



Phase transition behavior of the three-dimensional sixteen-vertex model
by Robert Adam Stern

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of
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Montana State University
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Abstract:

We have analyzed the critical behavior of a model describing phase transitions in KDP-type materials.

KDP-type materials are ferroelectric hydrogen-bonded crystals. Most of the members in this crystal family undergo a first-order ferroelectric transition, but the transition in KDP can be forced to second-order with pressure, and one member has a second-order transition at atmospheric pressure. It is generally accepted that the transition in these materials is intimately connected with the ordering of hydrogen nuclei in their bonds. However, precise details of the microscopic mechanism behind the ferroelectric phase transition is still, after half a century, a matter of debate.

For three decades the 3D sixteen-vertex model (16VM) has been used to describe ferroelectric phase transitions in KDP-type crystals, although its critical behavior has never been studied beyond a mean-field analysis. We have investigated the 3D 16VM on the diamond lattice with series expansions and Monte Carlo simulations. The model exhibits both first- and second-order transitions, depending on the magnitude of the interaction energies. When the transition is second-order, the 16VM belongs to the universality class of the 3D Ising model.

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APPROVAL

of a dissertation submitted by

Robert Adam Stern

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

George F. Tuthill

George F. Tuthill
(Signature)

4/23/01
(Date)

Approved for the Department of Physics

John. C. Hermanson

John C. Hermanson
(Signature)

4-23-01
(Date)

Approved for the College of Graduate Studies

Bruce R. McLeod

Bruce R. McLeod
(Signature)

4-23-01
(Date)

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ABSTRACT

We have analyzed the critical behavior of a model describing phase transitions in KDP-type materials.

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For three decades the 3D sixteen-vertex model (16VM) has been used to describe ferroelectric phase transitions in KDP-type crystals, although its critical behavior has never been studied beyond a mean-field analysis. We have investigated the 3D 16VM on the diamond lattice with series expansions and Monte Carlo simulations. The model exhibits both first- and second-order transitions, depending on the magnitude of the interaction energies. When the transition is second-order, the 16VM belongs to the universality class of the 3D Ising model.

CHAPTER ONE

INTRODUCING THE MAIN CHARACTERS

Introduction

A stimulating and perpetual problem in the field of statistical mechanics is the determination of critical properties of models used in describing real materials. The ferroelectric phase transition in KDP-type materials has been well studied experimentally, but the microscopic behavior underlying the transition is still, after fifty years, under debate. The theory of ferroelectric phase transitions in KDP-type crystals is founded upon a three-dimensional sixteen-vertex model (3D 16VM) on the diamond lattice, whose critical behavior is not at all well studied or understood. We report here our investigations into the 3D KDP 16VM with analyses of series expansions and Monte Carlo (MC) simulations, and we find the model displays both first- and second-order transitions. Furthermore, when the transition is second-order, the critical exponents belong to the 3D Ising model universality class. In this first chapter we place our work in context by introducing the reader to the flora and fauna residing in the wilderness of phase transitions in lattice models. We begin by discussing phase transitions in physical systems, then models displaying phase transitions, followed by a history of KDP-type crystals and a brief synopsis of their properties, and finally a general discussion of the 16VM.

Critical Phenomena

Phase transitions of various types occur in many different systems, yet they all display quite similar behavior. Whatever their precise nature, all phase transitions can be characterized by an *order parameter*, typically an extensive thermodynamic variable, which is zero in the high-temperature disordered phase, and nonzero in the low-temperature ordered phase. A sampling of common phase transitions and their order parameters are given in Table 1.

<u>Phase Transition</u>	<u>Order Parameter</u>
liquid-gas	density difference
ferromagnetic	- real scalar field magnetization
ferroelectric	- real scalar field polarization
superfluidity	- real scalar field phase of bosonic wave function
low-T superconductivity	- complex scalar field phase of Cooper pair wave function
helium ³	- complex scalar field phase of bosonic wave function
electroweak	- nine complex scalar fields - $\mathbb{C}^9$ vector gauge boson masses - $U(1) \times SU(2)$

Table 1. Examples of Phase Transitions and their Order Parameters

In the liquid-gas transition, for example, the order parameter ρ is the difference between the density of the gas and liquid: $\rho = \rho_{\text{liquid}} - \rho_{\text{gas}}$. At the critical temperature and pressure, ρ is zero, $\rho_{\text{liquid}} = \rho_{\text{gas}} \equiv \rho_c$, and phase coexistence is achieved. In ferromagnetic transitions, the order parameter is M , the average magnetization. This thesis is concerned with ferroelectric transitions in KDP-type crystals, for which the

order parameter is the polarization per unit volume P . Phase transitions can be labelled (a la Ehrenfest and Fisher^[1,2]) by discontinuities in thermodynamic functions; a transition is called n^{th} -order if the n^{th} derivative of the free energy is discontinuous. A first-order transition may exhibit a finite jump in the order parameter, while at a second-order transition the order parameter is continuous, and for example a susceptibility is discontinuous (usually it diverges).

Near second-order phase transitions, thermodynamic quantities behave as power laws. This is because at the critical temperature the correlation length $\xi(T, E_{\text{ext}})$ diverges and the system is left without any characteristic length scale. Power laws describe such scale invariant behavior, whereas an exponential, for example, does not. Given a coordinate l and a length scale L , the ratio of exponentials:

$$\frac{e^{\frac{l}{L}}}{e^{\frac{10l}{L}}} = e^{-\frac{9l}{L}} \quad (1.1)$$

obviously depends on L , but the ratio of powers:

$$\frac{\left(\frac{l}{L}\right)^{\alpha}}{\left(\frac{10l}{L}\right)^{\alpha}} = \frac{1}{10^{\alpha}} \quad (1.2)$$

does not. Thus power laws are naturally suited to describing systems without any characteristic length scale (such as phase transitions).

As a pertinent example, consider ferroelectric systems at a second-order transition. In zero external electric field, the polarization is zero above the critical

temperature T_c , and approaching T_c from below it vanishes as a power of the temperature difference from the critical point:

$$P \propto (T_c - T)^\beta, \quad T < T_c. \quad (1.3)$$

The parameter β is a *critical exponent*. Given the Gibbs free energy $G(T, E_{ext})$, the zero-

field dielectric susceptibility $\chi_T = -\frac{\partial^2}{\partial E^2} G(T, E_{ext}) \Big|_{E_{ext}=0}$ diverges at the transition

temperature as a power:

$$\chi_T \propto \begin{cases} |T - T_c|^{-\gamma} & T < T_c \\ |T - T_c|^{-\gamma'} & T > T_c \end{cases} \quad (1.4)$$

This defines the critical exponents γ, γ' . One often finds $\gamma = \gamma'$ in physical systems. The

specific heat $C_E = -T \frac{\partial^2}{\partial T^2} G(T, E_{ext} = 0)$ also diverges as a power at the phase transition:

$$C_E \propto \begin{cases} |T - T_c|^{-\alpha} & T < T_c \\ |T - T_c|^{-\alpha'} & T > T_c \end{cases} \quad (1.5)$$

Usually $\alpha = \alpha'$ within experimental error for most physical systems. Finally, the correlation length $\xi(T, E_{ext}=0)$ diverges with exponent ν :

$$\xi \propto \begin{cases} |T - T_c|^{-\nu} & T < T_c \\ |T - T_c|^{-\nu'} & T > T_c \end{cases} \quad (1.6)$$

Many different materials, even different phase transitions, often have the same critical exponents. Systems with the same critical exponents belong to the same *universality class*, and all physical phenomena fall into only a few universality classes. Table 2 gives a condensation by the author of data from many sources on some critical

exponents for a few experimental and theoretical systems (some theoretical models exhibiting phase transitions are described below).

<u>System</u>	<u>α</u>	<u>β</u>	<u>γ</u>	<u>Ref.</u>
<i>Ferromagnetic</i>				
Fe	0.12±0.01	0.34±0.02	1.333±0.015	[2,3]
Ni	0.10±0.03	0.33±0.03	1.320±0.023	[1,4,3]
Gd			1.33	[4,3]
YFeO ₃		0.354±0.005	1.33±0.05	[4,3] $\gamma \approx 7$ [4]
EuS		0.33±?		[1]
<i>Liquid-gas</i>				
CO ₂	0.125±?	0.3447±0.0005	1.20±0.02	[4]
Xe	0.08±0.02	0.350±0.015	1.3±0.1	[2,4]
Ar		0.33±0.05		[3]
<i>Superfluid</i>				
He ⁴	-0.014±0.016	0.34±0.01	1.33±0.03	[2]
He ³	≤0.3	0.361±0.001	1.15±0.03	[4]
<i>Ferroelectric</i>				
TGS			1.00±0.05	[4]
<i>Models</i>				
Mean Field	0 (discontinuity)	1/2	1	[3]
Ising 2D	0 (log)	1/8	7/4	[1,4]
Ising 3D	0.119±0.006	0.326±0.004	1.249±0.003	[4,5,6]
XY 3D	0.02±0.03		1.35±0.01	[4]
Heisenberg 3D	0.14±0.06	0.38±0.03	1.375±0.02	[1,4]

Table 2. Critical Exponents for Selected Models and Materials.

According to the universality hypothesis, all that determines the critical exponents of a system are the dimensionality of the system and the order parameter. Because there is no natural length scale near a phase transition, microscopic details become unimportant and the behavior of different systems near phase transitions are remarkable similar. Displaying this graphically are experimental data for liquid-gas and ferromagnetic transitions given in Figures 1 and 2. Plotted in Figure 1 (from

Guggenheim^[7]) is the scaled density versus temperature for eight different materials along the liquid-gas coexistence curve. Figure 2 is a plot of the scaled magnetization versus temperature, for five magnetic systems^[8]. After suitable scaling, all the data lie on the same curves.

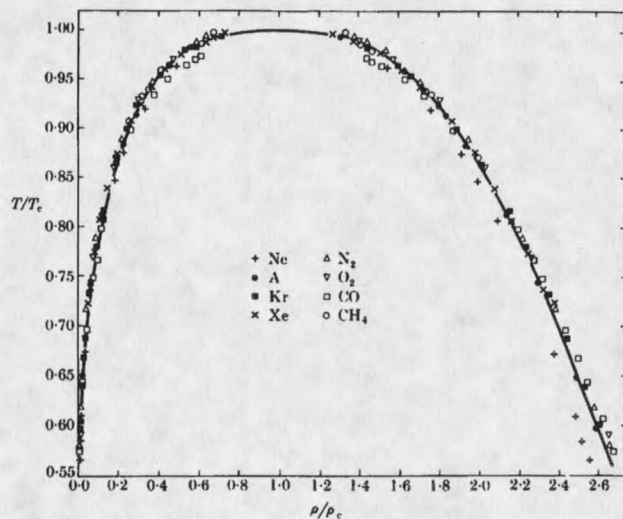


Figure 1. Liquid-Gas Transition^[7].

Shown are measurements of the coexistence curve on eight fluids.

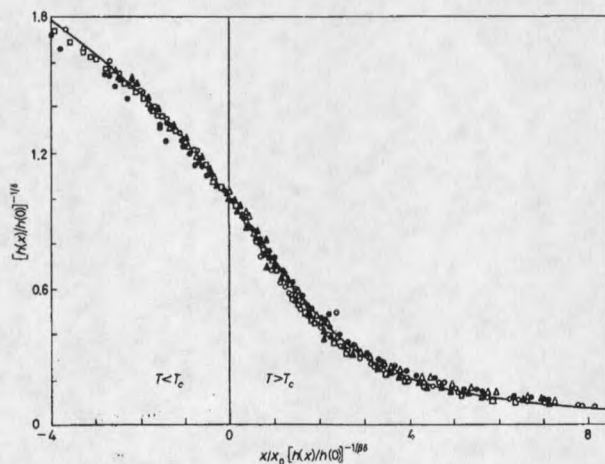


Figure 2. Ferromagnetic Transition^[8]. Experimental data for five various magnets.

▲ CrBr₂ ○ EuO₃ △ Ni ● Pd₃Fe □ YIG

The horizontal axis is scaled temperature, and the vertical axis is scaled magnetization.

Power law behavior in thermodynamic functions near a critical point are a consequence of the singular part of the free energy being a generalized homogeneous function (GHF) of its arguments. A GHF is one in which the following holds, for all λ :

$$G(\lambda^{a_E} E, \lambda^{a_T} \tau) = \lambda G(E, \tau) \quad (1.7)$$

and $\tau \equiv T - T_c$. a_E and a_T are the *external field-* and *temperature-scaling exponents*.

Equation (1.7) is for two arguments; it is straightforward to generalize a GHF to more than two variables. We can obtain expressions for α , β , and γ in terms of a_E and a_T . To find β , we take the derivative of equation (1.7) with respect to E :

$$\lambda^{a_H-1} P(\lambda^{a_E} E, \lambda^{a_T} \tau) = P(E, \tau) \quad (1.8)$$

Since this is true for any λ , it is certainly true for $\lambda = \tau^{-\frac{1}{a_T}}$. Using this and setting $E=0$ we obtain:

$$P(0, \tau) = P(0, 1) \tau^{\frac{1-a_E}{a_T}} \quad (1.9)$$

and thus $\beta = \frac{a_E - 1}{a_T}$. Playing exactly the same game with more derivatives we find:

$$\gamma = \frac{2a_E - 1}{a_T} \quad (1.10)$$

$$\alpha = \frac{2a_T - 1}{a_T} \quad (1.11)$$

Equations (1.10) and (1.11) imply the critical exponents are not all independent, and we can construct an example of a *scaling relation*:

$$\alpha + 2\beta + \gamma = 2. \quad (1.12)$$

What determines the universality class of a system are merely the values of the scaling exponents a_E and a_T .

Models of Critical Phenomena

There exists a hierarchy of models for systems exhibiting critical phenomena. The simplest and most widely used model is *mean-field theory* (MFT) (also known as “the Classical Theory,” Landau-Ginzburg theory and Weiss molecular field theory). MFT neglects all fluctuations in the system; each element interacts equally but weakly with every other element in the system. Most models are easily solvable within the MFT approximation, and treatments are straightforward and numerous^[1,4]. Suffice it to say, the scaling powers for MFT in any dimension are $a_T = 1/2$, and $a_E = 3/4$; the critical exponents are $\beta = 1/2$, $\gamma = 1$, and $\alpha = 0$ (the specific heat is discontinuous at T_c).

The spin-1/2 Ising model is a good beginning for discussions of lattice models. Originally conceived of by Wilhelm Lenz, it was the subject of Ernst Ising’s doctoral thesis in 1925. Ising solved the one-dimensional model and concluded it displayed no critical behavior at any finite temperature; he then gave a few heuristic arguments supporting the lack of phase transitions in the two- and three-dimensional models. After receiving his doctorate in Germany, he quit physics, worked for a German electric company, emigrated to the United States, and became a physics teacher in North Dakota^[9]. It was not until 1947 that he learned the model had acquired his name and that the derivation of the 2D zero-field partition function in 1944 by Lars Onsager^[10] was considered a pinnacle of mathematical physics. Nowadays the Ising model has been

extended to arbitrary-dimensional multi-configurational vertex models, used to model a variety of phase transitions in many physical systems, including liquids^[11], ferromagnets^[1,8], ferroelectrics^[12], particle physics^[13], and superstrings^[14].

Defining the Ising model is simple enough: on the vertices of a D -dimensional lattice are located spin variables $\sigma_i = \pm 1$, $i=1, \dots, 2N$. $2N$ is the total number of spins (we choose $2N$ spins so as to be consistent with the following chapters). In magnetic language, the spin variables represent localized spin moments, and in ferroelectric language they are electric dipole moments. These spins interact via the Hamiltonian:

$$H = -h \sum_{\langle i,j \rangle} \sigma_i \sigma_j - E_{ext} d \sum_i \sigma_i \quad (1.13)$$

d is the dipole moment of each spin, and E_{ext} is an external field. If we desire aligned spins to be energetically favored (i.e. a ferromagnet or ferroelectric), then $h > 0$. $\sum_{\langle i,j \rangle}$ is a sum over all nearest-neighbor spin pairs (although this restriction can be relaxed and one can consider next-nearest neighbors, etc.), and $\sum_i$ is a sum over all spins. The first term in (1.13) tends to align the spins, and the second term is a coupling of each spin to an external field.

It is easy to calculate thermodynamic quantities of the one-dimensional model with cyclic boundary conditions; defined on a row of N spins wrapped on a circle, the first spin identified with the last. To solve the model, a savage may exhibit the use of brute force, whereby one writes the partition function for a ring with two spins, then with three spins, then four spins, etc. A pattern is noticed, and the partition function in the thermodynamic limit is written down. Alternatively, one can reveal elegance and

sophistication by use of the transfer matrix^[15,16], a tool that finds wide application in lattice-model theory. However it is arrived at, in the thermodynamic limit, the partition function of the 1D Ising model is:

$$Z(T, E_{ext}) = e^J \cosh K + \sqrt{e^{2J} \sinh^2 K + e^{-2J}} \quad (1.14)$$

where:

$$J \equiv \frac{h}{k_B T} \quad (1.15)$$

$$K \equiv \frac{E_{ext} d}{k_B T} \quad (1.16)$$

The free energy is:

$$G(T, E_{ext}) = -k_B T \ln Z(T, E_{ext}) \quad (1.17)$$

The polarization per spin is:

$$P(T, E_{ext}) = -\frac{\partial G(T, E_{ext})}{\partial E_{ext}} = d \frac{e^J \sinh K}{\sqrt{e^{2J} \sinh^2 K + e^{-2J}}} \quad (1.18)$$

The susceptibility is:

$$\chi(T, E_{ext}) = \frac{\partial P(T, E_{ext})}{\partial E_{ext}} = \frac{d^2}{k_B T} \frac{e^{-J} \cosh K}{(e^{2J} \sinh^2 K + e^{-2J})^{\frac{3}{2}}} \quad (1.19)$$

We see that $\lim_{E_{ext} \rightarrow 0} P = 0$ for all non-zero temperatures. However, $\lim_{E_{ext} \rightarrow 0} \lim_{T \rightarrow 0} P = d$. A

phase transition thus occurs at zero field and zero temperature, and the value of the spontaneous magnetization depends strongly upon the path taken toward criticality.

$\chi(T, E_{ext})$ displays similar critical behavior: $\lim_{T \rightarrow 0} \chi = 0$ for all non-zero E_{ext} , but

$\lim_{E_{ext} \rightarrow 0} \chi = d^2 \frac{e^{2J}}{k_B T}$, and χ displays an essential singularity at $(T, E_{ext}) = (0, 0)$, see Figures 3

and 4.

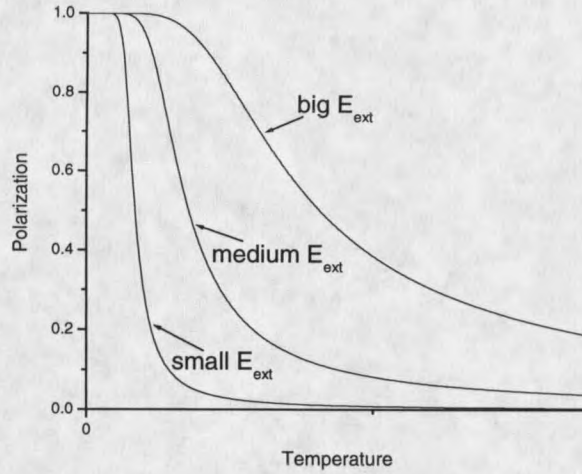


Figure 3. Polarization of the 1D Ising Model vs. Temperature, for various values of applied external field E_{ext} . $\mu = \frac{j}{k_B} = 1$.

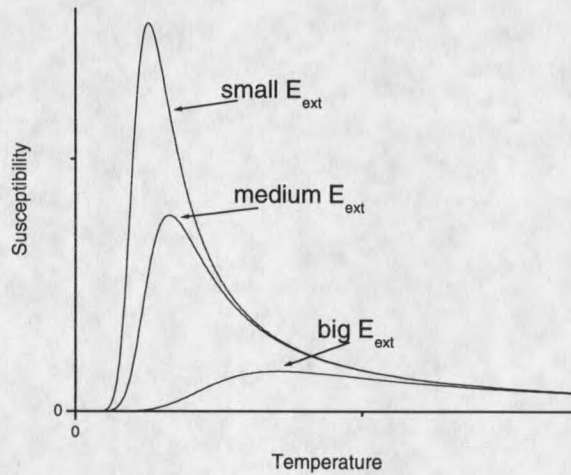


Figure 4. Susceptibility of the 1D Ising Model vs. Temperature, for various values of applied external field E_{ext} . $\mu = \frac{j}{k_B} = 1$.

The two-dimensional model was solved by Onsager in 1944 with an amazing display of applied Lie algebras and elliptic functions. Onsager examined the algebraic symmetries of the transfer matrix, which enabled him to derive functional relations for its eigenvalues, and with some analyticity arguments, the partition function. We state here for cultural value the free energy of the two-dimensional spin-1/2 zero-field Ising model^[10,15,16].

$$\begin{aligned}
 F &= -k_B T \lim_{n,m \rightarrow \infty} \frac{\ln Z}{mn} \\
 &= -k_B T \left[\ln(2) + \frac{1}{8\pi^2} \int_0^{2\pi} d\omega \int_0^{2\pi} d\omega' \ln(\cosh^2(2J) - \sinh(2J)(\cos \omega + \cos \omega')) \right]
 \end{aligned} \tag{1.20}$$

The three-dimensional model remains unsolved. Much numerical work has been done; the critical temperature, critical exponents, and corrections to scaling have been found with reasonable accuracy^[5,6]. The model is not likely to be solved analytically anytime soon; the class of functions required are *triply periodic* (much as elliptic functions, used in the 2D model, are doubly-periodic), about which nothing is known other than they can be both smooth and chaotic. The solution also involves algebraic varieties of high genus, of which very little is known, even by algebraic geometers^[17].

The XY model is much like the Ising model, except instead of just two discrete states, the spins are free to rotate in the x-y plane. The Hamiltonian is:

$$H = -j \sum_{\langle i,j \rangle} \vec{\sigma}_i \cdot \vec{\sigma}_j - \vec{E}_{ext} \cdot d \sum_i \vec{\sigma}_i \tag{1.21}$$

where $\vec{\sigma}_i$ is a two-dimensional vector representing the spin at site i . E_{ext} is in the plane of the spins. The order parameter of this model is two-dimensional. The XY model has as an obvious generalization the Heisenberg model, where the spins can point in any

direction. The Hamiltonian is the same for the XY model, but now the spins have three components, and the order parameter is three-dimensional. These models exhibit a wide variety of phase transition behavior^[18]

The 16VM is physically motivated by the theory of phase transitions in KDP-type crystals. Before discussing the 16VM, we present some properties of this crystal family.

KDP-Type Crystals

Modern ferroelectrics research began humbly enough in 1919 with the publication of an innocuous paper^[19] which largely escaped detection by the physics community, on the anomalous dielectric behavior of Rochelle salt (RS, a.k.a. $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$). Seignette first manufactured RS in LaRoche, France around 1655^[20]. Ferroelectricity, or "Seignette-electricity" as it was then called, was investigated in RS throughout the swinging twenties and thirties. The dielectric constant of RS as a function of temperature displays two prominent peaks, as shown in Figure 5. At two temperatures where the peaks occur, the spontaneous polarization vanishes, see Figure 6. This rather peculiar data suggest the occurrence of two separate phase transitions, a conclusion heartily reinforced by the realization that structural changes accompany the anomalous dielectric behavior^[20].

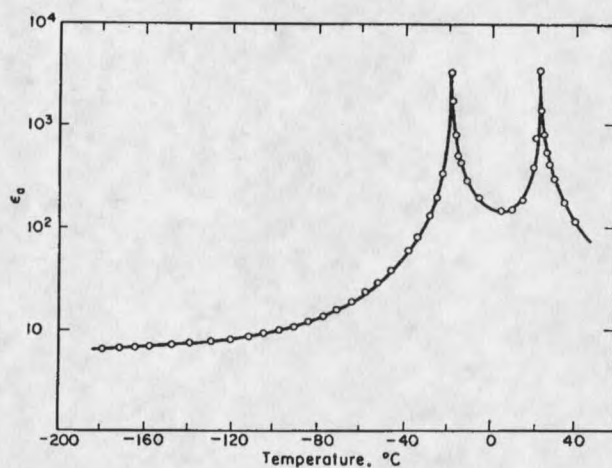


Figure 5. Dielectric Susceptibility of RS^[20]

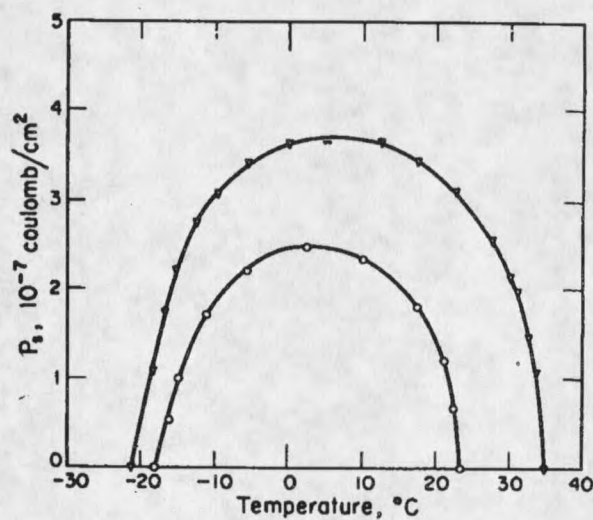


Figure 6. Spontaneous Polarization of RS^[20]
The lower curve is RS, and the upper curve is deuterated RS.

Unfortunately, theoretical understanding of the charge redistribution producing the macroscopic polarization in RS seemed difficult to acquire, if not unattainable. The complex chemical formula resisted any straightforward, intuitive explanation. Experimental reproducibility was low and quality samples difficult to maintain, due to

RS's high solubility in water and resulting sensitivity to humidity. In the face of such adversity much progress was gained over time, but in the early thirties RS "was some kind of physical curiosity and it was a good question to ask whether other substances might be found with similar properties."^[21] A great search was thus embarked upon to find a simpler, more stable, and altogether more benign material displaying Seignette-electricity. Ice was investigated.

On the morning of March 13, 1935, after two and a half years of disappointing experiments, a desperate graduate student named Georg Busch, working under Paul Scherrer at the ETH in Zurich, discovered ferroelectricity in a homely crystal widely held in disrepute named KDP (KH_2PO_4)^[22]. He then carried liquid hydrogen on a bus^[21].

Since then KDP has become the prototypical ferroelectric^[23], supporting a field of research and a line of industrial products. The distortive piezoelectric properties are exploited in speakers, microphones, guitar pickups, actuators and accelerometers. Large high-quality crystals of KDP are easy to fabricate because KDP is water soluble. The optics community commonly utilizes the birefringence of KDP^[24] to tune their lasers. Changes of crystal structure^[25-27], specific heat^[28,29], and dielectric properties^[39] at low temperatures and through the phase transition have been investigated. Pressure^[31], deuteration^[32], and isomorph effects^[33] on the phase transition have been reported. A pressure induced tricritical point in KDP was discovered in 1976^[34,35]. Hopping of hydrogen nuclei in and between their bonds has a rich and continuing history^[36-38]. Domains and domain wall motions are continuing to be observed and understood as new experimental methods become available^[39-44]. Relaxational dynamics have been

studied^[45-47]. Mixed crystals made from a ferroelectric (such as KDP) and an antiferroelectric (such as $\text{NH}_4\text{H}_2\text{PO}_4$, a.k.a. ADP) display glassy behavior^[48-50]. The chemical reactions occurring at high-temperature leading to breakdown of the crystal have been recently studied in detail^[51-53].

In the past half century, KDP has been eclipsed by perovskite ferroelectrics, of which the first to be investigated was BaTiO_3 (BT) during 1943-1946^[54]. These materials are ferroelectric at room temperature, and display much greater electromechanical responses at room temperature than KDP-type crystals: the dielectric, piezoelectric, and electromechanical coupling constants for BT are 40, 11, and 4 times larger at room temperature, respectively than of KDP^[55]. Of particular interest are ferroelectric-relaxor ferroelectric mixtures near the morphotropic phase boundary, displaying ultrahigh piezoelectric and electromechanical coupling, greater than BT by a factor of ten.^[56,57] Nonetheless research on KDP-type crystals continues apace.

Figures 7 and 8 show Busch's measurements of the dielectric constant and spontaneous polarization of KDP as a function of temperature. It can be said that KDP has nice curves. The susceptibility is negligible between zero K and 97 K (Figure 7 suggests about 75 K, but that was measured in 1935 with samples full of defects^[21]). At 97 K the susceptibility suddenly increases by an order of magnitude, remaining roughly constant, until about 150K, where it reaches its maximum. Above 150K it rapidly decreases, following the Curie-Weiss law $\chi_r = C/(T - T_c)$. The maximum at 150 K signifies a transition from the paraelectric tetragonal phase to the ferroelectric orthorhombic phase (the transition is at 123K in clean crystals). The sharp drop at 97 K

results from a freezing out of domain wall motions^[39-44]. These straightforward correspondences ought not to conceal the depth and complexity underlying the microscopic mechanisms, and the lack of completely satisfactory explanations for them.

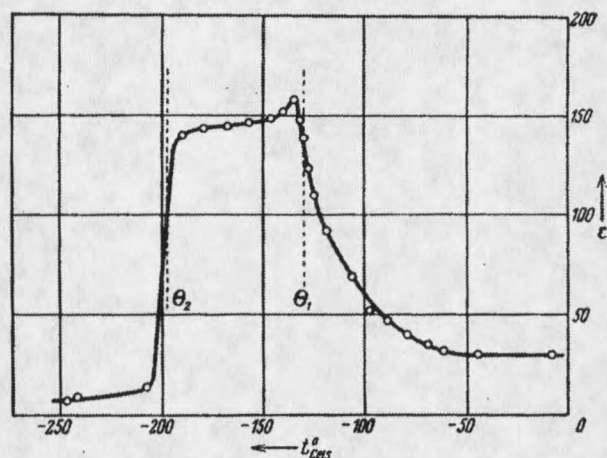


Figure 7. Dielectric Susceptibility of KDP^[22]

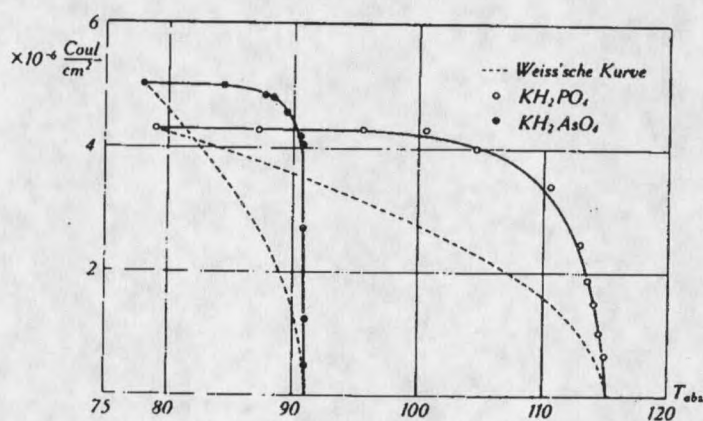


Figure 8. Spontaneous Polarization of KDP^[22]

KDP is a hydrogen-bonded crystal which gives its name to a whole family of ferroelectrics. Relatives include the isomorphs RbH_2PO_4 (RDP), KH_2AsO_4 (KDA), RbH_2AsO_4 (RDA), and CsH_2AsO_4 (CDA). CsH_2PO_4 (CDP), the ostracized uncle, has a different structure than KDP, as the cesium atoms are too big. CDP displays one-

dimensional behavior^[58]. Fully deuterated RDP also has a different structure than KDP. If an ammonium ion is exchanged for the cation, the crystal is the antiferroelectric second cousin ADP. The hydrogens can also be deuterated, yielding a dramatic increase in the critical temperature by almost a factor of two. Members of the KDP family and their ferroelectric critical temperatures are given in Table 3.

<u>Name</u>	<u>Chemical Formula</u>	<u>T_c (K)</u>
KDP	KH ₂ PO ₄	122.5
RDP	RbH ₂ PO ₄	146.9
KDA	KH ₂ AsO ₄	95.5
RDA	RbH ₂ AsO ₄	110
CDA	CsH ₂ AsO ₄	143
DKDP	KD ₂ PO ₄	213
DRDP	RbD ₂ PO ₄	218
DKDA	KD ₂ AsO ₄	160
DRDA	RbD ₂ AsO ₄	173
DCDA	CsD ₂ AsO ₄	212

Table 3. Members of the KDP Family and their Ferroelectric Transition Temperatures^[33].

The crystal structure of KDP consists of PO₄ groups located at the vertices of a diamond lattice, connected by hydrogen bonds lying nearly in the *a-b* plane perpendicular to the ferroelectric *c*-axis. Each phosphate is connected by four hydrogen bonds to four adjacent phosphate groups. Potassium ions lie above each phosphate group along the *c*-axis, and the spontaneous polarization results from a change in the relative displacement of the K and P ions along the *c*-axis^[59]. Every proton in its H-bond has two stable off-center positions, symmetrically placed about the bond center. The protons are ordered below the transition temperature, and disordered above^[60]. Figure 9 shows a drawing of KDP from the early thirties, reproduced in Slater's pioneering work^[61].

The ferroelectric transition is first-order for all family members but RDP, which has a second-order transition^[62]. The transition in KDP is only weakly first-order, and can be made second-order with the application of pressure^[34,35]. Pressure also decreases the critical temperature, and $T_c = 0$ for RDP at 16 kbar^[31].

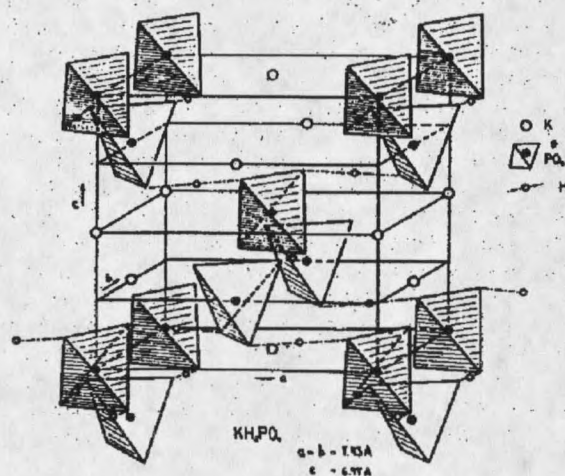


FIG. 1. Structure of KH_2PO_4 . Figure from Dr. C. C. Stephenson, by permission.

Figure 9. Structure of KDP^[61]

A simple and straightforward (albeit naïve and only partially true) mechanism for the phase transition follows from assuming the dipole moments are coupled to the hydrogens' positions, and the hydrogens' motion is dominated by tunneling (or thermally activated hopping) between their two stable off-center positions^[59,60,62]. The electric dipoles order when the hydrogens do. Most (not all) trends in variations of the critical temperature of KDP-family members as a function of deuteration (see Figure 10) are easily understood within this framework. When a crystal is deuterated, the critical

temperature increases, as the tunneling probability is smaller for a heavy deuteron than a light proton. Since the hydrogen tunneling is coupled to the cation displacement, increasing the cation mass inhibits tunneling, increasing the critical temperature. It is not a priori clear why the critical temperature decreases when the phosphate is replaced by an arsenate, as the O-H...O distance is greater in KDA than in KDP; perhaps the tunneling barrier in the hydrogen bond is decreased, or the mobility of the cation is enhanced. This question is well suited to first-principles density functional-type calculations.

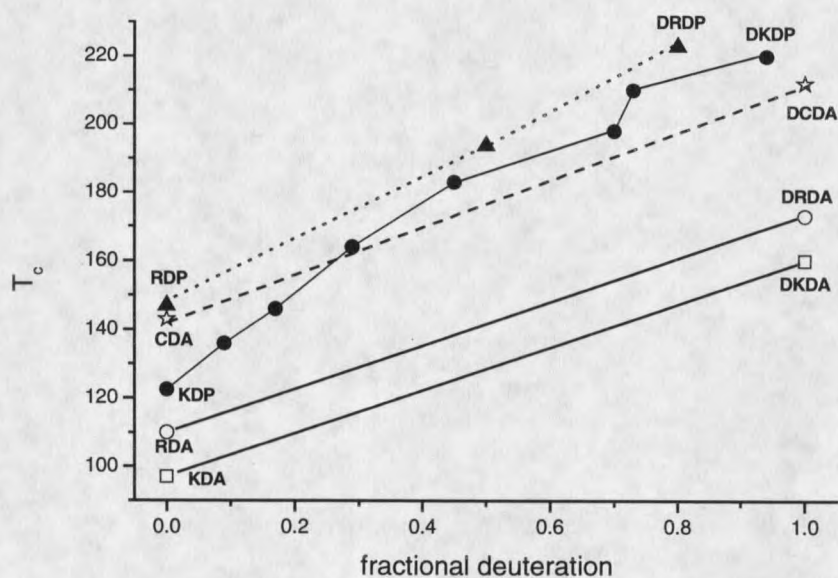


Figure 10. Transition Temperature for KDP-Family Members as a Function of Deuteration^[33]

The Sixteen Vertex Model

KDP theory began in earnest with the ice rules of Linus Pauling^[63] applied to a six vertex model (6VM) by J. C. Slater^[61]. The 2D 6VM was solved exactly by Lieb in 1967^[64]. Great progress was made in 1972 when Rodney Baxter calculated the free energy of the 2D eight vertex model (8VM)^[65] and showed Slater's 6VM was the solution of the 8VM at the critical temperature. Theoretical work on KDP continues unabated^[59,60,62,66-71] with investigations on various vertex models coupled to all sorts of long-range interactions, often accurately modeling the transition in KDP-type crystals.

The 16VM is a model of the hydrogen motion in KDP-type crystals, coupled to the local dipole moments. Since each phosphate group is attached to four hydrogen bonds, and since each hydrogen can sit in one of two places, "near" or "far" from the phosphate group, there are $2^4 = 16$ possible configurations of the four protons in the attached bonds. Assigning a specific energy to each configuration defines a particular 16VM on the diamond lattice, each vertex corresponding to a phosphate tetrahedron. The sixteen phosphate configurations, and energies we assign them are shown in Figure 11.

The six lowest energy configurations satisfy Pauling's "ice rule"^[63], with two protons close to, and two protons far from, each phosphate group. Of these configurations the two of lowest energy, giving rise to a polarization along the $+c$ ($-c$) axis, have the two near protons on the upper (lower) sides of the phosphate, as viewed along the c -axis. We assign energy zero (in zero external field) to these two configurations, and energy $\varepsilon_0 > 0$, the Slater energy, to each of the four remaining ice

rule states^[61]. Lying higher in energy yet with energy $\epsilon_1 > \epsilon_0$ are the eight Takagi configurations having one or three protons near the PO_4 group^[66]. The two remaining configurations each have zero or four protons nearby, and the PO_4 group is doubly ionized, with energy $\epsilon_2 > \epsilon_1$. In the presence of an external field applied along the c-axis, the ground states and Takagi states, which carry dipole moments $\pm 2\delta$ and $\pm\delta$ respectively, are split in energy. The 16VM considered here is adapted to the crystal anisotropy of KDP-type crystals, since $\epsilon_0 \neq \epsilon_2$ (see also the graphical representation of configurations in Figure 15, page 29).

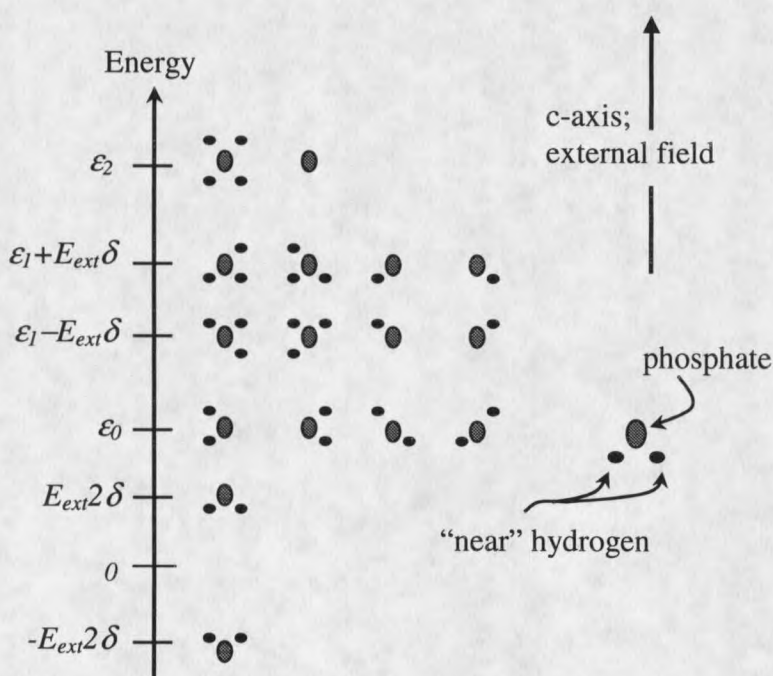


Figure 11. Assignments of Energies to Proton-Phosphate Configurations.

Slater originally considered a 6VM involving only the six lowest-energy states of Figure 11. With a mean-field type argument he showed the 6VM possessed only first-order transitions in which below the transition temperature the spontaneous polarization

P_s is independent of temperature, and at the transition temperature the polarization can take any value between zero and P_s . This behavior was confirmed in the 2D model with an exact solution^[64]. Critical behavior of this type is pathological, a consequence of the 6VM disallowing any dynamics. Later Takagi^[66] considered a fourteen vertex model (14VM) by including the eight vertices of higher energy, and concluded, also with a mean-field analysis, that the 14VM has only second-order transitions. The present work shows, without any mean-field-type analyses, that the 16VM has both first- and second-order transitions, depending on the relative strength of the energies ε_0 , ε_1 , and ε_2 . Inclusion of the two states with energy ε_2 also requires a four-spin interaction in the Hamiltonian (see equation (1.22)), the magnitude of which determines the order of the transition.

It is useful to view the 16VM on the diamond lattice as an Ising model on a different but related lattice^[72]. The transformation involves representing each H-bond by an Ising spin $\sigma = \pm 1$, where $+1$ (-1) designates the proton configuration compatible with the state completely polarized in the $+c$ ($-c$) direction. The lattice resulting from connecting nearest neighbor spins is constructed by placing tetrahedra around the sites of the old diamond lattice; we call this lattice the "Interaction-Round-a-Tetrahedron"^[16] (IRT) lattice, see Figure 12.

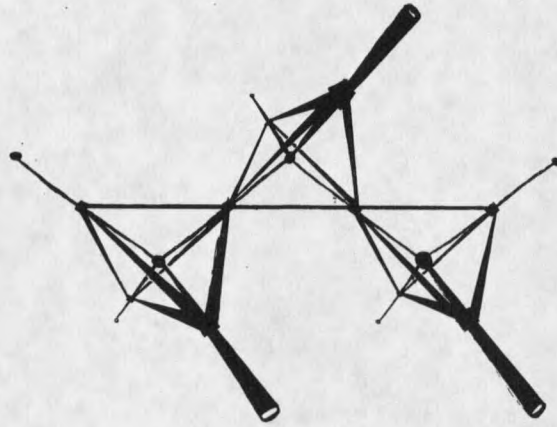


Figure 12. The IRT Lattice

IRT spins in a tetrahedron around individual PO_4 groups are coupled by 1-, 2-, and 4-spin interactions. The IRT model thus described has a Hamiltonian for each vertex of the form:

$$\begin{aligned}
 H = & J_0 - J_1(\sigma_i + \sigma_j + \sigma_k + \sigma_l) \\
 & - J_2'(\sigma_i\sigma_k + \sigma_i\sigma_l + \sigma_j\sigma_k + \sigma_j\sigma_l) \\
 & - J_2''(\sigma_i\sigma_j + \sigma_k\sigma_l) \\
 & - J_3(\sigma_i\sigma_j\sigma_k + \sigma_i\sigma_j\sigma_l + \sigma_i\sigma_k\sigma_l + \sigma_j\sigma_k\sigma_l) \\
 & - J_4\sigma_i\sigma_j\sigma_k\sigma_l
 \end{aligned} \tag{1.22}$$

where $\sigma_\alpha = \pm 1$ and

$$J_0 = \frac{\varepsilon_0}{4} + \frac{\varepsilon_1}{2} + \frac{\varepsilon_2}{8} \tag{1.23}$$

$$J_1 = -\frac{\delta}{2} E_{\text{ext}} \tag{1.24}$$

$$J_2' = \frac{\varepsilon_2}{8} \tag{1.25}$$

$$J_2'' = \frac{\varepsilon_0}{4} - \frac{\varepsilon_2}{8} \tag{1.26}$$

$$J_3 = 0 \quad (1.27)$$

$$J_4 = -\frac{\epsilon_0}{4} + \frac{\epsilon_1}{2} - \frac{\epsilon_2}{8} \quad (1.28)$$

The Ising interactions are shown graphically for a phosphate tetrahedra in Figure 13.

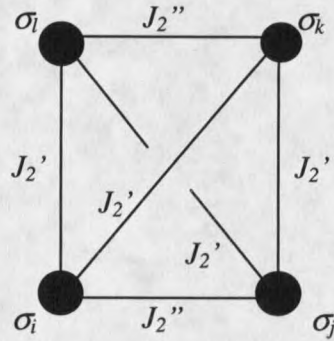


Fig. 13. Ising Model on a Tetrahedron of the IRT Lattice.
 J_2' and J_2'' are the two-spin interactions, and J_4 is the four- spin interaction.

The 2-spin interactions are anisotropic, since in general $J_2' \neq J_2''$. J_3 is zero due to symmetries in the grouping of configurations with respect to their energy assignments. The 4-spin interaction is in general non-zero. When $J_4 = 0$ the transition to the ordered phase is always second-order, becoming first-order when J_4 is large, compared to the two spin interactions.

Consideration of the 16VM shows that, as long as the ferroelectric phase is energetically favored (the case considered here), the ground state of the IRT model has all spins up or all spins down, despite the fact that J_2'' and J_4 may be positive or negative. When J_2' is negative while J_2'' and J_4 are positive, the model has competing interactions. If the groupings of configurations are left intact, but their ordering changed, we arrive at models with other possible ground states, see Figure 14. When the

Takagi groups are energetically favored, the vertex model is equivalent to a three dimensional dimer model, with a finite residual entropy. When the doubly ionized configurations are favored, the IRT model has a superantiferroelectric ground state consisting of alternating ferroelectric planes perpendicular to the c -axis. These other phases are sure to exhibit phase transitions of one type or another, a study of which would comprise a nice doctoral thesis.

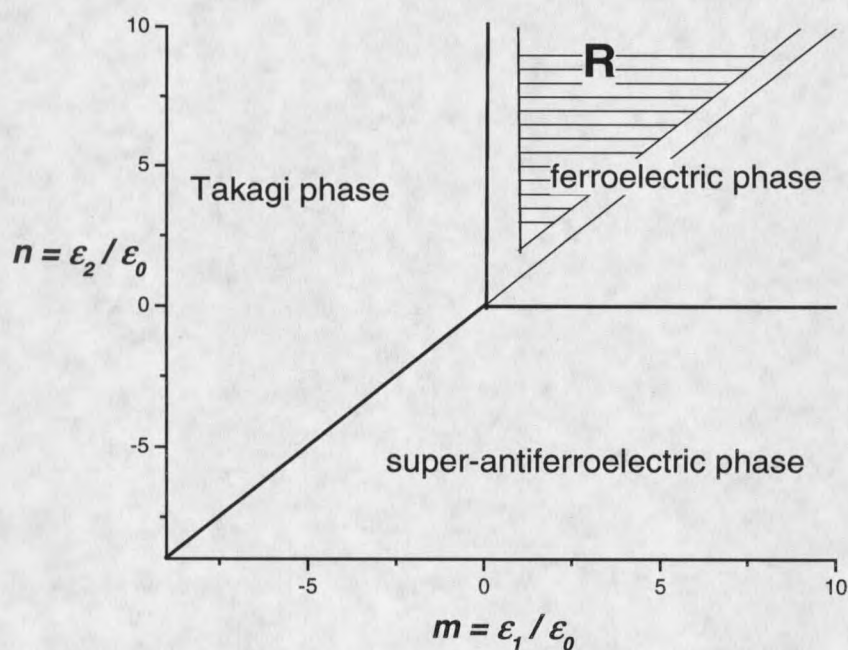


Figure 14. Possible Ground States of the 16VM.

This work considers only the ferroelectric phase.

The hatched region **R** is where low-T series expansions are defined, see discussion on page 33.

MC simulations probed the entire upper-right quadrant.

m and n are defined in equation (2.14) on page 32.

CHAPTER TWO

SERIES EXPANSIONS AND ANALYSES

Introduction

Since there is absolutely no hope of finding an exact solution to the 16VM before the defense of this thesis, we must resort to approximate methods when studying the model's critical behavior. The approximate methods used here are series expansions, described in this chapter, and Monte Carlo (MC) simulations, detailed in the next.

Series expansions come in two flavors: low-temperature and high-temperature. Terms in the low-T series correspond to deviations from the ground state. Terms in the high-T expansions represent correlations between spins in the paraelectric phase. Both series have graphical interpretations which enable their generation in a systematic manner. Once generated, the series must withstand a brutal ordeal of transformation and analysis, whereby the physical singularities of the model are hopefully revealed.

The most fruitful tool we used in analyzing our series were generalized differential approximants^[73], a generalization of Pade approximants^[74]. Unfortunately the asymptotic behavior of our series was not unambiguously reached, and the error bars in the analyses are rather large. This is a consequence of the loose-packed nature and low coordination number of the diamond lattice, and the presence of multi-spin interactions and anisotropy in the 16VM Hamiltonian (equation (1.22)). With the help of MC simulations in biasing the approximants, however, some critical properties were found with reasonable accuracy.

Low-Temperature Series Expansions

At low temperatures, the partition function $Z(T, E_{ext})$ is dominated by states of lowest energy. This motivates a low-temperature expansion of $Z(T, E_{ext})$ as a series of deviations from the ground state^[75]. Thermodynamic quantities can then be calculated from the Gibbs free energy $G(T, E_{ext}) = -k_B T \ln(Z(T, E_{ext}))$ by taking appropriate derivatives.

The ground state is uniquely specified with the application of a symmetry breaking external field E_{ext} . Without loss of generality the ground state energy is set to zero, since a translation of the energy results merely in the addition of a constant to the free energy, which has no physical consequences. The states are ordered in increasing energy, beginning with the ground state. The partition function $Z(T, E_{ext})$ is:

$$Z(T, E_{ext}) = \sum_{\{\alpha\}} \exp\left(-\frac{E_\alpha}{k_B T}\right) \quad (2.1)$$

$$= 1 + N_1 \exp\left(-\frac{E_1}{k_B T}\right) + N_2 \exp\left(-\frac{E_2}{k_B T}\right) + \dots \quad (2.2)$$

The sum $\sum_{\{\alpha\}}$ is over all states $\{\alpha\}$; in the second line, the first term (unity) represents the ground state, the second term represents N_1 states with energy E_1 , the third term represents N_2 states with energy E_2 , etc. Equation (2.2) has a graphical interpretation. Each term is represented by a graph on a lattice, the numbers N_1, N_2 , etc. will turn out to be *lattice constants* for each graph, and the Boltzmann weights $\left\{\exp\left(-\frac{E_i}{k_B T}\right)\right\}$ will weight the graphs according to our 16VM (see Figure 11, page 22).

The graphical representation arises by drawing a line along a hydrogen bond if the nuclei is not in the state consistent with the ground state^[72]. Thus with each phosphate-hydrogen configuration is associated an elementary vertex graph; all 16 of them are shown in Figure 15 below. To generate the graph representing an excitation of the lattice (equivalently, a state α), a line is drawn along all hydrogen bonds whose nuclei are not in the state consistent with the ground state.

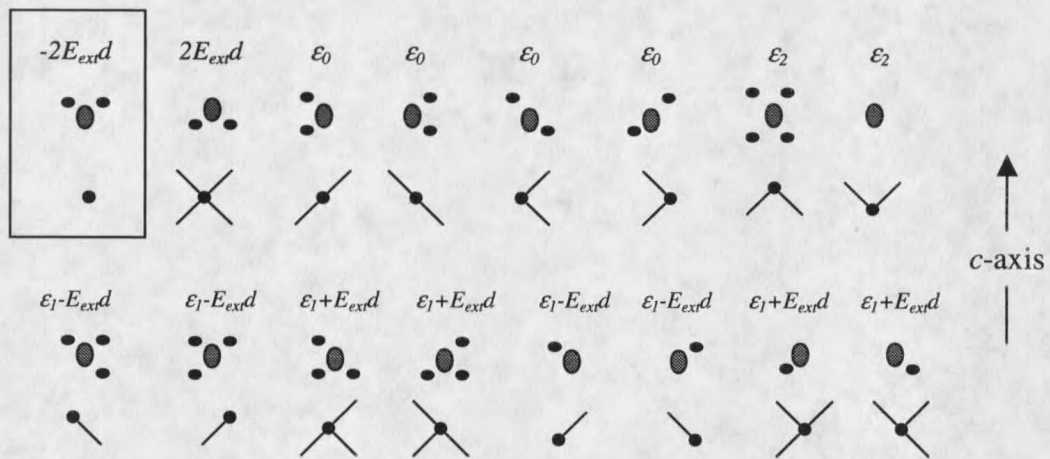


Figure 15. Graphical Representations and Energy of the Phosphate-Hydrogen-Vertex Configurations. Boxed configuration is the ground state.

Let us consider a few examples by calculating some lattice constants on a diamond lattice with N vertices and $2N$ bonds, wrapped on a 3-torus so surface effects can be neglected. The ground state α_0 with energy zero is given by the null graph. The first excited state α_l is obtained from the ground state by moving one hydrogen, producing two Takagi groups with energy $2\varepsilon_l + 2E_{ext}d$; the corresponding graph is $\diagup$. α_l can occur in $2N$ different ways, once for each bond, therefore the number N_l in

equation (2.2) (the lattice constant for the graph) is $2N$. The graphs representing states obtained by moving two adjacent hydrogens are $\angle (\alpha_2)$ with energy $2\varepsilon_1 + \varepsilon_0 + 4E_{ext}d$ and $\sphericalangle (\beta_2)$ with energy $2\varepsilon_1 + \varepsilon_2 + 4E_{ext}d$. There are four different graphs at each vertex equivalent to α_2 , i.e. α_2 can be placed (*embedded*) on the lattice $4N$ different ways, and β_2 in $2N$ ways. Moving two non-adjacent protons produces the excitation ζ_2 , with energy $4\varepsilon_1 + 4E_{ext}d$, represented by the disconnected graph $//$. ζ_2 can be embedded on the lattice $\frac{1}{2}2N(2N-7)$ ways (the first line can go on any of $2N$ bonds, the next can go anywhere except the occupied bond and the six connected to it, and the $\frac{1}{2}$ occurs because the two bonds are identical).

We can infer from these examples that the highest power of N occurring in the lattice constant equals the number of disconnected components of the graph. Because the free energy per site is an intensive variable in the thermodynamic limit, the partition function must be linear in N , and higher-order terms must cancel out. This amazing property of lattice models is proven within the graph theory formalism^[76], whereby Sykes *et al.*^[77] showed that if a model has an *extensive weighting system*, i.e.

$$w(G \cup G') = w(G) + w(G') \quad (2.3)$$

then the N -particle free energy $G(T, E)$ will be linear in N . $w(G)$ is the weight given to a graph G . Equation (2.3) says the weight of a disconnected graph with two components G and G' is simply the sum of the weights of each component. This result considerably reduces the work in calculating lattice constants, as only the linear contribution is required. (2.3) is true for the 16VM; the energy of excitation ζ_2 is twice the energy of

α_l . (2.3) holds for most lattice models, but fails in the presence of interactions between disconnected components, for example.

When ε_l and ε_2 are greater than ε_0 , the low-temperature series is dominated at low order by vertically connected Slater groups, called Slater chains. The partition function for a system where the only allowed excitations are a single Slater chain of arbitrary length is:

$$Z(T, E_{ext}) = 1 + 2Ny^2h + 4Ny^2xh^2 + 8Ny^2x^2h^3 + \dots \quad (2.4)$$

$$= 1 + 2Ny^2h \sum_{n=0}^{\infty} (2xh)^n \quad (2.5)$$

$$= 1 + \frac{Ny^2h}{1 - 2xh} \quad (2.6)$$

Thus in the thermodynamic limit, at low temperature, the free energy is:

$$G(T, E_{ext}) = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T \ln(Z)) \quad (2.7)$$

$$= \lim_{N \rightarrow \infty} \frac{1}{N} \left(-k_B T \ln \left[1 + \frac{Ny^2h}{1 - 2xh} \right] \right) \quad (2.8)$$

$$\approx_{T \rightarrow 0^+} -k_B T \frac{y^2h}{1 - 2xh} \quad (2.9)$$

This gives a polarization of:

$$P = -\frac{\partial G}{\partial E} = \frac{-2dy^2h}{(1 - 2xh)(1 - 2h(x - y^2))} \quad (2.10)$$

The zero-field ($h \rightarrow 0$) susceptibility $\chi_0(T)$ in the limit $\varepsilon_l, \varepsilon_2 \rightarrow \infty$, $\varepsilon_2 > \varepsilon_l$ has a *confluent*

singularity at $x = 1/2$:

$$\chi_0(T) = \frac{2dy^2}{k_B T} \left[(1-2x)^{-2} + 4x(1-2x)^{-3} \right] \quad (2.11)$$

A function has a confluent singularity if it diverges at the same point with more than one term. This confluent behavior dominates the first many terms in any low-temperature expansion of thermodynamic quantities for the 16VM. This series has as its first few terms (compare with the series in Appendix B):

$$\frac{k_B T}{2dy^2} \chi_0(T) = 1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + \dots \quad (2.12)$$

One must be very wary of this behavior. This is certainly not the physical series' asymptotic behavior, as the addition of Takagi and doubly ionized groups allow for dynamics and can change the order of the transition. Series which only gave information about the singularities in (2.11) were too short to provide us with physical quantities of any accuracy. This placed a limit on the parameter space available to analysis of the low-T series, given the series of finite lengths we generated.

To facilitate the following discussion of the 16VM, we introduce the four fundamental low-T expansion variables x , y , z , and h :

$$\begin{aligned} x &= \exp\left(-\frac{\varepsilon_0}{k_B T}\right) & y &= \exp\left(-\frac{\varepsilon_1}{k_B T}\right) \\ z &= \exp\left(-\frac{\varepsilon_2}{k_B T}\right) & h &= \exp\left(-\frac{2E_{ext}d}{k_B T}\right) \end{aligned} \quad (2.13)$$

Define the constants m and n as ratios of the interaction energies:

$$\begin{aligned} m &\equiv \frac{\varepsilon_1}{\varepsilon_0} & y &= x^m \\ n &\equiv \frac{\varepsilon_2}{\varepsilon_0} & z &= x^n \end{aligned} \quad (2.14)$$

When we restrict m and n to being integers, for each pair (m,n) we get a power series in x (or equivalently ε_0). In this way are obtained series expansions for the partition function in the presence of an external field over an entire region R of energy parameter space. For the present work, $R = (m \geq 2, n \geq m + 1)$. This is the shaded region in Figure 14, page 26 in Chapter One, which shows the various ground states of the model as a function of m and n . The anisotropy of the 16VM ($\varepsilon_2 \neq \varepsilon_0$) results in topologically similar graphs (such as α_2 and β_2) having different weights (xy^2 and zy^2). Unfortunately, existing tables of lattice constants^[75] on the diamond lattice are only provided for the isotropic case, and we have had to generate the necessary lattice constants.

We calculated lattice constants for all graphs contributing to the low-T series; they are tabulated in Appendix A. The low-T series themselves are given in Appendix B. When $m = 2, 3, 4, 5$ the susceptibility series has 9, 11, 13, and 15 terms. Asymptotic behavior sets in at lower order the lower m is. When m is greater than five the series are dominated by the confluent behavior (2.11). The expansions give decent quantitative information for $m = 2, 3$ and with biasing some qualitative information for $m = 4$. The region in parameter space for which the expansions provide useful information is somewhat meager, considering the authors' current perspective. After all, the MC simulations can probe all of Figure 14, not just part of the upper-right quadrant. A majority of the information on the 16VM was obtained through MC simulations. However, the problem was initially approached through series expansions, which led to

the Hamiltonian (1.22) and the phase diagram in Figure 14, both of which are generalizations of previous ideas.

Doubly ionized configurations with energy ε_2 have been omitted from most treatments of the 16VM in the context of KDP theory^[59,60,66,68], on the justification they were energetically too unfavorable to make much difference in thermodynamic quantities. In support of this is Figure 16, which displays a graph of the zero-field polarization series vs. temperature, for various values of m and n . The critical temperature definitely varies with m , but only insignificantly with n . More sophisticated techniques of series analysis are detailed below, followed by results of analysis on the low- and high-T series.

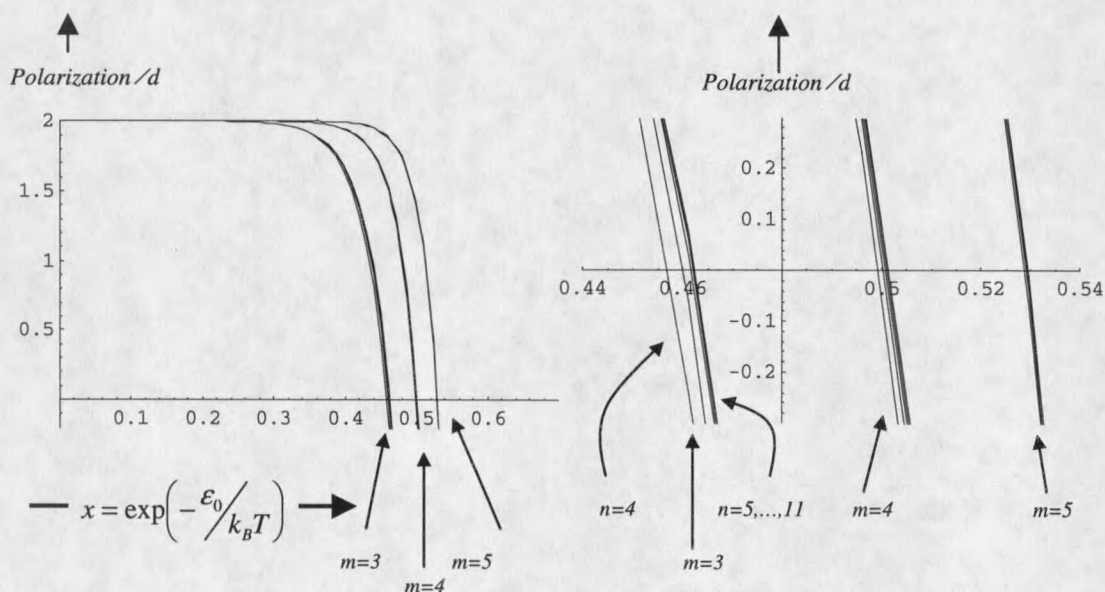


Figure 16. Zero-Field Polarization Given by Low-T Series Expansions, for $m = 3, 4, 5$. The polarization is shown for $n = m+1, \dots, 11$.

High-Temperature Series Expansions

High-temperature series^[72,75] are defined for the Ising Hamiltonian (1.22) on the IRT lattice (Figure 12). The problem is intractable in the presence of an external field, so E_{ext} is set to zero. The free energy series are interpreted graphically as a sum of closed loops on the IRT lattice, and the dielectric susceptibility is represented as a sum of nondirected paths connecting two vertices.

We will need the following identity for binary variables $\{\sigma = \pm 1\}$:

$$\exp(\sigma \cdot J) = \cosh(J) [1 + \sigma \tanh(J)] \quad (2.15)$$

Equation (2.15) can be verified by expanding the exponential and using $\sigma^2 = 1$.

We introduce somewhat cumbersome notation to explicitly exhibit all sums and products and keep track of factors of two in the high-T expansion of the free energy. The IRT lattice has N tetrahedra and $2N$ spins. Each tetrahedron j has four spins, which are thus labeled:

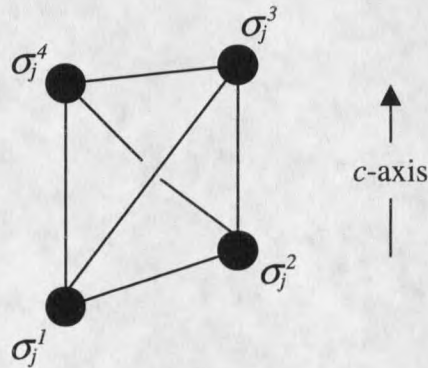


Figure 17. Labeling of spins in tetrahedra j on the IRT lattice.

The set of spins $\{\sigma_1^j, \sigma_2^j, \sigma_3^j, \sigma_4^j\}$ on tetrahedron j will be denoted Θ_j , and when those spins are in the state α , they will be denoted $\Theta_j(\alpha)$. The energy of the j^{th} tetrahedron when its spins $\Theta_j(\alpha)$ are in the state α is written $E_j[\Theta_j(\alpha)]$. E_j is given by the Hamiltonian in equation (1.22), concisely written as:

$$E_j = - \sum_{\zeta} K_{\zeta} \Omega_{\zeta} \quad (2.16)$$

where $\{K_2', K_2'', K_4\}$ are the normalized interactions $\left\{ \frac{J_2'}{k_B T}, \frac{J_2''}{k_B T}, \frac{J_4}{k_B T} \right\}$, and Ω_{ζ} are the

sets of spins that couple to the $\{K_{\zeta}\}$ (compare with equation (1.22)):

$$\begin{aligned} \Omega_2' &= \sigma_i \sigma_k + \sigma_i \sigma_l + \sigma_j \sigma_k + \sigma_j \sigma_l \\ \Omega_2'' &= \sigma_i \sigma_j + \sigma_k \sigma_l \\ \Omega_4 &= \sigma_i \sigma_j \sigma_k \sigma_l \end{aligned} \quad (2.17)$$

The energy of the j^{th} tetrahedron when its four spins Θ_j are in state α is written:

$$E_j[\Theta_j(\alpha)] = - \sum_{\zeta} K_{\zeta} \Omega_{\zeta}[\Theta_j(\alpha)] \quad (2.18)$$

We will ease the notational burden by writing:

$$\Omega_{\zeta}[\Theta_j(\alpha)] \equiv \Omega_{\zeta}(j; \alpha) \quad (2.19)$$

The energy E_{α} of the lattice when its spins are in the state α is:

$$E_{\alpha} = \sum_{j=1}^N E_j[\Theta_j(\alpha)] \quad (2.20)$$

The partition function $Z(T)$ can now be written as:

$$Z(T) = \sum_{\{\alpha\}} \exp\left(-\frac{E_{\alpha}}{k_B T}\right) \quad (2.21)$$

$$= \sum_{\{\alpha\}} \exp \left(\sum_{j=1}^N \sum_{\zeta} K_{\zeta} \Omega_{\zeta}(j; \alpha) \right) \quad (2.22)$$

$$= \prod_{j=1}^N \prod_{\zeta} \sum_{\{\alpha\}} \exp (K_{\zeta} \Omega_{\zeta}(j; \alpha)) \quad (2.23)$$

Equation (2.23) justifies the notation, for $Z(T)$ is now seen to be:

$$Z(T) = \left(\cosh^4(K_2') \cosh^2(K_2'') \cosh(K_4) \right)^N \prod_{j=1}^N \prod_{\zeta} \sum_{\{\alpha\}} [1 + \Omega_{\zeta}(j; \alpha) \omega_{\zeta}] \quad (2.24)$$

$$\equiv Z_0(T)^N \prod_{j=1}^N \prod_{\zeta} \sum_{\{\alpha\}} [1 + \Omega_{\zeta}(j; \alpha) \omega_{\zeta}] \quad (2.25)$$

where $\omega_{\zeta} \equiv \tanh(K_{\zeta})$ and the identity (2.15) was used. $\{\omega_{\zeta}\}$ are the basic high-T expansion variables. $Z_0(T)$ is analytic at any finite temperature, including the transition temperature. The free energy $G(T)$ is written in the thermodynamic limit as:

$$G(T) = -k_B T \ln(Z_0) - k_B T \ln \left(\prod_{j=1}^N \prod_{\zeta} \sum_{\{\alpha\}} [1 + \Omega_{\zeta}(j; \alpha) \omega_{\zeta}] \right) \quad (2.26)$$

$$= -k_B T \ln(Z_0) - k_B T \ln(S_G) \quad (2.27)$$

S_G is a series of excitations on the IRT lattice composed of products of the $\{\sigma\}$ variables and expansion variables $\{\omega_{\zeta}\}$. When the sum over all states $\{\alpha\}$ is performed, terms where any spin variable appears an odd number of times will vanish. Terms where every spin variable appears an even number of times will be nonzero. In this way the high-T free energy series is represented as a sum of closed loops on the IRT lattice, connecting the spins appearing in each nonvanishing term of the series.

In constructing the zero-field free energy high-T series S_G and the zero-field susceptibility high-T series S_{χ} , we will build polynomials (*decorations*) representing

excitations in and around a tetrahedron. The counting of closed loops and two-spin correlations simplifies considerably when bonds are *decorated* with the polynomials.

For clarity, the expansion variables are renamed:

$$\begin{aligned} b &\equiv \omega_2' \\ c &\equiv \omega_2'' \\ d &\equiv \omega_4 \end{aligned} \tag{2.28}$$

Graphically, these variables label the bonds on an elementary tetrahedron:

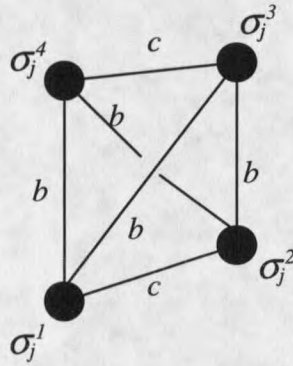


Figure 18.
Expansion Variables for the High-T Series.
 d is the four-spin interaction.

The first step in building the decorations is defining elementary tetrahedral graphs which all have vertices of even degree:

$$\text{with three vertices: } t_3 = b^2 c \tag{2.29}$$

$$\text{with four vertices: } t_4 = b^4 + 2b^2 c^2 + (2b^2 + c^2 + 4b^2 c + b^4 c^2) d \tag{2.30}$$

t_3 in (2.29) represents a closed loop on an IRT tetrahedron with three vertices, see Figure 19. There are four different possible ways of placing t_3 on a tetrahedron, but this multiplicity factor is not yet considered; the interested reader can find it in the first term of equation (2.35). t_4 in (2.30) has two pieces: configurations with the four-spin

interaction d , and loops with four vertices. The loops are shown in Figure 20. There are two ways of embedding the loop b^2c^2 on a tetrahedra, thus the factor of two in (2.30). Some contributions to t_4 containing d are shown in Figure 21. There are two ways to place b^2d on a tetrahedra, thus the factor of two in (2.30)

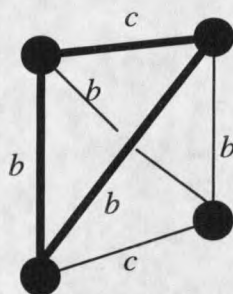


Figure 19. $t_3 = b^2c$.

There are four ways to place t_3 on a tetrahedron, but this multiplicity factor is not built into t_3 .

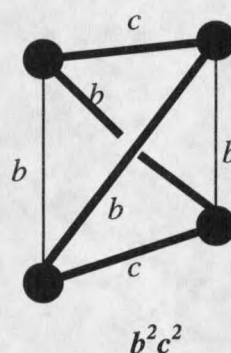
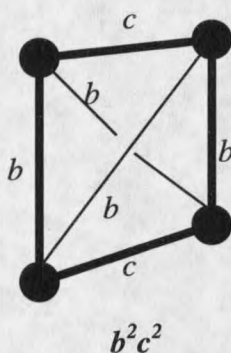
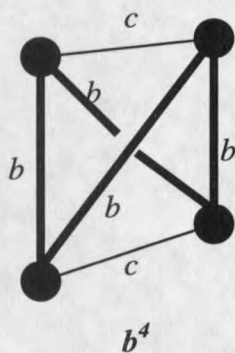


Figure 20. Closed Loops Contributing to t_4 .

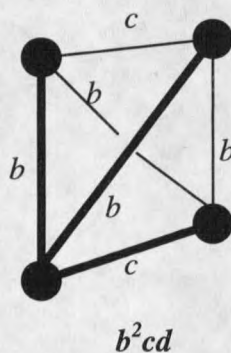
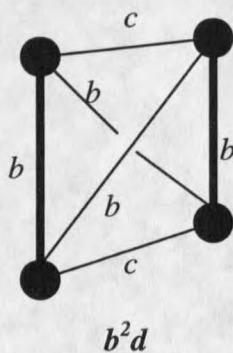


Figure 21. Two contributions to t_4 containing the four-spin interaction d .

t_3 and t_4 are internal to one tetrahedron. They ignore paths that leave the *home* tetrahedron, describe a closed loop in one or more neighboring tetrahedra, and re-enter the home tetrahedron at the original vertex. To account for these external loops, we introduce a vertex weight $\tilde{v}$ that sums all loops passing through the neighboring tetrahedron and its neighbors.

$$\tilde{v} = 1 + 3b^2c\tilde{v}^2 + \left[2b^2c^2 + b^4 + d(4b^2c + b^4c^2 + 2b^2 + c^2) \right] \tilde{v}^3 + \dots \quad (2.31)$$

To be useful, (2.31) must be expanded self-consistently to the desired order by substituting $\tilde{v}$ back into itself. Doing so produces equation (2.32), valid for up to two tetrahedra away from the home tetrahedron:

$$\begin{aligned} \tilde{v} = & 1 + b^4 + 3b^2c + 2b^2c^2 + 15b^6c + 18b^4c^2 + 30b^4c^3 \\ & + d(2b^2 + 4b^2c + 30b^4c + c^2 + 15b^2c^3 + 12b^2c^4 + 12b^6 + 91b^4c^2) \\ & + d^2(12b^4 + 48b^4c + 12b^2c^2 + 24b^2c^3 + 3c^4) \end{aligned} \quad (2.32)$$

Using $\tilde{v}$, we define new bond weights $\tilde{b}$ and $\tilde{c}$, which are dressed two-point interactions (see Figure 18, with b and c replaced with $\tilde{b}$ and $\tilde{c}$):

$$\tilde{b} = b + 2bc\tilde{v} + \left[b^3 + bc^2 + b^3c^2 + 2b^3c + d(b + 2bc + b^3 + bc^2 + b^3c^2 + 2b^3c) \right] \tilde{v}^2 \quad (2.33)$$

$$\tilde{c} = c + 2b^2\tilde{v} + \left[2b^2c + b^4c + 2b^2c^2 + d(c + 2b^2 + 2b^2c + b^4c + 2b^2c^2) \right] \tilde{v}^2 \quad (2.34)$$

Define a *fundamental graph* to be a directed walk with no three consecutive vertices belonging to the same tetrahedron. Each fundamental graph of n steps contributes to each series at n^{th} and higher orders. Each step of the fundamental graph is along the edge of a tetrahedron from, say, σ_i to σ_k , and we write its contribution to the graph weight as either $\tilde{b}$ or $\tilde{c}$. Doing so means we have included all graphs in which (before summing over spin configurations in constructing the thermodynamic average)

the spins σ_i and σ_k appear linearly or cubed, and the remaining spins in between appear to the 2^{nd} or 4^{th} powers. We also include in the graph weight a factor of $\tilde{v}$ for each endpoint and any interior vertex in the graph.

S_G in equation (2.27) can now be written to eighth order:

$$S_G = 4t_3 + t_4 + 2(3t_3 + t_4)^2 + 4(9t_3^3 + 27t_3^2t_4 + 12t_3t_4^2 + t_4^3) + 2\tilde{b}^4\tilde{c} + 2\tilde{b}^4\tilde{c}^2(\tilde{c}^2 + 2\tilde{b}^2) + 2\tilde{b}^4\tilde{c}^2(\tilde{c}^4 + 2\tilde{b}^4 + (\tilde{c}^2 + 2\tilde{b}^2)^2) \quad (2.35)$$

Now we construct the zero-field dielectric susceptibility series S_χ . S_χ is written with the help of the fluctuation-dissipation theorem^[1] (FDT) as a sum of two-point correlation functions:

$$k_B T \chi_T = d^2 S_\chi - P^2 \quad (2.36)$$

$$S_\chi \equiv \sum_{i,j=1}^{2N} \langle \sigma_i \sigma_j \rangle \quad (2.37)$$

In a similar (but not identical) way to S_G , S_χ is interpreted graphically as a sum of graphs with two vertices of degree one, and all other vertices having even degree.

Since each succeeding step of a fundamental graph can take one of three possible directions (two of type $\tilde{b}$ and one of type $\tilde{c}$) into a tetrahedron, and the initial step has two tetrahedra to choose from, the fundamental graphs of order n contribute a factor $2\tilde{v}^2(2\tilde{b} + \tilde{c})^n$ to the susceptibility. Expanded and truncated, a sum of such terms up to $n = 5$ would yield the correct expansion up to fifth order:

$$S_\chi = 1 + 2\tilde{v}^2 \sum_{n=1}^5 (2\tilde{b} + \tilde{c})^n + \dots \quad (2.38)$$

Extending the sum to $n = 6$ will overcount diagrams, since there are twelve six-step paths that return to the initial site by traversing six separate tetrahedra. However, each such path contributes the same weight, namely $b^4 c^2$, which can be subtracted off. Such paths also cause overcounting at $n = 7$, but in a similar way we can correct for this by subtracting $12b^4 c^2 (2b + c)$, yielding

$$S_z = 1 + 2\tilde{v}^2 \sum_{n=1}^7 (2\tilde{b} + \tilde{c})^n - 12\tilde{b}^4 \tilde{c}^2 (1 + 2\tilde{b} + \tilde{c}) + \dots \quad (2.39)$$

expanded and truncated at seventh order.

Now that we have the low-T series for the partition function (Appendix B), and the high-T zero-field free energy and susceptibility series (equations (2.35) and (2.39), and Appendix C), we are ready to learn about the 16VM. To this end we discuss methods of analyzing series expansions.

Interlude: Methods of Series Analysis

When faced with an everywhere analytic finite series in a real variable which approximates a singular function, one has recourse to a few methods of discerning the singular behavior. The choice of method should be, if possible, determined by an assumed functional form of the singularity, and different methods work well for different types of functions. The methods discussed here are the *ratio method*, *Pade approximants* and their generalization, *generalized differential approximants* (GDA)^[73,74].

The dominant singularity of a function is what determines the function's radius of convergence, defined as the distance between the point of expansion and the nearest singularity. When the dominant singularity is an isolated pole at z_0 on the real axis, so that near z_0 the function $f(z)$ can be approximated by:

$$f(z) = \frac{A(z)}{\left(1 - \frac{z}{z_0}\right)^\alpha}, \quad z_0 \in \mathbb{R}, \quad \alpha \in \mathbb{R}^+, \quad A(z) \text{ is analytic at } z_0, \quad (2.40)$$

then the ratio test works splendidly.

When $f(z)$ has the functional form of (2.40) but the physical singularity is not the dominant one, and/or $z_0 \in \mathbb{C}$, then Pade approximants will accurately reveal the series' singular behavior. If the physical singularity is a *confluent singularity*:

$$f(z) = \frac{A_1(z)}{\left(1 - \frac{z}{z_0}\right)^{\alpha_1}} + \frac{A_2(z)}{\left(1 - \frac{z}{z_0}\right)^{\alpha_2}}, \quad z_0 \in \mathbb{C}, \quad \alpha_1, \alpha_2 \in \mathbb{R}^+, \quad A_1(z), A_2(z) \text{ analytic} \quad (2.41)$$

or if the beginning of the series is dominated by an additive function analytic at z_0 :

$$f(z) = \frac{A(z)}{\left(1 - \frac{z}{z_0}\right)^\alpha} + B(z), \quad z_0 \in \mathbb{C}, \quad n \in \mathbb{R}^+, \quad A(z), B(z) \text{ analytic at } z_0, \quad (2.42)$$

or any combinations thereof, then one ought to use GDA's. GDA's are powerful tools. They should be used with care and caution, like a chainsaw, and are a natural choice when there exists no a priori information about the functional form one is approximating with a series.

The Ratio Method

The ratio method is useful for analyzing the singular behavior of power series approximations to *well behaved functions*, as in equation (2.40). Such a function $f(z)$ has a power series expansion about $z = 0$:

$$f(x) = \sum_{q=0}^{\infty} f_q z^q \quad (2.43)$$

The $\{f_q\}$ are easily calculated:

$$f_q = \frac{\alpha(\alpha+1)\dots(\alpha+q-1)}{q! z_0^q} \quad (2.44)$$

The ratio method is motivated by the observation that selective ratios of the coefficients $\{f_q\}$ are independent of q and contain information about z_0 and α . Define:

$$a_q \equiv \frac{f_{q-1}}{f_q} = \frac{q}{q+\alpha-1} z_0 \quad (2.45)$$

Note that

$$\lim_{q \rightarrow \infty} a_q = z_0. \quad (2.46)$$

Armed with (2.46) one can plot a_q vs. $1/q$ and thereby obtain an estimate for z_0 , see

Figure 22 for an example.

To estimate α , define:

$$r_q \equiv \frac{1}{a_q} - \frac{1}{a_{q-1}} = \frac{1-\alpha}{q(q-1)z_0} \quad (2.47)$$

$$p_q \equiv \frac{1}{q} - \frac{1}{q-1} = \frac{-1}{q(q-1)} \quad (2.48)$$

$$\tau_q \equiv \frac{r_q}{p_q} = \frac{\alpha - 1}{z_0} \quad (2.49)$$

Note τ_q is independent of q . Equation (2.49) gives:

$$\alpha = \tau_q z_0 + 1 \quad (2.50)$$

Successive approximations to α can be obtained by using the estimate of z_0 and (2.50), see Figure 23.

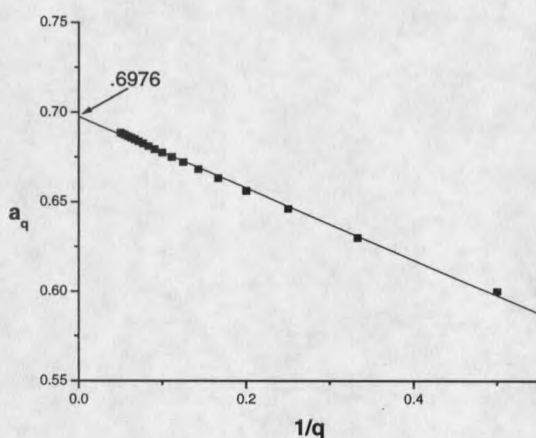


Figure 22. a_q Plotted Against $1/q$ for the Function $f(z) = \left(1 - \frac{z}{.7}\right)^{-1.3333}$, expanded to 20th-order. This gives an estimate of the critical point as $z_0 = 0.6976 \pm 0.0036$.

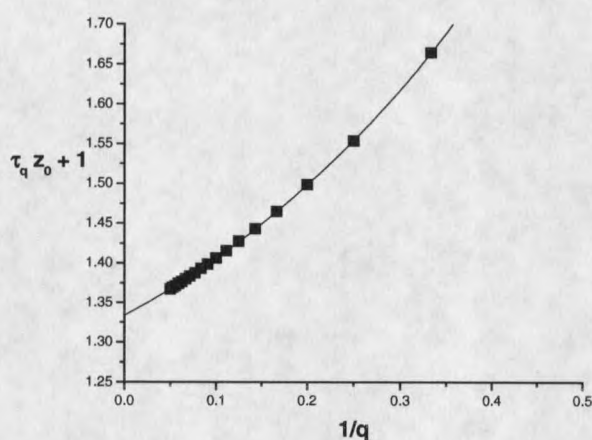


Figure 23. Estimates of the Critical Exponent γ of $f(z) = \left(1 - \frac{z}{.7}\right)^{-1.3333}$. The fit is exponential, and gives an estimate of $\gamma = 1.334 \pm 0.0021$.

Pade Approximants

The domain of convergence often exceeds the circle of convergence for a power series. Pade approximants and GDA's exploit this fact by analytically continuing a series past its circle of convergence. Pade approximants involve approximating the series expansion to a function by a ratio of polynomials:

$$\sum_{q=0}^W f_q z^q = \frac{R_B(z)}{P_A(z)} \quad (2.51)$$

where $P_A(z)$ and $R_B(z)$ are polynomials in z of degree A and B , respectively:

$$P_A(z) = \sum_{q=0}^A p_q z^q \quad (2.52)$$

$$R_B(z) = \sum_{q=0}^B r_q z^q. \quad (2.53)$$

We adopt the normalization $p_0 = 1$. In order for equation (2.51) to yield a unique solution for the constants $\{p_q\}$ and $\{r_q\}$, W must equal $A+B$. Then (2.51) is equivalent to a set of linear equations for $\{p_q\}$ and $\{r_q\}$, which can be easily solved. When the linear system is ill-conditioned, the corresponding approximant does not exist.

$\frac{R_B(z)}{P_A(z)}$ is called the $[A,B]$ approximant, although many other notations exist in

the literature (such as $[B/A]$, etc.). Singularities in $f(z)$ are approximated by the zeros of $P_A(z)$. Pade approximants can represent simple poles ($\alpha = 1$) exactly. If a series approximates a function with $\alpha \neq 1$, one must use the logarithmic derivative of the series:

$$\frac{d}{dz} \ln(f(z)) = \frac{f'(z)}{f(z)} = \frac{-\alpha}{z - z_0} \quad (2.54)$$

The residue of the approximants will then give estimates of $-\alpha$.

The diagonal approximants $[A,A]$ have the property of being invariant under the Euler transformation $z = \frac{\theta z}{1 + \phi w}$. This transformation is often used to increase the rate

of convergence of a series. Thus the diagonal approximants converge at least as fast as the series obtained by the best Euler transformation. Usually one examines sequences of diagonal and almost-diagonal approximants $[A, A+j]$, $j = 0, \pm 1$.

Generalized Differential Approximants

If we form the Pade approximant for the logarithmic derivative of a function:

$$\frac{f'(z)}{f(z)} = \frac{R_B(z)}{P_A(z)} \quad (2.55)$$

and rearrange the terms in equation (2.55), we get

$$P_A(z) f'(z) - R_B(z) f(z) = 0 \quad (2.56)$$

When $f(z)$ is a finite series, the above is a set of linear equations for the $\{p_n\}$ and $\{r_n\}$.

If $f(z)$ consists of a singularity plus an analytic piece:

$$f(z) = A(z) \left(1 - \frac{z}{z_0}\right)^{-\alpha} + B(z) \quad (2.57)$$

with $B(z_0)$ finite; then the logarithmic derivative transformation (2.54) does not work, and neither will (2.55). A natural generalization of dlog Pade approximants is to add higher derivative terms or analytic pieces to (2.56). If an analytic polynomial is added to (2.56):

$$P_A(z) f'(z) + R_B(z) f(z) + S_C(z) = 0 \quad (2.58)$$

where $S_C(x)$ is a polynomial in z of degree C , then *first-order, inhomogeneous* approximants are obtained. (2.58) is called the $[A, B, C]$ approximant. Dlog Pade

approximant are *first-order, homogeneous* approximants. Divergences of $f(z)$ occur at the zeros of $P_A(z)$, and the critical exponent α is given by:

$$\alpha = \frac{R_B(z_0)}{P'_A(z_0)}. \quad (2.59)$$

The equivalent of diagonal approximants for (2.61) are the $[A, A-2, A-2]$ approximants^[74].

In the case of a confluent singularity, a zero of $P_A(z)$ and $R_B(z)$ will coincide.

When this happens, one should use *second-order, homogeneous* approximants:

$$P_A(z) f''(z) + R_B(z) f'(z) + S_C(z) f(z) = 0 \quad (2.60)$$

The critical exponents are found to be:

$$\alpha_{\pm} = \frac{1}{2} \left[1 - \frac{r_0}{p_0} \pm \frac{1}{p_0} \sqrt{r_0^2 + p_0^2 - 2r_0 p_0 - 4p_0 r_0} \right] \quad (2.61)$$

where

$$p_0 \equiv \frac{1}{2} P''(z_0) \quad (2.62)$$

$$r_0 \equiv R'(z_0). \quad (2.63)$$

One can also construct inhomogeneous approximants of any order.

Results of Analyzing the Series Expansions

Although generating the high-temperature series with lattice decorations was exciting and interesting, the expansions are too short from which to infer any quantitative conclusions. The low-T series are quite a bit longer, but the asymptotic

behavior was not unambiguously reached. In particular, estimates of the critical temperature only vaguely converge, and the susceptibility exponent only hinted at.

The MC simulations provide decent estimates of the transition temperatures, which when used with the ratio test gave reasonable estimates of the critical exponent. In Figures 24 through 27 are estimates of the susceptibility exponent γ from the low-T series, using the ratio test and T_c estimates from the MC simulations. The estimates are grouped close to the 3D Ising value of 1.250, but not so well that the author feels comfortable extrapolating a value for γ .

Table 4 gives the results of the Pade analysis of the low-T susceptibility series. Numbers in bold refer to m and n . Dlog approximants and first-order inhomogeneous approximants were the most useful. No evidence was seen of confluent behavior. For each series, the first column (labelled $[A,B,C]$) is the approximant. Approximants with two numbers (such as 3-4) are dlog Pade approximants, and with three numbers (such as 4-2-2) are first-order inhomogeneous approximants. The second column is estimates of the transition temperature z_0 , and the third column is estimates of the susceptibility exponent γ . It can be seen from the table that the critical point and exponent estimates are not well converged, although general trends are evident. The critical point estimates are not too far off from the MC simulations, and the critical exponents are not too far away from the 3D Ising value of 1.250.

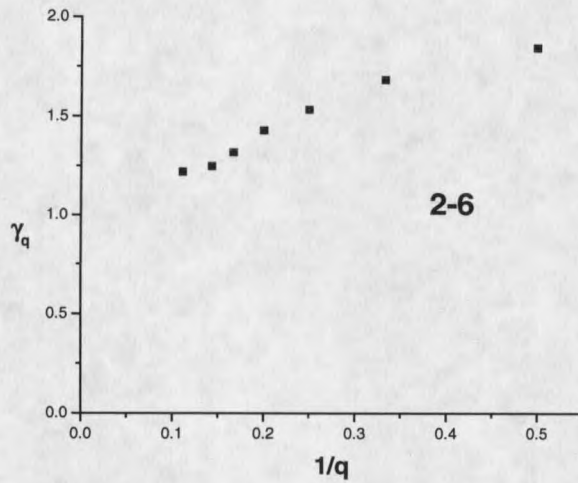


Figure 24. Estimates of γ from the Low-T Series, using the ratio test.
 $(m,n) = (2,6)$. $z_0 = 0.505$ was estimated from the MC simulations.
 $\gamma = 1.250$ is the 3D Ising value.

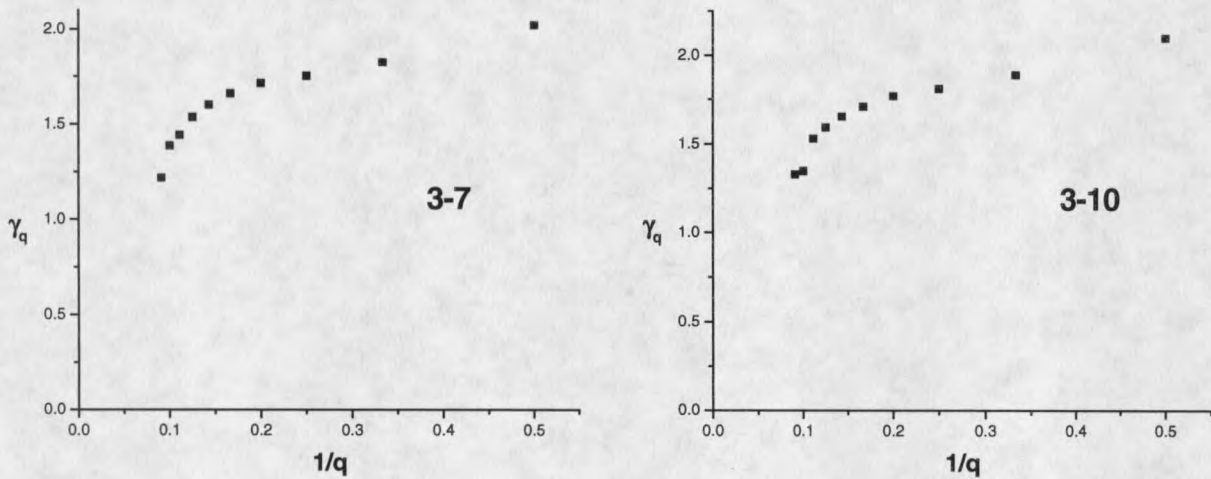


Figure 25. Estimates of γ from the Low-T Series, using the ratio test.
 $(m,n) = (3,7)$ and $(3,10)$. $z_0 = 0.520$ and 0.535 was estimated from the MC simulations.
 $\gamma = 1.250$ is the 3D Ising value.

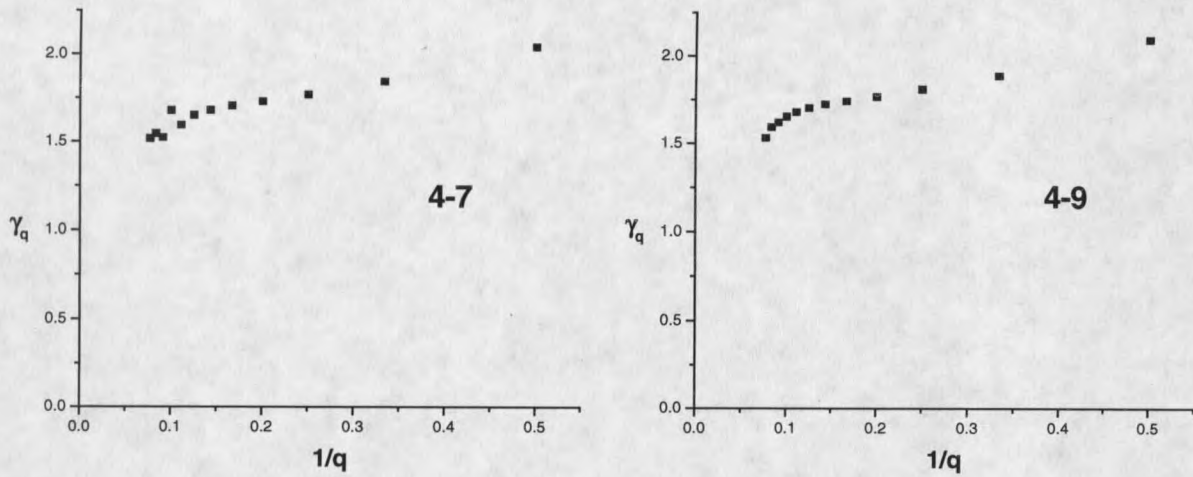


Figure 26. Estimates of γ from the Low-T Series, using the ratio test.
 $(m,n) = (4,7)$ and $(4,9)$. $z_0 = 0.530$ and 0.540 was estimated from the MC simulations.
 $\gamma = 1.250$ is the 3D Ising value.

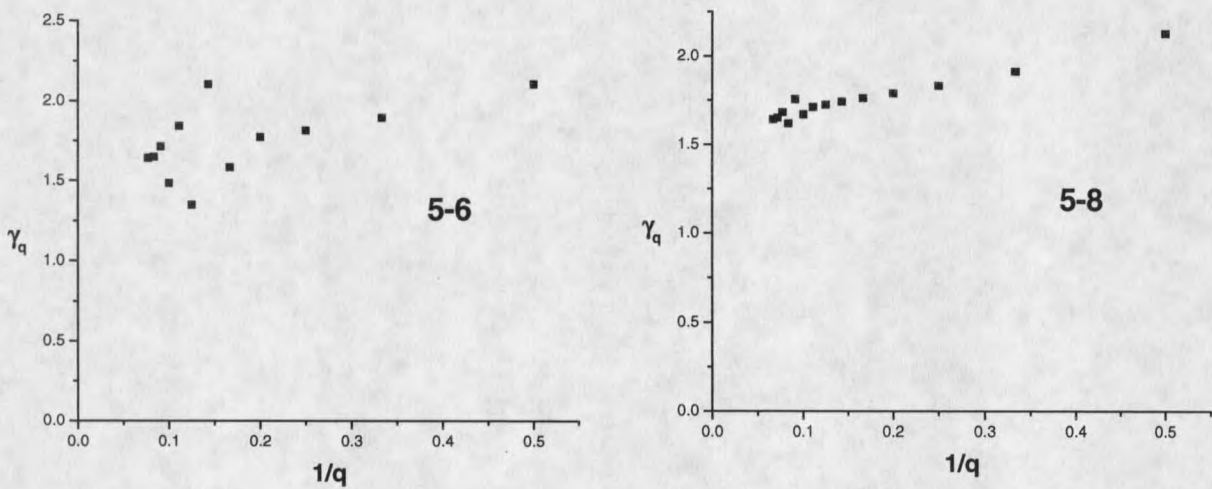


Figure 27. Estimates of γ from the Low-T Series, using the ratio test.
 $(m,n) = (5,6)$ and $(5,8)$. $z_0 = 0.545$ and 0.555 was estimated from the MC simulations.
 $\gamma = 1.250$ is the 3D Ising value.

<u>[A,B,C]</u>	<u>z₀</u>	<u>γ</u>	<u>[A,B,C]</u>	<u>z₀</u>	<u>γ</u>	<u>[A,B,C]</u>	<u>z₀</u>	<u>γ</u>
<u>2-3</u>			<u>2-9</u>			<u>3-9</u>		
3-1-1	0.995	1.820	3-4	0.991	1.201	3-3	1.181	1.325
3-2-2	0.979	1.425	4-4	1.105	1.795	3-4	1.173	1.256
			2-2-2	0.988	1.195	4-4	1.183	1.334
<u>2-5</u>			3-1-1	1.064	1.741	4-5	1.176	1.281
4-3	0.911	0.752	3-2-2	0.686	1.755	5-4	1.176	1.282
4-4	0.951	1.043				5-5	1.182	1.329
4-5	0.950	1.031	<u>3-4</u>					
5-4	0.917	0.790	2-2-1	1.051	1.382	<u>3-10</u>		
3-2-2	0.953	1.063	2-3-1	0.998	1.048	3-3-3	0.684	1.184
			4-3-3	1.127	1.327	3-4-3	0.735	1.116
<u>2-6</u>			<u>3-5</u>			4-3-1	1.037	0.969
2-2	1.073	1.692	3-4	1.149	1.520	4-3-3	0.680	0.546
2-3	0.953	0.987	2-2-2	1.101	1.268	4-4-2	0.797	1.409
3-3	0.988	1.361	2-3-2	1.078	1.062	5-4-1	0.790	1.201
3-4	0.965	1.053	3-4-2	1.184	1.615			
2-2-2	0.948	0.773	4-3-3	1.116	1.106	<u>3-11</u>		
3-1-1	1.077	1.830				3-3-3	0.686	1.170
3-2-2	0.709	1.489	<u>3-6</u>			3-4-2	0.849	0.824
			3-3	1.168	1.388	3-4-3	0.734	1.109
<u>2-7</u>			4-5	1.202	1.659	4-3-1	1.037	0.966
2-2	1.073	1.692	5-5	1.195	1.608	4-4-2	0.797	1.413
2-3	0.987	1.176	5-6	1.202	1.663	5-4-1	0.790	1.210
3-3	0.945	1.375						
3-4	1.000	1.191	<u>3-7</u>			<u>3-12</u>		
2-2-1	1.010	1.324	3-4	1.165	1.281	5-4-1	0.791	1.209
2-2-2	0.985	1.183	2-2-2	1.191	1.502	5-3-2	0.782	0.878
3-1-1	1.053	1.677	2-3-1	1.187	1.470			
3-2-2	0.687	1.719	3-2-1	1.177	1.383	<u>4-5</u>		
			3-4-3	1.124	1.035	5-4-1	0.603	1.778
<u>2-8</u>			<u>3-8</u>					
2-2	1.073	1.692	3-3	1.182	1.325	<u>4-6</u>		
2-3	0.987	1.760	5-5	1.190	1.384	5-4-2	0.873	1.082
3-3	1.023	1.412	2-3-3	1.210	1.592			
3-4	0.991	1.201	3-2-1	1.172	1.279	<u>4-7</u>		
4-4	1.104	1.795	3-3-2	1.165	1.238	4-4-2	0.861	1.022
2-2-2	0.985	1.201	4-4-1	1.212	1.473	5-4-2	0.927	0.929
3-1-1	1.064	1.741	4-4-2	0.841	0.959			
3-2-2	0.685	1.771				<u>5-6</u>		
						5-3-1	0.901	0.904

Table 4. Analysis of Low-T Susceptibility Series with GDA's.

Numbers in bold refer to m and n .

For each series, the first column (labelled $[A,B,C]$) is the approximant. Approximants with two numbers (such as 3-4) are dlog Pade approximants, and with three numbers (such as 4-2-2) are first-order inhomogeneous approximants.

In the second column are estimates of the transition temperature, and in the third column are estimates of the susceptibility exponent γ .

CHAPTER THREE

MONTE CARLO SIMULATIONS

Introduction to Monte Carlo Simulations

Series expansions are certainly interesting and entertaining to generate, but the quantitative information they can provide on the 16VM is marginal, for two reasons. First is the loose-packed nature of the diamond lattice, which prevents long-range correlations from contributing to a series until very high order is reached. A. J. Guttman^[5] has argued that a series on the diamond lattice is effectively half as long as a series of equal length on a cubic lattice. The second reason is the model anisotropy, which pushes the asymptotic behavior of the series out to high order. Thus considerable time and effort have been invested in numerical simulations as an additional method of investigating the 16VM.

The simplicity of models with Ising-like binary variables makes them highly amenable to computer simulations. The Monte Carlo (MC) algorithm is a straightforward and efficient method of sampling the phase space available to a system and generating statistical ensembles from which thermodynamic quantities can be calculated. Furthermore, errors due to finite-sized effects and statistical averaging can be analyzed and controlled. Included in this chapter is a brief review of the ideas behind MC simulations, and the results of applying them to the 16VM.

The MC algorithm proceeds by calculating physical quantities for a bunch of states available to the system, creating an ensemble. The most obvious method of

sampling phase space, called *simple sampling*, is to choose the bunch of states independently, and then use those states to calculate thermodynamic averages according to the standard formula:

$$\langle A \rangle = \frac{\sum_{\{\alpha\}} A_{\alpha} \exp\left(-\frac{E_{\alpha}}{k_B T}\right)}{\sum_{\{\alpha\}} \exp\left(-\frac{E_{\alpha}}{k_B T}\right)} \quad (3.1)$$

$\langle A \rangle$ is the average quantity of interest, A_{α} is the value of A when the system is in the state α , E_{α} is the energy of state α , and $\sum_{\{\alpha\}}$ is a sum over the states generated. Simple sampling works well for percolation-type models^[78], but unfortunately is terribly inefficient for studying thermal phase transitions. Consider the ordered low-T state of a system. Simple sampling chooses states randomly distributed throughout phase space, and the probability distribution of the order parameter $Q(\alpha)$ is symmetric about $\langle P \rangle = 0$, because plus and minus spins are chosen on average with equal probability. Thermal systems, however, spend most of their time in a small region of phase space, with a probability distribution centered on the equilibrium polarization $\langle P \rangle \neq 0$ with width $1/\sqrt{M}$, where M is the number of systems in the ensemble. The most likely systems are thus only rarely sampled.

A way around this problem is *importance weighted sampling*^[78,79], whereby states are chosen according to a probability distribution centered around the equilibrium polarization. The probability distribution can be chosen so that thermal averages reduce to arithmetic averages:

$$\langle A \rangle = \frac{\sum_{\{\alpha\}} A_{\alpha}}{|\alpha|}. \quad (3.2)$$

where $|\alpha|$ stands for the number of configurations sampled. Justifying an algorithm that realizes this sampling technique requires the law of detailed balance^[78] for $Q(\alpha)$ for the states generated by one's particular sampling technique:

$$Q(\alpha)W(\alpha \rightarrow \alpha') = Q(\alpha')W(\alpha' \rightarrow \alpha). \quad (3.3)$$

$W(\alpha \rightarrow \alpha')$ is the transition probability of going from state α to state α' . Equation (3.3) is a form of conservation of probability. Metropolis, *et al.*^[80] showed in 1953 that if (3.3) holds, then the probability distribution of generated states approaches in the limit $|\alpha| \rightarrow \infty$ the equilibrium probability distribution for the system:

$$Q_{eq}(\alpha) = \frac{1}{Z} \exp\left(-\frac{E_{\alpha}}{k_B T}\right). \quad (3.4)$$

Z is the partition function for the system. Equations (3.3) and (3.4) combine to give

$$\frac{W(\alpha \rightarrow \alpha')}{W(\alpha' \rightarrow \alpha)} = \exp(-(E_{\alpha'} - E_{\alpha})/k_B T) \equiv \exp(-\Delta E/k_B T). \quad (3.5)$$

This does not yet determine $W(\alpha \rightarrow \alpha')$ uniquely; we adopt the common choice:

$$W(\alpha \rightarrow \alpha') = \begin{cases} \exp(-\Delta E/k_B T) & \Delta E > 0 \\ 1 & \text{otherwise} \end{cases}. \quad (3.6)$$

Many other forms for $W(\alpha \rightarrow \alpha')$ exist in the literature^[78]. The transition probability (3.6) is realized in practice by placing the system in an initial state, randomly selecting a spin σ and a real number $s \in [0,1]$, and calculating the energy change ΔE of flipping σ .

If s is less than $\exp(-\Delta E/k_B T)$, the spin is flipped, otherwise, nothing happens. This is done $2N$ times (recall $2N$ is the number of spins on the lattice, and N is the number of tetrahedra); such a cycle is called one *Monte Carlo step per site* (MCS/S). A number of MCS/S serve to equilibrate the lattice, after which thermodynamic quantities are calculated and stored, yielding data on a single element of the thermodynamic ensemble. Once adequate data have been generated for an ensemble at a particular temperature, the temperature is forwarded incrementally, and the whole procedure is repeated.

Computational Details

We performed simulations on the IRT lattice, with the Hamiltonian of equation (1.22), in zero external field, on lattices with $2N = (2L)^3$ spins, and $L = 5$ to 10 . Simulations were run mostly on personal computers in our lab and office. Runs on lattices of sizes $L = 5, 6, 7$ required a day or less of computer time, $L = 8, 9$ required almost two days, and $L = 10$ about three days, depending on the specific computer used and temperature range explored. Finite-size behavior was systematic for $L \geq 6$.

Calculated during each run were the polarization per spin $P(T)$:

$$P(T) = \frac{1}{2N} \left\langle \sum_{i=1}^{2N} \sigma_i \right\rangle, \quad (3.7)$$

the energy per spin $E(T)$:

$$E(T) = \frac{1}{N} \left\langle \sum_{j=1}^N E_j(\alpha) \right\rangle, \quad (3.8)$$

the dielectric susceptibility $\chi_T(T)$:

$$\chi_T(T) = \frac{2N}{k_B T} (\langle P^2 \rangle - \langle P \rangle^2), \quad (3.9)$$

and the heat capacity $C(T)$:

$$C_E(T) = \frac{2N}{k_B T} (\langle E^2 \rangle - \langle E \rangle^2). \quad (3.10)$$

Every point in (m, n) -space (see equation (2.14)) with m, n integers between 3 and 18, was sampled at least once on lattices with $L = 8$ and 9, and often with $L = 10$. At multiple points in parameter space, many runs (5×10) were performed for each L , to obtain finite-size information and study the statistical scatter of the data. At each temperature in the region of the critical temperature, 3500 MCS/S per site were performed, with a temperature step between $0.0002 \frac{\epsilon_0}{k_B}$ and $0.0001 \frac{\epsilon_0}{k_B}$. Data from both heating and cooling runs were collected. The critical temperature was determined by the maximum of χ_T or C_E , and estimates from heating and cooling were often averaged.

The C++ computer code we wrote is reproduced in Appendix D.

Results and Discussion

We have found that the 16VM displays both first- and second-order transitions, depending on the values of J_2' , J_2'' , and J_4 . This is easily seen in Figures 28 through 31, which show the polarization and energy near the critical temperature for second- and first-order transitions, respectively. Both heating and cooling are shown in each graph, superimposed upon each other. The second-order transition displays no hysteresis, and the curves are relatively smooth and continuous. The first-order transition displays significant hysteresis and discontinuities at the transition temperature.

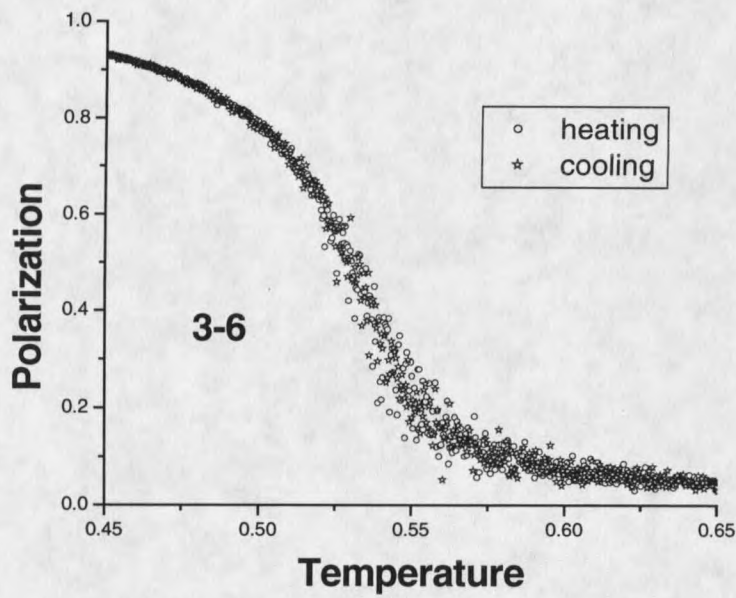


Figure 28. Absolute Value of the Polarization vs. Temperature for $(m,n) = (3,6)$. Transition is second-order. $L = 9$. Heating and cooling are shown.

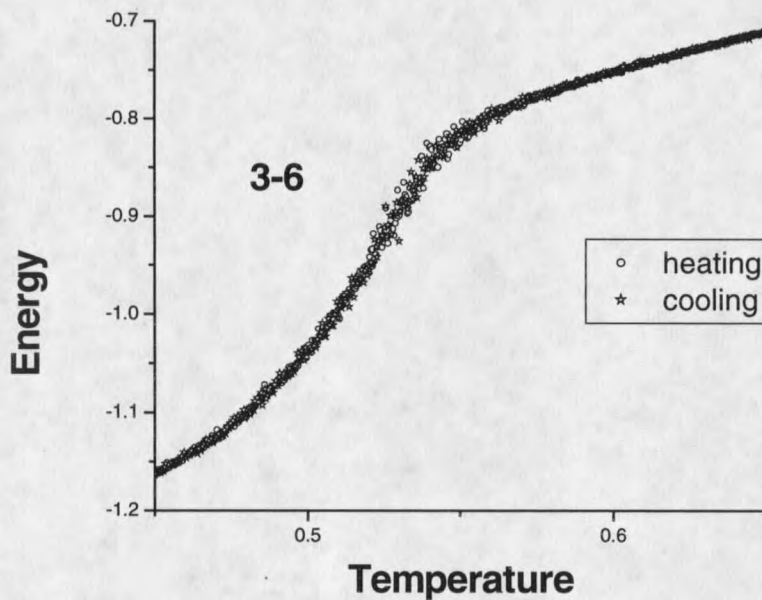


Figure 29. Energy vs. Temperature for $(m,n) = (3,6)$. Transition is second-order. $L = 9$. Heating and cooling are shown.

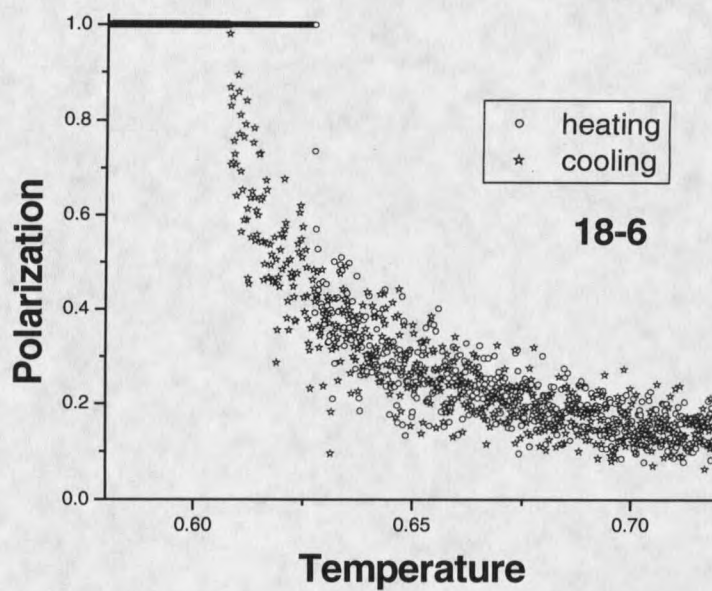


Figure 30. Absolute Value of Polarization vs. Temperature for $(m,n) = (18,6)$. Transition is first-order. $L = 9$. Heating and cooling are shown.

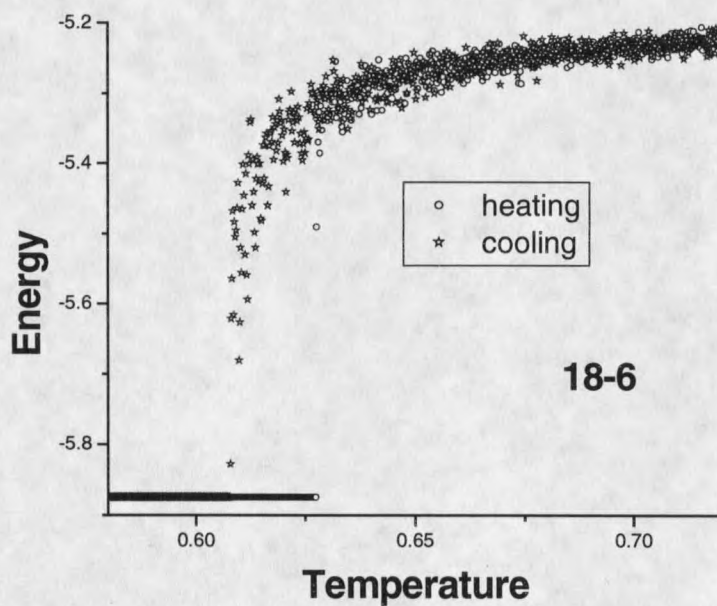


Figure 31. Energy vs. Temperature for $(m,n) = (18,6)$. Transition is first-order. $L = 9$. Heating and cooling are shown.

When the transition is strongly first-order, the hysteresis does not decrease as the system size or number of equilibration steps is increased, in contrast with second-order transitions. It is was impossible to discern between transitions that are weakly first-order or barely second-order, but we identified a tricritical region (TCR) where the nature of the transition changes order.

Results from the simulations are nicely summarized in Figures 32 and 33, which show contour diagrams of the critical temperature as a function of m and n . Figure 32 was obtained from susceptibility data, and Figure 33 from the heat capacity. It is seen that the critical temperature depends only weakly on n , and strongly on m , consistent with the series expansions. This is a consequence of the fact that for fixed n , increasing m increases J_4 , leaving J_2' and J_2'' fixed, see equations (1.25-1.28). The weak behavior of the critical temperature with n also partially justifies the approximation of neglecting ε_2 in previous vertex models of KDP-type crystals. However, neglecting ε_2 yields an Ising Hamiltonian without a four-spin interaction, and it is precisely this four-spin interaction that is responsible for the first-order transitions. Restricted vertex models predict nearly the same behavior as the 16VM when the transition is second-order, but they completely miss the (TCR) and first-order transitions.

The behavior of the model as it passes through the TCR is shown in Figures 34 and 35, which display graphs of the polarization and energy as m varies from 4 to 18, with $n = 14$. The onset of first-order transitions is evident at roughly $m = 10-12$, where a finite jump in the polarization and energy appears.

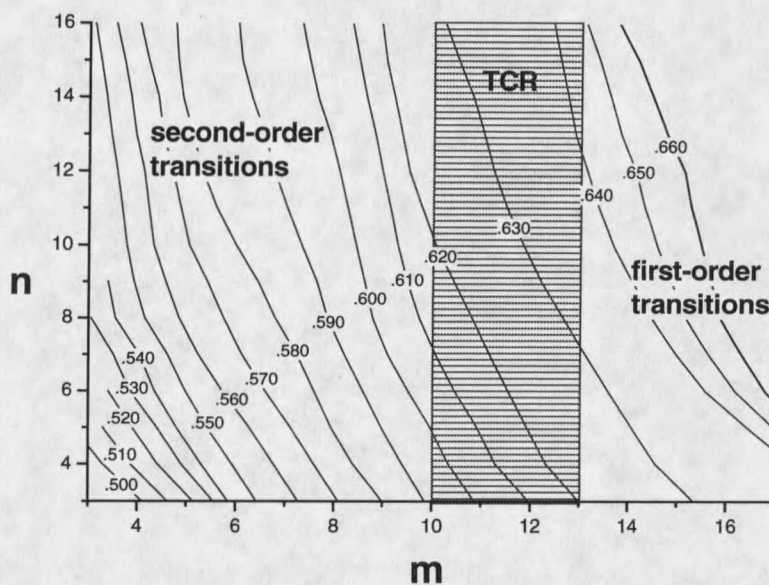


Figure 32. Transition Temperature as a Function of m and n , in units of ε_0/k_B ,
Obtained from χ_r .

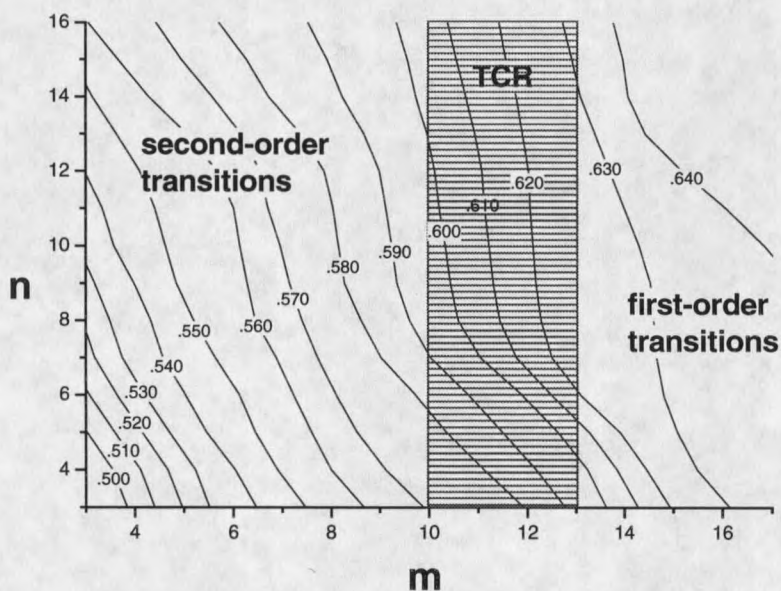


Figure 33. Transition Temperature as a Function of m and n , in units of ε_0/k_B ,
Obtained from C_E .

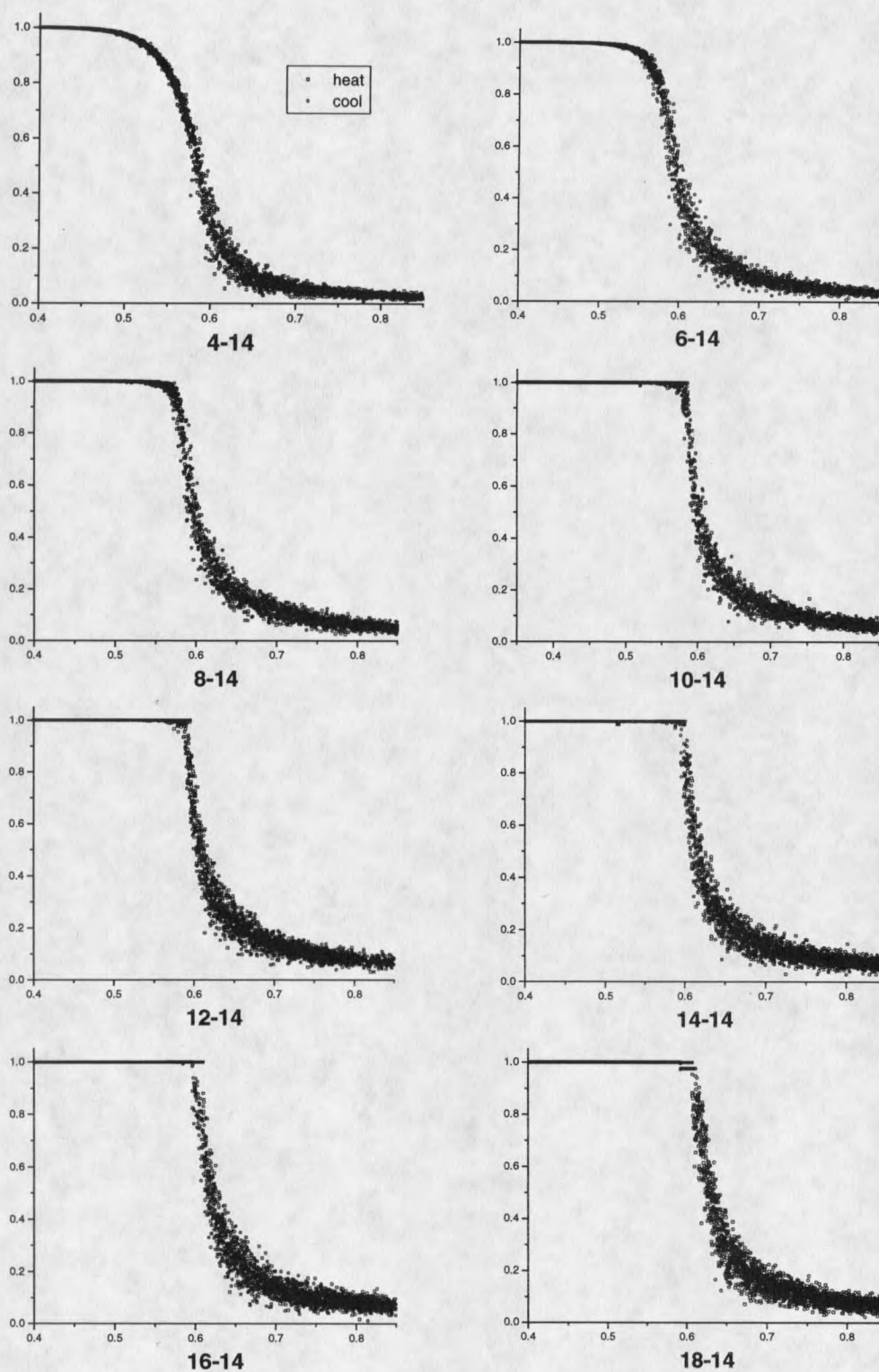


Figure 34. Polarization vs. $k_B T / \epsilon_0$ for $n = 14$, with Variation in m . $L = 9$. Both heating and cooling runs are shown. m - n for each run is given under each graph.

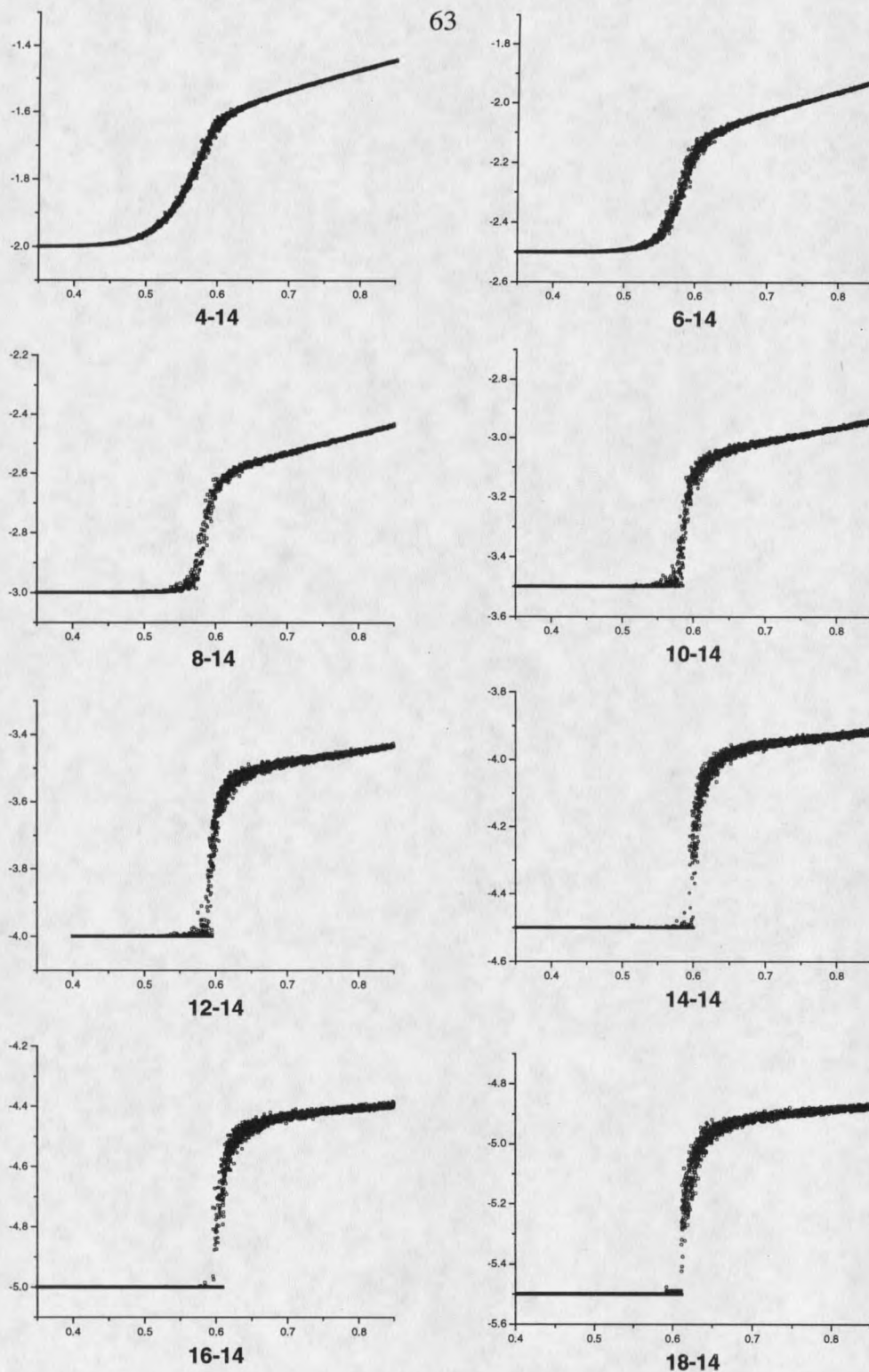


Figure 35. Energy vs. $k_B T / \epsilon_0$ for $n = 14$, with Variation in m . $L = 9$.

Both heating and cooling runs are shown. $m-n$ for each run is given under each graph.

The dielectric susceptibility and the heat capacity also behave differently, depending on the nature of the transition. When the transition is second-order, the data appear on fairly smooth curves. At a first-order transition, both response functions display a δ -function singularity, see Figures 36 and 37.

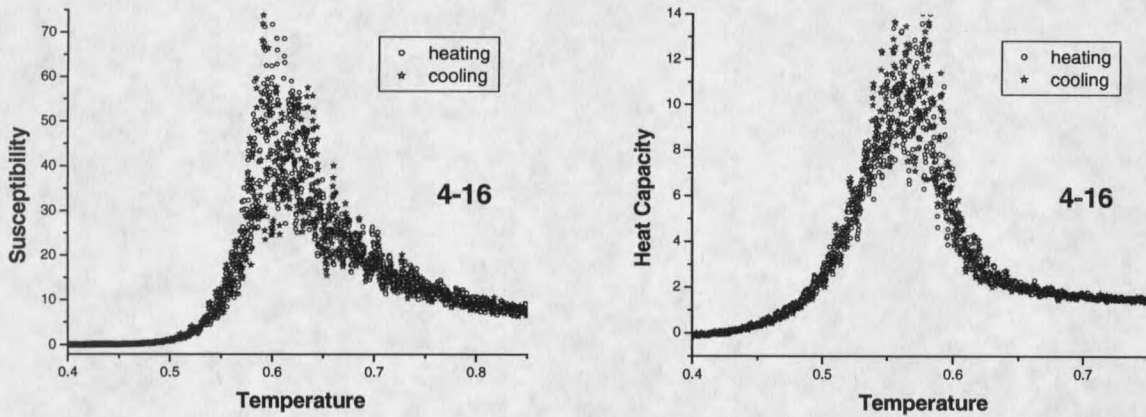


Figure 36. Dielectric Susceptibility and Heat Capacity for a Single Run with $(m,n) = (4,16)$. $L = 9$. Transition is second-order. Both heating and cooling are shown.

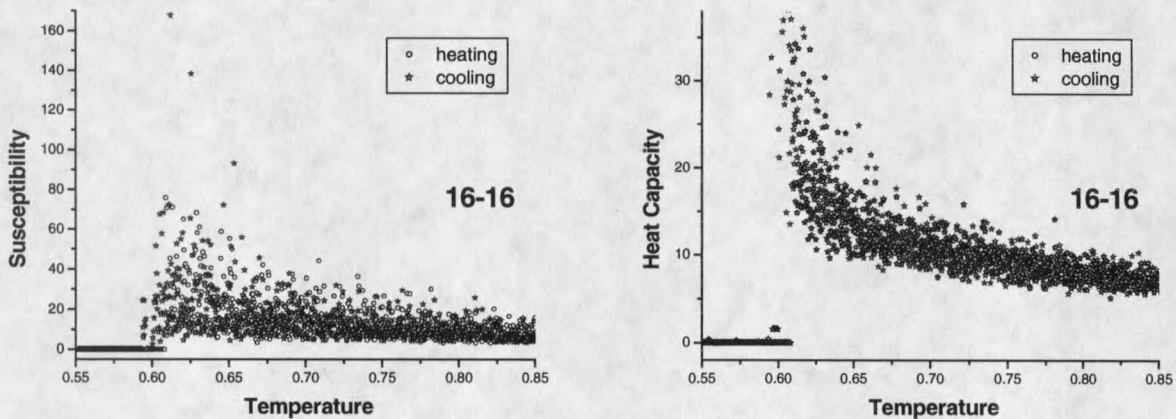


Figure 37. Dielectric Susceptibility and Heat Capacity for a Single Run with $(m,n) = (16,16)$. $L = 9$. Transition is first-order. Both heating and cooling are shown.

The transition temperature can be determined in the thermodynamic limit ($L \rightarrow \infty$) by plotting $T_c(L)$ against an inverse power of L . Finite-size scaling theory^[80,81] predicts $|T_c(L) - T_c(\infty)| \approx L^{-\theta}$, where $\theta = 1/\nu$ at a second-order transition (ν is the correlation length critical exponent), and $\theta = d$ at a first-order transition (d is the dimension of the lattice). Figure 38 displays this for $(m,n) = (3,3)$, where the transition is second-order. Figure 39 displays $(m,n) = (12,12)$, inside the TCR, where finite-size scaling is not expected to be valid. Figure 40 shows $(m,n) = (16,16)$, where the transition is first-order.

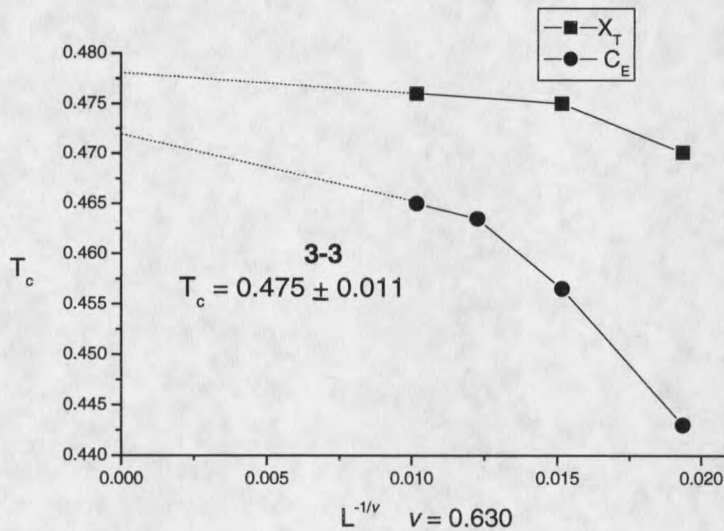


Figure 38. Critical Temperature Extrapolated from Finite Size Data for $(m,n) = (3,3)$.

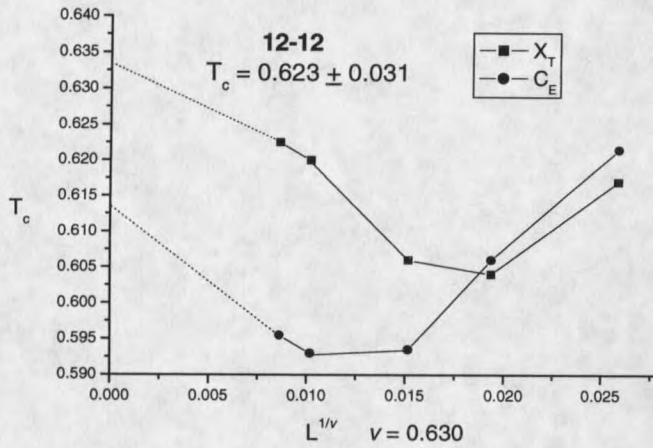


Figure 39. Critical Temperature Extrapolated from Finite Size Data for $(m,n) = (12,12)$.

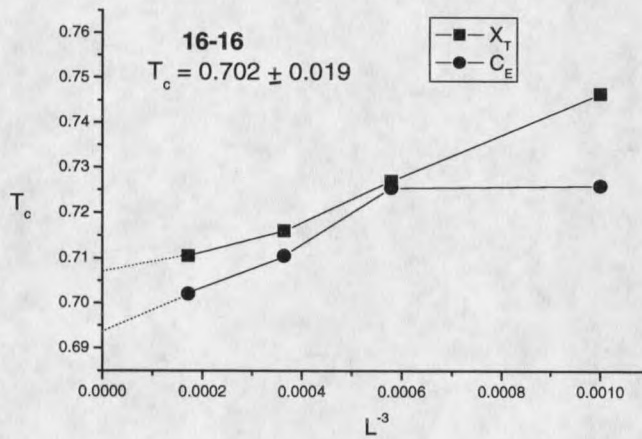


Figure 40. Critical Temperature Extrapolated from Finite Size Data for $(m,n) = (16,16)$.

Finite-size scaling also states that near a second order phase transition, the polarization and susceptibility have the functional forms:

$$P(T, E_{ext}) = L^{-\frac{\beta}{\nu}} \tilde{P}\left(L \cdot \left|1 - \frac{T}{T_c}\right|^\nu\right) \quad (3.11)$$

$$\chi(T, E_{ext}) = L^{\frac{\gamma}{\nu}} \tilde{\chi}_2 \left(L \cdot \left| 1 - \frac{T}{T_c} \right|^{\nu} \right) \quad (3.12)$$

$\tilde{P}$ and $\tilde{\chi}_2$ are *universal scaling functions*. If one plots $L^{\frac{\beta}{\nu}} P$ or $L^{\frac{\gamma}{\nu}} \chi$ against $L^{\frac{1}{\nu}} \left(1 - \frac{T}{T_c} \right)$ for various values of L , the data should collapse near T_c onto a single curve, either $\tilde{P}$ or $\tilde{\chi}_2$. Collapsing should not occur near a first-order transition. A drawback of this approach is the necessity of fitting three parameters: β (or γ), ν , and T_c . This data collapsing, and lack thereof, is shown for the polarization in Figures 41 through 43, for various values of m and n , and the critical exponents are assumed to take their 3D Ising values^[5,6]: $\nu = 0.630$, $\beta = 0.325$, $\gamma = 1.250$, and T_c is found through the finite-size analysis described above. This behavior breaks down in the presence of first-order transitions, as shown in Figures 42 and 43.

The upper branch of the scaling functions corresponds to $T < T_c$, and the lower branch to $T > T_c$. The high-temperature data all appear to be universal, but the low- T functions cease to be universal when the transition is first-order. The curves are fairly insensitive to the precise value of the exponents used, as the curves look pretty much the same whether $\beta = 0.325$ or $\beta = 0.375$, for example. The most these pictures can do is reinforce the belief that our model does indeed display scaling behavior near second-order transitions, and does not at a first-order transitions. The susceptibility data collapses nicely for $T < T_c$, but the high-temperature data are too scattered to collapse. This is due to the lack of self-averaging of the susceptibility, whereby errors do not decrease as the thermodynamic limit is approached.

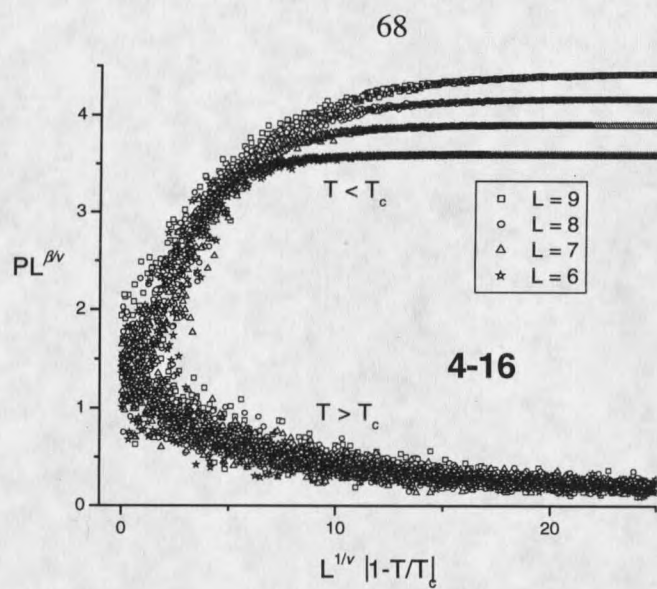


Figure 41. Scaling Plot for the Polarization with $(m,n) = (4,16)$.

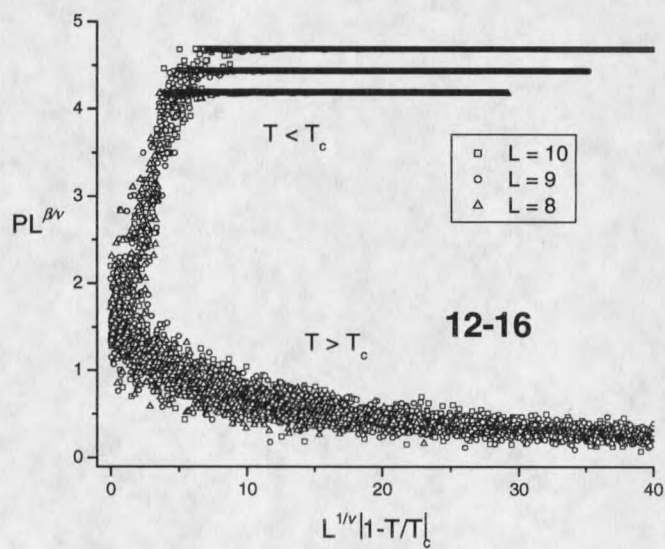


Figure 42. Scaling Plot Function for the Polarization with $(m,n) = (12,16)$.

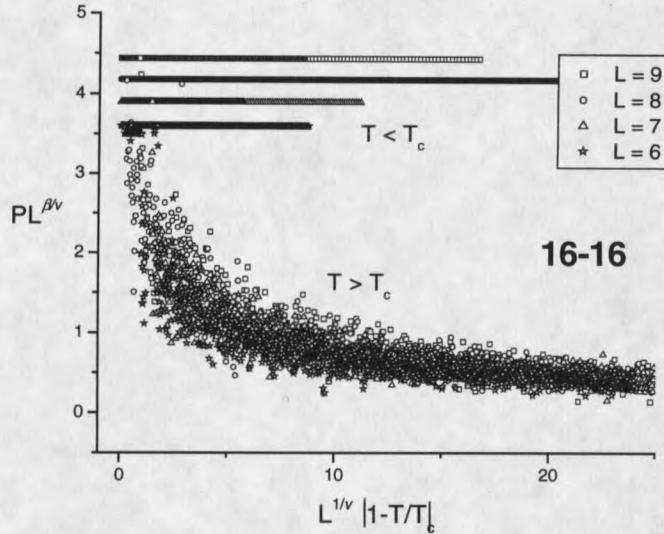


Figure 43. Scaling Plot Function for the Polarization with $(m,n) = (16,16)$.

Estimates of the exponents β and γ can be obtained by using the scaling formulae:

$$P(T_c) \propto (2L)^{-\frac{\beta}{\nu}} \quad (3.13)$$

$$\frac{\gamma}{\nu} = \frac{\ln \left[\frac{\chi(b2L, T_c)}{\chi(2L, T_c)} \right]}{\ln(b)} \quad (3.14)$$

Using equations (3.13) and (3.14) requires data of exceptional quality; unfortunately our data are only pretty good. Figures 44 and 45 show log-log plots of $P(T_c)$ vs. $2L$; the slope of the line is β/ν . $\beta/\nu = 0.516$ for the 3D Ising universality class. We used the 3D Ising value $\nu = 0.630$ to estimate β at 0.303 and 0.379, for $(m,n) = (3,3)$ and $(6,6)$, respectively. Finally, Figure 46 shows estimates of γ/ν as a function of $\ln(b)$ for $(m,n) = (6,6)$, where b is the scale factor in equation (3.14). This is as good as our data

gets for estimates of the susceptibility index. $\gamma/\nu = 1.98$ for the 3D Ising universality class, and with $\nu = 0.630$, we estimate γ at 1.386 ± 0.143 . While not as accurate as one would desire, the estimates are not inconsistent with the 16VM belonging to the 3D Ising universality class.

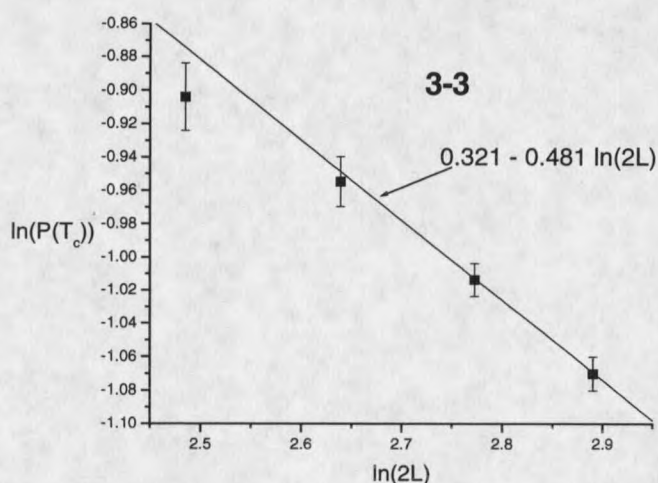


Figure 44. $P(T_c)$ vs. $2L$, for $(m,n) = (3,3)$.

Slope of the line is equal to β/ν . $\beta/\nu = 0.516$ for the 3D Ising universality class.

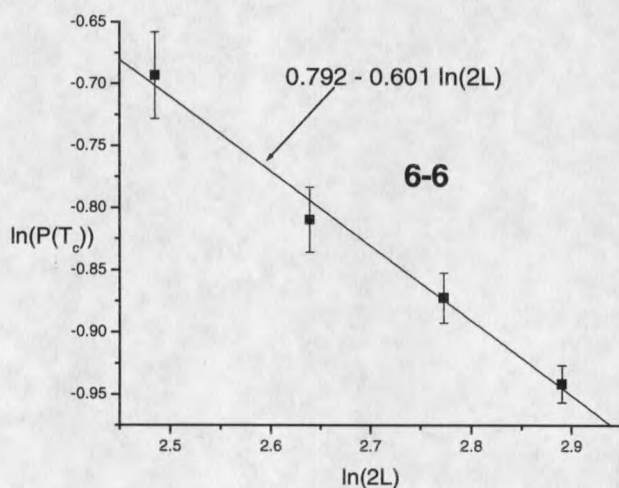


Figure 45. $P(T_c)$ vs. $2L$, for $(m,n) = (6,6)$.

Slope of the line is equal to β/ν . $\beta/\nu = 0.516$ for the 3D Ising universality class.

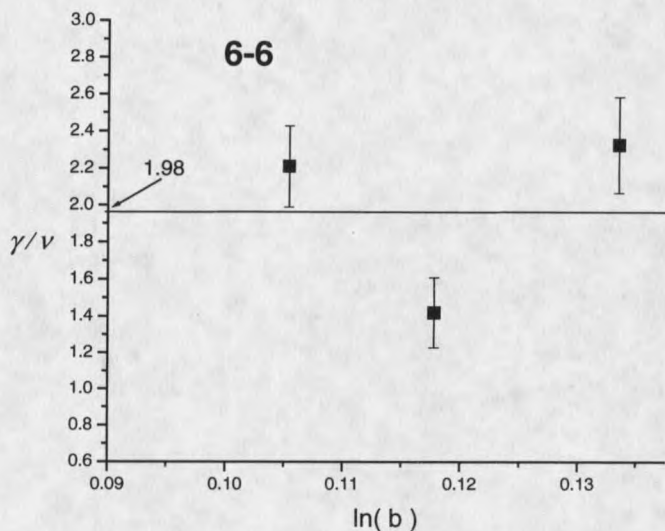


Figure 46. $\frac{\gamma}{v}$ vs. Scaling Constant b , for $(m, n) = (6, 6)$.
 $\frac{\gamma}{v} = 1.98$ for the 3D Ising universality class.

These conclusions are consistent with previous MC simulations of 3D models with multi-spin interactions on cubic lattices^[82]. These investigations revealed a TCR, and the transitions were first-order when the four-spin interaction was large compared to the two-spin interactions. They used lattices twice as big as ours with the same number of equilibration steps, but our temperature steps were $100 \square 500$ times smaller, and consequently our equilibration times were that much longer. Consequently our hysteresis loops are smaller and data on the order parameter and energy is more precise. However, we did not calculate the fourth-order cumulant of the order parameter^[78] which is quite useful in obtaining quality estimates of critical exponents, and so our estimates of the exponents are not nearly as good as those in [82]. We can state with a fair amount of confidence, however, that the critical behavior of the 16VM has been accurately determined, and it does indeed belong to the 3D Ising universality class.

CHAPTER FOUR

FIN

Here we are at the end, after studying the 3D 16VM in detail, having determined its phase transition behavior. The model exhibits both first- and second-order transitions, depending on the relative strength of the energy parameters. When the transition is second-order, critical exponents belong to the 3D Ising universality class. It is reassuring our results do not conflict with the universality hypothesis.

The MC simulations provided a wealth of information, but the series expansions are too short from which to infer highly accurate conclusions. Consequently the critical temperatures determined by the series analyses correspond only roughly to those determined by the MC simulations, although they are not inconsistent with each other. When critical temperatures from the MC simulations were used to bias the series analyses, reasonable agreement with the 3D Ising model was found, and from the MC simulations themselves we estimate the susceptibility critical exponent γ at 1.386 ± 0.143 , reasonably close to the 3D Ising value of 1.250.

We can estimate the model's parameters with a few simple arguments. KDP is weakly first-order at atmospheric pressures, so m is close to 10 (see Figures 32 and 33, page 61). Pressure decreases the transition temperature, and forces the transition to be second-order at 2.4 kbar, so to be consistent with Figures 32 and 33, pressure simultaneously decreases both m and n .

ϵ_0 can be found as a function of m and n by using the transition temperature obtained from MC simulations. The “height” of the contours in Figures 32 and 33 are estimates of

$$\frac{k_B T_c}{\epsilon_0} \equiv \tau_c(m, n). \quad (4.1)$$

If we use the following relic from the Slater theory^[61]:

$$\frac{\epsilon_0}{k_B} = T_c \ln(2) \quad (4.2)$$

we obtain $\tau_c(m, n) = \ln(2) \approx .693$, independent of m and n . This is undoubtedly in the region of strong first-order transitions. Using (4.1), Figure 32 (page 61), and the transition temperature for various crystals, one can draw contour diagrams of $\epsilon_0(m, n)$ for each KDP-family member. We have chosen to do this for KDP with its weakly first-order transition, RDA with its second-order transition, and DKDP and CDA which are both strongly first-order.

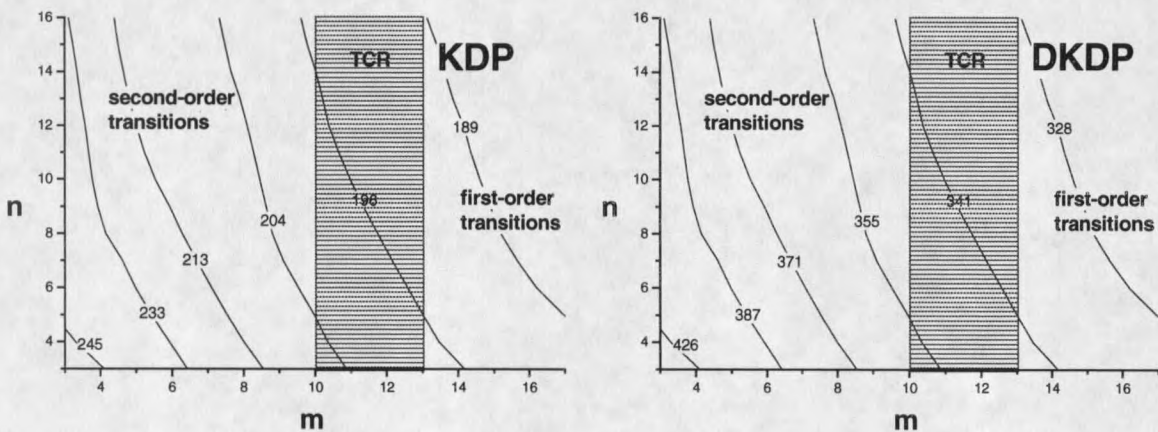


Figure 47. ϵ_0/k_B (in degrees Kelvin) as a function of m and n , for KDP and DKDP.

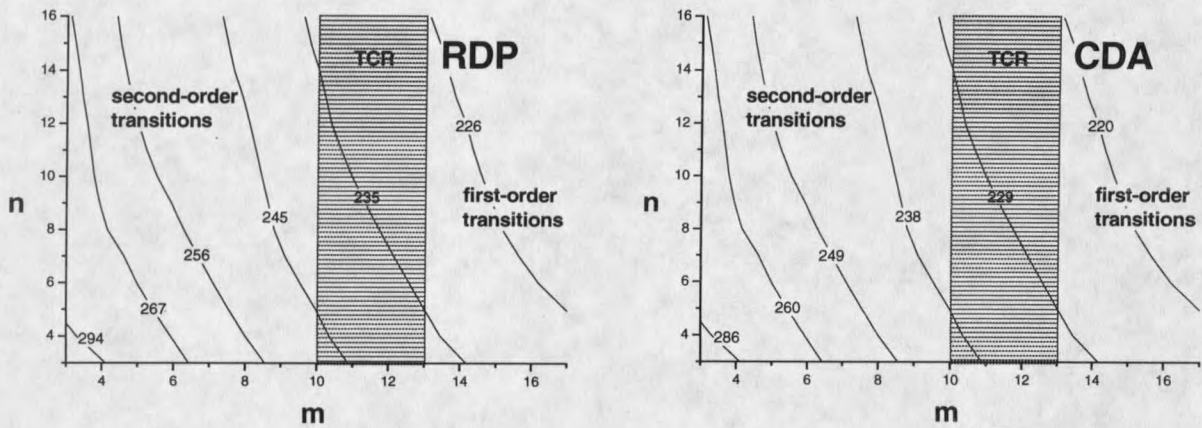


Figure 48. ε_0/k_B (in degrees Kelvin) as a function of m and n , for RDP and CDA.

It is important to realize the interaction energies ε_0 , ε_1 , and ε_2 are only parameters in the theory; they do not necessarily correspond to physical energies in the crystals. The 16VM is only one ingredient in the theoretical recipe of KDP-type crystals. In all likelihood an accurate description of KDP would require ε_0 , ε_1 , and ε_2 to be temperature dependent, perhaps changing discontinuously through the transition. ε_0 , ε_1 , and ε_2 also contain information about structural strain, although how they do so is far from obvious. At some point, long-range strain must be introduced into the theory to reproduce the experimentally determined mean-field exponents.

It might be possible for an enthusiastic young investigator to program a computer to generate many lattice constants, extending the series considerably. Another ten terms added to the low-T series would considerably aid the convergence, and is an entirely attainable goal. It is unclear what can be done for the high-T series, as their generation appears much less systematic than their low-T counterparts, but progress is definitely possible.

We have provided information on one more animal in the zoo of lattice models. The 16VM is also the foundation for most theoretical treatments of KDP-type crystals. These treatments included many different long-range interactions and often neglected any explicit reference to the 16VM. More often than not, the four-spin interaction was ignored. The four-spin interaction is what drives the transition first-order; one does not need long-range interactions to do so. It would be interesting to rework some of these older treatments in light of what we now know about their underlying statistical theory.

APPENDICES

APPENDIX A

LOW-TEMPERATURE SERIES LATTICE CONSTANTS

In this appendix are tabulated the lattice constants we generated for the low-temperature series. The table is to be used as follows:

To each graph is associated an identification number, a lattice constant, and a statistical weight. The weights are not given in the table, as they are trivial to produce. The weight of a graph is the product of the weights of the graph's individual vertices. Given a graph, every vertex of degree one or three gets a y . Of the six possible vertices of degree two, $\wedge$ and $\vee$ contribute a z , and $\rangle$, $\langle$, $/$, and $\backslash$ each contribute an x . A vertex of degree zero or four contributes nothing (technically a one) to the weight. Each bond in the graph contributes an h to the weight. For example, graph number 3 gets the weight y^2zh^2 , and graph number 5 gets $x^2y^2zh^4$.

To construct a series for the partition function from the table use the formula:

$$Z(T, E_{ext}) = 1 + \sum_g p_g w_g \quad (\text{A.1})$$

$\sum_g$ is a sum over all graphs in the table, p_g is the lattice constant for each graph, and w_g

is the weight of each graph. The highest degree term in a series depends on m :

$$\text{highest degree term} = 4m + 5. \quad (\text{A.2})$$

<u>ID #</u>	<u>Graph</u>	<u>Lattice Constant</u>	<u>ID #</u>	<u>Graph</u>	<u>Lattice Constant</u>
1		2	23		12
2		2^n	24		72
3		2	25		480
4		8	26		1432
5		32	27		1
6		64	28		8
7		156	29		40
8		368	30		160
9		848	31		556
10		1920	32		1772
11		2	33		5304
12		12	34		4
13		48	35		40
14		156	36		240
15		456	37		1120
16		4	38		18
17		24	39		180
18		96	40		1080
19		320	41		12
20		952	42		144
21		2648	43		864
22		7472	44		2

<u>ID #</u>	<u>Graph</u>	<u>Lattice Constant</u>	<u>ID #</u>	<u>Graph</u>	<u>Lattice Constant</u>
45		28	67		16
46		224	68		32
47		2	69		64
48		8	70		-7
49		16	71		-40
50		32	72		-104
51		64	73		-256
52		8	74		-608
53		32	75		-1408
54		96	76		-3200
55		4	77		-56
56		16	78		-288
57		48	79		-704
58		128	80		-1664
59		312	81		-3840
60		736	82		-362
61		8	83		-1776
62		48	84		-4192
63		192	85		-2128
64		2	86		-20
65		16	87		-56
66		80	88		-144

<u>ID #</u>	<u>Graph</u>	<u>Lattice Constant</u>	<u>ID #</u>	<u>Graph</u>	<u>Lattice Constant</u>
89		-352	111		1160
90		-104	112		1136
91		-288	113		-523/2
92		-128			
93		-736			
94		-704			
95		-352			
96		-608			
97		-52			
98		-144			
99		-368			
100		-384			
101		-1824			
102		-1056			
103		-16			
104		-44			
105		-112			
106		-152			
107		-416			
108		-840			
109		116/3			
110		388			

APPENDIX B

LOW-TEMPERATURE SERIES EXPANSIONS

In this appendix we have tabulated the low-T susceptibility series, for the range of parameters we found useful. This way one does not have to use the lattice constants in Appendix A to generate the series. The numbers before each series are m, n . The expansion variable is $x = \exp\left(-\frac{\varepsilon_0}{k_B T}\right)$.

2-3

$$1 + 8x + 36x^2 + 132x^3 + 444x^4 + 1484x^5 + 4429x^6 + 13538x^7 + 40478x^8 + 124806x^9 + \dots$$

2-4

$$1 + 8x + 36x^2 + 128x^3 + 412x^4 + 1264x^5 + 3840x^6 + 11072x^7 + 32769x^8 + 95074x^9 + \dots$$

2-5

$$1 + 8x + 36x^2 + 128x^3 + 408x^4 + 1232x^5 + 3620x^6 + 10528x^7 + 30354x^8 + 87824x^9 + \dots$$

2-6

$$1 + 8x + 36x^2 + 128x^3 + 408x^4 + 1228x^5 + 3588x^6 + 10308x^7 + 29810x^8 + 85454x^9 + \dots$$

2-7

$$1 + 8x + 36x^2 + 128x^3 + 408x^4 + 1228x^5 + 3584x^6 + 10276x^7 + 29590x^8 + 84910x^9 + \dots$$

2-8

$$1 + 8x + 36x^2 + 128x^3 + 408x^4 + 1228x^5 + 3584x^6 + 10272x^7 + 29558x^8 + 84690x^9 + \dots$$

2-9

$$1 + 8x + 36x^2 + 128x^3 + 408x^4 + 1228x^5 + 3584x^6 + 10272x^7 + 29554x^8 + 84658x^9 + \dots$$

3-4

$$1 + 8x + 36x^2 + 128x^3 + 404x^4 + 1188x^5 + 3436x^6 + 9068x^7 + 24325x^8 + 63552x^9 + 164158x^{10} + 419946x^{11} + \dots$$

3-5

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1156x^5 + 3180x^6 + 8524x^7 + 22020x^8 + 56412x^9 + 142873x^{10} + 358860x^{11} + \dots$$

3-6

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3148x^6 + 8304x^7 + 21440x^8 + 54080x^9 + 135856x^{10} + 338070x^{11} + \dots$$

3-7

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3144x^6 + 8272x^7 + 21220x^8 + 53536x^9 + 133488x^{10} + 331026x^{11} + \dots$$

3-8

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3144x^6 + 8268x^7 + 21188x^8 \\ + 53316x^9 + 132944x^{10} + 328694x^{11} + \dots$$

3-9

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3144x^6 + 8268x^7 + 21184x^8 \\ + 53284x^9 + 132724x^{10} + 328150x^{11} + \dots$$

3-10

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3144x^6 + 8268x^7 + 21184x^8 \\ + 53280x^9 + 132692x^{10} + 327930x^{11} + \dots$$

4-5

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1156x^5 + 3208x^6 + 8448x^7 + 21544x^8 \\ + 54408x^9 + 134537x^{10} + 327920x^{11} + 790312x^{12} + 1664316x^{13} + \dots$$

4-6

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3140x^6 + 8228x^7 + 21036x^8 \\ + 52076x^9 + 127484x^{10} + 307168x^{11} + 731849x^{12} + 1727414x^{13} + \dots$$

4-7

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8196x^7 + 20780x^8 \\ + 51532x^9 + 125188x^{10} + 300124x^{11} + 711184x^{12} + 1669446x^{13} + \dots$$

4-8

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + 20748x^8 \\ + 51312x^9 + 124608x^{10} + 297792x^{11} + 704176x^{12} + 1648790x^{13} + \dots$$

4-9

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + 20744x^8 \\ + 51280x^9 + 124388x^{10} + 297248x^{11} + 701808x^{12} + 1641746x^{13} + \dots$$

4-10

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + 20744x^8 \\ + 51276x^9 + 124356x^{10} + 297028x^{11} + 701264x^{12} + 1639414x^{13} + \dots$$

5-6

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3176x^6 + 8228x^7 + 20992x^8 \\ + 52000x^9 + 127044x^{10} + 305164x^{11} + 723513x^{12} + 1696512x^{13} \\ + 3718248x^{14} + 8486982x^{15} + \dots$$

5-7

$$1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8196x^7 + 20808x^8 \\ + 51456x^9 + 124712x^{10} + 298120x^{11} + 702848x^{12} + 1638544x^{13} \\ + 3783897x^{14} + 8444150x^{15} + \dots$$

5-8

$$\begin{aligned}
 &1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + 20740x^8 \\
 &+ 51236x^9 + 124204x^{10} + 295788x^{11} + 695804x^{12} + 1617888x^{13} \\
 &+ 3726016x^{14} + 8510294x^{15} + \dots
 \end{aligned}$$

5-9

$$\begin{aligned}
 &1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + 20736x^8 \\
 &+ 51204x^9 + 123948x^{10} + 295244x^{11} + 693508x^{12} + 1610844x^{13} \\
 &+ 3705360x^{14} + 8452422x^{15} + \dots
 \end{aligned}$$

5-10

$$\begin{aligned}
 &1 + 8x + 36x^2 + 128x^3 + 400x^4 + 1152x^5 + 3136x^6 + 8192x^7 + 20736x^8 \\
 &+ 51200x^9 + 123916x^{10} + 295024x^{11} + 692928x^{12} + 1608512x^{13} \\
 &+ 3698352x^{14} + 8431766x^{15} + \dots
 \end{aligned}$$

APPENDIX C

HIGH-TEMPERATURE SERIES EXPANSIONS

In this appendix we have tabulated the high-T susceptibility series, for the range of parameters we found useful. The numbers before each series are m, n . The expansion variable is $x = \frac{\epsilon_0}{k_B T}$.

3-4

$$1 + \frac{3}{2}x + \frac{9}{4}x^2 + \frac{11}{4}x^3 + \frac{499}{128}x^4 + \frac{12807}{2560}x^5 + \frac{172627}{30720}x^6 + \frac{6208171}{860160}x^7 + \dots$$

3-5

$$1 + \frac{3}{2}x + \frac{9}{4}x^2 + \frac{11}{4}x^3 + \frac{499}{128}x^4 + \frac{12807}{2560}x^5 + \frac{172627}{30720}x^6 + \frac{6208171}{860160}x^7 + \dots$$

3-6

$$1 + 2x + \frac{9}{4}x^2 + \frac{71}{24}x^3 + \frac{9}{4}x^4 + \frac{1111}{960}x^5 - \frac{59}{160}x^6 + \frac{711881}{322560}x^7 + \dots$$

3-7

$$1 + \frac{9}{4}x + \frac{33}{16}x^2 + \frac{173}{64}x^3 - \frac{2415}{2048}x^4 - \frac{40211}{20480}x^5 - \frac{6765523}{983040}x^6 + \frac{237218319}{18350080}x^7 + \dots$$

3-8

$$1 + \frac{5}{2}x + \frac{7}{4}x^2 + \frac{13}{6}x^3 - \frac{2755}{384}x^4 - \frac{3889}{1536}x^5 - \frac{1330907}{92160}x^6 + \frac{178260431}{2580480}x^7 + \dots$$

3-9

$$1 + \frac{11}{4}x + \frac{21}{16}x^2 + \frac{253}{192}x^3 - \frac{33671}{2048}x^4 + \frac{276193}{61440}x^5 - \frac{7111697}{327680}x^6 + \frac{38190634357}{165150720}x^7 + \dots$$

4-6

$$1 + 2x + \frac{13}{4}x^2 + \frac{55}{12}x^3 + \frac{47}{6}x^4 + \frac{9031}{960}x^5 + \frac{94049}{11520}x^6 + \frac{2005841}{129024}x^7 + \dots$$

4-7

$$1 + \frac{9}{4}x + \frac{51}{16}x^2 + \frac{293}{64}x^3 + \frac{12869}{2048}x^4 + \frac{78179}{20480}x^5 - \frac{439477}{327680}x^6 + \frac{384890897}{55050240}x^7 + \dots$$

4-8

$$1 + \frac{5}{2}x + 3x^2 + \frac{103}{24}x^3 + \frac{309}{128}x^4 - \frac{5857}{1536}x^5 - \frac{472459}{30720}x^6 + \frac{38758859}{2580480}x^7 + \dots$$

4-9

$$1 + \frac{11}{4}x + \frac{43}{16}x^2 + \frac{709}{192}x^3 - \frac{27553}{6144}x^4 - \frac{642917}{61440}x^5 - \frac{96038869}{2949120}x^6 + \frac{14042820961}{165150720}x^7 + \dots$$

4-10

$$1 + 3x + \frac{9}{4}x^2 + \frac{11}{4}x^3 - \frac{243}{16}x^4 - \frac{13903}{1280}x^5 - \frac{130939}{2560}x^6 + \frac{64774859}{215040}x^7 + \dots$$

5-6

$$1 + 2x + \frac{17}{4}x^2 + \frac{149}{24}x^3 + \frac{161}{12}x^4 + \frac{22831}{960}x^5 + \frac{117503}{5760}x^6 + \frac{3862331}{80640}x^7 + \dots$$

5-7

$$1 + \frac{9}{4}x + \frac{69}{16}x^2 + \frac{413}{64}x^3 + \frac{28729}{2048}x^4 + \frac{397329}{20480}x^5 + \frac{9253861}{983040}x^6 + \frac{2130645397}{55050240}x^7 + \dots$$

5-8

$$1 + \frac{5}{2}x + \frac{17}{4}x^2 + \frac{77}{12}x^3 + \frac{4849}{384}x^4 + \frac{14567}{1536}x^5 - \frac{921487}{92160}x^6 + \frac{57588887}{2580480}x^7 + \dots$$

5-9

$$1 + \frac{11}{4}x + \frac{65}{16}x^2 + \frac{1165}{192}x^3 + \frac{52243}{6144}x^4 - \frac{297587}{61440}x^5 - \frac{21836653}{589824}x^6 + \frac{851030729}{33030144}x^7 + \dots$$

APPENDIX D

MONTE CARLO C++ COMPUTER CODE

```

#include <fstream.h>
#include <math.h>
#include <time.h>
#include <stdio.h>
#include <string.h>
#include <process.h>

#define sig(a,b,c,d) lattice[x+a + (y+b)*MP2 + (z+c)*MP2S][d-1] //function to find site in lattice
//#define fs flip=(ec>fran2()); lattice[x + (y)*MP2 + (z)*MP2S][s]^=flip; if(x==1 && flip) lattice[MP1 + y*MP2 +
z*MP2S][s]=sig(0,0,0,s+1); else if(x==M && flip) lattice[y*MP2 + z*MP2S][s]=sig(0,0,0,s+1); if(y==1 && flip) la
ttice[x + MP1*MP2 + z*MP2S][s]=sig(0,0,0,s+1); else if(y==M && flip) lattice[x + z*MP2S][s]=sig(0,0,0,s+1); if(
z==1 && flip) lattice[x + y*MP2 + MP1*MP2S][s]=sig(0,0,0,s+1); else if(z==M && flip) lattice[x + y*MP2][s]=sig(0
,0,0,s+1);
#define fs if(ec>1 || ec>fran2()) {lattice[x + (y)*MP2 + (z)*MP2S][s]=!sig(0,0,0,s+1); if(x==1) lattice[MP1 + y*
MP2 + z*MP2S][s]=sig(0,0,0,s+1); else if(x==M) lattice[y*MP2 + z*MP2S][s]=sig(0,0,0,s+1); if(y==1) lattice[x +
MP1*MP2 + z*MP2S][s]=sig(0,0,0,s+1); else if(y==M) lattice[x + z*MP2S][s]=sig(0,0,0,s+1); if(z==1) lattice[x +
y*MP2 + MP1*MP2S][s]=sig(0,0,0,s+1); lattice[x + y*MP2][s]=sig(0,0,0,s+1);}

float energy_change[2][2][2][2][2][2][2];
float arrayec[2][2][2][2][2][2][2];
bool (*lattice)[8];
void calculate_arrayec(float temp);
void MC();
float polarization();
double total_energy();
float fran2();
int iran2(int input);
int toint(double input);
inline float G(int s1,int s2,int s3,int s4,int s5,int s6);

int idum; //for random numbers
int M,eq_st,data_st,eq_b_data, eq_crit, start_temp, end_temp,temp_step, crit_low, crit_high, crit_st, num_runs;
int *a_M,*a_eq_st,*a_data_st,*a_eq_b_data, *a_eq_crit, *a_start_temp, *a_end_temp,*a_temp_step, *a_crit_low, *a_
crit_high, *a_crit_st;
float J2H, J2V, J4;
float *a_J2H, *a_J2V, *a_J4;
char (*a_filename)[30], filename[30];

void main()
{
    char filepath[80];
    idum = (-1)*(int)((unsigned) time(NULL))& 0xFFFFFFFF; //initialize random number generator

```

```

fran2();
iran2(100);
double input;

fstream infile("c:\\kdpinput.txt", ios::in);
if(!infile.is_open())
{
    cout<<"Couldn't open input file"<<endl;
    exit(-1);
}

//cout<<"Number of Runs" << endl <<"?";
infile>>num_runs;

a_M=new int[num_runs]; a_eq_st=new int[num_runs]; a_data_st=new int[num_runs]; a_eq_b_data=new int[num_runs]
;
a_eq_crit=new int[num_runs]; a_start_temp=new int[num_runs]; a_end_temp=new int[num_runs]; a_temp_step=new i
nt[num_runs];
a_crit_low=new int[num_runs]; a_crit_high=new int[num_runs]; a_crit_st=new int[num_runs];
a_J2H = new float[num_runs]; a_J2V = new float[num_runs]; a_J4 = new float[num_runs];
a_filename = new char[num_runs][30];

for(int run = 0; run<num_runs; run++)
{
    //cout<<endl <<"Run #" << run+1 << endl;
    //cout<<"Enter filename" << endl <<"?";
    infile>>a_filename[run];
    //cout<<"Number of blocks per side of the cube" << endl << "?";
    infile>>a_M[run];
    //cout<<"Number of Equilibrate Steps" << endl << "?";
    infile>>a_eq_st[run];
    //cout<<"Number of data steps" << endl << "?";
    infile>>a_data_st[run];
    //cout<<"Number of Equilibrate Steps between Data Steps" << endl << "?";
    infile>>a_eq_b_data[run];
    //cout<<"Starting Temperature" << endl << "?";
    infile>>input;
    a_start_temp[run]=toint(input);
    //cout<<"Final Temperature" << endl << "?";
    infile>>input;
    a_end_temp[run]=toint(input);
    //cout<<"Temperature Step" << endl << "?";
    infile>>input;
    a_temp_step[run]=toint(input);
}

```

```

//cout<<"Critical Temperature Range Start" << endl << "?";
infile>>input;
a_crit_low[run]=toint(input);
//cout<<"Critical Temperature Range End" << endl << "?";
infile>>input;
a_crit_high[run]=toint(input);
//cout<<"Critical Temperature Step" << endl << "?";
infile>>input;
a_crit_st[run]=toint(input);
//cout<<"Equilibrate Steps in Critical Range" << endl << "?";
infile>>a_eq_crit[run];

//cout<<"J2H" << endl << "?";
infile>>a_J2H[run];
//cout<<"J2V" << endl << "?";
infile>>a_J2V[run];
//cout<<"J4" << endl << "?";
infile>>a_J4[run];

```

```

}
infile.close();

```

```

for(run = 0; run<num_runs; run++) //Loop to do each run

```

```

{
    unsigned int start_time=time(NULL);
    //get values to be used for this run from arrays
    M=a_M[run]; eq_st=a_eq_st[run]; data_st=a_data_st[run]; eq_b_data=a_eq_b_data[run];
    eq_crit=a_eq_crit[run]; start_temp=a_start_temp[run]; end_temp=a_end_temp[run]; temp_step=a_temp_step[ru

```

n];

```

    crit_low=a_crit_low[run]; crit_high=a_crit_high[run]; crit_st=a_crit_st[run];
    J2H = a_J2H[run]; J2V = a_J2V[run]; J4 = a_J4[run];
    strcpy(filename, a_filename[run]);

```

```

//sprintf(filepath, "c:\\windows\\desktop\\%s.dat", filename);
sprintf(filepath, "c:\\%s.dat", filename); //for win 2000
fstream outfile(filepath, ios::app | ios::out);

```

```

//Fill energy_change array
for(int s1=0; s1<2; s1++)
    for(int s2=0; s2<2; s2++)
        for(int s3=0; s3<2; s3++)
            for(int s4=0; s4<2; s4++)
                for(int s5=0; s5<2; s5++)
                    for(int s6=0; s6<2; s6++)
                        for(int s7=-1; s7<2; s7+=2)

```

```

        energy_change[s1][s2][s3][s4][s5][s6][(s7+1)/2]=-2.0*s7*G(s1,s2,s3,s4,s5,s6)

lattice = new bool[(M+2)*(M+2)*(M+2)][8]; //create lattice array
for(int i = 0; i<((M+2)*(M+2)*(M+2)); i++)
    for(int j = 0; j<8; j++) //fill lattice with plus one spin
        lattice[i][j]=1;

outfile<<"Temp\tPolar\tEnergy\tSusp"<<endl;
cout<<endl << "Run #" << run+1 << endl;

int mode=1; //mode 1 going up, mode 2 going down, 0 done
int temp=start_temp;

float *pol_array=new float[data_st]; //Stores polarization and energy for each data run
float *eng_array=new float[data_st];

while(mode)
{
    calculate_arrayec(temp/10000.0); //Calculte array_ec for this Temp
    if(temp>=crit_low && temp<=crit_high)
        for(i=0; i<eq_crit; i++) //Equilibrate steps for Non-Critical Region
            MC();
    else
        for(i=0; i<eq_st; i++) //Equilibrate steps for Critical Region
            MC();
    for(i=0; i<data_st; i++) //Data Steps
    {
        if(i!=0) //Add extra steps in between if not the first data step
            for(int j=0; j<eq_b_data; j++)
                MC();
        MC(); //Data step
        pol_array[i]=polarization(); //Add polarization for this data step to array
        eng_array[i]=total_energy(); //Add energy to array
    }

    float t_pol=0;
    float t_pol_s=0;
    float t_eng=0;
    float t_eng_s=0;
    for(i=0; i<data_st; i++) //Calculate average polarization and energy
    { //and average square of these
        t_pol+=pol_array[i];
        t_pol_s+=(pol_array[i]*pol_array[i]);
        t_eng+=eng_array[i];
        t_eng_s+=(eng_array[i]*eng_array[i]);
    }
}

```

```

    }
    t_pol/=data_st;
    t_pol_s/=data_st;
    t_eng/=data_st;
    t_eng_s/=data_st;

    //Output data
    cout<<temp/10000.0<<"\t"<<t_pol<<"\t"<<t_eng<<"\t"<<8*M*M*M*(t_pol_s-(t_pol*t_pol))/(temp/10000.0)<<
"\t"<<(t_eng_s-(t_eng*t_eng))/((temp/10000.0)*(temp/10000.0))<<endl;
    outfile<<temp/10000.0<<"\t"<<t_pol<<"\t"<<t_eng<<"\t"<<8*M*M*M*(t_pol_s-(t_pol*t_pol))/(temp/10000.0
)<<"\t"<<(t_eng_s-(t_eng*t_eng))/((temp/10000.0)*(temp/10000.0))<<endl;

    if(temp>=crit_low && temp<crit_high && mode==1)    //Step through temperatures
        temp+=crit_st;
    else if(temp>crit_low && temp<=crit_high && mode==2)
        temp-=crit_st;
    else if(mode==1)
        temp+=temp_step;
    else
        temp-=temp_step;

    if(temp>=end_temp && mode==1)    //Change direction if at final temp
        mode=2;
    if(temp<start_temp)    //Stop if at start temp
        mode=0;
}
outfile<<endl<<endl;
outfile.close();
delete lattice;
delete pol_array;
cout<<endl<<"Run Time: "<<time(NULL)-start_time<<" s" <<endl;
}

void calculate_arrayec(float temp) //This function fills the arrayec with  $e^{(-\text{energy\_change}/\text{temp})}$ 
{
    float *p_energy_change = reinterpret_cast<float*>(&energy_change);
    float *p_arrayec = reinterpret_cast<float*>(&arrayec);
    for(int i = 0; i<128; i++)
        p_arrayec[i] = exp(-p_energy_change[i]/temp);
}

void MC2() //monte carlo simulator
{
    int MSQ=M*M;

```

```

int MP1=M+1;
int MC8=M*M*M*8;
int MP2=M+2;
int MP2S=(M+2)*(M+2);
for(int i=0; i<MC8; i++) //Iterate through test sequence M^3*8 times.
{
    float ec;

    int x=iran2(M);
    int y=iran2(M);
    int z=iran2(M);
    int s=iran2(8)-1;
    switch(s)
    {
        /*      1      2      3      4      5      6
7*/
        case 0:
            ec=arrayec[sig(0,0,0,3)][sig(0,0,0,4)][sig(1,-1,-1,7)][sig(1,0,-1,8)][sig(0,0,0,2)][sig(1,0,0,2)][s
ig(0,0,0,1)];
            break;
        case 1:
            ec=arrayec[sig(0,0,0,3)][sig(0,0,0,4)][sig(0,-1,-1,7)][sig(0,0,-1,8)][sig(0,0,0,1)][sig(-1,0,0,1)][s
ig(0,0,0,2)];
            break;
        case 2:
            ec=arrayec[sig(0,-1,0,5)][sig(0,-1,0,6)][sig(0,0,0,1)][sig(0,0,0,2)][sig(0,-1,0,4)][sig(0,0,0,4)][si
g(0,0,0,3)];
            break;
        case 3:
            ec=arrayec[sig(0,0,0,5)][sig(0,0,0,6)][sig(0,0,0,1)][sig(0,0,0,2)][sig(0,1,0,3)][sig(0,0,0,3)][sig(0
,0,0,4)];
            break;
        case 4:
            ec=arrayec[sig(1,0,0,7)][sig(1,0,0,8)][sig(0,0,0,4)][sig(0,1,0,3)][sig(1,0,0,6)][sig(0,0,0,6)][sig(0
,0,0,5)];
            break;
        case 5:
            ec=arrayec[sig(0,0,0,7)][sig(0,0,0,8)][sig(0,0,0,4)][sig(0,1,0,3)][sig(-1,0,0,5)][sig(0,0,0,5)][sig(
0,0,0,6)];
            break;
        case 6:
            ec=arrayec[sig(0,1,1,2)][sig(-1,1,1,1)][sig(0,0,0,6)][sig(-1,0,0,5)][sig(0,1,0,8)][sig(0,0,0,8)][sig
(0,0,0,7)];
            break;
        case 7:

```

```

        ec=arrayec[sig(0,0,1,2)][sig(-1,0,1,1)][sig(0,0,0,6)][sig(-1,0,0,5)][sig(0,-1,0,7)][sig(0,0,0,7)][sig(0,0,0,8)];
    }

```

```

    if(ec>1 || ec>fran2()) //Check to see if spin flips
    {

```

```

        lattice[x + (y)*MP2 + (z)*MP2S][s]=!sig(0,0,0,s+1); //Flip spin

```

```

        if(x==1)

```

```

            lattice[MP1 + y*MP2 + z*MP2S][s]=sig(0,0,0,s+1); //If the spin is on the edge

```

```

        else if(x==M) //of th lattice change the

```

```

            lattice[y*MP2 + z*MP2S][s]=sig(0,0,0,s+1); //equivalent spin on the

```

```

        if(y==1) //opposite edge

```

```

            lattice[x + MP1*MP2 + z*MP2S][s]=sig(0,0,0,s+1);

```

```

        else if(y==M)

```

```

            lattice[x + z*MP2S][s]=sig(0,0,0,s+1);

```

```

        if(z==1)

```

```

            lattice[x + y*MP2 + MP1*MP2S][s]=sig(0,0,0,s+1);

```

```

        else if(z==M)

```

```

            lattice[x + y*MP2][s]=sig(0,0,0,s+1);
        }
    }
}

```

```

float polarization() //check polarization of lattic
{

```

```

    int numup=0;

```

```

    int MP1=M+1;

```

```

    int MP2=M+2;

```

```

    int MP2S=MP2*MP2;

```

```

    for(int x=1; x<MP1; x++)

```

```

        for(int y=1; y<MP1; y++)

```

```

            for(int z=1; z<MP1; z++)

```

```

                for(int s=0; s<8; s++)

```

```

                    numup += lattice[x + y*MP2 + z*MP2S][s];

```

```

    return ((float)2*numup-(M*M*M*8))/((float)(M*M*M*8));
}

```

```

double total_energy()
{

```

```

    int MP1=M+1;

```

```

    int MM1=M-1;

```

```

    int MP2= M+2;
}

```

```

int MP2S = MP2*MP2;

double energy=0;
for(int x=1; x<MP1; x++)      //Add up energys for each site
    for(int y=1; y<MP1; y++)
        for(int z=1; z<MP1; z++)
            {
                energy+=energy_change[sig(0,0,0,3)][sig(0,0,0,4)][sig(1,-1,-1,7)][sig(1,0,-1,8)][sig(0,0,0,2)][s
ig(1,0,0,2)][sig(0,0,0,1)];
                energy+=energy_change[sig(0,0,0,3)][sig(0,0,0,4)][sig(0,-1,-1,7)][sig(0,0,-1,8)][sig(0,0,0,1)][s
ig(-1,0,0,1)][sig(0,0,0,2)];
                energy+=energy_change[sig(0,-1,0,5)][sig(0,-1,0,6)][sig(0,0,0,1)][sig(0,0,0,2)][sig(0,-1,0,4)][s
ig(0,0,0,4)][sig(0,0,0,3)];
                energy+=energy_change[sig(0,0,0,5)][sig(0,0,0,6)][sig(0,0,0,1)][sig(0,0,0,2)][sig(0,1,0,3)][sig(
0,0,0,3)][sig(0,0,0,4)];
                energy+=energy_change[sig(1,0,0,7)][sig(1,0,0,8)][sig(0,0,0,4)][sig(0,1,0,3)][sig(1,0,0,6)][sig(
0,0,0,6)][sig(0,0,0,5)];
                energy+=energy_change[sig(0,0,0,7)][sig(0,0,0,8)][sig(0,0,0,4)][sig(0,1,0,3)][sig(-1,0,0,5)][sig
(0,0,0,5)][sig(0,0,0,6)];
                energy+=energy_change[sig(0,1,1,2)][sig(-1,1,1,1)][sig(0,0,0,6)][sig(-1,0,0,5)][sig(0,1,0,8)][sig
(0,0,0,8)][sig(0,0,0,7)];
                energy+=energy_change[sig(0,0,1,2)][sig(-1,0,1,1)][sig(0,0,0,6)][sig(-1,0,0,5)][sig(0,-1,0,7)][s
ig(0,0,0,7)][sig(0,0,0,8)];
            }
        return energy/(-2*(M*M*M*8));
    }

int toint(double input)      //Converts float entered(for temps) to int
{
    input*=10000;
    if(input-floor(input)>ceil(input)-input)
        return (int)ceil(input);
    else
        return (int)floor(input);
}

inline float G(int s1,int s2,int s3,int s4,int s5,int s6) //Calculates energy
{
    if(s1==0) s1=-1;if(s2==0) s2=-1;if(s3==0) s3=-1;
    if(s4==0) s4=-1;if(s5==0) s5=-1;if(s6==0) s6=-1;
    return -0.5*(J2V*(s1+s2+s3+s4)+J2H*(s5+s6))-0.25*J4*(s1*s2*s5+s3*s4*s6);
}

void MC() //monte carlo simulator

```

```

{
    int MSQ=M*M;
    int MP1=M+1;
    int MC8=M*M*M;
    int MP2=M+2;
    int MP2S=(M+2)*(M+2);
    int i;
    for(i=0; i<MC8; i++) //Iterate through test sequence M^3*8 times.
    {
        float ec;
        register bool flip;

        int x=iran2(M);
        int y=iran2(M);
        int z=iran2(M);
        int s=0;
        ec=arrayec[sig(0,0,0,3)][sig(0,0,0,4)][sig(1,-1,-1,7)][sig(1,0,-1,8)][sig(0,0,0,2)][sig(1,0,0,2)][sig(0,
0,0,1)];
        fs

        s=1; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(0,0,0,3)][sig(0,0,0,4)][sig(0,-1,-1,7)][sig(0,0,-1,8)][sig(0,0,0,1)][sig(-1,0,0,1)][sig(0
,0,0,2)];
        fs

        s=2; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(0,-1,0,5)][sig(0,-1,0,6)][sig(0,0,0,1)][sig(0,0,0,2)][sig(0,-1,0,4)][sig(0,0,0,4)][sig(0,
0,0,3)];
        fs

        s=3; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(0,0,0,5)][sig(0,0,0,6)][sig(0,0,0,1)][sig(0,0,0,2)][sig(0,1,0,3)][sig(0,0,0,3)][sig(0,0,0
,4)];
        fs

        s=4; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(1,0,0,7)][sig(1,0,0,8)][sig(0,0,0,4)][sig(0,1,0,3)][sig(1,0,0,6)][sig(0,0,0,6)][sig(0,0,0
,5)];
        fs

        s=5; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(0,0,0,7)][sig(0,0,0,8)][sig(0,0,0,4)][sig(0,1,0,3)][sig(-1,0,0,5)][sig(0,0,0,5)][sig(0,0,
0,6)];
        fs
    }
}

```

```

        s=6; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(0,1,1,2)][sig(-1,1,1,1)][sig(0,0,0,6)][sig(-1,0,0,5)][sig(0,1,0,8)][sig(0,0,0,8)][sig(0,0,0,7)];
        fs
        s=7; x=iran2(M); y=iran2(M); z=iran2(M);
        ec=arrayec[sig(0,0,1,2)][sig(-1,0,1,1)][sig(0,0,0,6)][sig(-1,0,0,5)][sig(0,-1,0,7)][sig(0,0,0,7)][sig(0,0,0,8)];
        fs
    }
}

/*inline void flipspin(int x, int y, int z, int s, double ec)
{
    bool flip=(ec>fran2()); //Check to see if spin flips
    lattice[x + (y)*MP2 + (z)*MP2S][s]^=flip; //Flip spin

    if(x==1)
        lattice[MP1 + y*MP2 + z*MP2S][s]=sig(0,0,0,s+1); //If the spin is on the edge
    else if(x==M && flip) //of th lattice change the
        lattice[y*MP2 + z*MP2S][s]=sig(0,0,0,s+1); //equivalent spin on the
    if(y==1) //opposite edge
        lattice[x + MP1*MP2 + z*MP2S][s]=sig(0,0,0,s+1);
    else if(y==M)
        lattice[x + z*MP2S][s]=sig(0,0,0,s+1);
    if(z==1)
        lattice[x + y*MP2 + MP1*MP2S][s]=sig(0,0,0,s+1);
    else if(z==M)
        lattice[x + y*MP2][s]=sig(0,0,0,s+1);
}*/

```

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