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The Haus–Tanaka Model for the Ice VII – Ice VIII Phase Transition

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Abstract

The high temperature susceptibility series of the model proposed by Haus and Tanaka (1977) to account for the transition of the orientationally disordered ice VII phase to the orientationally ordered ice VIII phase does not provide evidence for the possible occurrence of a first-order transition, as predicted by the mean field approximation, but gives a second-order transition instead.

1. Introduction

The phase of ice VIII was first identified by Whalley *et al.* (1966). The phase transition between ice VII and ice VIII occurs at about 273 K when the pressure exceeds $2\cdot 14\times 10^9$ Pa and is a first-order transition. As shown by dielectric measurements, ice VII is orientationally disordered and ice VIII is orientationally ordered.

Brown and Whalley (1966) and Johari *et al.* (1974) have shown that the ice VII and VIII phases have a common b.c.c. lattice in which the sites are occupied by the oxygen ions. Each oxygen is hydrogen-bonded to four of its neighbours in such a way that the lattice can be viewed as being composed of two interwoven diamond sublattices. The structure of the lattice is illustrated in Fig. 1*a*. The state of order of the lattice is determined by the positions of the hydrogen ions in the bonds (Wong and Whalley 1976). For the ordered ice VIII phase, only two hydrogen atoms are close to the oxygen atom at each site, and the electric dipole moments associated with the water molecules are either parallel or antiparallel according to whether the molecules are on the same or different sublattices.

Recently, Haus and Tanaka (1977) proposed a theoretical model, referred to hereafter as the Haus–Tanaka model, to simulate the transition between the ice VII and ice VIII phases. The lattice which they considered is constructed from the midpoints of the bond edges of the two diamond sublattices and can subsequently be visualized as two interpenetrating tetrahedron sublattices, labelled I and II. As shown in Fig. 1*b*, each site is 12 coordinated, 6 of its nearest neighbours being on sublattices I and II respectively. The Haus–Tanaka model of the lattice is then defined by the hamiltonian:

$$\begin{aligned}\mathscr{H} = & -J_2 \sum_{<i,j>} \sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{I}} - J_2 \sum_{<i,j>} \sigma_i^{\mathrm{II}}\sigma_j^{\mathrm{II}} - J_2' \sum_{<i,j>} \sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{II}} \\ & - J_4 \sum_{<i,j,k,l>} \sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{I}}\sigma_k^{\mathrm{I}}\sigma_l^{\mathrm{I}} - J_4 \sum_{<i,j,k,l>} \sigma_i^{\mathrm{II}}\sigma_j^{\mathrm{II}}\sigma_k^{\mathrm{II}}\sigma_l^{\mathrm{II}}, \end{aligned} \tag{1}$$

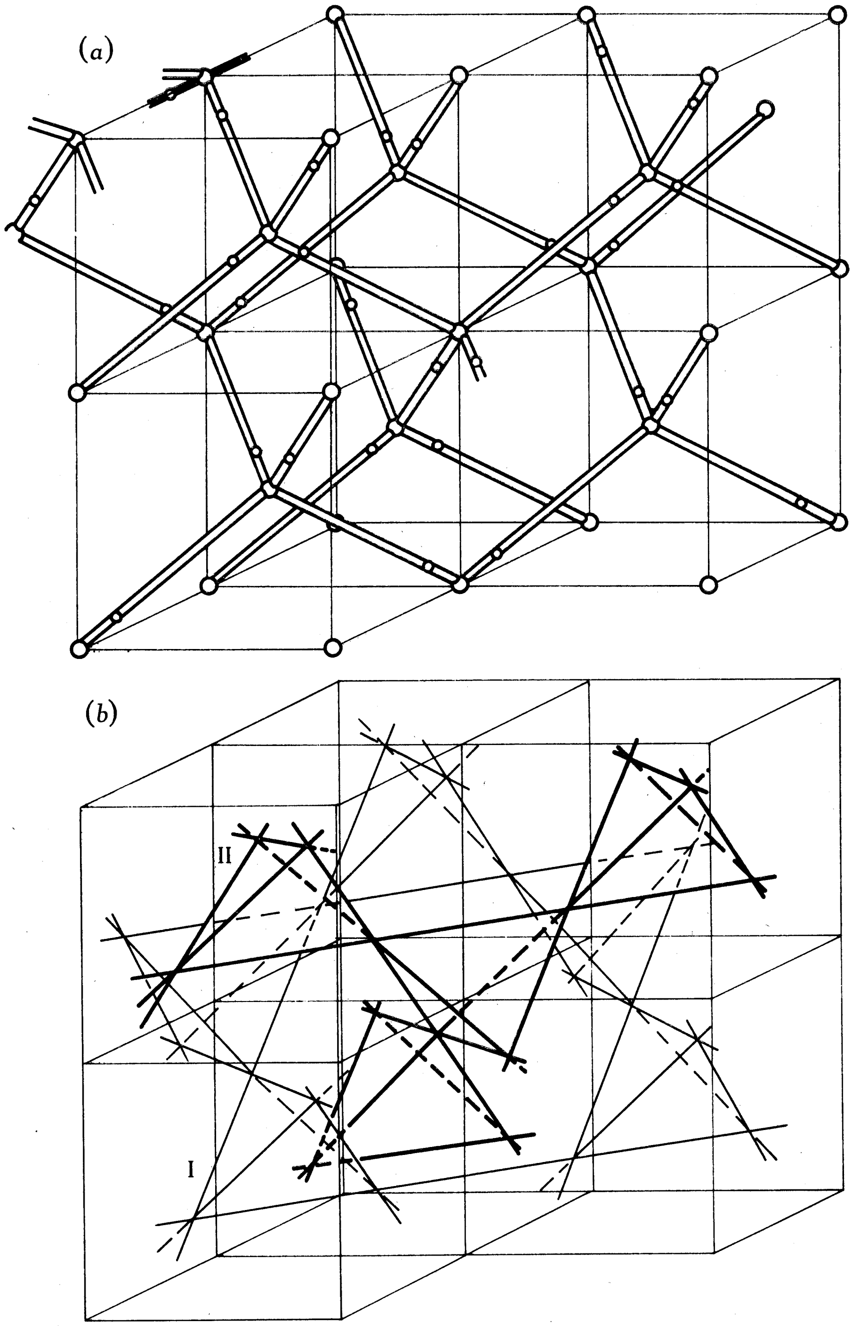

Fig. 1. Haus–Tanaka model of the ice VII–ice VIII phase transition, showing:

(*a*) two interpenetrating diamond sublattices of the ice VII and ice VIII structures, with large and small circles representing oxygen and hydrogen atoms respectively;

(*b*) two interpenetrating tetrahedron sublattices I and II, formed by joining the midpoints of the hydrogen bonds in the two diamond sublattices.

where each spin σ has values ± 1, depending on whether the hydrogen ion in the original bond is above or below the lattice site. To correspond with the features of the ordered ice VIII phase, the interactions within each sublattice are ferromagnetic (J_2 and $J_4 > 0$), while the interaction between sublattices is antiferromagnetic ($J_2' < 0$). The four-spin interaction J_4 is included to satisfy the ice rule approximately. Haus and Tanaka computed the free energy of the model by the cluster variation method. With the mean field approximation and a suitable choice of parameters, they showed the phase transition to have a first-order transition, thus leading to the conclusion that the model is suitable to account for the ice transition. However, the results of other similar models cast doubts on their solution.

For the four-spin interaction Ising models investigated by Bolton *et al.* (1972), Oitmaa and Gibberd (1973) and Thompson (1974), the mean field approximation has predicted the occurrence of a first-order transition when the four-spin coupling is sufficiently large. Nevertheless, the exact series expansion method predicts that such models on the square lattice (Oitmaa and Gibberd 1973; Oitmaa 1974) and tetrahedron lattice (Ho-Ting-Hun and Oitmaa 1976) have a second-order transition for all values of the coupling strength. We therefore investigate here the proposed model by means of the exact series method.

2. High Temperature Susceptibility Series

Assuming that there are N lattice sites, we have for the zero-field partition function of the model:

$$\begin{aligned} Z = \sum_{\{\sigma\}} \exp(-\beta\mathscr{H}) &= (\cosh K_2)^{3N}(\cosh K_2')^{3N}(\cosh K_4)^{\frac{1}{2}N} \\ &\quad \times \sum_{\{\sigma\}} \prod_{<i,j>} (1+v\sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{I}}) \prod_{<i,j>} (1+v\sigma_i^{\mathrm{II}}\sigma_j^{\mathrm{II}}) \prod_{<i,j>} (1+\mu\sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{II}}) \\ &\quad \times \prod_{<i,j,k,l>} (1+w\sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{I}}\sigma_k^{\mathrm{I}}\sigma_l^{\mathrm{I}}) \prod_{<i,j,k,l>} (1+w\sigma_i^{\mathrm{II}}\sigma_j^{\mathrm{II}}\sigma_k^{\mathrm{II}}\sigma_l^{\mathrm{II}}), \end{aligned} \tag{2}$$

where $\beta = 1/kT$, $K_2 = \beta J_2$, $K_2' = \beta J_2'$, $K_4 = \beta J_4$, $v = \tanh K_2$, $\mu = \tanh K_2'$ and $w = \tanh K_4$. Grouping the products taken over $\langle i,j\rangle$ and $\langle i,j,k,l\rangle$ over each tetrahedron of lattices I and II, and then expanding them in an appropriate way, we obtain

$$\begin{aligned} Z &= (\cosh K_2)^{3N}(\cosh K_2')^{3N}(\cosh K_4)^{\frac{1}{2}N}\{1+4v^3+3v^4 + (3v^2+4v^3+v^6)w\}^{\frac{1}{2}N} \\ &\quad \times \sum_{\{\sigma\}} \prod_{\in \mathrm{I}} \{1+A(\sigma_1^{\mathrm{I}}\sigma_2^{\mathrm{I}}+\sigma_1^{\mathrm{I}}\sigma_3^{\mathrm{I}}+\sigma_1^{\mathrm{I}}\sigma_4^{\mathrm{I}}+\sigma_2^{\mathrm{I}}\sigma_3^{\mathrm{I}}+\sigma_2^{\mathrm{I}}\sigma_4^{\mathrm{I}}+\sigma_3^{\mathrm{I}}\sigma_4^{\mathrm{I}})+B\sigma_1^{\mathrm{I}}\sigma_2^{\mathrm{I}}\sigma_3^{\mathrm{I}}\sigma_4^{\mathrm{I}}\} \\ &\quad \times \prod_{\in \mathrm{II}} \{1+A(\sigma_1^{\mathrm{II}}\sigma_2^{\mathrm{II}}+\sigma_1^{\mathrm{II}}\sigma_3^{\mathrm{II}}+\sigma_1^{\mathrm{II}}\sigma_4^{\mathrm{II}}+\sigma_2^{\mathrm{II}}\sigma_3^{\mathrm{II}}+\sigma_2^{\mathrm{II}}\sigma_4^{\mathrm{II}}+\sigma_3^{\mathrm{II}}\sigma_4^{\mathrm{II}}) \\ &\qquad + B\sigma_1^{\mathrm{II}}\sigma_2^{\mathrm{II}}\sigma_3^{\mathrm{II}}\sigma_4^{\mathrm{II}}\} \prod_{<i,j>} (1+\mu\sigma_i^{\mathrm{I}}\sigma_j^{\mathrm{II}}), \end{aligned} \tag{3}$$

where

$$A = \frac{(v+2v^2+2v^3+2v^4+v^5)(1+w)}{1+4v^3+3v^4+(3v^2+4v^3+v^6)w}, \qquad B = \frac{3v^2+4v^3+v^6+(1+4v^3+3v^4)w}{1+4v^3+3v^4+(3v^2+4v^3+v^6)w}. \tag{4a, b}$$

In equation (3) we see that there exist three types of bonds: A, B and μ. After further expansion of the products, terms of the form $A^m B^n$ have at most one contribution from A or B for each tetrahedron. Therefore, in the derivation of the series for thermodynamic quantities, bonds A or B from the same tetrahedron cannot occur more than once in a contributing graph. The bond μ, which is not associated with any tetrahedron, does not follow such a restriction.

We adopt the same idea in enumerating magnetic graphs for the high temperature zero-field susceptibility series. With the aid of a computer, the following series is derived:

$$
\begin{aligned}
\chi = {} & 1 + 6A + 18A^2 + 54A^3 + 162A^4 + 486A^5 + 1446A^6 + 12BA^5 + \ldots \\
& + \mu(6 + 72A + 432A^2 + 1944A^3 + 7776A^4 + 29160A^5 + \ldots) \\
& + \mu^2(30 + 540A + 6B + 4854A^2 + 72AB + 30828A^3 \\
& \qquad + 504A^2B + 161538A^4 + 2808A^3B + \ldots) \\
& + \mu^3(150 + 3588A + 72B + 42876A^2 + 1296AB + 353652A^3 + 12432A^2B + \ldots) \\
& + \mu^4(738 + 21852A + 570B + 324936A^2 + 11970AB + 126B^2 + \ldots) \\
& + \mu^5(3636 + 128184A + 3672B + \ldots) \\
& + 17664\mu^6 + \ldots .
\end{aligned} \tag{5}
$$

Using the equations (4a) and (4b) we can re-express this series in terms of v, μ and w as

$$
\begin{aligned}
\chi(v, \mu, w) = {} & 1 + 6v + 30v^2 + 138v^3 + 618v^4 + 2766v^5 + 12378v^6 + 6vw \\
& + 48v^2w + 300v^3w + 1728v^4w + 9480v^5w + 18v^2w^2 + 216v^3w^2 \\
& + 1812v^4w^2 + 54v^3w^3 + \ldots \\
& + \mu(6 + 72v + 576v^2 + 3816v^3 + 22752v^4 + 127368v^5 + 72vw \\
& \qquad + 1008v^2w + 9216v^3w + 69552v^4w + 432v^2w^2 + 7344v^3w^2 + \ldots) \\
& + \mu^2(30 + 540v + 5952v^2 + 51564v^3 + 386490v^4 + 60w + 612vw \\
& \qquad + 11436v^2w + 135960v^3w + 72vw^2 + 5988v^2w^2 + \ldots) \\
& + \mu^3(150 + 3588v + 50268v^2 + 536508v^3 + 72w + 4884vw \\
& \qquad + 107952v^2w + 1296vw^2 + \ldots) \\
& + \mu^4(738 + 21852v + 370350v^2 + 570w + 33822vw + 126w^2 + \ldots) \\
& + \mu^5(3636 + 128184v + 3672w + \ldots) \\
& + 17664\mu^6 + \ldots .
\end{aligned} \tag{6}
$$

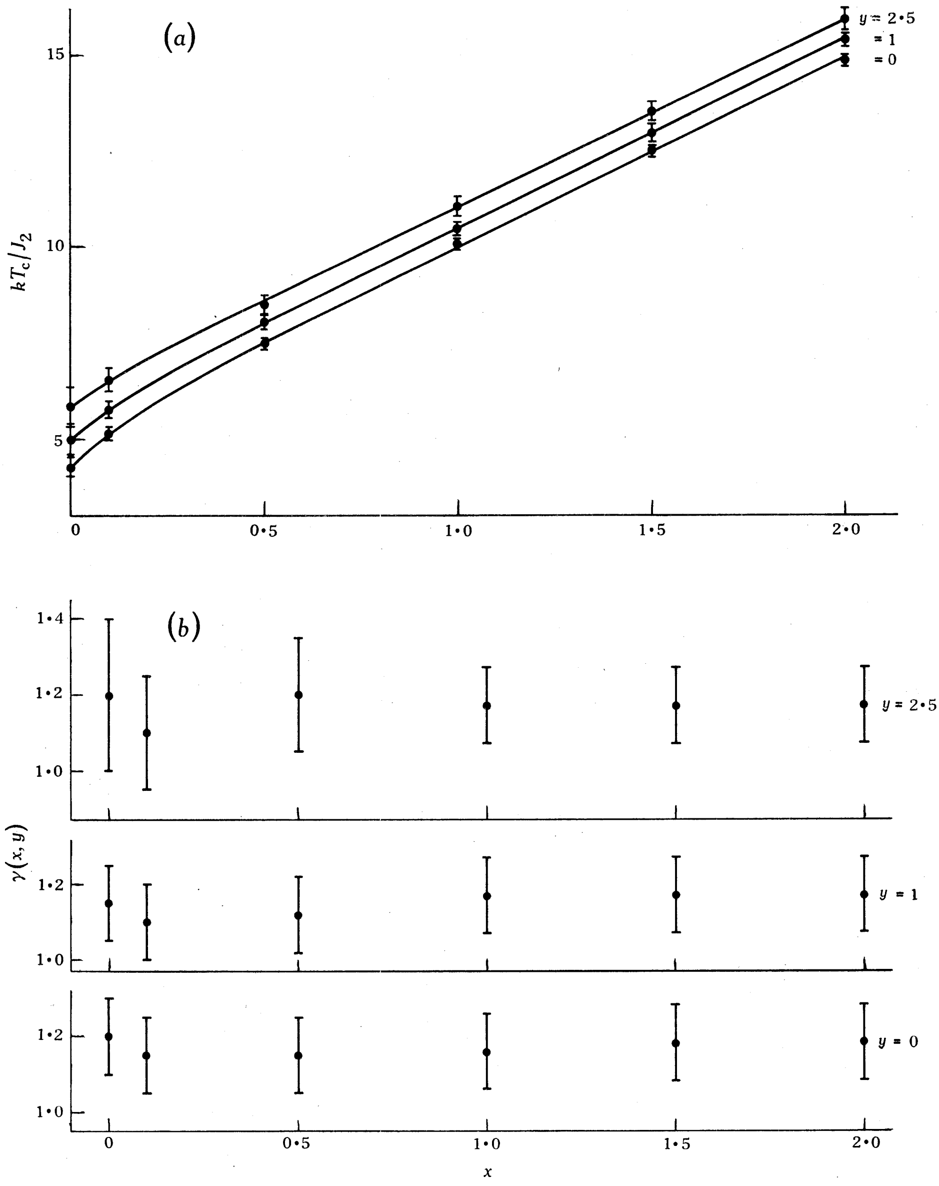

Fig. 2. Dependence on the coupling strengths x and y of (*a*) the estimated value of kT_c/J_2 and (*b*) the critical exponent γ.

3. Series Analysis and Results

As the partition function is invariant when the sign of J_2' changes, the model is equivalent for the same positive and negative J_2'. Therefore, in the series analysis, it is sufficient to consider the case $J_2' > 0$. On introducing the coupling strengths $x = J_2'/J_2$ and $y = J_4/J_2$ and assigning particular values to these variables, we reduce the series $\chi(v, \mu, w)$ to a form in v, which is then analysed by the standard ratio and Padé approximant methods (Gaunt and Guttmann 1974). In general, the estimates of the critical parameter $v_c(x, y)$ and critical exponent $\gamma(x, y)$ obtained by the two methods are consistent. Fig. 2*a* shows that the estimated kT_c/J_2 value increases smoothly with respect to both x and y. The marked improvement in accuracy for estimates away from $x = 0$ is due to the increase of coordination number from 6 to 12. With the $v_c(x, y)$ thus determined, $\gamma(x, y)$ can be estimated; its dependence on x and y is illustrated in Fig. 2*b*. However, at $x = 0$ the model reduces to a pair-quartet Ising model on two decoupled tetrahedron lattices, for which γ has been determined to be $1\cdot25$ and is independent of the four-spin interaction strength y (Ho-Ting-Hun and Oitmaa 1976).

Our estimated $\gamma(0, y)$ value, which lies within the range $1\cdot20 \pm 0\cdot20$ for various y, thus appears to be slightly low. Such a result is not unexpected, as earlier investigations by several authors (Jasnow and Moore 1968; Lambeth *et al.* 1974) on the pairwise Ising model upon the tetrahedron lattice, which corresponds to x and y being zero, have indicated the impossibility of assessing this critical exponent accurately by a short series. It is only with the use of a relatively long susceptibility series of 16 terms (Ho-Ting-Hun and Oitmaa 1975) that the critical behaviour of the model has been ascertained with some certainty. We therefore anticipate that our short series cannot give a highly accurate estimate of $\gamma(x, y)$.

As shown in Fig. 2*b*, the consistency of the estimates at nonzero x with $\gamma(0, y)$, together with their trends of remaining constant, lead us to believe that γ should be $1\cdot25$ and be independent of the coupling strengths x and y. To confirm this surmise we re-estimated the $v_c(x, y)$ from Padé approximants to $\chi^{1/1\cdot25}$, and found them to converge to the corresponding estimated values shown in Fig. 2*a*. Hence the result for the critical exponent upholds the universality hypothesis and implies that the phase transitions for various x and y are all of second order.

4. Conclusions

Our results for the Haus–Tanaka model are different from those obtained by the mean field approximation. We have shown by means of the high temperature susceptibility series that the model has a second-order transition for all x and y. On the other hand, the mean field approximation adopted by Haus and Tanaka predicts that a change from a second- to a first-order transition occurs for $y > 1+x$. However, evidence is lacking to support such a prediction. Models that exhibit such a change in the nature of the phase transitions (Oitmaa 1972; Harbus and Stanley 1973*a*, 1973*b*) possess high temperature susceptibility series which show signs of irregularity and anomalies in the series analysis. Our series, however, does not display any such symptoms. Thus the Haus–Tanaka model does not appear to have a first-order transition. Based on similarities in both nature and results between the present model and the pair-quartet Ising model mentioned in Section 3, we feel that the occurrence of a first-order transition is not an inherent property of the model but a spurious consequence of the approximation. Hence the model is not capable of accounting for the transition between the ice VII and ice VIII phases.

Acknowledgments

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