

Statistical Mechanics of Finite Ice-Rule Ferroelectric Models!

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We study the statistical mechanics of the KDP , F and modified KDP models defined on a 4×4 lattice. Direct fields that are parallel and perpendicular to the crystal axis as well as staggered field are considered. Numerical results on the energy, specific heat, polarization and polarizability are given.

I. INTRODUCTION

THE statistical mechanics of hydrogen-bonded ferroelectric and antiferroelectric models has been a subject of interest in recent years. The modified potassium dihydrogen phosphate ($MKDP$) model of a ferroelectric was solved in 1967.⁽¹⁾ Soon afterward the ice-rule ferroelectric KDP and the antiferroelectric F models also yielded to analysis.⁽²⁾ The detailed thermodynamic properties of these ice-rule models have been discussed in a recent review.⁽³⁾ In the presence of a nonzero external electric field, the partition function of the ice-rule models is expressed in terms of the solution of coupled integral equations. These equations are rather cumbersome to solve numerically. On the other hand, it is possible to carry out numerical studies for small lattices. Such studies are often useful in indicating general behavior of such systems. Thus Katsura et al. discussed the distribution of zeros of the partition function for finite KDP and F models with a vertical field.⁽⁴⁾ Some of their findings led to the discovery of general theorems on the

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(1) F. Y. Wu: Phys. Rev. Letters 18, 605 (1967).

(2) E. H. Lieb: Phys. Rev. Letters 18, 1046; 19, 108 (1967).

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zero distributions.⁵⁾ In a recent publication⁶⁾ we have extended these discussions to include horizontal and staggered fields. In this paper we report further results on numerical studies of the statistical mechanics of the ice-rule models with both direct (horizontal and vertical) and staggered fields. These results are instructive especially in the case of F model which has not been solved with a nonzero staggered field.

II. ENUMERATION OF THE PARTITION FUNCTION

Consider a square lattice with periodic boundary conditions. We place arrows on the lattice edges subject to the condition that there are always two arrows in and two arrows out at a given vertex (the ice rule). Then there are six allowed vertex configurations as shown in Fig. 1. We may characterize the "State" of the crystal by its arrow configuration. To each vertex configuration we assign an energy, and the energy of a state, E , is taken to be the sum of all vertex energies: Then the partition function is defined by

$$Z = \sum_{states} e^{-\beta E}, \quad (1)$$

where $\beta = 1/kT$, k being the Boltzmann constant.

The basic energy assignments appear in Fig. 1. Note that both the KDP and the $MKDP$ models favor a polarized arrow configuration and hence are

	(1)	(2)	(3)	(4)	(5)	(6)
Arrow Configuration						
"Bond" Configuration		+				
KDP	0	0	ϵ	ϵ	ϵ	ϵ
F	ϵ	ϵ	ϵ	ϵ	0	0
MKDP	∞	0	ϵ	ϵ	ϵ	ϵ
Energy due to vertical field	-v	+v	+v	-v	0	0
Energy due to horizontal field	-h	+h	-h	+h	0	0
Energy due to staggered field	0	0	0	0	$-s(\epsilon B)$ $s(\epsilon A)$	$s(\epsilon B)$ $-s(\epsilon A)$

Fig. 1. Vertex energies of the ice-rule ferroelectric models. The staggered field energy varies sign for vertices belonging to sublattices A and B .

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ferroelectric. whereas the F model favors an antiferroelectric ground state. If each arrow denotes a unit. electric dipole, then there are also the electric energies $(\pm h, \pm v)$ due to the presence of a horizontal field h and vertical field v . Finally, to complete the description of the long-range order in the F model, we introduce a fictitious staggered field $\pm s$ which varies its sign from site to site. This completes the description of the ice-rule models. In the KDP and $MKDP$ models with zero field, the ground state has a net polarization in the northeast-southwest direction. This direction plays the role of the crystal axis in three-dimensions.

We have enumerated the partition function (1) for a periodic 4×4 lattice in the following cases:

- (a) KDP model with a direct field $h=v$, i.e., the external field is in the direction of the crystal axis. We denote this case by $KDP(//)$.
- (b) KDP model with a direct field $h=-v$, i.e., the external field is perpendicular to the crystal axis. We denote this case by $KDP(\perp)$.
- (c) F model with a staggered field s .
- (d) $MKDP$ model with a direct field $h=v$, which we denote by $MKDP(//)$.

In the enumeration of the partition functions we found it convenient to use the "bond description" of the states instead of using the arrows. These bond configurations are also shown in Fig. 1. To facilitate our procedures we have used an electronic computer in generating the allowed bond configurations. The partition functions in the cases (a)-(d) take the form

$$Z = \sum_{l,n} g(l, n) y^l (z^n + z^{-n}) \quad (2)$$

in which

$$y = e^{-\beta \epsilon} \quad z = e^{-2\beta v}, \text{ or } z = e^{-\beta s}. \quad (3)$$

and $g(l, n)$ is the number of graphs for given powers l and n . The resulting expressions of the partition functions are: ⁽⁷⁾

$$\begin{aligned} \text{(a) } Z_{KDP(//)} &= (z^{16} + z^{-16}) + 8y^4(z^{12} + z^{-12}) + (136y^8 + 16y^6)(z^8 + z^{-8}) \\ &\quad + (256y^{12} + 496y^{10} + 48y^8)(z^4 + z^{-4}) \\ &\quad + (16y^{16} + 192y^{14} + 680y^{12} + 528y^{10} + 40y^8), \end{aligned} \quad (4)$$

$$\begin{aligned} \text{(b) } Z_{KDP(\perp)} &= y^{16}(z^{16} + z^{-16}) + 8y^{12}(z^{12} + z^{-12}) + (4y^{16} + 48y^{14} \\ &\quad + 124y^{12} + 16y^{10} + 12y^8)(z^8 + z^{-8}) + (248y^{12} + 496y^{10} \\ &\quad + 48y^8 + 8y^4)(z^4 + z^{-4}) + (6y^{16} + 96y^{14} + 432y^{12} \\ &\quad + 496y^{10} + 288y^8 + 32y^6 + 2), \end{aligned} \quad (5)$$

(7) Expressions (4) and (6) for $Z_{KDP(//)}$ and $Z_{F(s)}$ have been given in Ref. 6.

$$(c) \quad Z_{F(s)} = (z^{16} + z^{-16}) + 16y^4(z^{12} + z^{-12}) + (140y^8 + 32y^6) \\ \times (z^8 + z^{-8}) + (256y^{12} + 384y^{10} + 144y^8)(z^4 + z^{-4}) \\ + (256y^{14} + 640y^{12} + 384y^{10} + 152y^8), \quad (6)$$

$$(d) \quad Z_{MDKP(\dots)} = z^{16} + 8y^4z^{12} + 136y^8z^8 + 256^{12}z^4 + 16y^{16}. \quad (7)$$

Note that as a consequence of the imposed periodic boundary conditions, the external field v or s enters the partition function as z^4 . This is due to the conservation of the number of down arrows from row to row.

III. THERMODYNAMIC PROPERTIES

We present in this section results on numerical calculations of the thermodynamic properties of the ice-rule models based on the partition functions (4) to (7). The zero-field internal energy, U , and the specific heat, C , the polarization, P and the polarizability, χ , are given by, respectively,

$$U = -\frac{\partial}{\partial \beta} \ln Z|_{z=1} = \epsilon \left[\frac{y}{Z} \left(\frac{\partial Z}{\partial y} \right) \right]_{z=1}, \quad (8)$$

$$C = \frac{\partial U}{\partial T} = k\beta^2 \left\{ \frac{\epsilon^2 y}{Z^2} \left[Z \frac{\partial Z}{\partial y} + yZ \frac{\partial^2 Z}{\partial y^2} - y \left(\frac{\partial Z}{\partial y} \right)^2 \right] \right\}_{z=1}, \quad (9)$$

$$P = -\frac{z}{Z} \frac{\partial Z}{\partial z}, \quad (10)$$

$$\chi = \beta \frac{z}{Z^2} \left[Z \frac{\partial Z}{\partial z} + zZ \frac{\partial^2 Z}{\partial z^2} - z \left(\frac{\partial Z}{\partial z} \right)^2 \right]. \quad (11)$$

In the case of F model with a staggered field, P and χ represent, respectively, the staggered polarization and the staggered polarizability. We also remark that the polarization P has been normalized so as to yield a maximum value of 16 for completely ordered states.

Plots of energy and specific heat per vertex for the **KDP**, **F** and **MKDP** models with zero field are shown in Figs. 2 and 3. It is of interest to compare our plot with the known values of energy per vertex, u , of an infinite lattice in the infinite temperature limit.⁽⁸⁾

$$\begin{aligned} \mathbf{KDP}: \quad \frac{u}{\epsilon} &= \frac{3}{4} \sqrt{3} - \frac{1}{2\pi} \sqrt{3} - \frac{1}{3} = 0.690040324\dots \\ \mathbf{F} : \quad \frac{u}{\epsilon\epsilon} &= \frac{8}{3} + \frac{1}{\pi} \sqrt{\frac{3}{\pi}} - \frac{3}{2} \sqrt{3} = 0.619919351\dots \\ \mathbf{MKDP}: \quad \frac{u}{\epsilon} &= \frac{2}{3} = 0.66666666\dots \end{aligned} \quad (12)$$

(8) The values for **KDP** and **F** are taken from Ref. 3. The value for **MKDP** is computed from Eq. (10) in F. Y. Wu: Phys. Rev. 168, 539 (1968).

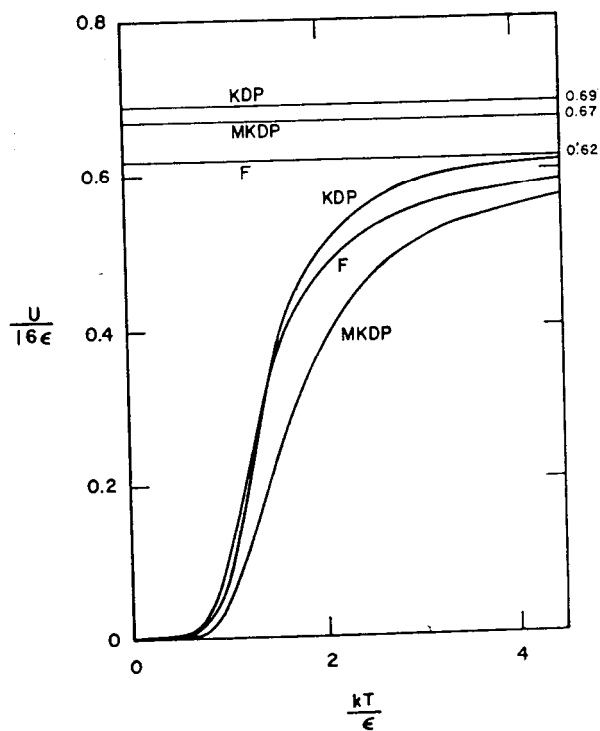


Fig. 2. Internal energy of the 4×4 *KDP*, *F* and *MKDP* lattices. The horizontal lines denote the infinite temperature limits of the energy in infinite lattices.

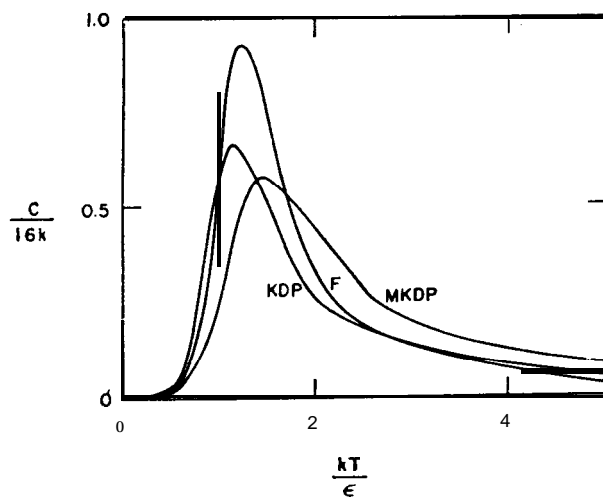


Fig. 3. Specific heat of the 4×4 *KDP*, *F* and *MKDP* lattices.

We see that the energies never exceed the infinite temperature limits of a large lattice. The polarization of *KDP*(//) is shown in Fig. 4 for two different values of the applied field v . Similarly, we show in Fig. 5 the staggered polarization of the *F* model for two different values of the staggered field s . These two sets of curves behave similarly, as one would expect from the fact that the staggered

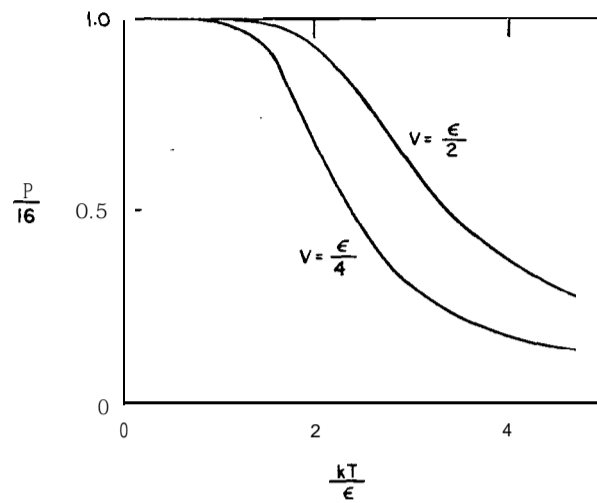


Fig. 4. Polarization of the 4×4 **KDP** lattice with field along the crystal axis ($h=v$).

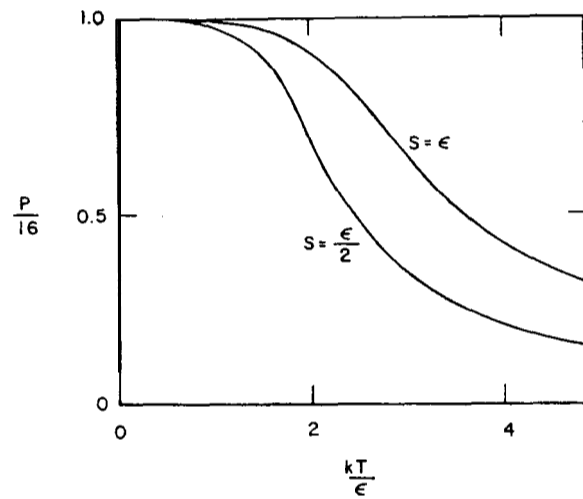


Fig. 5 Staggered polarization of the 4×4 **F** Lattice

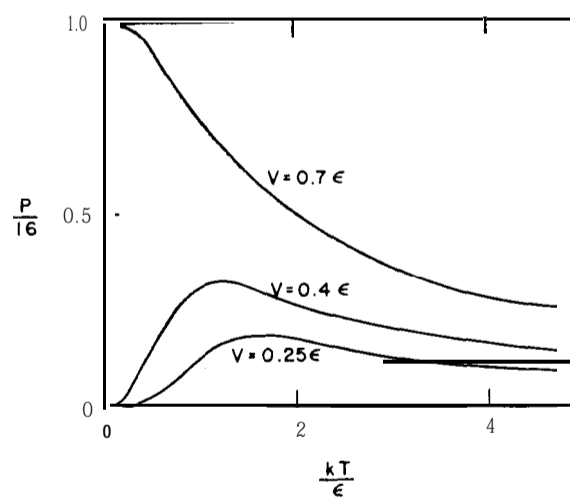


Fig. 6. Polarization of the 4×4 **KDP** lattice with field perpendicular to the crystal axis ($h=-v$).

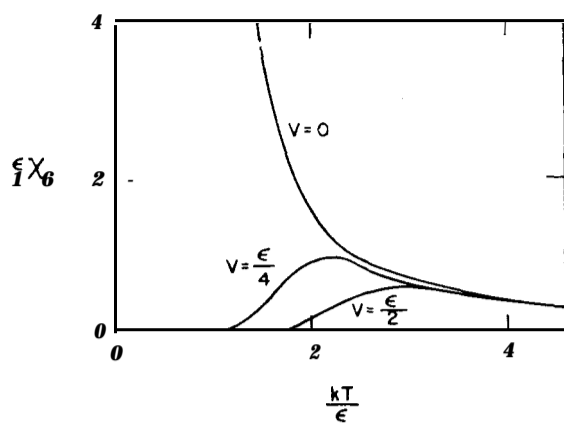


Fig. 7. Polarizability of the 4x4 **KDP** lattice with field along the crystal axis ($h=v$)

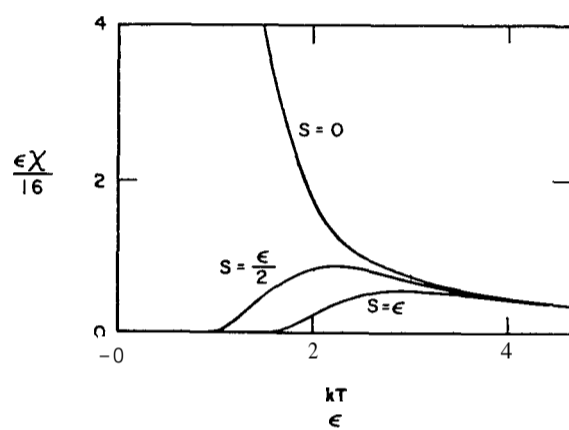


Fig. 8. Staggered polarizability of the 4x4 **F** lattice.

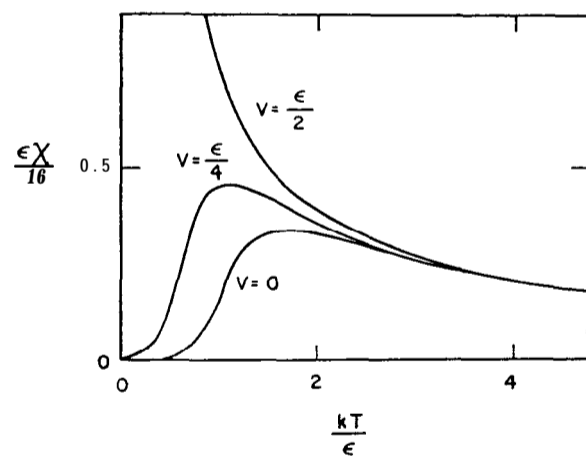


Fig. 9. Polarizability of the 4x4 **KDP** lattice with field perpendicular to the crystal axis ($h=-v$).

field in an antiferroelectric model plays the same role as a direct field in a ferroelectric model. In both Figs. 4 and 5 the polarization saturates at zero temperature and decreases monotonically as temperature rises with the magnitude of polarization increasing with the applied field.

The direct polarization for $KDP(\perp)$ is plotted in Fig. 6 for three different values of v . In the zero temperature limit, the dominant term in $Z_{KDP(\perp)}$ is

$$Z_{KDP(\perp)} \cong y^{16} (z^{16} + z^{-16}) = e^{16\beta(2|v|-\epsilon)}, \text{ if } |v| > \frac{1}{2}\epsilon$$

$$\cong 2, \text{ if } |v| < \frac{1}{2}\epsilon.$$

It follows then that the magnitude of the zero temperature polarization per vertex will be unity if $|v| > \frac{1}{2}\epsilon$, and zero if $|v| \leq \frac{1}{2}\epsilon$. This accounts for the different behavior of the three curves at $T=0$. This difference can also be seen from the energy considerations. At absolute zero the lattice will assume its ground state. For $|v| > \frac{1}{2}\epsilon$ the preferred vertex is the type (4) of Fig. 1, which is polarized in the direction of the external field. Hence we have full polarization. On the other hand, if $|v| < \frac{1}{2}\epsilon$ the favored vertices are of types (1) and (2) which are polarized perpendicular to the applied field. Consequently, there is zero polarization in the field direction.

The polarizability is plotted in Figs. 7, 8 and 9 for the $KDP(\parallel)$, F and $KDP(\perp)$ models, respectively. For $KDP(\parallel)$, the ground state is ordered in the direction of the external field. In fact, the polarization per vertex in the ground state jumps from -1 to $+1$ at $v=0$. Therefore the zero-field ($v=0$) polarizability diverges at absolute zero. Similarly the staggered polarization jumps from -1 to $+1$ at $s=0$ in the F model and the zero-field ($s=0$) staggered polarizability diverges at absolute zero. These results contrast with that of $KDP(\perp)$. In the $KDP(\perp)$ case the discontinuity of the ground state polarization occurs at $v=-h = -\frac{1}{2}\epsilon$. When $v = -h = -\frac{1}{2}\epsilon - 0$, the ground state is composed of vertices of type (1) or (2) which have zero polarization in the direction of the applied field. When $v = -h = -\frac{1}{2}\epsilon + 0$, however, the ground state is composed of vertices of type (4) which has a net polarization in the direction of the field. Therefore the polarization perpendicular to the crystal axis jumps from 0 to 1 at $v = -\frac{1}{2}\epsilon$. As a result, the polarizability diverges at $v = -\frac{1}{2}\epsilon$ at absolute zero.