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EXACT SOLUTION OF THE F MODEL OF AN ANTIFERROELECTRIC

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The Rys F model of an antiferroelectric is solved by the transfer-matrix method. The result is different in many respects from the analogous Ising antiferromagnet, i.e., an infinite-order phase transition and a natural boundary in the complex T plane. It can also be solved when an external electric field is included. Above the transition temperature the behavior is normal while below T_c there is no polarization unless the electric field is sufficiently large.

The F model, which was originally proposed by Rys[1] as an interesting statistical mechanics problem, has since[2] become a meaningful model of hydrogen bonded ferroelectrics (e.g., $NH_4H_2PO_4$), at least in the sense that the two-dimensional Ising model is a reasonable model for an antiferromagnet. We have succeeded in solving this model by an extension of the method used to find the residual entropy of square ice.[3]

The solution has several unusual features:

(1) The free energy has a branch point at the critical temperature (as usual), but the cut is a natural boundary instead of a movable cut (e.g., $\ln|T-T_c|$).

(2) The phase transition is infinite order, i.e., the free energy and all its derivatives are finite and continuous at T_c. The free energy has an asymptotic power series about T_c with a zero radius of convergence. In particular, there is no latent heat.[2]

(3) Unlike the Ising model, the F model can be solved when an external electric field $\mathcal{E}$ is included (we wish to thank Professor J. Lebowitz for suggesting we treat the application of an electric field). For $T > T_c$, the polarization versus $\mathcal{E}$ is the usual S-shaped curve, saturating at $\mathcal{E} = \infty$. For $T < T_c$, however, the polarization is 0 for $\mathcal{E} < \mathcal{E}_c$ (where $\mathcal{E}_c$ depends on T). For $\mathcal{E} > \mathcal{E}_c$, the polarization behaves normally. The Ising antiferromagnet does not have this property.

The statement of the problem is the following: Place arrows on the bonds of a square $N \times N$ lattice and allow only those configurations with precisely two arrows pointing into each vertex. (Thus far we have the ice problem.) Next, we assign energies to the six kinds of vertices (Fig. 1): $e_1 = e_2 = e_3 = e_4 = \epsilon > 0$, $e_5 = e_6 = 0$. If, in addition, we apply an electric field $\mathcal{E}$ in the vertical direction, there is an additional energy $-\mathcal{E}d(N^2 - 2n)$, where d is the dipole moment and $2n$ is the number of downward vertical arrows. The partition function is

$$Z = \sum \exp[-Km + E(N^2 - 2n)], \tag{1}$$

where the sum is over allowed configurations; $E = \mathcal{E}d/kT$, $K = \epsilon/kT$, and m is the number of types 1, 2, 3, and 4 vertices.

Let φ and φ' be the configurations of two successive rows of vertical bonds and introduce the transfer matrix

$$A(\varphi, \varphi') = \sum \exp(-Km), \tag{2}$$

where m is now the number of types 1, 2, 3,

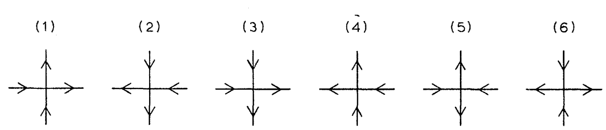

FIG. 1. The six kinds of vertex configurations allowed by the "ice condition." The associated energies for the F model are $e_1 = e_2 = e_3 = e_4 = \epsilon > 0$; $e_5 = e_6 = 0$. From F. Y. Wu, Phys. Rev. Letters 18, 605 (1967).

and 4 on the single row of vertices and where the sum is now over allowed arrangements of intervening horizontal arrows. If n is the number of downward vertical arrows in φ then A is replaced by $A' = \exp[E(N-2n)]A(\varphi, \varphi')$ with an electric field. Thus, $Z = \mathrm{Tr}[A'^N] =$ (largest eigenvalue)^N. As we showed previously,[3] A conserves the number n. Let $y = 1-2n/N$ and let $\Lambda_N(y)$ be the largest eignevalue of A in any given n subspace. Then

$$Z = \max_y [\Lambda_N(y)]^N \exp[N^2 Ey]. \tag{3}$$

Let $f(x_1, \cdots, x_n)$ be the amplitude in some eigenvector for having downward vertical arrows at sites $x_1, \cdots, x_n$. The eigenvalue equation is similar to the ice problem[3]:

$$\Lambda f(x_1, \cdots, x_n) = \left(\sum_{y_1=1}^{x_1} \cdots \sum_{y_n=x_{n-1}}^{x_n} + \sum_{y_1=x_1}^{x_2} \cdots \sum_{y_n=x_n}^{N} \right) \times f(y_1, \cdots, y_n) D(X, Y), \tag{4}$$

where

$$D = \exp\left[-NKy - 2K \sum_{i,j=1}^{n} \delta(x_i - y_j)\right]$$

Again, the plane-wave Ansatz works:

$$f(x_1, \cdots, x_n) = \sum_P ! a(P) \exp\left[i \sum_{j=1}^{n} k_{P(j)} x_j \right], \tag{5}$$

and we find (for n even) the following: (1) If $P = \cdots p, q, \cdots$ and $Q = \cdots q, p, \cdots$ then $a(P) = a(Q)B(p,q)$ with $B(p,q) = -[1 + T(p)T(q) - 2\Delta T(p)] \times [1 + T(p)T(q) - 2\Delta T(q)]^{-1}$, where $\Delta = 1 - \frac{1}{2}\exp(2K)$ and $T(p) = \exp(ip)$; (2) for all $i = 1, \cdots, n$,

$$\exp(ik_i N) = \prod_{j \neq i} B(k_i, k_j);$$

and (3)

$$\Lambda = \prod_j \{e^{-2K} - (1 - e^{ikj})^{-1}\} + \prod_j \{e^{-2K} - (1 - e^{-ikj})^{-1}\}. \tag{6}$$

It will be recognized that we have constructed the eigenvectors of the Heisenberg chain

$$H = -\sum_1^N S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z, \tag{7}$$

although with different eigenvalues. The maximum Λ corresponds to the ground state of (7) because both are positive.

The properties of the set $\{k\}$ for the ground state of (7) are well understood and we quote the results[4]: (1) For each k, there is a $-k$. (2) For large N, the k's are distributed between $-Q$ and Q (which depends on y) with a distribution function $\rho(k)$. (3) It is convenient to change variables to $e^{ik} = (e^{i\mu} - e^{\alpha})(e^{i\mu + \alpha} - 1)^{-1}$ for $\Delta > -1$, with $\Delta = -\cos\mu$, and to $e^{ik} = (e^{\lambda} - e^{-i\alpha}) \times (e^{\lambda - i\alpha} - 1)^{-1}$ for $\Delta < -1$, with $\Delta = -\cosh\lambda$. The critical point is thus $\Delta = -1$ corresponding to a critical temperature $e^K = 2$. (4) In the new variables we introduce $R(\alpha)$ [such that $R(\alpha)d\alpha = 2\pi\rho(k)dk$] in terms of which

$$N^{-2} \ln Z(y) = N^{-2} \ln \Lambda_N(y) + Ey \equiv f(y) \to \frac{1}{4\pi} \int_{-b}^{b} R(\alpha) C(\alpha) d\alpha + Ey - K, \tag{8}$$

and free energy per vertex $= -kT \max_y f(y)$;

$$C(\alpha) = \ln[(\cosh\alpha - \cos 2\mu)/(\cosh\alpha - 1)], \quad \Delta > -1:$$
$$= \ln[(\cosh 2\lambda - \cos\alpha)/(1 - \cos\alpha)], \quad \Delta < -1. \tag{9}$$

The distribution R and the limit b are determined by the integral equation

$$R(\alpha) = \xi(\alpha) - \int_{-b}^{b} K(\alpha - \beta) R(\beta) d\beta, \tag{10}$$

$$\pi(1-y) = \int_{-b}^{b} R(\alpha) d\alpha, \tag{11}$$

where

$$\xi(\alpha) = \sin\mu[\cosh\alpha - \cos\mu]^{-1}, \quad \Delta > -1,$$
$$= \sinh\lambda[\cosh\lambda - \cos\alpha]^{-1}, \quad \Delta < -1; \tag{12}$$

$$K(\alpha) = (2\pi)^{-1}(\sin 2\mu)[\cosh\alpha - \cos 2\mu]^{-1}, \quad \Delta > -1,$$
$$= (2\pi)^{-1}(\sinh 2\lambda)[\cosh 2\lambda - \cos\alpha]^{-1}, \quad \Delta < -1. \tag{13}$$

When $y = 0$, $b = \infty$ for $\Delta > -1$ and $b = \pi$ for $\Delta < -1$. Equation (10) may then be solved by Fourier transforms:

$$R(\alpha) = \pi[2\mu \cosh(\pi\alpha/2\mu)]^{-1}, \quad \Delta > -1,$$
$$= (\pi/2\lambda) \sum_{n=-\infty}^{\infty} \mathrm{sech}[\pi(\alpha + 2\pi n)/2\lambda], \quad \Delta < -1. \tag{14}$$

Now, it can be shown on general grounds that, as $N\to\infty$, $N^{-2}\ln\Lambda_N(y)$ is a continuous concave, symmetric function of y. Hence, for $E=0$ the optimum choice is $y=0$. The free energy is obtained by inserting (14) and (9) into (8). The resulting function of temperature has a cut which is a natural boundary and we shall discuss its properties elsewhere. When the second form of (14) and (9) is inserted into (8) the integral can be done explicitly term by term and we thus obtain the following expression for $\mathcal{E}=0$ and $\Delta<-1$:

$$N^{-2}\ln Z=\tfrac{1}{2}\lambda-K+\tfrac{1}{2}\sum_{n=1}^{\infty}(1-e^{-2n\lambda})(n\cosh n\lambda)^{-1}. \quad (15)$$

For small μ or λ (i.e., $T\sim T_c$), the free energy has an asymptotic, divergent power series which is the same above and below T_c. In terms of μ it is

$$N^{-2}\ln Z=-K+2\ln[\Gamma(\tfrac{1}{4})/2\Gamma(\tfrac{3}{4})] + \tfrac{1}{2}\sum_{n=1}^{\infty}\frac{B_{2n}\mu^{2n}}{n(2n)!}[(-1)^n-|E_{2n}|]. \quad (16)$$

If we differentiate (16) with respect to μ, we find at T_c

$$\text{Energy/vertex}=\tfrac{1}{3}\epsilon,$$
$$\text{Specific heat/vertex}=k(\ln 2)^2(28/45). \quad (17)$$

By virtue of the concavity mentioned above, as E increases y increases continuously. For small y one does perturbation theory on (10) and (11). b decreases with increasing y. For $\Delta>-1$, $b\approx\infty$ so that $N^{-2}\ln[Z(y)/Z(0)]\approx Ey-\text{const}\times y^2$ and the polarization $(=N^2y)$ is proportional to E. For $\Delta<-1$, b is finite $(\approx\pi)$ and $N^{-2}\times\ln[Z(y)/Z(0)]\sim Ey-\text{const}\times y$. Hence, there is no polarization unless E is large enough.

For $y\approx 1$, on the other hand, (10) and (11) are simple because $b\approx 0$. Thus $b\approx\pi(1-y)\times[2\xi(0)]^{-1}$. When this is inserted into (8) one finds $N^{-2}\ln Z\approx -K+Ey+s(1-y)+t(1-y)\ln(1-y)$, with s and t constants. Hence, for large E, the polarization is

$$y\approx 1-(2/\pi)\exp(-2E+2K). \quad (18)$$

This result is in marked contrast to the analogous magnetization of the Heisenberg chain which, in the ground state, saturates with a finite magnetic field. The difference is a consequence of the logarithmic divergence of (9) at $\alpha=0$.

Dr. F. Y. Wu has kindly informed me (private communication) that he has evaluated the partition function by the dimer method for the particular case $\Delta=0$ ($e^K=\sqrt{2}$ or $\mu=\frac{1}{2}\pi$), but for all y. Indeed, when $\Delta=0$, $K(\alpha)=0$ so that $R(\alpha)=\xi(\alpha)=(\cosh\alpha)^{-1}$ and $\sinh b=\tan\frac{1}{2}\pi(1-y)$. If we insert this result into (8) and change variables to $(\cosh\alpha)^{-1}=\cos k$ we obtain

$$N^{-2}\ln Z(y)=Ey-\tfrac{1}{2}\ln 2+\frac{1}{4\pi}\int_{-Q}^{Q}dk\,\ln\frac{1+\cos k}{1-\cos k}, \quad (19)$$

where $Q=\frac{1}{2}\pi(1-y)$. The integral in (19) can be evaluated for $y=0$, whence

$$N^{-2}\ln Z(0)=-\tfrac{1}{2}\ln 2+(2/\pi)(\text{Catalan's constant}) = 0.236\,548\,2. \quad (20)$$

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