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[1]I. M. Lifshitz, Usp. Fiz. Nauk 83, 617 (1964) [Sov. Phys. Usp. 7, 549 (1965)].

[2]Yu. Izyumov, Proc. Phys. Soc. (London) 87, 505 (1966).

[3]R. C. Jones, J. Phys. C 4, 2903 (1971).

[4]G. A. Murray, Proc. Phys. Soc. (London) 89, 87 (1966).

[5]E. Frikkee, J. Phys. C 2, 345 (1969).

[6]E. Shiles and D. Hone, Phys. Rev. 5, 1915 (1972).

[7]R. M. White and C. M. Hogan, Phys. Rev. 167, 480 (1968).

[8]N. Kroò and L. Bata, Phys. Letters 24A, 22 (1967).

[9]N. Kroò and L. Pâl, J. Appl. Phys. 39, 453 (1968).

[10]W. J. DeBonte and H. Callen, Phys. Rev. 188, 831 (1969).

[11]S. F. Edwards, Phil. Mag. 3, 1020 (1958).

[12]D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1959) [Sov. Phys. Usp. 3, 320 (1960)].

[13]W. Kohn and J. M. Luttinger, Phys. Rev. 108, 590 (1957).

[14]F. Yonezawa, Progr. Theoret. Phys. (Kyoto) 31, 357 (1964).

[15]E. Shiles, thesis (University of California, Santa Barbara, 1970) (unpublished).

[16]T. Wolfram and J. Callaway, Phys. Rev. 130, 2207 (1963).

[17]D. Hone, H. Callen, and L. R. Walker, Phys. Rev. 144, 283 (1966).

[18]L. Van Hove, Phys. Rev. 95, 1374 (1954).

[19]W. J. L. Buyers, T. M. Holden, E. C. Svensson, R. A. Cowley, and R. W. H. Stevenson, Phys. Rev. Letters 27, 1442 (1971).

[20]D. Hone, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 335.

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Phase Transition in a Sixteen-Vertex Lattice Model*

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We consider a sixteen-vertex ferroelectric model defined on a square lattice and deduce the nature of the phase transition in this model from its equivalence with an Ising model with a nonzero magnetic field. We find that, as the value of a parameter which occurs linearly in the Hamiltonian is varied, the model may exhibit a first-order transition, a second-order transition with an infinite specific heat, or no phase transition.

INTRODUCTION

There has been considerable recent interest in the eight-vertex lattice model which is a generalization of the Ising and ice-rule ferroelectric models of phase transitions.[1] In vew of the unexpected behavior of a variable exponent found to exist in the eight-vertex model,[2] it seems appropriate to investigate a further generalization of these models, the sixteen-vertex model. The sixteen-vertex model can be defined on any lattice of coordination number 4, and encompasses, among others, the eight-vertex model and the Ising model in a nonzero magnetic field as special cases.[1] Very little is known about the behavior of this general lattice model, except in a few special cases in which the model can be shown to be directly equivalent to an Ising model, hence exhibiting the usual Ising-type transition.[3] Any result which leads to different types of phase transition would be very useful and illuminating.

In this paper some new findings are reported in this connection. A certain class of the sixteen-vertex model is considered and the behavior of this model at the transition point is deduced. It is found that, as the value of a parameter which occurs linearly in the Hamiltonian is varied, the model may exhibit a first-order transition, a second-order transition with an infinite specific heat, or no phase transition. It is of interest to note that a first-order transition results and persists in a region in the parameter space. In the potassium-dihydrogen-phosphate (KDP) model of a ferroelectric which also exhibits a first-order transition,[4] the transition becomes a second-order one when an infinitesimal electric field is present.[1]

DEFINITION OF THE MODEL

We first define the sixteen-vertex problem. Consider a lattice of coordination number 4, which has N vertices. Each of the $2N$ lattice edges (assuming periodic boundary conditions) may or may not be covered by a bond. A definite bond covering of the lattice will be called a state so that there are 2^{2N} distinct states. A fixed energy is assigned to each of the $2^4 = 16$ bond configurations that may occur at a vertex, and the energy E of a state is taken to be the sum of all vertex energies. The partition function of the sixteen-vertex model is then

$$Z=\sum e^{-\beta E}\ , \tag{1}$$

where $\beta=1/kT$ and the summation is extended over the 2^{2N} states. This completes the definition of the model, which can also be interpreted as a general ferroelectric model without the ice rule.[1]

The model we propose to consider has the following energy assignment:

$$\begin{aligned}\text{vertex energy} &= n\epsilon \quad \text{for vertices having } n(=0,\ 1,\ 2,\ 3) \text{ bonds}\\ &= a\epsilon \quad \text{for vertices having 4 bonds}\ ,\end{aligned} \tag{2}$$

where a is a variable parameter. Furthermore, we shall restrict our considerations to a square lattice. The key step is that, using a result due to Mermin,[5] one can relate the partition function of this model in the case of a square lattice to that of an Ising model with a nonzero magnetic field. One can then deduce the nature of the phase transition in the present model from the established results of the Ising model. We first summarize the main findings: (i) For $\epsilon>0$ and $a_0<a<0$, where

$$\begin{aligned}a_0&=4-2\ln(18+12\sqrt{2})/\ln(2+2\sqrt{2})\\ &=-0.515033\ldots\ ,\end{aligned} \tag{3}$$

the model exhibits a first-order phase transition with a latent heat. The transition is also characterized by discontinuities in the order parameter and the specific heat. The specific heat does not diverge. (ii) For $\epsilon>0$ and $a=a_0$, the model exhibits a second-order phase transition with an infinite specific heat. Both the energy and the order parameter are continuous. (iii) For $\epsilon>0$, $a\geq 0$ and $\epsilon<0$, $a\leq 4+\delta$ for some positive δ, the model exhibits no phase transition. The regions of no transition can presumably be extended to $\epsilon>0$, $a<a_0$ and $\epsilon<0$, $a>4+\delta$, but we have no rigorous proof in the latter cases. Some of these results can be easily checked. For $a=4$ the model can be alternately described by assigning an energy 2ϵ to each bond. Since a bond may or may not be present on a given lattice edge, the partition function can be trivially summed in this case to yield $Z=(1+e^{-2\beta\epsilon})^{2N}$ which shows no phase transition.[6] This is in agreement with (iii). For $\epsilon<0$ and $a<3$, the vertices with the lowest energy are those with three bonds. The ground state is highly degenerate and, consequently, there can be no phase transition.

DETAILS AND DISCUSSIONS

To deduce the behavior of our model, it is useful to introduce the dual lattice D which is constructed by drawing a perpendicular bisector to each lattice edge. The dual lattice is also a square lattice of N vertices. If on each edge of D we draw a bond whenever the corresponding edge of the original lattice has a bond, our model can be restated as follows: Each edge of D may or may not be covered by a bond. To each bond we associate an energy 2ϵ and to every four bonds forming a square we associate an extra energy $(a-4)\epsilon$. This is then the bar model considered by Mermin.[5] In fact, the partition function (1) is precisely the grand partition function of Mermin's bar model provided that we identify $e^{-2\beta\epsilon}$ as the fugacity z. By considering the system as a mixed two-component model, Mermin showed that the bar model is equivalent to a nearest-neighbor lattice-gas model. Since the latter system is also known to be identical to an Ising model in a nonzero magnetic field,[7] we can therefore relate the partition function (1) to that of an Ising model. The related Ising Hamiltonian

$$\mathcal{H}_{\text{Ising}}=-J\sum\sigma_i\sigma_j-H\sum\sigma_i \tag{4}$$

is also defined on the square lattice. In (4), $-J$ is the nearest-neighbor interaction and $-H$ represents the magnetic energy of a spin. Let $K\equiv\beta J$, $L\equiv\beta H$, and denote the Ising partition function by $Z_{\text{Ising}}(L,\ K)$. Using Mermin's result and the relationship between a lattice gas and an Ising model,[7] we are led to the identity

$$Z=e^{-4N\beta\epsilon}[(e^{(4-a)\beta\epsilon}-1)(1+e^{2\beta\epsilon})]^{N/2}Z_{\text{Ising}}(L,\ K)\ , \tag{5}$$

where

$$\begin{aligned}L&=\ln[(1+e^{2\beta\epsilon})(e^{(4-a)\beta\epsilon}-1)^{-1/2}]\ ,\\ K&=\tfrac{1}{4}\ln(1+e^{2\beta\epsilon})>0\ .\end{aligned} \tag{6}$$

Here $K>0$ implies that the related Ising model is ferromagnetic. Let

$$z=\lim_{N\to\infty}\frac{1}{N}\ln Z\ .$$

Equation (5) leads to

$$z(a,\ \beta)=-4\beta\epsilon+\tfrac{1}{2}\ln[(e^{(4-a)\beta\epsilon}-1)(1+e^{2\beta\epsilon})] +z_{\text{Ising}}(L,\ K)\ . \tag{7}$$

Clearly the analytic properties of z will follow from that of z_{Ising}. It is therefore useful to first summarize the established analytic properties of $z_{\text{Ising}}(L,\ K)$ for $K>0$: (a) $z_{\text{Ising}}(L,\ K)$ is analytic in L and K for $L\neq 0$.[8] (b) For $K>K_0\equiv\frac{1}{2}\ln(\sqrt{2}+1)$

$=0.44069\ldots$ (or $K^{-1}<K_0^{-1}=2.26919\ldots$), the magnetization per spin,

$$M(L,\ K)=\frac{\partial}{\partial L}\ z_{\text{Ising}}(L,\ K)\ , \tag{8}$$

is discontinuous at $L=0$. The amount of discontinuity is[9]

$$M(K)\equiv M(0+,\ K)-M(0-,\ K)$$
$$=2(1-\sinh^{-4}2K)^{1/8},\quad K>K_0\ . \tag{9}$$

(c) As $K\to K_0$ we have[10,11]

$$\left(\frac{\partial^2}{\partial L^2}\,z_{\text{Ising}}(L,\ K)\right)_{L=0}\sim|K-K_0|^{-7/4}\ , \tag{10}$$

$$\frac{\partial^2}{\partial K^2}\,z_{\text{Ising}}(0,\ K)\sim\ln|K-K_0|\ . \tag{11}$$

(d) For sufficiently small $K(K=\alpha K_0,\ \alpha<1)$, $z_{\text{Ising}}(L,K)$ is analytic in L and K at $L=0$.[12] The current belief is that this analyticity can be extended to $K=K_0-$ but there has been no rigorous proof.

We now proceed to examine the analytic properties of z using (a)–(d). Since both L and K are analytic in β, we observe from (a) that $z(a,\ \beta)$ can be nonanalytic in β only when $L=0$, or

$$(1+e^{2\beta\epsilon})^2=e^{(4-a)\beta\epsilon}-1\ . \tag{12}$$

This then defines the transition temperature T_c if a phase transition exists. Equation (12) has no solution for $\epsilon<0$, $a\leq 4$ and $\epsilon>0$, $a\geq 0$. This establishes the first statement in (iii).

To see whether indeed a phase transition occurs at the temperature defined by (12), we compute the corresponding value of K, which we denote by K_c. One finds that, in the case of $\epsilon<0$ and $a>4$ [for which (12) has a solution], K_c is always less than K_0. In particular, the value $a=4+$ corresponds to $K_c=0+$. It then follows from (d) that no phase transition exists for $a>4+\delta$, for some positive δ, and presumably for all $a>4$.[13] Similarly for $\epsilon>0$ one finds that, as a decreases from $0-$, K_c decreases monotonically from ∞ to $\frac{1}{4}\ln 2<K_0$ and equals K_0 at $a=a_0$. The remaining part of (iii) now follows from (d).

A phase transition can therefore occur only in the region $\epsilon>0$, $a_0\leq a<0$. What happens in this case can be visualized from Fig. 1 where L is plotted against K^{-1} for different values of a. The heavy line segment on the $L=0$ axis is the points at which $Z_{\text{Ising}}(L,\ K)$ becomes nonanalytic. As temperature varies, L and K^{-1} vary along the curves in Fig. 1. The nonanalytic points are reached only when $a_0\leq a<0$. The temperature at which the nonanalyticity occurs is the transition temperature T_c defined by (12). In Fig. 2, T_c is plotted as a function of a. The solid curve denotes the physical transition temperature, whereas the dashed curve

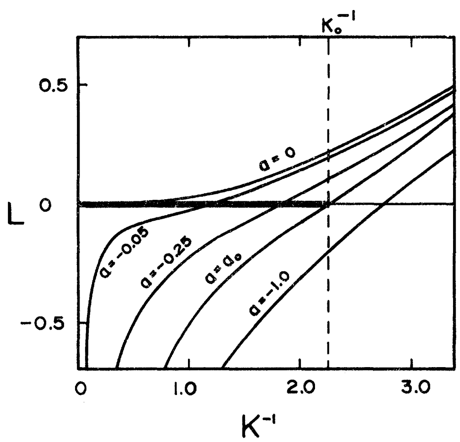

FIG. 1. L vs K^{-1} for $\epsilon>0$. $K_0^{-1}=2.26919\ldots$.

does not correspond to any physical transition. It is a curious fact that T_c should be discontinuous at $a=a_0$ [corresponding to $kT_c/\epsilon=2/\ln(2+2\sqrt{2})$ $=1.27022\ldots$].

In the region $\epsilon>0$, $a_0\leq a<0$ where a phase transition occurs, we can compute the energy per vertex E and the specific heat per vertex c at $T_c\pm$. The derivatives $\partial z/\partial L$, $\partial z/\partial K$, etc., occurring in the expressions

$$E=-\frac{\partial z}{\partial\beta}=-\left(\frac{\partial z}{\partial L}\,\frac{\partial L}{\partial\beta}+\frac{\partial z}{\partial K}\,\frac{\partial K}{\partial\beta}\right),$$
$$c=k\beta^2\,\frac{\partial^2 z}{\partial\beta^2}\ , \tag{13}$$

can be computed at $T_c\pm$. It follows from (9) that the energy is discontinuous at T_c for $a_0<a<0$. The latent heat

$$h=E(T_c+)-E(T_c-) \tag{14}$$

can be computed using (7)–(9) and the fact that $(\partial L/\partial\beta)<0$ at T_c. The result is

$$h=\left|\frac{\partial L}{\partial\beta}\right|M(K_c),\quad a_0<a<0 \tag{15}$$

where all quantities are evaluated at T_c. The transition is therefore of first order. Similarly we find that the specific heat is finite but discontinuous at T_c. As $a\to a_0$ which corresponds to $K_c\to K_0$, the latent heat approaches zero and the energy becomes continuous. When $a=a_0$ the energy attains the value $E/\epsilon=23\sqrt{2}-32+(9-6\sqrt{2})a_0$ $=0.261814\ldots$ at T_c. The specific heat diverges in this limit because of (c). Since the dominant divergence is that of (10), we find, after using the fact that K_c is analytic in a,

$$c(T_c)\sim|a-a_0|^{-7/4}\ . \tag{16}$$

Therefore a second-order transition with an infinite specific heat occurs when $a=a_0$.

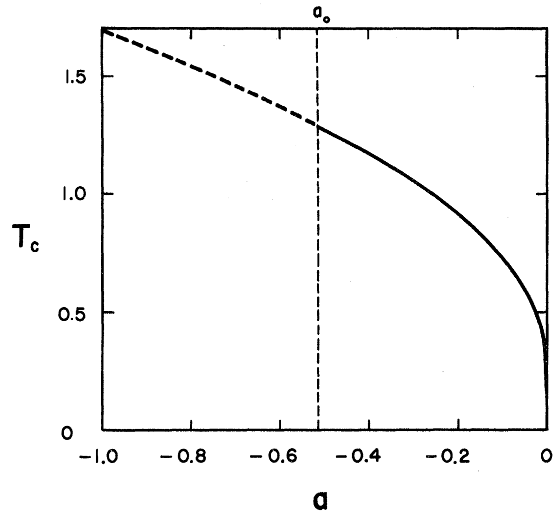

FIG. 2. Transition temperature T_c vs a for $\epsilon < 0$. $a_0 = -0.515033\ldots$ and T_c is in units of ϵ/k.

For $\epsilon > 0$ and $a < 0$, the favored vertex configurations are those with four bonds. We can therefore consider the fraction of vertices having four bonds, s, as an order parameter:

$$s = \frac{1}{\beta\epsilon}\frac{\partial}{\partial a} z(a, \beta) . \tag{17}$$

Following the same reasoning as above, we find that s is discontinuous at T_c for $a_0 < a < 0$. The amount of discontinuity can be computed, and we find

$$s(T_c -) - s(T_c +) = [1 + (1 + e^{2\beta\epsilon})^{-2}]M(K_c), \quad a_0 < a < 0 \tag{18}$$

where all quantities are evaluated at T_c. When $a = a_0$ the order parameter becomes continuous and attains the value $s = 9 - 6\sqrt{2} = 0.514718\ldots$ at T_c.

Finally, to those who are accustomed to the spin language, it is useful to point out another connection of the present model with the Ising model. As in the case of the eight-vertex model, the general sixteen-vertex model can also be transformed into an Ising model whose interaction strengths are some linear combinations of the vertex energies.[1] In the equivalent Ising model the spins are located on the lattice edges. For the present model the Ising Hamiltonian turns out to be[14]

$$\mathcal{H}_{\text{Ising}} = \frac{\epsilon}{16}\left[2(a+4)\sum\sigma + (4-a)\sum\sigma\sigma' + (a-4)\sum\sigma\sigma'\sigma'' + (4-a)\sum\sigma\sigma'\sigma''\sigma''' - (a+28)N\right], \tag{19}$$

where except in the first term all interactions are within the sets of four spins surrounding every vertex of the square lattice. It is an interesting result that the Ising model described by the Hamiltonian (19) leads to a first-order phase transition for $\epsilon > 0$ and $a_0 < a < 0$.

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[1]For a review on the ferroelectric models and discussions on the eight-vertex and sixteen-vertex models, see E. H. Lieb and F. Y. Wu, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972).

[2]R. J. Baxter, Phys. Rev. Letters 26, 832 (1971); Ann. Phys. (N. Y.) 70, 193 (1972).

[3]F. Y. Wu, Phys. Rev. Letters 22, 1174 (1969); 24, 1476 (1970); Solid State Commun. 10, 115 (1972); M. Suzuki and M. E. Fisher, J. Math. Phys. 12, 235 (1971).

[4]E. H. Lieb, Phys. Rev. Letters 19, 108 (1967).

[5]N. D. Mermin, Phys. Rev. Letters 26, 169 (1971).

[6]Since the case $a = 4$ can be trivially solved, one may wish to restrict to $a \neq 4$ in the ensuing discussions.

[7]T. D. Lee and C. N. Yang, Phys. Rev. 87, 410 (1952).

[8]J. L. Lebowitz and O. Penrose, Commun. Math. Phys. 11, 99 (1968).

[9]C. N. Yang, Phys. Rev. 85, 808 (1952).

[10]M. E. Fisher, Physica 25, 521 (1959).

[11]L. Onsager, Phys. Rev. 65, 117 (1944).

[12]G. Gallavotti, S. Miracle-Solé, and D. Robinson, Phys. Letters 25A, 693 (1967).

[13]Using some recent results on the Ising model by Lebowitz (report in Yeshiva Symposium, December 1971), one can show at least that all first derivatives of z are continuous in the regions $\epsilon > 0$, $a < a_0$ and $\epsilon < 0$, $a > 4 + \delta$.

[14]This is also the Ising Hamiltonian corresponding to the bar lattice gas of Ref. 5.