Exact Solution of a Model of an Antiferroelectric Transition*

F. Y. Wu
Department of Physics, Northeastern University, Boston, Massachusetts 02115
(Received 18 February 1969)

A modified version of the Rys F model of an antiferroelectric is solved exactly. In addition to the six kinds of vertices allowed by the ice rule, the model considered also includes two kinds of doubly ionized vertices. For a particular choice of the energy for these new vertices, the partition function is evaluated in a closed form. The phase transition is of second-order (in contradistinction to the infinite-order transition of the Rys F model), and the specific heat has a logarithmic singularity.

I. INTRODUCTION

THE statistical problem of two-dimensional hydrogen-bonded crystals as soluble models of phase transitions has been considered by a number of authors.[1–3] The mathematical problem is the following: Consider a periodic square lattice which has one hydrogen atom sitting off center on each lattice edge. Each vertex has an energy which depends on the surrounding hydrogen-atom configuration. The problem is to evaluate the partition function. In the models that were previously solved, one explicitly assumes and uses the "ice rule" which says that each vertex has precisely two near and two distant hydrogen atoms, so that each vertex is electrically neutral. For real physical systems, however, one must allow the formation of ionic vertices. Therefore, in order to make a meaningful comparison of the theory with experiments, it is quite important to investigate the effect of the inclusion of these ionized vertices.[4] The delicate nature of the previous exact solutions indicates that this is likely to be a question which can be answered only through exact analysis. Therefore, it is very unfortunate that the previous methods of solution do not seem to provide a straightforward extension to this more realistic problem.

The purpose of the present paper is to report some exact results in this connection. We consider the Rys F model[5] of an antiferroelectric, and, in addition to the six kinds of vertices allowed by the ice rule, we also permit the formation of doubly ionized vertices. For a particular, but realistic, choice of the energy value for these new vertices, we are able to solve this model exactly. Our result shows that the critical behavior is modified drastically by the inclusion of these new vertices.

Following the usual convention,[1–3] we represent each lattice edge by a directed arrow. Let us number the different types of vertices from 1 to 8, as shown in Fig. 1, with vertex energies $e_1=e_2=e_3=e_4=\epsilon>0$, $e_5=e_6=0$, $e_7=e_8=2\epsilon$. We note that the Rys F model includes only the vertices (1)–(6), while the model that we now propose includes all eight vertices. The vertices (7) and (8) have the highest energy because they are expected to be less populated. The Rys F model was solved exactly by Lieb.[2] The main feature of the solution is that the transition is of infinite order. In particular, the specific heat is continuous at the transition temperature. We shall show that with the inclusion of the two new kinds of vertices the phase transition becomes second-order and the specific heat possesses a logarithmic singularity.

In Sec. II, we consider a slightly more general version and obtain the solution through the use of the weak-graph expansion method formulated by Nagle.[6] While it can be shown (see Appendix) that this model is equivalent to a planar Ising model and from this our conclusions follow immediately, we prefer the method of solution presented in Sec. II[7] because it is more general and may find applications in other problems. In Sec. III, the thermodynamic properties of the present model are obtained and compared with those of the F model.

II. METHOD OF SOLUTION

Our problem is to evaluate the partition function

$$Z=\sum_{G}\prod_{i=1}^{N}\omega(\xi_i), \tag{1}$$

where $\xi_i=1, 2, \cdots, 8$ specifies the configuration of the ith vertex, N is the total number of vertices, and G

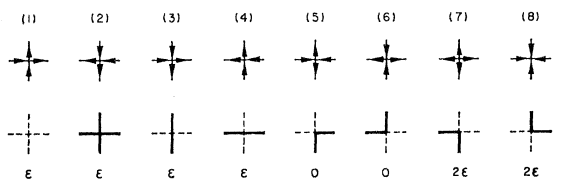

FIG. 1. The eight kinds of vertex configurations and the associated vertex energies.

* Work supported in part by National Science Foundation Grant Nos. GP-6851 and GP-9041.

[1] F. Y. Wu, Phys. Rev. Letters **18**, 605 (1967); Phys. Rev. **168**, 539 (1968).

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

[3] B. Sutherland, Phys. Rev. Letters **19**, 103 (1967); C. P. Yang, *ibid.* **19**, 586 (1967); B. Sutherland, C. N. Yang, and C. P. Yang, *ibid.* **19**, 588 (1967).

[4] Y. Takagi, J. Phys. Soc. Japan **3**, 273 (1948).

[5] F. Rys, Helv. Phys. Acta **36**, 537 (1963).

[6] J. F. Nagle, J. Math. Phys. **9**, 1007 (1968).

[7] This model can also be solved by the transfer matrix method proceeding along the lattice diagonal direction [E. H. Lieb (private communication)].

denotes the set of allowed lattice arrow configurations. For the present model, the vertex weights $\omega(\xi)$ are the Boltzmann factors

$$\begin{aligned}&\omega(1)=\omega(2)=\omega(3)=\omega(4)=e^{-\beta\epsilon},\\&\omega(5)=\omega(6)=1,\\&\omega(7)=\omega(8)=e^{-2\beta\epsilon}.\end{aligned}\tag{2}$$

In a previous paper,[8] an expression in closed form has been obtained for Z when the condition

$$\omega(1)\omega(2)+\omega(3)\omega(4)=\omega(5)\omega(6)+\omega(7)\omega(8)\tag{3}$$

is fulfilled. It is easily seen that the vertex weights given by (2) fail to satisfy this condition. Therefore, the previous result is not directly applicable to this problem. However, through a rearrangement of terms in (1), we shall be able to find a set of new vertex weights which satisfies the condition (3) and the previous result may then be used.

The procedure of rearranging terms in the partition function is known as the method of weak-graph expansion in the lattice statistical theory. It was first introduced by DiMarzio and Stillinger[9] in their evaluation of the residual entropy of ice. Later developments are largely due to Nagle[6] who formulated the weak-graph expansion method and applied it to a number of problems. We shall follow Nagle's notations with slight simplifications.[10]

Let us consider in the remainder of this section a more general model with vertex weights

$$\begin{aligned}&\omega(1)=\omega(2)=e^{-\beta\epsilon_1}=u_1,\\&\omega(3)=\omega(4)=e^{-\beta\epsilon_2}=u_2,\\&\omega(5)=\omega(6)=1,\\&\omega(7)=\omega(8)=e^{-\beta(\epsilon_1+\epsilon_2)}=u_1u_2,\end{aligned}\tag{4}$$

which reduces to our modified F model on taking $u_1=u_2=u=e^{-\beta\epsilon}$. We shall now show that for this problem a closed expression can be obtained for the partition function. First, it is convenient to use the language of bonds instead of arrows.[10] As pointed out elsewhere,[1] this can be accomplished by replacing all arrows pointing downward and arrows pointing toward the left by bonds. The resulting correspondences of the vertex configurations are shown in Fig. 1. It is to be noted that for our problem the degree of a vertex, or the number of bonds attached to a vertex, is always even (0, 2, or 4). The next step is to remove the restriction imposed by G on the summation (1). By independently summing over the eight vertex configurations at all N vertices, we naturally include in the summation a number of configurations which contain some unmatched neighboring vertex configurations. In order to exclude these unwanted configurations, we introduce for each lattice edge an edge factor $A(\xi_i,\xi_j)$ with the property

$$\begin{aligned}A(\xi_i,\xi_j)&=1, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are compatible}\\&=0, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are incompatible.}\end{aligned}\tag{5}$$

Here i and j refer to the two vertices connected by the edge ij and the configurations ξ_i and ξ_j are compatible if they both have or both do not have a bond on the edge ij. A simple way to accomplish this is to write

$$A(\xi_i,\xi_j)=\tfrac{1}{2}[1+c_{ij}(\xi_i)c_{ij}(\xi_j)],\tag{6}$$

where

$$\begin{aligned}c_{ij}(\xi_i)=c_{ji}(\xi_i)&=1,\\&\text{if } \xi_i \text{ has a bond on the edge } ij,\\&=-1,\\&\text{if } \xi_i \text{ does not have a bond on the edge } ij.\end{aligned}$$

Then the partition function Z takes the form

$$Z=\sum_{\xi_i=1}^{8}\prod_{\text{edges}}\tfrac{1}{2}[1+c_{ij}(\xi_i)c_{ij}(\xi_j)]\prod_{i=1}^{N}\omega(\xi_i).\tag{7}$$

At first sight the expression (7) appears to be more complicated than the original expression (1). However, because of the factorability of the compatibility function $c_{ij}(\xi_i)c_{ij}(\xi_j)$, as observed by Nagle,[6] one may multiply out the product of the $2N$ edge factors and regroup the terms to form a new expansion (the weak-graph expansion). Each term in the expansion is now a product of many $c_{ij}(\xi_i)c_{ij}(\xi_j)$ factors. If for each $c_{ij}(\xi_i)c_{ij}(\xi_j)$ factor we draw a bond between the vertices i and j, then we have again a graphical representation for all terms in the expansion. The summation in the expansion is now extended over all graphs which include all vertices of even and odd degrees.

After expanding the product of the edge factors and collecting all factors for a given graph, (7) can be rewritten as

$$Z=\sum_{\text{all graphs}}\prod_{i=1}^{N}[\tfrac{1}{4}\sum_{\xi_i=1}^{8}\omega(\xi_i)\prod_{\substack{k\\ ik \text{ in } G}}c_{ik}(\xi_i)].\tag{8}$$

Now the expression (8) is similar to the original expression (1) if one considers the quantity inside the square bracket as a new weight for the ith vertex. It is straightforward to evaluate the weights for all 16 kinds of vertex configurations now appearing in this new scheme. We shall now specialize to the case specified by (4). For these special $\omega(\xi)$ weights, one finds without difficulty that, again, the vertices of odd degrees turn out to have identically zero weights. Consequently (8) reduces to precisely (1), except that the eight vertices

[8] C. Fan and F. Y. Wu, Phys. Rev. **179**, 560 (1969). See also, H. S. Green and C. A. Hurst, *Order-Disorder Phenomena* (Wiley-Interscience, Inc., New York, 1964), Sec. 5.3.

[9] E. A. DiMarzio and F. H. Stillinger, Jr., J. Chem. Phys. **40**, 1577 (1964).

[10] In Ref. 6, the structure of two sublattices is introduced in transforming the arrow configurations into bond configurations. Our consideration appears to be simpler and more direct.

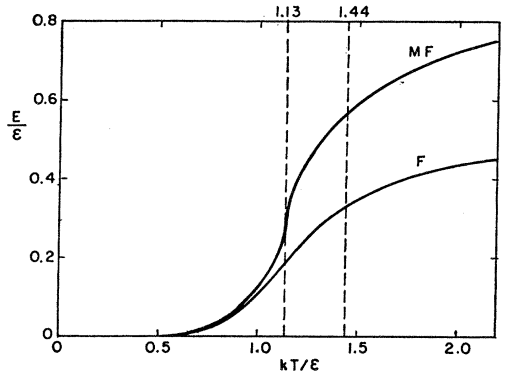

FIG. 2. The energy per vertex of the F model (F) and the modified F model (MF).

of even degrees now have the following weights:

$$\begin{aligned}
&\omega'(1)=\omega'(2)=\tfrac{1}{2}(u_1+u_2-1+u_1u_2),\\
&\omega'(3)=\omega'(4)=\tfrac{1}{2}(u_1+u_2+1-u_1u_2),\\
&\omega'(5)=\omega'(6)=\tfrac{1}{2}(u_1-u_2-1-u_1u_2),\\
&\omega'(7)=\omega'(8)=\tfrac{1}{2}(u_1-u_2+1+u_1u_2).
\end{aligned} \tag{9}$$

In computing $\omega'(\xi)$ from the quantity inside the square bracket in (8), we have taken $\omega(5)=\omega(6)=-1$ instead of the original value $+1$. This is permissible because the vertices (5) and (6) always occur in pairs.

It is now a simple matter to confirm that the solubility condition (3) is an identity for the set of weights (9). Consequently, the result of Ref. 8 can be used. In particular, Eq. (8) of Ref. 8 in conjunction with (9) gives the free energy f per vertex for the model specified by (4),

$$\begin{aligned}
-\beta f&=\lim_{N\to\infty}\frac{1}{N}\ln Z\\
&=\frac{1}{8\pi^2}\int_0^{2\pi}d\theta\int_0^{2\pi}d\varphi\,\ln[(1+u_1^2)(1+u_2^2)\\
&\qquad+2u_1(1-u_2^2)\cos(\theta+\varphi)\\
&\qquad+2u_2(1-u_1^2)\cos(\theta-\varphi)].
\end{aligned} \tag{10}$$

One recognizes that, aside from the addition of a constant, f is the free energy for a quartic Ising lattice with interactions $-\frac{1}{2}\epsilon_1$ and $-\frac{1}{2}\epsilon_2$. That this eventually reduces to the Onsager-Ising solution is quite interesting and somewhat mystifying. We shall include in the Appendix a direct proof which demonstrates this equivalence.

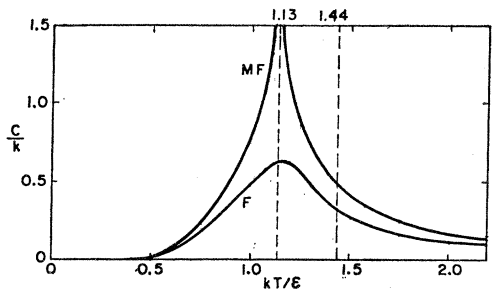

FIG. 3. The specific heat per vertex of the F model (F) and the modified F model (MF).

III. RESULTS AND DISCUSSION

Now returning to the modified F model of Sec. I, we use $u_1=u_2=u=e^{-\beta\epsilon}$ and obtain for the free energy f

$$\begin{aligned}
-\beta f&=\frac{1}{8\pi^2}\int_0^{2\pi}d\theta\int_0^{2\pi}d\varphi\,\ln[(1+u^2)^2\\
&\qquad-4u(1-u^2)\cos\theta\cos\varphi]\\
&=\ln(1+u^2)-\tfrac{1}{2}\ln 2+\frac{1}{4\pi}\int_0^{2\pi}d\theta\\
&\qquad\times\ln[1+(1-\kappa^2\cos^2\theta)^{1/2}],
\end{aligned} \tag{11}$$

where

$$\kappa=4u(1-u^2)/(1+u^2)^2=2\sinh\beta\epsilon/\cosh^2\beta\epsilon.$$

The evaluations of the thermodynamic functions are identical to those for the Ising solution.[11] The energy E per vertex is

$$E/\epsilon=1-\tfrac{1}{2}\coth(\beta\epsilon)[1+(2/\pi)\kappa' K(\kappa)] \tag{12}$$

and the specific heat c per vertex takes the form

$$\begin{aligned}
c/k&=\pi^{-1}(\beta\epsilon\coth\beta\epsilon)^2\{K(\kappa)-E(\kappa)\\
&\qquad-\tfrac{1}{2}(1-\kappa')[\tfrac{1}{2}\pi+\kappa' K(\kappa)]\}.
\end{aligned} \tag{13}$$

Here

$$\kappa'=(1-\kappa^2)^{1/2}=2\tanh^2\beta\epsilon-1$$

and

$$K(\kappa)=\int_0^{\pi/2}(1-\kappa^2\sin^2\theta)^{-1/2}d\theta,$$

$$E(\kappa)=\int_0^{\pi/2}(1-\kappa^2\sin^2\theta)^{1/2}d\theta$$

are, respectively, the complete elliptical integrals of the first and second kinds. The phase transition occurs at $\kappa=1$ or

$$kT_c/\epsilon=1/\ln(\sqrt{2}+1)=1.13459\cdots \quad \text{(modified } F \text{ model)}.$$

This is to be compared with the transition temperature of the F model

$$kT_c/\epsilon=1/\ln 2=1.44269\cdots \quad (F \text{ model}).$$

We have plotted in Figs. 2 and 3 the temperature dependences of the energy and the specific heat for both models.[12] For the Rys F model the transition is of

[11] See, for example, K. Huang, *Statistical Mechanics* (Wiley-Interscience, Inc., New York, 1963), p. 371.

[12] The numerical evaluations of the energy and the specific heat of the F model are from a forthcoming paper by E. Lieb and F. Y. Wu.

infinite-order so that the specific heat is continuous at T_c, whereas for the modified F model the specific heat possesses a logarithmic singularity with the critical behavior

$$c/k \sim (2/\pi) \ln^2(\sqrt{2}+1) \ln|1-T/T_c|, \quad T \sim T_c. \quad (14)$$

To summarize, we have constructed a realistic model of a hydrogen-bonded antiferroelectric (by breaking the ice rule) and obtained its exact solution. The model exhibits a logarithmically second-order phase transition. However, further investigations along the following directions are essential in testing the general validity of our conclusions: (i) the inclusion of the singly ionized vertices, (ii) consideration of some other energy values for the ionized vertices, and (iii) the inclusion of an external electric field. Unfortunately, neither of these problems can be treated rigorously. The effect of the singly ionized vertices is expected to be more important and has been considered by Takagi[4] for the KDP (potassium dihydrogen pohsphate) ferroelectric. Using a mean-field approach, Takagi found a second-order transition for the KDP model whereas with the ice rule the transition is of first-order.[2] This is consistent with our result. We have also investigated the effect of (ii) and (iii) using an approximation procedure formulated in Ref. 8. The results also indicate that the transition is of second-order for realistic energy assignments. From these considerations, it appears that models of hydrogen-bonded crystals in general will exhibit second-order phase transitions. The KDP and the F models are perhaps two isolated special cases which happen to behave differently exhibiting, respectively, first- and infinite-order phase transitions.[13]

Note added in proof: Our speculation on the critical behavior of general models of hydrogen-bonded crystals appears to be partially justified by the further results obtained after the submission of the present paper. By mapping a general antiferroelectric model with both singly and doubly ionized vertices into an Ising problem, we are able to establish the logarithmically second-order transition for a large class of models with realistic energy parameters. Details have been reported in F. Y. Wu, Phys. Rev. Letters **22**, 1174 (1969).

[13] These are the results when there is no external field. The phase transitions are of second-order for both models if an external electric field is included (these discussions will be included in a forthcoming paper by E. Lieb and F. Y. Wu).

ACKNOWLEDGMENT

It is a pleasure to thank Professor Elliott Lieb for a stimulating conversation.

APPENDIX

We use a result of Ref. 8 to prove that the model considered in Sec. II is equivalent to a planar Ising problem. In Ref. 8, it is shown that the problem of a quartic Ising lattice with first- and second-neighbor interactions is equivalent to a problem of hydrogen-bonded crystals. This result can be extended to the Ising lattice with unequal interactions in all directions. Denoting the first-neighbor interactions by $-J_1$ and $-J_2$ and the second-neighbor interactions by $-J$ and $-J'$, then in the notion of Fig. 1, the corresponding hydrogen-bonded crystal will have the following vertex energies:

$$\begin{aligned} &e_1=-J_1-J_2-J-J', \quad e_2= J_1+J_2-J-J', \\ &e_3=J_1-J_2+J+J', \quad e_4=-J_1+J_2+J+J', \\ &e_5=e_6=J'-J, \quad e_7=e_8=J-J'. \end{aligned} \quad (A1)$$

Let us now take $J_1=J_2=0$, $J=\frac{1}{2}\epsilon_1$, and $J'=\frac{1}{2}\epsilon_2$. Then on one hand the Ising lattice reduces to a planar quartic lattice with interactions $-\frac{1}{2}\epsilon_1$ and $-\frac{1}{2}\epsilon_2$; on the other hand, the hydrogen-bonded crystal has the following vertex energies:

$$\begin{aligned} &e_1=e_2=-\tfrac{1}{2}(\epsilon_1+\epsilon_2), \quad e_3=e_4=\tfrac{1}{2}(\epsilon_1+\epsilon_2), \\ &e_5=e_6=\tfrac{1}{2}(-\epsilon_1+\epsilon_2), \quad e_7=e_8=\tfrac{1}{2}(\epsilon_1-\epsilon_2). \end{aligned} \quad (A2)$$

It can be shown[14] that the partition function is symmetric in the two sets of energies $\{e_1=e_2, e_3=e_4\}$ and $\{e_5=e_6, e_7=e_8\}$. Hence, (A2) is equivalent to

$$\begin{aligned} &e_1=e_2= \tfrac{1}{2}(\epsilon_1-\epsilon_2), \quad e_3=e_4=\tfrac{1}{2}(-\epsilon_1+\epsilon_2), \\ &e_5=e_6=-\tfrac{1}{2}(\epsilon_1+\epsilon_2), \quad e_7=e_8=\tfrac{1}{2}(\epsilon_1+\epsilon_2). \end{aligned} \quad (A3)$$

Adding a constant energy $\frac{1}{2}(\epsilon_1+\epsilon_2)$ to (A3), the vertex energies are then identical to those specified by (4). This completes our proof. More precisely, we have shown the following:

$$f=\tfrac{1}{2}(\epsilon_1+\epsilon_2)+f_{\text{Ising}}(-\tfrac{1}{2}\epsilon_1, -\tfrac{1}{2}\epsilon_2), \quad (A4)$$

where f is the free energy per vertex of the hydrogen-bonded crystal specified by (4) and $f_{\text{Ising}}(-\frac{1}{2}\epsilon_1, -\frac{1}{2}\epsilon_2)$ is the free energy per spin of a simple quartic Ising lattice with interactions $-\frac{1}{2}\epsilon_1$ and $-\frac{1}{2}\epsilon_2$.

[14] F. Y. Wu (unpublished).