulty, the DLREs are approximately linearized and the nonlinearity is retained in the form of a *self-consistent* system of equations [in our case Eqs. (8)–(10)].

III. THERMODYNAMICS OF THE MODEL WITH DIPOLE-DIPOLE FORCES

The full solution of the above system of nonlinear equations can only be obtained by numerical methods. An analytic solution is out of the question unless additional approximations are made. This is related to the fact that the thermodynamics of the model crucially depends on the lattice Green function which, as already remarked, includes the dimension, geometry of lattice and the Fourier-transform of the relevant potential.

TABLE I. Values of the coefficients in expressions (36) and (44) for cubic lattices.

Lattice	z	v_a	$U(0)$	α	β	γ
sc	6	1	$4\pi/3$	-0.1649	-0.4945	4π
bcc	8	1	$3^{1/2}\pi$	0.247	0.709	$3\pi 3^{1/2}$
fcc	12	$2^{-1/2}$	$4(2^{1/2})\pi/3$	0.237	0.713	$4\pi 2^{1/2}$

In the theory of magnetic models with short-range interactions the Fourier-transform of the potential can be determined *exactly*; in some cases even the analytic expression for the lattice Green function can be found. However, in the theory of structural phase transitions, the problem is much more complicated. In that case we have a long-range potential, presumably with an anisotropic dipole-dipole interaction. The exact analytic evaluation of the Fourier-transform of this potential is not possible; so is the corresponding calculation of the lattice Green function. Major simplifications are needed if progress is to be made in this respect.

Thus, having demonstrated qualitatively the effects of the local-field quadratic fluctuations, we shall limit ourselves to the *long-wavelength* approximation. Another simplification will be the restriction to monoaxial crystals. The archetype of such ferroelectrics is threeglycinsulphate (TGS). This ferroelectric of the order-disorder type has been studied carefully both experimentally and theoretically; it has been shown that it exhibits a critical phenomenon in the vicinity of T_c [6]. Accordingly, it is reasonable to assume that monoaxial crystals of the TGS type can be described by the present model.

Unfortunately, however, the long-wavelength approximation of $U(\mathbf{k})$ cannot lead to a closed expression; so we are forced to consider only the expansion of the lattice Green function near T_c as the most interesting region in the whole temperature range.

In the long-wavelength approximation for the monoaxial ferroelectric, then, the potential $U(\mathbf{k})$ has the form [7]

$$U(k_x, k_y, k_z) = U(0) - \alpha k^2 + \beta k_z^2 - \gamma\left(\frac{k_z^2}{k^2}\right) + O(k_z^4, k^4). \tag{36}$$

The expansion coefficients depend on the structure; these are given for some types of lattices in Table I [8]. The corresponding expansion for the Green function near the critical point has the form (see the Appendix):

$$G(\varepsilon) = G(0) - \sum_{n=0}^{\infty} a_n \varepsilon^{n+2}\ln(\varepsilon) + \sum_{n=1}^{\infty} b_n \varepsilon^n;$$

$$\varepsilon \equiv (1-p)^{1/2}. \tag{37}$$

Having obtained the analytic expression for the lattice Green function near T_c, one can consider the corresponding specific-heat behavior. The specific heat C_h is defined by

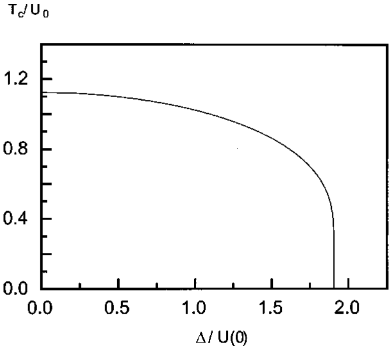

FIG. 1. The dependence of the critical temperature $T_c/U(0)$ of the fcc lattice on the tunneling parameter $\overline{\Delta}=\Delta/U(0)$. The maximum value of $T_c/U(0)$ at $\overline{\Delta}=0$ equals 1.1230; $T_c=0$ at $\overline{\Delta}=1.905$.

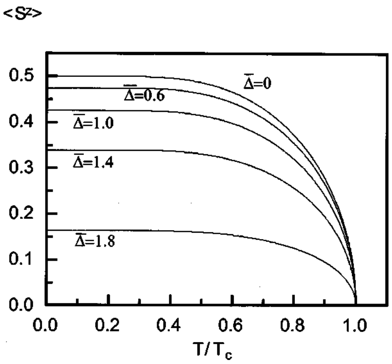

FIG. 3. The dependence of the spontaneous polarization ($\propto\langle S^x\rangle$) of the fcc lattice on the reduced temperature for some values of $\overline{\Delta}$.

$$C_h=\frac{1}{N}\frac{d\langle H\rangle}{dT},\tag{38}$$

the average energy $\langle H\rangle$ being given by Eq. (24) and the temperature T by Eq. (22). In the paraelectric phase ($\langle S\rangle=0$):

$$\begin{aligned}C_h&=\frac{1}{N}\frac{(d\langle H\rangle/dp)}{dT/dp}\\&=\frac{p\Omega^2(p)}{T(p)}\\&\quad\times\left[\frac{[\Omega^2(p)-2\Delta^2]/U(0)-[U(0)/4p][dG(p)/dp]}{R(p)\{\Delta^2+[U^2(0)/8p][dG(p)/dp]\}-\Omega^2(p)}\right],\end{aligned}\tag{39}$$

$$R(p)=1-\frac{4pT(p)}{U(0)\{2-G(p)-[2p\Delta/U(0)^2]\}}.\tag{40}$$

To first approximation we can put in Eq. (39) $p=1$, since all the quantities in this expression are finite at the critical point, except the derivative $dG(p)/dp$. Expansion (37) yields

$$\frac{dG(p)}{dp}\cong\left(\frac{a_0}{2}-b_2\right)-\frac{b_1}{2\varepsilon}-a_0\ln(\varepsilon),\tag{41}$$

which is divergent at the critical point. However, *in the limit as* $p\rightarrow1$, we find that the specific heat at the transition point remains finite with the value

$$C_h=-\frac{2\Omega^2(1)}{R(1)U(0)T_c}.\tag{42}$$

Clearly, it is impossible to find an expansion for the specific heat in terms of the temperature. This is related to the fact that the expansion of the temperature deviation $\tau(\varepsilon)\equiv T(\varepsilon)/T_c-1$ has the form

$$\tau(\varepsilon)\approx u_1\varepsilon+u_2\varepsilon\ln(\varepsilon)+O(\varepsilon^2),\tag{43}$$

which does not have an inverse $\varepsilon(\tau)$. The explicit forms of the coefficients u_1 and u_2 are somewhat cumbersome and are not given here.

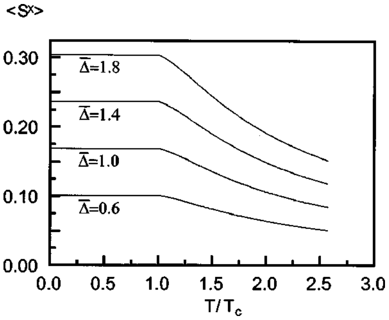

FIG. 2. The dependence of $\langle S^x\rangle$ for the fcc lattice on T/T_c for some values of $\overline{\Delta}$.

Similarly, it can be readily shown that to the left of the critical point the specific heat also remains finite with the same value as Eq. (42). Thus, *the* SFA *predicts the absence of the specific-heat jump at the critical point with long-range dipole-dipole forces*.

The values of the lattice Green function can be determined for the whole range of the parameter $p\in[0,1]$ only numerically. To this end we use

$$G(p)=\frac{v_a}{(2\pi)^3}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\frac{d^3k}{1-pU(\mathbf{k})/U(0)},\tag{44}$$

where the integration runs over the main Brillouin zone, $U(\mathbf{k})$ being given by Eq. (36). The temperature dependence of thermodynamic quantities can then be readily determined in the present model.

Figure 1 gives the dependence of the critical temperature $T_c/U(0)$ on the tunnel splitting $\overline{\Delta}\equiv\Delta/U(0)$. In Fig. 2, $\langle S^x\rangle$ is plotted as a function of T/T_c. As already pointed out, $\langle S^x\rangle$ remains constant for the temperature range $T/T_c\leqslant1$. Figure 3 shows the spontaneous polarization ($\propto\langle S^z\rangle$) as a function of T/T_c for several values of $\overline{\Delta}$. The tendency of $\langle S^z\rangle$ decreasing with increasing Δ is evident. In Fig. 4, the temperature dependence of the specific heat $C_h(T/T_c)$ is given for various values of $\overline{\Delta}$. It is interesting to note this nonstandard behavior of C_h, especially in the interval $\overline{\Delta}\in[1.5,1.9]$, the local maximum appearing in the temperature range $T/T_c\geqslant1$. This behavior can only be ascribed to the long-range anisotropic dipole forces.

Two remarks are in order here. The first is that, near the critical point, C_h behaves almost logarithmically—a conse-

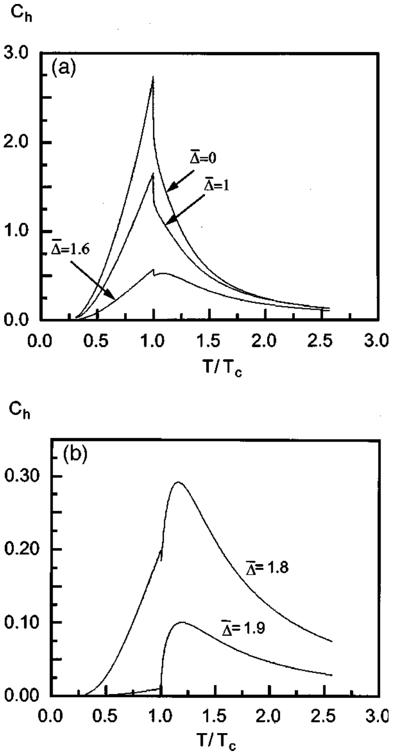

FIG. 4. The dependence of the dimensionless specific heat $C_h/U(0)$ of the fcc lattice on T/T_c for some values of $\bar{\Delta}$.

quence of the *approximate* inversion of Eq. (43). This agrees *qualitatively* with experimental observations [9]. However, for a detailed comparison with experiment, a separate investigation is called for. The second remark is that Figs. 4(a) and 4(b) demonstrate clearly the competition between the singular component of C_h (predominating at small Δ values) and the regular contribution (predominantly at large Δ values; $\bar{\Delta}\rightarrow\bar{\Delta}_c\approx 1.9$, where the order parameter $\langle S^z\rangle$ is close to zero). This effect has been known for some time in the theory of the anisotropic Ising model [10]; in Ref. [9] it was taken into account qualitatively by adding a constant to the fitting expression for C_h.

The pair CF is defined by Eq. (17) in terms of $p(T)$, the relative distance R and $U(\mathbf{k})$. It is interesting to compare the asymptotic behavior ($R\rightarrow\infty$) of this function to the well-known Ornstein-Zernike result. The symmetry of $U(\mathbf{k})$ defines the extreme anisotropy of the correlations involved. It therefore makes sense to consider the behavior of this function as $R\rightarrow\infty$ along the axis of anisotropy (longitudinal correlations) as well as perpendicular to the axis (transverse correlations).

Using Eqs. (17) and (36), we can write the following expression for $\langle S_f^z S_{f+R}^z\rangle$:

$$\langle S_f^z S_{f+R}^z\rangle_c = \frac{1-\langle S^z\rangle^2}{4N} \times \sum_k \frac{\exp(i\mathbf{k}\cdot\mathbf{R})}{1-p[1-\alpha k^2+\beta k_z^2-\gamma(k_z/k)^2]/U(O)}, \tag{45}$$

the long-wavelength contributions dominating. Replacing the summation by an integration, we conclude that this problem is reduced to the investigation of the following integral (for longitudinal correlations):

$$\langle S_f^z S_{f+R}^z\rangle_c = \frac{1-\langle S^z\rangle^2}{32\pi^3} \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\exp(iRz)\,dx\,dy\,dz}{1-p[1-\alpha r^2+\beta z^2-\gamma(z/r)^2]}; \tag{46}$$

$r^2\equiv x^2+y^2+z^2$. A similar expression for the transverse CF can be obtained, but with exp(*iRx*) replacing exp(*iRz*). Similar integrals are considered in Ref. [11].

It is concluded that the asymptotic expansion of the *longitudinal* CF consists of two components

$$\langle S_f^z S_{f+R}^z\rangle = \langle S_f^x S_{f+R}^z\rangle_1 + \langle S_f^z S_{f+R}^z\rangle_{\mathrm{osc}}. \tag{47}$$

The first two terms of the first component are of the form

$$\langle S_f^z S_{f+R}^z\rangle_1 \underset{R\rightarrow\infty}{\approx} \frac{1}{4}\left(\frac{A(p)}{R^3}+\frac{B(p)}{R^5}\right). \tag{48}$$

In turn, the Ornstein-Zernike theory for isotropic potentials *predicts* the asymptotic form $(1/R)\exp[-R/\chi^{1/2}]$ (χ being the homogeneous part of the static susceptibility). The second component defines the oscillating part of the longitudinal correlation function

$$\langle S_f^z S_{f+R}^z\rangle_{\mathrm{osc}} \underset{R\rightarrow\infty}{\approx} \frac{1}{4}\left(C(\rho)\frac{\cos(\xi R)}{\xi R}-D(p)\frac{\sin(\xi R)}{(\xi R)^2}\right), \tag{49}$$

where $\xi\equiv\sqrt{(1-p)/(1-p+\gamma p)}$.

A similar result applies to *transverse* correlations. In that case, the first two terms of the first component read

$$\langle S_f^z S_{f+R}^z\rangle_1 \underset{R\rightarrow\infty}{\approx} \frac{1}{4}\left(\frac{M(p)}{R^3}+\frac{N(p)}{R^5}\right), \tag{50}$$

At the critical point ($p=1$), the first two terms have the asymptotic form

$$\langle S_f^z S_{f+R}^z\rangle \underset{R\rightarrow\infty}{\approx} \frac{1}{8\pi\alpha R}-\frac{(3\alpha-\beta)}{8\pi\alpha\sqrt{\alpha\gamma}R^2} \quad \text{(longitudinal part of the CF)}. \tag{51}$$

This behavior remains valid for the temperature range $T \leqslant T_c$. The above expression is proportional to $(1-\langle S^z\rangle^2)$, because in the ferroelectric phase $p=1$ and the spontaneous polarization is the order parameter.

The dependence of the CFs on T and R can be found numerically. This has been undertaken for the face-centered cubic lattice in the long-wavelength approximation for $U(\mathbf{k})$. The results are given in Figs. 5–8.

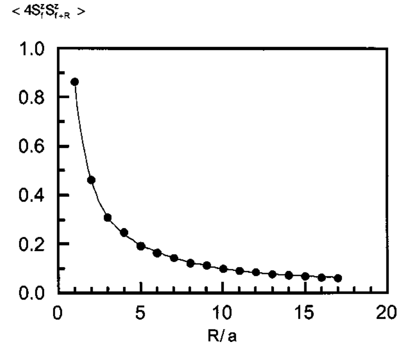

FIG. 5. The dependence on the relative distance R of the *longitudinal* CF for the sc lattice at the critical point.

IV. CONCLUSION

In this work we have suggested an approximation (the SFA) for calculating the thermodynamic characteristics of the proton model with tunneling. Our method can undoubtedly be generalized for more complex spin Hamiltonians with an arbitrary interparticle interaction.

The *physical meaning* of this approximation is the following. The true quantum-mechanical spectrum of the operator σ_f [defined by Eq. (3)] is replaced with a distribution. As a first step, we have calculated *self-consistently* the *quadratic fluctuations* of σ_f^z which lead to the approximate but *linearized* DLREs [Eqs. (8) and (9)]; these equations can, in turn, be solved by well-known mathematical methods. The SFA has allowed us to consider the complete thermodynamics of the model; specifically, we have obtained the analytic expressions for the spontaneous polarization, the specific heat, the pair CF, and the static susceptibility of the order-disorder ferroelectric. We have then determined numerically the main characteristics of the system versus the reduced temperature T/T_c and the relative distance R/a (a being the lattice constant). The logarithmic behavior of the specific heat to the right side of the critical point has been predicted; it is a consequence of the long-range and axial anisotropy of the dipole-dipole interaction. The SFA has enabled us to explore the asymptotics of the CFs at large interparticle separations. In fact, our present approach can be regarded as a basic theory for determining all integral characteristics of the transverse Ising model. No other systematic microscopic approaches exist except the mean-field approximation and renormalization group theory [6]. Our results are essentially generalizations of those obtained within that approximation.

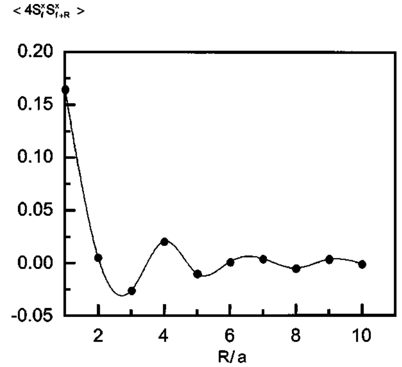

FIG. 6. The dependence on the R/a of the *transverse* CF for the sc lattice at the critical point.

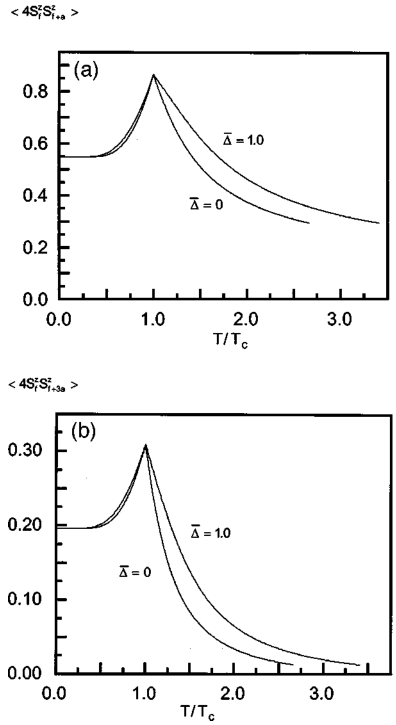

FIG. 7. The dependence on T/T_c of the *longitudinal* CFs (a) $\langle 4S_f^z S_{f+a}^z \rangle$ and (b) $\langle 4S_f^z S_{f+3a}^z \rangle$, for the sc lattice for two values of $\bar{\Delta}$.

The main deficiency of the SFA is that it cannot take into account the *dynamics* of the local fields (the operator σ_f is, in effect, the approximate integral of the motion). This is

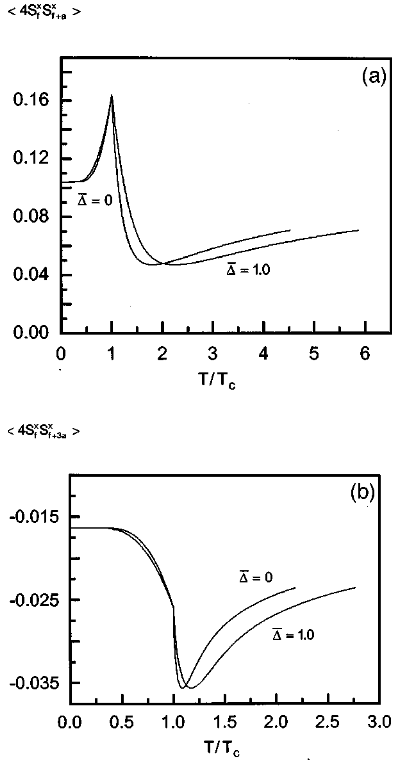

FIG. 8. The dependence on T/T_c of the *transverse* CFs (a) $\langle 4S_f^x S_{f+a}^x \rangle$ and (b) $\langle 4S_f^x S_{f+3a} \rangle$, for the sc lattice for two values of $\bar{\Delta}$.

precisely why we have qualified this approach as the *static* fluctuation approximation. However, this approximation can boast the following features:

(1) Its simplicity and transparent physical content. In addition, it can readily be applied to a wide class of physical systems with an arbitrary interparticle potential and an arbitrary integral dimension.

(2) Critical phenomena in the system can be described by invoking the controllable approximation (5) and nothing else. In particular, it is not necessary to develop any specific methods for phase-transition phenomena; the critical behavior is obtained *automatically* for some value of the control parameter (in our case, $p=1$). The possibility to calculate CFs of *any order* by means of DLREs distinguishes the SFA from other approaches based on some modification or another of the mean-field approximation.

(3) The SFA gives reasonable accuracy in estimating T_c and other thermodynamic parameters for a wide range of temperature and external fields.

(4) The *principal difference* between the exact solution and the SFA is the following. The attempt to obtain the exact solution leads to DLREs containing higher order (not only quadratic) fluctuations of the local field (infinite in general). It yields a system of nonlinear difference equations; analytic methods of solution are *not known*. In the SFA we are forced to consider only quadratic fluctuations of the local field, higher-order fluctuations being incorporated only in some average sense [see Eq. (35)]. The DLREs obtained in this case are *linear and self-consistent*; they have enabled us to use well-known mathematical methods to determine the complete thermodynamic solutions.

ACKNOWLEDGMENTS

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APPENDIX: BEHAVIOR OF THE LATTICE GREEN FUNCTION FOR THE ANISOTROPIC DIPOLE-DIPOLE POTENTIAL NEAR THE CRITICAL POINT

The investigation of the critical behavior of the model considered requires the evaluation of the lattice Green function

$$G(p)=\frac{v_a}{(2\pi)^3}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\frac{d^3k}{1-pU(\mathbf{k})/U(0)}, \tag{A1}$$

v_a being an elementary volume of the reciprocal lattice and $U(\mathbf{k})$ the Fourier transform of the interaction potential. In the long-wavelength approximation for the monoaxial ferroelectric, $U(\mathbf{k})$ has the form [7]

$$U(k_x,k_y,k_z)=U(0)-\alpha k^2+\beta k_z^2-\gamma\left(\frac{k_z^2}{k^2}\right)+O(k_z^4,k^4), \tag{A2}$$

where α,β,γ are the expansion coefficients depending on the dimension of the lattice (for some types of lattices these are given in Table I).

As can be seen from Eq. (A1), the integration runs over the main Brillouin zone representing a cube with side $2\pi/a$. To proceed further the true first zone is replaced with a sphere whose radius Q given by $4\pi Q^3/3=(2\pi)^3$. $G(p)$ will then assume the form

$$G(p)=\frac{v_a}{2\pi^2}\int_0^Q k^2dk\int_0^1 dx\left[p(\gamma-\beta k^2)\left(x^2+\frac{1-p+p\alpha k^2}{p(\gamma-\beta k^2)}\right)\right]^{-1}, \tag{A3}$$

$x\equiv\cos\theta$. Integration over the angular variable becomes trivial and we get

$$G(p)=\frac{v_a}{2\pi^2}\int_0^Q k^2dx\,\frac{a\tan\sqrt{p(\gamma-\beta k^2)/(1-p+p\alpha k^2)}}{\sqrt{p(\gamma-\beta k^2)/(1-p+p\alpha k^2)}}$$

$$=\frac{v_a}{4\pi^2p\sqrt{\alpha}}\int_0^{Q^2}\sqrt{\frac{k}{k+\lambda^2}}\,\Psi(k,\lambda)dk. \tag{A4}$$

Here

$$\lambda\equiv[(1-p)/\alpha p]^{1/2}\cong\varepsilon/\alpha^{1/2};$$

$$\Psi(k,\lambda)=\frac{a\tan\sqrt{(\gamma-\beta k)/\alpha(k+\lambda^2)}}{\sqrt{(\gamma-\beta k^2}}. \tag{A5}$$

The function $\Psi(k,\lambda)$ is continuous in the region $\{[0,Q^2]\times[0,\lambda_0]\},[\lambda_0>0,\ (\gamma/\beta>Q^2)]$, but differentiable only in the region $\{[0,Q^2]\times(0,\lambda_0)\}$ because its derivative $\Psi'(0,\lambda)\propto 1/\lambda$. A Taylor-series expansion is therefore out of the question at this stage. To circumvent this difficulty we introduce the variable $t\equiv\sqrt{(\lambda^2+k)[1-(\beta/\gamma)k]}$. After some transformations we obtain the following expression for the integral (A4):

$$G(p)=\frac{v_a}{2\pi^2p\sqrt{\alpha\gamma}}\int_\lambda^B\frac{\sqrt{t^2-\lambda^2}}{[1+(\beta/\gamma)t^2]^{3/2}}\,a\tan\left(\sqrt{\frac{\alpha}{\gamma}}t\right)dt$$

$$\cong\frac{v_a}{2\pi^2\sqrt{\alpha\gamma}}\int_0^B\sqrt{t(t+2\lambda)}\;\overline{\Psi}(t,\lambda)dt, \tag{A6}$$

where

$$B\equiv\sqrt{\frac{Q^2+\lambda^2}{1-(\beta/\gamma)Q^2}}\approx\frac{1}{\sqrt{1-(\beta/\gamma)}}; \tag{A7}$$

$$\overline{\Psi}(t,\lambda)=\frac{a\tan[(t+\lambda)\sqrt{\alpha/\gamma}]}{[1+(\beta/\gamma)(t+\lambda)^2]^{3/2}}. \tag{A8}$$

The function $\overline{\Psi}'(t,\lambda)\in\{[0,B]\times[0,\lambda_0]\}$; so it *can* be expanded into a Taylor series over t:

$$\overline{\Psi}(t,\lambda)=\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{\partial^m\overline{\Psi}(t,\lambda)}{\partial t^m}\right)_{t=0}t^m\equiv\sum_{m=0}^{\infty}c_m(\lambda)t^m. \tag{A9}$$

Inserting this expansion into Eq. (A6), we find

$$G(\lambda)\cong\frac{v_a}{2\pi^2\sqrt{\alpha\gamma}}\sum_{m=0}^{\infty}c_m(\lambda)\int_0^B t^{m+1/2}\sqrt{1+2\lambda}dt$$

$$=\frac{v_a}{2\pi^2\sqrt{\alpha\gamma}}\sum_{m=0}^{\infty}c_m(\lambda)\Phi\left(\frac{1}{2};m+\frac{3}{2};2\lambda\right),\quad\text{(A10)}$$

The asymptotic expansion of the integral

$$\lim_{\varepsilon\to 0}\Phi(\sigma,\delta,\varepsilon)=\int_0^L t^{\delta-1}(t+\varepsilon)^{\sigma}dt,\qquad\text{(A11)}$$

is standard. For the case $\sigma+\delta$ ($\equiv$ an integer) this has the following form:

$$\Phi(\sigma,\delta,\varepsilon)=\varepsilon^N\left[\binom{N}{\sigma}\ln\left(\frac{L}{\varepsilon}\right)+(-1)^{N+1}\frac{\Gamma(N-\sigma+\rho)}{\Gamma(-\sigma)\Gamma(N+1+\rho)}\times[\psi(N-\sigma)-\psi(N+1)]\right]+\sum_{n=0,(\neq N)}\frac{L^{N-n}}{N-n}\varepsilon^n,\qquad\text{(A12)}$$

$\Gamma(x)$ being the gamma function and $\psi(x)$ the digamma function. In our case $\sigma\equiv\frac{1}{2}$, $\delta\equiv m+\frac{3}{2}$, $N\equiv m+2$, $L\equiv B$, $\varepsilon\equiv 2\lambda$. Thus,

$$G(\lambda)=\frac{v_a}{2\pi^2\sqrt{\alpha\gamma}}\sum_{m=0}^{\infty}c_m(\lambda)\left\{(2\lambda)^{m+2}\frac{\Gamma(m+3/2)}{\sqrt{\pi}(m+2)!}\times\left[\ln\left(\frac{B}{2\lambda}\right)+(-1)^m\frac{\psi(m+3/2)-\psi(m+1)}{2}\right]+\sum_{n=0,\neq m+2}^{\infty}\frac{B^{m+2-n}}{m+2-n}(2\lambda)^n\right\}.\qquad\text{(A13)}$$

Expanding the coefficients $c_m(\lambda)$ in a Taylor series

$$c_m(\lambda)=\sum_{l=0}^{\infty}\frac{c_m^{(l)}}{l!}\lambda^1,\qquad\text{(A14)}$$

we finally obtain

$$G(\varepsilon)=G(0)-\sum_{n=0}^{\infty}a_n\varepsilon^{n+2}\ln\varepsilon+\sum_{n=1}^{\infty}b_n\varepsilon^n,\qquad\text{(A15)}$$

where

$$G(0)=\frac{v_a}{\pi^2\sqrt{\alpha\gamma}}\sum_{m=0}^{\infty}\frac{c_m(0)B^{m+2}}{m+2},\quad a_0\equiv\frac{v_a}{4\pi\sqrt{\alpha\gamma}}.\qquad\text{(A16)}$$

The remaining coefficients a_0,b_n $(n=1,2,\ldots)$ are somewhat cumbersome and will not be given here.

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