



# Three-dimensional Ising model of polarity formation in molecular crystals



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## ARTICLE INFO

### Article history:

Received 16 February 2017

Available online 10 May 2017

### Keywords:

Ising model

Symmetry breaking

Polarity formation

Molecular crystals

## ABSTRACT

Polarity formation in a three-dimensional array of molecules is described as a symmetry breaking effect of a generalized Ising Hamiltonian. Geometrical constraints in conjunction with asymmetric multipole interactions are able to break the spin flip symmetry generating a non-vanishing average local polarization.

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## 1. Introduction

In the attempt to describe ferromagnetism W. Lenz in 1920 argued: “atoms are dipoles which flip between two positions” [1]. Based on this intuition he introduced the following model, known as the Ising model. At each site  $i$  of a lattice a variable  $S_i$  which can only assume value 1 or  $-1$  is defined. The interactions between the  $\{S_i\}$  are restricted to the nearest neighboring sites only, with a coupling term  $J$ , yielding the legendary formula for the internal energy of the system

$$H = -J \sum_{(i,j)} S_i S_j. \quad (1)$$

Even if the early Lenz's dipole assumption is incorrect it caught the core ingredients for a theoretical approach to ferromagnetism. A few years later, with the discovery of the spin, the Ising model gained full consistency, its power was proved beyond the very ferromagnetism becoming a fundamental model in statistical mechanics [2]. Its strength is definitely in its simplicity, for instance in its ability to describe the building up of long range correlations, typical of the phase transition, by only including short range interactions. Yet, in many respects the simplicity of the Ising model is only apparent and a high degree of complexity arises from the presence of the  $2^N$  with  $N \sim 10^{24}$  possible states. In fact, it is only in the thermodynamic limit that a phase transition can be recovered as the result of the spin flip symmetry breaking in the Hamiltonian Eq. (1) which would otherwise cause a zero ensemble average of the order parameter, i.e. zero spontaneous magnetization [3]. Analogously, it is only in the thermodynamic limit that the analyticity of the free energy is broken at the critical point of the ferromagnetic transition.

The present work is a generalization to three dimensions of our previous work [4], where we have shown that spontaneous polar ordering, experimentally observed in molecular crystals [5–8], can be described by an Ising model in which a symmetry breaking effect occurs due to the simultaneous presence of asymmetrical electrostatic interactions and the breaking of the translational invariance. The former enter the model in a very natural way once we express the coupling

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in a multipole expansion. The latter is of a pure geometric nature and is caused by the boundary conditions. The model is in fact used in a different context from phase transitions, but the “two states” Lenz’s inspiring idea is still present, being now defined by the parity operator (see next section). Notice that now the symmetry breaking, which ensures a non-vanishing polarization, has a significantly different fundamental origin.

## 2. Ising Hamiltonian in multipole expansion

Let us denote by  $\mathcal{C}$  the set of identical molecules constituting our system. The parity operator  $\Pi$  defines a unitary transformation on  $\mathcal{C}$ . With a slight abuse of notation we will write  $\Pi(M)$ , and  $\Pi^2(M) = M$ , meaning that the operator acts on the coordinate of all the atoms of  $M$ , and will refer to  $\Pi(M)$  and  $\Pi^2(M)$  as the state of the molecule  $M \in \mathcal{C}$ .

In spherical coordinates the parity operator can be represented as

$$\Pi : \begin{pmatrix} r \\ \theta \\ \phi \end{pmatrix} \rightarrow \begin{pmatrix} r \\ \pi - \theta \\ \phi + \pi \end{pmatrix}.$$

Let us consider a distribution of  $N$  point-like charges  $q_i$  at positions  $\mathbf{r}_i$ ,  $i = \{1, \dots, N\}$ . The  $l$ -order multipole moment in spherical coordinates is given by

$$Q_l^m = \sum_i^N q_i R_l^m(\mathbf{r}_i), \quad (2)$$

where  $R_l^m(\mathbf{r}_i)$  are the regular solid harmonics given by

$$R_l^m(r, \theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_l^m(\theta, \phi), \quad (3)$$

where  $Y_l^m$  are the spherical harmonics. Since  $r$  is invariant by parity the  $R_l^m$  and consequently the general quadrupole moment  $Q_l^m$  has the same parity as the  $Y_l^m$ , i.e.  $(-1)^l$

$$\Pi Q_l^m = (-1)^l Q_l^m.$$

Consider two non-overlapping charge distributions centered around  $\mathbf{R}_A$  and  $\mathbf{R}_B$ . The electrostatic energy in multipole expansion can be written as [9,4]:

$$V(R_{AB}) = k_C \sum_{l_A=0}^{\infty} \sum_{l_B=0}^{\infty} (-1)^{l_B} (Q_A)_{l_A} B_{l_A, l_B} (Q_B)_{l_B}, \quad (4)$$

where  $\mathbf{R}_{AB} = \mathbf{R}_B - \mathbf{R}_A$ ,  $k_C$  is the Coulomb constant whose value depends on the units, and where for each  $l_A, l_B \in [0, \infty)$  the  $(2l_A + 1) \times (2l_B + 1)$  matrix  $B_{l_A, l_B}$  is defined by

$$B_{l_A, l_B}^{m_A, m_B}(\mathbf{R}_{AB}) = \left( \frac{2(l_A + l_B)}{2l_A} \right)^{1/2} (-1)^{m_A + m_B} I_{l_A + l_B}^{-(m_A + m_B)}(\mathbf{R}_{AB}) C_{l_A m_A, l_B m_B}^{l_A + l_B} \quad |m_A| \leq l_A, |m_B| \leq l_B, \quad (5)$$

where  $I_l^m(\mathbf{r})$  are the irregular solid harmonics given by

$$I_l^m(r, \theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} \frac{Y_l^m(\theta, \phi)}{r^{l+1}}, \quad (6)$$

$C_{l_A m_A, l_B m_B}^{l_A + l_B}$  are the Clebsch–Gordan coefficients, and  $(Q_A)_l^m$  (resp.  $(Q_B)_l^m$ ) are the multipole moments of distribution  $A$  (resp.  $B$ ). It is easily seen from the symmetry of the Clebsch–Gordan coefficients that  $B_{l_A, l_B}^{m_A, m_B}$  is invariant under a transformation that exchanges  $\{l_A, m_A\}$  with  $\{l_B, m_B\}$

$$B_{l_B, l_A}^{m_B, m_A} = B_{l_A, l_B}^{m_A, m_B}. \quad (7)$$

Consider a three-dimensional lattice of  $N = N_x N_y N_z$  sites having coordinates  $(i, j, k) \in \{1, \dots, N_x\} \times \{1, \dots, N_y\} \times \{1, \dots, N_z\}$  with periodic boundary conditions (PBC) in the  $x$  and  $y$  directions and free boundary conditions (FBC) on the  $z$ . At each lattice point  $(i, j, k)$  is located an identical (microscopic) charge distribution with multipole moments  $q_i^m$  resembling a molecule of  $\mathcal{C}$ . We assume such an arbitrary configuration as a reference state of the system. Any other can be obtained from it by multiple applications of the parity operator. The two states of a molecule can be more conveniently formalized by defining a binary variable,  $S_{i,j,k} = \pm 1$  (often called spin by analogy with magnetism) at each lattice point. A general multipole moment of a molecule  $M \in \mathcal{C}$  in any arbitrary state can, therefore, be expressed as

$$Q_{i,j,k}^{l,m} = S_{i,j,k}^l q^{l,m}, \quad S_{i,j,k} = \pm 1,$$

where  $S_{i,j,k}^l$  denotes the variable  $S_{i,j,k}$  to the power of  $l$ .

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