THE 16-VERTEX MODEL OF A FERROELECTRIC WITH PROTON TUNNELING

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Thermodynamics of the 1D ferroelectric model with proton tunneling has been reduced to the calculation of the grand partition function of the 1D Ising model of spin $S = 1$ in the transverse field $\Gamma$. This allows the behavior of the initial model to be calculated in the vicinity of its thermodynamic anomaly. In the second order, the dependence of the free energy on temperature and the tunneling parameter $\Gamma$ was found.

1. Introduction

It is known [1, 2] that in ferroelectrics with proton tunneling, quantum effects dramatically change the thermodynamic picture of the phase transitions from proton-disordered to proton-ordered states. The standard theoretical description of these phenomena [1, 2] uses the Ising model for spins $S = 1/2$ in the "transverse field $\Gamma$," where $\Gamma$ is the energy of the tunnel splitting. This model, however, does not account for two essential features which define the character of phase transitions in ferroelectrics: the geometry of local proton complexes (LC) and the electroneutrality principle for LC configurations, known as "Pauling's ice rule" [3]. It is desirable when considering quantum effects in ferroelectrics to have a model that accounts for both of these features.

The simplest model satisfying these conditions was considered in [4]. This model is depicted by the one-dimensional sequence of $N$ sites connected in a chain by bonds. Each pair $((i - 1), i)$ of sites is connected by the $i$th pair $((i, 1), (i, 2))$ of bonds. The sites with four adjacent bonds form a geometrical vertex. One proton is placed on each bond and a proton on a bond can tunnel between two localized states. At the $i$th pair of bonds, these localized states are described by the pair of variables $(\sigma_{i,1}^{t}, \sigma_{i,2}^{t})$, where $\sigma_{i,1}^{t}$ and $\sigma_{i,2}^{t}$ are the Pauli matrices. The $i$th geometrical vertex has $2^4$ proton configurations, each of which we call a vertex (without the term "geometrical"). The energies of the vertices are described in terms of the spin variables as follows:

$$H_0(i) = -v_1[\sigma_{i,1}^{t}\sigma_{i+1,1}^{t} + \sigma_{i,2}^{t}\sigma_{i+1,2}^{t}] - \frac{1}{2}v_2[\sigma_{i,1}^{t}\sigma_{i,2}^{t} + \sigma_{i+1,1}^{t}\sigma_{i+1,2}^{t}] - v_3[\sigma_{i,1}^{t}\sigma_{i+1,2}^{t} + \sigma_{i+1,1}^{t}\sigma_{i,2}^{t}].$$

(1)

In addition, the term "tunnel splitting" is associated with each $i$th pair of bonds $((i, 1), (i, 2))$,

$$v(i) = \left(\frac{\Gamma}{2}\right)[\sigma_{i,1}^{t} + \sigma_{i,2}^{t}].$$

(2)

The energy of vertex (1) can have five values $w_i$ ($i = 1, 2, \ldots, 5$). The energies $w_1$, $w_2$, $w_3$ correspond to the six neutral vertices consisting of all possible positions of two protons on the four bonds of the vertex. The three parameters in model (1) are defined by the three vertex energies

$$v_1 = -\frac{1}{4}(w_1 + w_3), \quad v_2 = \frac{1}{2}(w_1 + w_2), \quad v_3 = -\frac{1}{4}(w_2 + w_3).$$

(3)
The energies of the other vertices have the following values: 8 one-fold charged vertices have the energies \( w_4 = 0 \) and 2 two-fold charged vertices have the energies \( w_5 = -w - \frac{3}{4}(w_2 + w_3) \). In all that follows, we investigate only the special case \( w_1 = w_2 = -w, \ w_3 = -w - \epsilon_0, \) and \( 0 < \epsilon_0 < w \). Here the energy \( w \) plays the role of the Coulomb gap between the energies of the charged and neutral vertices [4]. The energy \( \epsilon_0 \) separates the energies \( w_3 \) of the neutral polarized vertices from the energies \( w_1 = w_2 \) of the neutral nonpolarized vertices.

The Hamiltonian of the considered model is found by the summation of expressions (1), (2) over \( i \):

\[
H_N = H_N^0 + V_N = 2w \sum_{i=1}^{N} \left[ (S_i^z)^2 - (1 + \varepsilon) S_i^x S_i^z - g S_i^z \right] - Nw, \tag{4}
\]

where \( \varepsilon = \epsilon_0/2w, \ g = \Gamma/w, \) and

\[
S_i^\alpha = \frac{1}{2} (\sigma_{i,1}^\alpha + \sigma_{i,2}^\alpha), \quad i = 1, 2, \ldots, N, \quad \alpha = x, z; \quad S_{N+1}^z = 0. \tag{5}
\]

The conditions \( S_{N+1}^z = 0 \) are called the free-end conditions and all Hamiltonians considered below obey these conditions. Operators \( S_i^\alpha \) act in the four-dimensional spaces \( X_i \) \( (i = 1, 2, \ldots, N) \). Each \( X_i \) can be broken into the direct sum of one-dimensional (\( X_i^0 \)) and three-dimensional (\( X_i^1 \)) subspaces,

\[
X_i = X_i^0 + X_i^1. \tag{6}
\]

On the subspaces \( X_i^0 \) and \( X_i^1 \), the irreducible representations of the Lie algebra of the spin operators with the weights \( S = 0 \) and \( S = 1 \) are realized. Model (4) was considered in the classical case of \( g = 0 \) in [5].

In the infinite Coulomb gap limit, \( w \gg \epsilon_0, \ \epsilon_0 \sim T \), configurations of the neutral vertices form an autonomous thermodynamic system. This system has the first type of phase transition from the nonpolarized high-temperature state to the polarized low-temperature state at the temperature \( T_c = \epsilon_0/\log 2 \). Accounting for the finite \( w \)-effects smears this phase transition into the region of the thermodynamic anomaly in the vicinity of \( T_c \) [5]. In [4], the tunneling influence on the critical temperature \( T_c \) was considered using operator perturbation theory techniques [6]. The influence of tunneling on the form of the thermodynamic anomaly was beyond the scope of the methods of [4]. Here, we are interested in thermodynamic behavior of model (4) in the vicinity of its thermodynamic anomaly, \( T \sim T_c \), for the conditions \( \varepsilon < 1, \ g < 1 \). Because of the sharp change in the thermodynamic characteristics in this temperature region, it is difficult to use perturbation theory or computer methods for the investigation. Our approach consists of the reduction of model (4) to the 1D Ising problem of spins \( S = 1 \) in a transverse field. The advantage of this approach is that the reduced model has no thermodynamic anomalies and, therefore, is accessible for investigations by analytic or computer methods. The Hamiltonian \( H_N^1 = H_N^0 + V_N^1 \) of the reduced model has the form (4), as the initial model, but now the symbols \( S_i^z, S_i^x \) mean the operators acting in the \( X_i^1 \) subspaces of decomposition (6).

The paper is organized as follows. In Sec. 2, the above-mentioned reduction technique is developed. In Sec. 3, the reduction technique of Sec. 2 and thermodynamic perturbation theory [7] are applied to the investigation of the free energy of the 1D ferroelectric model (4). Our conclusions are given in Sec. 4.

### 2. The reduction technique

The Hamiltonians \( H_N \) and \( H_N^1 \) act respectively in the spaces

\[
\overline{X}_N = \bigotimes_{i=1}^{N} X_i, \quad \overline{X}_N^1 = \bigotimes_{i=1}^{N} X_i^1. \tag{7}
\]