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The Cluster Variation Method proposed by Morita is shown to yield a development of the entropy into an alternating series when applied to the Lenz-Ising Model. Truncation of this series to its first N terms gives an N-th order variationally based approximation to the exact statistical behavior of this system. The first four orders of this sequence of approximations have been carried out in this work.

Curious behaviors such as complex Curie temperatures have been observed by others and this work shows that such behavior is due to the alternating sign of the terms in the entropy expansion. The effect is large enough to cause a non-physical global minimum to appear on the boundary of the variation space, starting with the third order approximation and requires the use of non-calculus type of minimization. Even in the second approximation, the entropy becomes negative for certain regions of the variation space, which is certainly unphysical.

A modification of the Cluster Variation Method is effective in suppressing these undesired effects. The (2n+1)-cluster results are then an improvement over those of the (2n+1)-cluster approximation. The (2n)-cluster results are less affected by spurious minima.

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A Study of the Free Energy of the Lenz-Ising Model Using the Cluster Variation Method of Morita

CHAPTER I

CLUSTER VARIATION METHOD

Objectives of This Work

The purpose of this work can be described by considering these answers to the following questions. (1) What are we studying? The free energy of the Lenz-Ising model will be examined. (2) Why are we studying this model? We are interested in obtaining a method that will permit the calculation of the free energy for systems of interacting particles. The Lenz-Ising model is the simplest of all the models of interacting particles. No exact solutions in three dimensions for arbitrary T,B yet exist. (3) How shall we study this model? The Morita Cluster Variation Method (CVM) will be used to calculate an approximate value for the free energy of this model. (4) Why do we use this method? Variational methods have a track record as a superior approximation method. The Morita Variational Method has been found to behave strangely; we wish to resolve this strangeness.

In addition to obtaining answers to the above questions, this work will assist in gaining insight into the phase transitions exhibited by various systems at a critical temperature peculiar to each system. Examples of phase

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changes are the transition from a non-ferromagnetic to a ferromagnetic state in Fe and Ni i.e. the long range ordering that causes the material to become magnetic. Other examples are a lattice gas and a binary alloy such as Cu-Zn.

Application of the CVM to Calculate the Free Energy of the Lenz-Ising Model

One way to study the behavior of an N-particle system is to analyze this behavior into the behavior of the N **1-particle** subsystems, the N*(N-1)/2 **2-particle** subsystems, the N*(N-1)*(N-2)/(3!) **3-particle** subsystems, and so on. This method replaces the study of one object --the N-particle system--by the study of 2^N-1 objects. Why would one do this?

One always does this for systems whose particles (1) do not interact with each other whence, the system's behaviors are entirely determined by the N 1-particle properties and (2) are all similar in their properties, whence, all N 1-particle properties are the same. Then this approach replaces the study of an N-particle system by a 1-particle system. Examples of this approach include the standard studies of the ideal classical and quantal gases, and the ideal paramagnet.

This approach has been extended to include those systems of interacting particles for which "normal coordinates" have been located, coordinates in which there are no interactions. The main example here is the set of vibrations of lattice ions in the harmonic approximation, which are replaced by non-interacting "quasiparticles". In this case, however, the 1-quasiparticle properties are not all the same; each class must be treated individually, and the final results obtained by summation.

However, arguments that "only small subsystems are important" are rarely rigorous for non-ideal systems. Nor do all of these sorts of arguments include estimates of the errors made in ignoring the remaining (enormously many) subsystems. Further, it is often difficult to see how to improve a treatment of this type, which might be promising, but not quite good enough. These difficulties all come from the same sources:

1. the choice of which subsystems are included in the study is usually made on an intuitive basis, and not on the basis of a general principle, and
2. ignored subsystems are not explicitly considered at all, so that it is difficult to judge the error that ignoring them incurs, or how to include them in a better approximation.

The usual criterion for including subsystems is that their particles are all physically close, and in intense interactions; subsytems whose particles are all distant, and not interacting, are usually ignored. This is why the systems studied are often called "clusters"; i.e. a number of similar things in close proximity, somewhat separate from other things. There does not seem to be a common name for particles that are not parts of clusters. That is, common language reflects the procedure sketched above: we know how to treat N-particle systems that obviously separate into essentially independent subsystems (clusters), but we have difficulty when this separation is not perfect.

T. Morita[1] has presented a formalism for the equilibrium statistical mechanical study of N-particle systems in which all 2^N subsytems explicitly appear. One then makes an explicit choice as to which will be retained and which will be ignored in further study. This leads to an approximate expression for the free energy of the N-particle system in terms of quantities related to the retained subsytems[2-4]. Minimizing this approximate free energy by varying these quantities:

1. gives an estimate of the exact equilibrium free energy , and
2. gives estimates for all equilibrium thermal behaviors of the system.

It had been thought that it gave an upper bound to the free energy -- we now know that this is wrong!

There is only one sort of approximation involved in this procedure: the choice of which subsystems to retain for further consideration, and which to ignore. Many other strategies require a series of nested approximations; it is frequently difficult to determine their relative affects on the accuracy of the result. We now know that Morita's method is also of this uncontrolled type!

Morita's method can be systematically improved by retaining previously ignored subsystems. Since these explicitly enter the original expression for the free energy, it is possible to form some estimate of their importance. It is easy to incorporate any "physical intuitions" one may have as to the importance of certain clusters.

Morita has called his procedure the **CLUSTER VARIATION METHOD**. We shall present it by defining a "cluster" in a general way, one that does not rely on some particular attribute such as physical proximity. We shall restrict ourselves to classical systems, and we shall suppose that the particles are arranged on a crystal lattice. Then we shall define the **microstates** and the **macrostates** of clusters, and then distinquish between **cluster functions** and **cluster quantities**. We shall introduce the distinction between **extrinsic** and **intrinsic** variables, recall the usual development of the Hamiltonian into a series of intrinsic terms, and exhibit Morita's novel development of the entropy into such a series. We exhibit the free energy of the system as a sum of a series of intrinsic terms, each due to a particular cluster. This series is exact, but, as it contains 2^N -1 terms, it is too difficult for direct calculation of results for macroscopic systems. But this series is ideal as a starting point for approximations -- one partitions the set of clusters into those which one will retain in subsequent work, and those which one will ignore, and then deletes from the sum all the terms relating to ignored clusters. In this work the truncated expansions of the free energy are also called approximations. Thus the expansion retaining only the first term is called the first approximation and the expansion retaining only the first and second terms is called the second approximation and so on. In this work the free energy will be calculated for the first through the fourth approximation using the Morita expansion.

The calculation of the free energy using these concepts can be outlined as follows. The Helmholtz free energy of the Lenz-Ising model[5] is expressed as a function of its macrostate, $F = F(P_o)$, for the first through the fourth approximation using the Morita expansion. For each approximation, that macrostate P_o for which the free energy is stationary is found, using either the calculus methods or the Simplex algorithm[6]. The stationary free energy is obtained with the calculus methods by setting the first derivative of F to zero: $(\delta F/\delta P_o)_{P_o} = 0$ and determing the mini-max nature of the stationary state P_o with the second derivative. For the higher approximations the Simplex algorithm is used to find the stationary free energy.

The method can be summarized as: Write the free energy (using the Hamiltonian) for the Lenz-Ising model using the Morita cluster expansion and minimize it. Remembering that the equilibrium free energy is the one which is the least of all possible free energies (F), the minimization will give two results: (1) the equilibrium macrostate P_0, and (2) the equilibrium free energyy $F_0 = F(P_0)$. This method is completely analogous to the quantum mechanics procedure: minimizing the expectation of the energy <E> = (psi,Hpsi) gives not only the correct ground state energy of the system E_0 but also the correct ground state psi_0.

The results for the Lenz-Ising model in the presence of a magnetic field will be calculated with the Morita method and compared with exact calculations for systems which contain only N=1,2,3,4 particles (see Chapter III).

Boltzmann, Gibbs, Morita

Boltzmann expressed the entropy of composite systems whose sub-systems do not interact as[7],

$$S_B = -k_B \Sigma_{i=1}^{N} tr_i^{(1)} P_i^{(1)} \ln P_i^{(1)}$$

where k_B is Boltzmann's constant

$tr_i^{(1)}$ is a (generalized) summation over all the microstates of the ith sub-system,

$P_i^{(1)}$ is the probability law for the microstates of the ith sub-system, that is, $P_i^{(1)}$ is the MACROSTATE of the ith SUB-SYSTEM.

Later this was extended by Gibbs[8] to calculate the entropy for composite systems with arbitrarily interacting subsystems as,

$$S_G = k_B \, tr^{(N)} P^{(N)} \ln P^{(N)}$$

where,

$tr^{(N)}$ is a (generalized) sum over the microstates of the composite system,

$P^{(N)}$ is the probability law for the macrostates of the composite system, that is, $P^{(N)}$ is the MACROSTATE of the COMPOSITE SYSTEM.

For a composite system of many interacting particles the calculation of S_G is prohibitively difficult. Morita expresses the total or extrinsic entropy of the composite system as the sum of the entropies associated with each cluster of the composite system. In the cluster expansion he refers to the extrinsic entropy of the complete system as given by,

$$S_G = S^{(N)}\text{extrinsic} = \tilde{S}^{(1)}\text{intrinsic} + \tilde{S}^{(2)}\text{intrinsic} + \ldots \tilde{S}^{(N)}\text{int.}$$

where, $\tilde{S}^{(1)}$ is the intrinsic entropy of all particles taken one at a time (singlets) with no interaction between the particles and would be the same as Boltzmann's S_B. Therefore, $S_B = \tilde{S}^{(1)}$. The next term $\tilde{S}^{(2)}$ is the intrinsic entropy of a pair of interacting particles and then $\tilde{S}^{(3)}$ is the intrinsic entropy of a triple of interacting particles and so on. This resolution of the entropy also clarifies the relation of S_G and S_B since we could write the expansion as

$$S^{(N)} = S_G = S_B + \tilde{S}^{(2)} + \tilde{S}^{(2)} + \tilde{S}^{(3)} + \ldots \tilde{S}^{(N)}.$$

If there are no correlations among the particles, i.e., if

$P^{(N)} = \Sigma_{i=1}{}^{N} P^{(1)}{}_{i}$,

then $S^{(n)} = 0$ for each $n > 1$,

and $S_G = S_B$.

Then Gibbs' entropy reduces to Boltzmann's entropy. If there are interactions among subsystems (particles), then S_G will differ from S_B .

The complete Morita expansion for the free energy (F) is exact but typically we only use the first few terms. We refer to the terms as clusters or approximations i.e., 1st approximation or 1-cluster etc.

Morita decomposes a system of N particles into the collection of all subsets of these particles:

"1-clusters" are sets, each containing 1 particle; there are N of these.

"2-clusters" are sets, each containing 2 particles; there are N(N-1)/2 of these.

"n-clusters" are sets, each containing n particles; there are N!/(N-n)!n! of these.

The entire system, then is "the N-cluster"; there is one of these. We could use the familiar notation for "combinatorial factor":

$$Cn(N) = N!/(N-n)!n!$$

There are 2^N-1 clusters in all, for a system of N particles.

Any particular n-cluster is labeled by the particles it contains:

$C^{(n)}_{i1,i2,i3,\ldots in}$. The microstate of the n-cluster $C^{(n)}_{i1,\ldots,in}$ is $\mu^{n}_{i1,\ldots,in} = (\mu_{i1},\ldots\mu_{in})$. The microstate of the ith particle is μ_i; the microstate of the whole system is $\mu^N = (\mu_1,\mu_2, \ldots \mu_N)$. The macrostate of the whole system is $P^{(N)}$ = probability of each value of μ^N. The macrostate of an n-cluster is

$P^{(n)}_{i1,\ldots in} = \Sigma P^{(N)}$ where sigma is summed over all the microstates of the particles not in the n-cluster.

The following approximations from Morita's expansion for the free energy are the expressions that we will minimize. Only the first two approximations are shown here.

<u>First Approximation</u> (first term) (see also p.41,68)

This first term in the Morita cluster expansion, known as the first approximation, is the free energy for single clusters-one particle at a time, with no interaction between clusters. All correlations at the pair level and up are ignored.

$F = U - TS$

$U = \langle H \rangle$

$H = -\mu_0(\Sigma_{i=1}^{N} x_i)B - \frac{1}{2}J(\Sigma_{i=1}^{N} x_i^2)Z$

$U = N(-\Sigma\mu_0 Bx - \frac{1}{2}ZJx^2)$

where F = free energy T = temperature

U = internal energy S = entropy

Z = coordination number*

H = Hamiltonian

x = magnetization per particle

B = external magnetic field

J = exchange integral

μ_0 = magnetic moment

x^2 = interaction between n.n. (see p.48)

*Z is the number of n.n. : $Z = 2$ in one dimension
n.n. = nearst neighbors $Z = 4$ in 2-dim (square lattice)
$Z = 12$ in 3-dim

In this study of the free energy using the Morita cluster expansion the results will be obtained for an FCC lattice[9]. A unit cell of an FCC lattice is shown in Fig.1.

The Morita expansion for only the first term is,

$$S^{(N)} = S^{\sim(1)}$$

where

$$S^{\sim(1)} = S^{(1)} = \Sigma[\text{all singlets}]S^{(1)}{}_i$$

and $S^{(1)}{}_i = k_B \mathrm{tr}^{(1)}{}_i P^{(1)}{}_i \ln P^{(1)}{}_i$ is the entropy of each single subsystem (or particles) and $S^{(1)}$ is the entropy of all the N subsystems, each taken one at a time, so that there are no interactions among the systems, and $S^{\sim(1)} = S^{(1)}$ is the INTRINSIC entropy of these NONINTERACTING subsystems.

$$S = -k_B N[\tfrac{1}{2}(1+x)\ln(.) + \tfrac{1}{2}(1-x)\ln(.)]$$

$$F = N\{-\mu_0 Bx - \tfrac{1}{2}ZJx^2 + k_B T[\tfrac{1}{2}(1+x)\ln(.)+\tfrac{1}{2}(1-x)\ln(.)]\}$$

$$\text{or } F/Nk_B T = \beta F/N = -(\mu_0 B/k_B T)x - (ZJx^2/2k_B T) + [\tfrac{1}{2}(1+x)\ln(.)+\tfrac{1}{2}(1-x)\ln(.)]$$

When the factor that precedes the natural log is repeated as its function then the notation ln(.) is used.

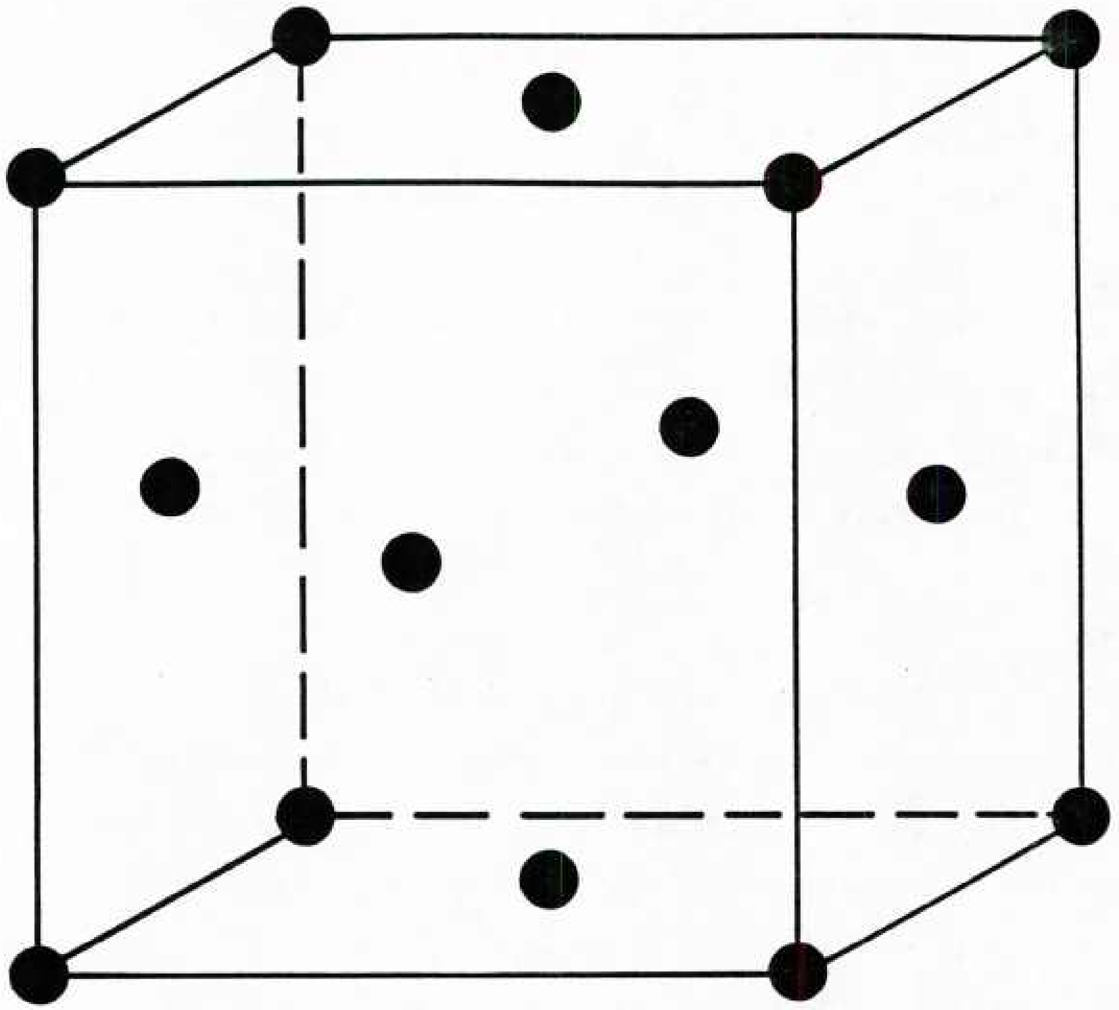

Fig. 1. THE UNIT CELL FOR A FACE CENTERED CUBIC (FCC) LATTICE. THE NUMBER OF NEAREST NEIGHBORS IS 12.

$\Phi = \beta F/N = -(\mu_0 \beta B)x - (\frac{1}{2}\beta JZ)x^2 + [\frac{1}{2}(1+x)\ln(.)+\frac{1}{2}(1-x)\ln(.)]$

Using a reduced temperature T_r an alternate form can be obtained ($\beta = 1/k_B T$)

$T_r = k_B T/J = 1/\beta J$

Then $\mu_0 B/k_B T = \mu_0 B/k_B T * J/J = \mu_0 B/JT_r = B_r/T_r$

where $B_r = \mu_0 B/J$

$\Phi = -(B_r/T_r)x - (Z/2T_r)x^2 + \frac{1}{2}(1+x)\ln(.) + \frac{1}{2}(1-x)\ln(.)$

For $B_r = 0$

$\Phi = -(Z/2T_r)x^2 + \frac{1}{2}(1+x)\ln(.) + \frac{1}{2}(1-x)\ln(.)$

We find the "best" values for x by minimizing Φ.

$0 = d\Phi/dx = -(Z/T_r)x + \frac{1}{2}\ln\frac{1}{2}(1+x) - \frac{1}{2}\ln\frac{1}{2}(1-x)$

$= -(Z/T_r)x + \frac{1}{2}\ln[(1+x)/(1-x)]$

$x = \frac{1}{2}(T_r/Z)\ln[(1+x)/(1-x)]$

Second Approximation (second term) or 2-clusters + 1-cluster

The second approximation is the sum of the first term (first approximation) plus the 2-cluster term of Morita's expansion,

$$S^{(N)} = \tilde{S}^{(1)} + \tilde{S}^{(2)}$$

where

$$\tilde{S}^{(2)} = \Sigma(\text{all pairs})\tilde{S}^{(2)}_{i,j}$$

and $\tilde{S}^{(2)}_{i,j} = S^{(2)}_{i,j} - \tilde{S}^{(1)}_{i} - \tilde{S}^{(1)}_{j}$ is the INTRINSIC entropy for subsystems of pairs of particles $\tilde{S}^{(1)}_{i}$ and $\tilde{S}^{(1)}_{j}$, including any interactions they may have, and $S^{(2)}_{i,j} = -k_B \mathrm{tr}^{(2)}_{i,j} P^{(2)}_{i,j} \ln P^{(2)}_{i,j}$ is the entropy of $\tilde{S}^{(1)}_{i}$ and $\tilde{S}^{(1)}_{j}$ including interactions. The entropy due only to the single particles $S^{\sim(1)}$ is subtracted from the pair entropy.

$$F = U - TS$$

$$U = -(N\mu_0 B)x - (\tfrac{1}{2}NZJ)y$$

$$S = S^{\sim(1)} + S^{\sim(2)}$$

$$= -k_B N\{\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)$$

$$+ \tfrac{1}{2}Z[\tfrac{1}{4}(1+2x+y)\ln\tfrac{1}{4}(1+2x+y) + 2*\tfrac{1}{4}(1-y)\ln\tfrac{1}{4}(1-y)$$

$$+\tfrac{1}{4}(1-2x+y)\ln\tfrac{1}{4}(1-2x+y)]$$

$$-2[\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)]\}.$$

$$F = N\{-\mu_0 Bx - \tfrac{1}{2}ZJy + Tk_B[\tfrac{1}{2}(1\pm x)\ln\tfrac{1}{2}(1\pm x)$$

$$+ \tfrac{1}{2}Z\{\tfrac{1}{4}(1\pm 2x+y)\ln\tfrac{1}{4}(1\pm 2x+y) + \tfrac{1}{2}(1-y)\ln\tfrac{1}{4}(1-y)$$

$$- (1\pm x)\ln\tfrac{1}{2}(1\pm x)\}]\}.$$

$$F/Nk_B T = \Phi = -(\mu_0\beta B)x - \tfrac{1}{2}\beta JZy + \tfrac{1}{2}(1\pm x)\ln\tfrac{1}{2}(1\pm x)$$

$$+ \tfrac{1}{2}Z\{\tfrac{1}{4}(1\pm 2x+y)\ln(.) + \tfrac{1}{2}(1-y)\ln\tfrac{1}{4}(1-y)$$

$$- (1\pm x)\ln\tfrac{1}{2}(1\pm x)\}.$$

$$\Phi = -(B_r/T_r)x - \tfrac{1}{2}(Z/T_r)y + \tfrac{1}{2}(1\pm x)\ln\tfrac{1}{2}(1\pm x)$$

$$+ \tfrac{1}{2}Z\{\tfrac{1}{4}(1\pm 2x+y)\ln(.) + \tfrac{1}{2}(1-y)\ln\tfrac{1}{4}(1-y)$$

$$- (1\pm x)\ln\tfrac{1}{2}(1\pm x)\}.$$

For $B_r = 0$

$$\Phi = -\tfrac{1}{2}(Z/T_r)y + \tfrac{1}{2}(1\pm x)\ln\tfrac{1}{2}(1\pm x) + \tfrac{1}{2}Z[\tfrac{1}{4}(1\pm 2x+y)\ln(.)$$

$$+ \tfrac{1}{2}(1-y)\ln\tfrac{1}{4}(1-y) - (1\pm x)\ln\tfrac{1}{2}(1\pm x)]$$

$$0 = f_1(x,y) = d\Phi/dx \;; \quad 0 = f_2(x,y) = d\Phi/dy$$

It is helpful to recall that the first few terms of the Morita expansion are known by other names - the names of their inventors, and later reappeared as terms in the cluster expansion for the free energy. (See the names of the inventors associated with the approximations shown in figure 5, Chapter II.) This is interesting since in their original form it was sometimes difficult to see how their inventors were able to logically derive the equations for the free energy. As these results are rederived in the Morita expansion they appear as a consequence of a very orderly and logical development and the relation of the approximations to each other is now understood. The physics is clear in this new derivation as compared to the original derivations where it was sometimes obscure. The first term or first approximation, known as the 1-cluster term in the Morita expansion, is the same as the Weiss model which uses the self-consistent field or molecular field approximation for ferromagnets. The Bragg-Williams model (1934) is a more rigorous statement of the Weiss model and gives similar results, (see figure 5). The second term is the 2-cluster term and was originally known as the Bethe-Pierls approximation used to describe Cu-Zn alloys and is an improvement over the Bragg-Williams approximation. The Bethe-Pierls model (1936) takes into account specific short-range order, i.e. local correlations between spins. The second approximation is the sum of the 1-cluster and 2-cluster terms.

<u>Some items of procedural interest</u>

A. **Particle Names**

Label the N particles of a system using the N counting: 1,2,...,N. This labeling is arbitrary. The same same labeling is used unchanged throughout this work.

A "cluster" of particles is a set of particles, that is, an unordered list of particles. For example, $\{i_1,...,i_n\} = \{i_\alpha\}^n_{\alpha=1}$ is a particular cluster of n particles. This is also called an n-cluster of the particles of the system. The individual particles in that cluster are called $i_1, i_2, ... i_n$. In a system of N particles, there are the following n-clusters:

size of cluster	generic name	specific names
N	1-clusters $\{i\}$	$\{1\},\{2\},...,\{N\}$
½N(N-1)	2-clusters $\{i_1,i_2\}$	$\{1,2\}$
(1/6)N(N-1)(N-2)	3-clusters $\{i_1,i_2,i_3\}$	...
-		
-		
N(N-1)	N-cluster $\{i_1,...,i_n\}$	...

In all, there are $2^N -1$ n-clusters.

Cluster function:

A "cluster function" is a function of the microstate of the particles making up a cluster. For example, $f^{(N)}(i_1,...,i_n) = f(\mu_{i1},\mu_{i2},\mu_{i3},...,\mu_{in})$ is an n-cluster function, where μ_i is the microstate of the i^{th} particle and $\mu_{i1},\mu_{i2},...,\mu_{in}$ is the microstate of $\{i_1,...,i_n\}$.

So μ_1 is the microstate of particle i_1

μ_2 " " " " " i_2

In particular, the macrostate of an n-cluster is a cluster function.

Names:

There are N particles arranged on N sites of a lattice. Sites are located at the positions

$$r = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + \dots n_3\mathbf{b}_3$$

where

$\mathbf{b}_i$ is the i^{th} base vector of a unit cell of the lattice, and each n_i is an integer.

Sometimes it will be convenient to name a particle for the site it occupies. Then we speak of the particle n_1, n_2. However, for much of the formal discussion of this work, it will be convenient to assign the cardinal numbers {1,2,...,N} to the particles in some way, and then denote a particle by this cardinal number. So, we speak of the i^{th} particle.

$P^{(n)}_{i_1,i_2,\dots,i_n} = P^{(n)}_{i_1,i_2,\dots i_n}(\mu_{i_1},\mu_{i_2},\dots\mu_{i_n})$ is the <u>macrostate</u> of the cluster $C^{(n)}_{i_1,\dots i_n}$, i.e., $P^{(n)}_{i_1,\dots,i_n}$ is the probability of the microstate $\mu_{i_1},\dots,\mu_{i_n}$.

A "<u>cluster quantity</u>" is the average of a cluster function; it depends on the macrostate of the cluster.

A "<u>cluster variable</u>" is either a "<u>cluster function</u>", or a "<u>cluster quantity</u>". Cluster variables can be "extrinsic" or "intrinsic". We suppose we can obtain, perhaps by a direct measurement, the value of a cluster variable for any isolated cluster: these are extrinsic. We then define the intrinsic cluster variables:

$$f^{(1)}_{i} = \hat{f}^{(1)}_{i}$$

$$f^{(2)}_{ij} = (\hat{f}^{(1)}_{i} + \hat{f}^{(1)}_{j}) + \hat{f}^{(2)}_{ij}$$

$$f^{(3)}_{ijk} = (\hat{f}^{(1)}_{i} + \hat{f}^{(1)}_{j} + \hat{f}^{(1)}_{k}) + (\hat{f}^{(2)}_{ij} + \hat{f}^{(2)}_{ik} + \hat{f}^{(2)}_{jk}) + (\hat{f}^{(3)}_{ijk})$$

$-$

$-$

$-$

$$f^{(n)}_{i1,i2,...in} = (\Sigma_{j=1}^{n} \hat{f}^{(1)}_{ij}) + (\Sigma_{jk} \hat{f}^{(2)}_{ijik})$$

$-$

$-$

$-$

These can be inverted to define any particular intrinsic cluster variable entirely in terms of extrinsic cluster variables only.

$$\hat{f}^{(1)}_{i} = f^{(1)}_{i}$$

$$\hat{f}^{(2)}_{ij} = f^{(2)}_{ij} - (f^{(1)}_{i} + f^{(1)}_{j})$$

$$\hat{f}^{(3)}_{ijk} = f^{(3)}_{ijk} - (f^{(2)}_{ij} + f^{(2)}_{ik} + f^{(2)}_{jk}) + (f^{(1)}_{i} + f^{(1)}_{j} + f^{(1)}_{k})$$

$-$

$-$

$-$

$$\hat{f}^{(n)}_{i1,i2,\ldots in} = f^{(n)}_{i1,i2,\ldots in} - (\Sigma f^{(n-1)}_{i\ldots i}) + (\Sigma f^{(n-2)}_{i\ldots i}) - \ldots \quad .$$

Examples:

$H = \Sigma \hat{h}^{(1)}_{i} + \Sigma \hat{h}^{(2)}_{ij} + \ldots \Sigma h^{(N)}_{12\ldots N}$

The Hamiltonian H is an extrinsic, N-cluster function.

It is expanded into intrinsic n-cluster functions.

$U = \Sigma \langle \hat{h}^{(1)}_{i} \rangle + \Sigma \langle \hat{h}^{(2)}_{ij} \rangle + \ldots$

The internal energy U is an extrinsic N-cluster quantity.

It is expanded into intrinsic n-cluster quantities.

$S = -k_B \Sigma_{\mu_1} \Sigma_{\mu_2} \ldots \Sigma_{\mu_N} P^{(N)} \ln P^{(N)}$

$= \hat{S}^{(1)} + \hat{S}^{(2)} + \ldots + \hat{S}^{(N)}$

where

$\hat{S}^{(1)} = \Sigma_i \hat{S}_i^{(1)}$

$\hat{S}^{(2)} = \Sigma_{ij} \hat{S}^{(2)}_{ij}$

$\hat{S}^{(3)} = \Sigma_{ijk} \hat{S}^{(3)}_{ijk}$

$-$

$-$

The entropy S is an extrinsic N-cluster quantity. It is expanded into

$S^{(1)}_{i} = \hat{S}^{(1)} = -k_B \Sigma (\mu_i) P^{(1)}_{i} \ln P^{(1)}_{i}$

$S^{(2)}_{ij} = S^{(1)}_{i} + S^{(1)}_{j} + \hat{S}^{(2)}_{ij}$

$= -k_B \Sigma_{\mu_i} \Sigma_{\mu_2} P^{(2)}_{ij} \ln P^{(2)}_{ij}$

etc.

B. Summing over clusters, and the effects of symmetries

An n-cluster is defined by the n particles it contains: the order of these particles is of no consequence to the definition of the n-cluster, [So {1,2} is the same as {2,1}, and $\{i\alpha\}(\alpha=1\text{-->}n)$, is the same cluster as $\{Pi\alpha)\}(\alpha=1\text{-->}n)$, where P is any one of the n! permutations of the n numbers 1,2,...,n.] So, while there are n! distinct lists, i.e. arrangements, of the n numbers 1,2,...,n, all these lists name the same cluster: {1,2,...,n}, $\{i\alpha\}\alpha$.

Sums of 1-cluster quantities:

$$\Sigma V(i) \quad \Sigma(\text{all 1-clusters})\, Q^{(1)}{}_{i}$$

$$= \Sigma_{i=1}{}^{N} Q^{(1)}{}_{i}$$

$$= Q^{(1)}{}_{1} + Q^{(1)}{}_{2} + \ldots + Q^{(1)}{}_{3}$$

$$\Sigma V_{ij} \quad \Sigma_{\text{all 2-clusters}}\, Q^{(2)}{}_{ij}$$

$$= \tfrac{1}{2}\Sigma_{i=1}{}^{N}\Sigma_{j=1}{}^{N} Q^{(2)}{}_{ij}$$

$$(i =/\ j)$$

$$= \tfrac{1}{2}(Q^{(2)}{}_{12} + \ldots + Q^{(2)}{}_{1N}$$

$$Q^{(2)}{}_{21} + \ldots + Q_{N1}$$

-

-

-

$$Q^{(2)}{}_{N1} + Q^{(2)}{}_{N2} + \ldots\ )$$

$$= \Sigma_{i=1}{}^{N-1}\Sigma_{j=i+1}{}^{N} Q^{(2)}{}_{ij}$$

$$= Q^{(2)}{}_{12} + Q^{(2)}{}_{13} + \ldots + Q^{(2)}{}_{1N}$$

$$+ \ldots + Q^{N(2)}{}_{N-1}$$

[Note that $Q^{(2)}{}_{ij} = Q^{(2)}{}_{ji}$]

$$\Sigma V_{ijk}$$

$$\Sigma_{\text{all 3-clusters}}\, Q^{(3)}{}_{ijk}$$

$=(1/3!)\Sigma_i\Sigma_j\Sigma_k Q^{(3)}_{ijk}$

$(i{=}/j{=}/k)$

$=\Sigma_{i=1}^{N-2}\Sigma_{j=i+1}^{N-1}\Sigma_{k=j+1}^{N} Q^{(3)}_{ijk}$

[Note that $Q^{(3)}_{ijk} = Q^{(3)}_{ikj} = Q^{(3)}_{jik} = Q^{(3)}_{jki}$
$= Q^{(3)}_{kij} = Q^{(3)}_{kji}$]

$-$

$-$

$-$

$\Sigma_{\text{all n-clusters}} Q^{(n)}_{i1,i2...in}$

$=(1/n!)\Sigma_{i1=1}^{N}\Sigma_{i2=1}^{N}\ldots$
$\Sigma_{in=1}^{N} Q^{(n)}_{i1i2...in}$

$(i\alpha$ /= $i\beta$ for any $\alpha,\beta = 1,N$ except when $\alpha = \beta$

$=\Sigma_{i1=1}^{N-n}\Sigma_{i2=i1+1}^{N-n+1}\ldots$
$\Sigma_{in=in-1+1}^{N} Q^{(n)}_{i1i2...in}$

$-$

$-$

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For <u>similar particles on a regular lattice</u>, we can drastically simplify the above sums. We use the "n-coordination numbers", defined as follows:

$Z^{(2)}_{p}$ = pair coordination number for spacing p
= number of 2-clusters whose spacing is p,

$Z^{(3)}_{pqr}$ = tri-coordination number for spacings p,q,r
= number of 3-clusters whose sides have lengths p,q,r, with $p \leq q \leq r$.

$Z^{(4)}_{pqrs}$ = quad-coordination number...

etc.

$\Sigma_{\text{all 1-clusters}} Q^{(1)}_{i} = N*Q^{(1)}_{\alpha}$

for α = any one of $\{1,2,\ldots,N\}$.

$\Sigma_{\text{all 2-clusters}} Q^{(2)}_{ij} = \frac{1}{2} N \Sigma_{p} Z^{(2)}_{p} Q^{(2)}_{\alpha,\beta}$,

for α,β,=any of $\{1,2,\ldots N\}$ such that

$|\vec{r}_{\alpha} - \vec{r}_{\beta}| \rightarrow p$

$\Sigma_{\text{all 3-clusters}} Q^{(3)}_{ijk} = (1/3!) N \Sigma_{p} \Sigma_{q} \Sigma_{r} Z^{(3)}_{pqr} Q^{(3)}_{\alpha,\beta,\gamma}$

for any α,β,γ or any permutation of these.

etc.

C. Microstates and Macrostates

The microstate of the ith particle is μ_i; its values fall in some discrete or continuous set. For the Lenz-Ising model, the values are +1 and -1. The microstate of an n-cluster is the set of the microstates of each particle contained in it:

$$\mu^{(n)}_{i1,\ldots in} = \{\mu_{i1}, \mu_{i2}, \ldots \mu_{in}\}$$

In particular, the microstate of the N-particle system is the set of the microstates of each particle:

$$\mu^{(n)} = \{\mu_1, \mu_2, \ldots, \mu_n\} .$$

The macrostate of the N-particle system is a probability law defined on the set of possible microstates $\mu^{(N)}$:

$$P^{(N)}(\mu^{(N)}) = \text{probability of } \mu^{(N)}$$

The task of equilibrium statistical mechanics is to determine this macrostate.

From the macrostate of the system, $P^{(N)}$, we can extract the macrostate of any subsystem:

$$P^{(n)}(\mu_{i1},\ldots,\mu_{in})$$

$$= \Sigma\mu_i\ldots\Sigma\mu_N P^{(N)}(\mu_1,\mu_2,\ldots,\mu_N)$$

(except $\mu_1,\mu_2,\ldots\mu_{in}$)

(1) From this, it follows that the macrostate of any n-cluster determines the macrostate of all the n'-clusters (n'< n) contained within it.

(2) We note that all macrostates are normalized:

$$\Sigma\mu_{i1}\ldots\Sigma\mu_{in}P^{(n)}_{i1,\ldots,in} = 1$$

(for all n and all $\{i\alpha\}[\alpha=1 \to n]$) .

D. A note on summing over n-clusters

We often sum over all the various n-clusters, for a given value of n. We also often sum over all the various microstates of a given n-cluster (e.g., when computing a thermal average). It is convenient to represent these very different sorts of sums with very different sorts of notations. So, henceforth we will use

$$\Sigma_{i1}\Sigma_{i2}\ldots\Sigma_{in}[.] = \Sigma_{\text{all n-cluster}}[.]$$

$(i\alpha \neq i\beta\ \forall\alpha,\beta$ xxx $\alpha=\beta)$

$$\Sigma\mu_{i1}\Sigma\mu_{i2}\ldots\Sigma\mu_{in}[..] = \mathrm{tr}^{(n)}_{i1,i2\ldots in}[.]$$

respectively, for the two different sorts of sums.

E. Representation of macrostates

It is a well-known result that a probability law is equivalent with the set of all of its moments.

A common (sketch of a) proof is:

(1) $P(x)$ = probability law for a random variable x.

(2) $R(k) = ∩-\infty\infty P(x)\exp(ikx)dx$
is the Fourier transform of $P(x)$.
[∩ represents an integral sign]

(3) $R(k) = R(0) + R'(0)k + R''(0)k^2/2 + \ldots$
is the Taylor's series of $R(k)$.

(4) By inspection of (2) :

$R(0) = ∩-\infty\infty P(x)dx =1$
by normalization of $P(x)$.

$R'(0) = i∩-\infty\infty xP(x)dx = x^-$ is
the 1st moment of x.

Note: x^- represents x with a "bar" superscript.

$R''(0) = (i^2)∩-\infty\infty x^2P(x)dx$
$= (x^2)^-$
is the 2nd moment of x.

$-$

$-$

$-$

(5) Hence, $R(k) = 1 + ikx^- + \frac{1}{2}(i^2)k^2x^{2-} + \ldots$

(6) Hence, if we are given $P(x)$, then we can calculate all the moments, either directly,

$(x^n)^- = ∩-\infty\infty x^nP(x)dx$,

or indirectly,

$(x^n)^- = (d^nR/dk^n)_{k=0}$.

If we are given all the moments, then we can construct

$$R(k) = 1 + ikx^{-} + (i^2)k^2(x^2)^{-} + \ldots ,$$

and inverse-Fourier transform it to get $P(x)$:

$$P(x) = \frac{1}{2}\pi\int_{-\infty}^{\infty} \exp(-ikx)R(k)dk \quad .$$

QED.

This rule extends to the case of a set of (possible) correlated random variables :

$P(x)$ is equivalent with $\prod_{\alpha=1}^{n} x_{i\alpha}$ for all n.

When the microstate of each particle is bi-valued, $\mu_i = \pm 1$, then the macrostate of the particle is

$$P^{(1)}_i(\mu_i) = P^{(1)}_i \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1+x^{(1)}_i \\ 1-x^{(1)}_i \end{pmatrix}$$

where

$$x^{(1)}_i = \langle\mu_i\rangle = tr^{(1)}_i[P^{(1)}_i(\mu_i)\mu_i] \quad .$$

clearly, $P^{(1)}_i(\mu_i)$ is equivalent with $\langle\mu_2\rangle$ each determines the other.

The macrostate of larger clusters can also be expressed in terms of moments:

$$P^{(2)}_{ij}(\mu_i\mu_j) = \frac{1}{4}\begin{bmatrix} 1 + x^{(1)}_i - x^{(1)}_j + x^{(2)}_{ij} \\ 1 + x^{(1)}_i - x^{(1)}_j + x^{(2)}_{ij} \\ 1 - x^{(1)}_i + x^{(1)}_j - x^{(2)}_{ij} \\ 1 - x^{(1)}_i - x^{(1)}_j + x^{(2)}_{ij} \end{bmatrix}$$

where

$$x^{(2)}_{ij} = \langle\mu_i\mu_j\rangle = tr^{(2)}_{ij}[P^{(2)}_{ij}(\mu_i,\mu_j)\mu_i\mu_j]$$

$$P^{(3)}_{ijk}(\mu_i\mu_j\mu_k) = P^{(3)}_{ijk}\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \\ 1 & -1 & 1 \\ 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & -1 \\ -1 & -1 & 1 \\ -1 & -1 & -1 \end{bmatrix}$$

$$=1/8 \begin{bmatrix} 1+x^{(1)}_{i} & +x^{(1)}_{j} & +x^{(1)}_{k} & +x^{(2)}_{ij} & +x^{(2)}_{ik} & +x^{(2)}_{jk} & +x^{(3)}_{ijk} \\ 1+ & + & - & + & - & - & - \\ 1+ & - & + & - & + & - & - \\ 1+ & - & - & - & - & + & + \\ 1- & + & + & - & - & + & - \\ 1- & + & - & - & + & - & + \\ 1- & - & + & + & - & - & + \\ 1- & - & - & + & + & + & - \end{bmatrix}$$

where

$$\begin{aligned} x^{(3)}_{ijk} &= \langle \mu_i \mu_j \mu_k \rangle \\ &= tr^{(3)}_{ijk}[P^{(3)}_{ijk}(\mu_i \mu_j \mu_k)\mu_i \mu_j \mu_k] \end{aligned}$$

And so on.

CHAPTER II

SHORT HISTORY OF THE LENZ-ISING MODEL

The following remarks are intended to provide some additional background information for the Lenz-Ising model with particular reference to ferromagnetic systems.

We focus attention on the Lenz-Ising model as a mathematical object existing independently of any particular physical system. The Hamiltonian used in the Lenz-Ising model is a definition of this model. The Hamiltonian we are using is for nearest neighbor (n.n.) interaction only between the particles in the system. This system for interacting particles, is the simplest one that it is possible to study. It is not an exact description of any specific physical system such as a ferromagnet, an alloy or a liquid. The results can be expected to give the general shape of the magnetization curve and the value of the critical temperature but not the details for any particular physical system. This however is only a limitation of the Hamiltonian that is used and the mathematics necessary to study it. Results that more accurately describe a specific physical system can be obtained by using a Hamiltonian that is an improved representation of that system.

History

To explain the experimental results obtained by Stern and Gerlach in 1922 it was proposed by Uhlenbeck and Goudsmit in 1925 that the electron possesses a spin S=1/2 and that it is oriented either parallel or anti-parallel to the field[10]. Ising published in the same year the results for a model based on a suggestion of his thesis advisor Wilhelm Lenz, that if electrons were located on a lattice and if an interaction were introduced between nearest neighbor spins that favored parallel alignment of spins, then at sufficiently low temperatures the spins would all be parallel, and the model might provide an atomic description of ferromagnetism[11,12]. The Hamiltonian corresponding to this model, and which expresses the internal energy of the system can be written in the form,

$$H = -\mu_0 B \Sigma \mu_i - J\Sigma_{ij}(\text{sum over all n.n. pairs})\mu_i \mu_j$$

where the interaction integral (J > 0) represents the interaction between spins, B is the magnetic field, μ_0 the magnetic moment of a single spin, and μ_i or $\mu_j = \pm 1$ is the spin state of the ith electron on the lattice. The suffix i runs over all sites of the lattice, and <i,j> over all pairs of sites i and j which are nearest neighbors.

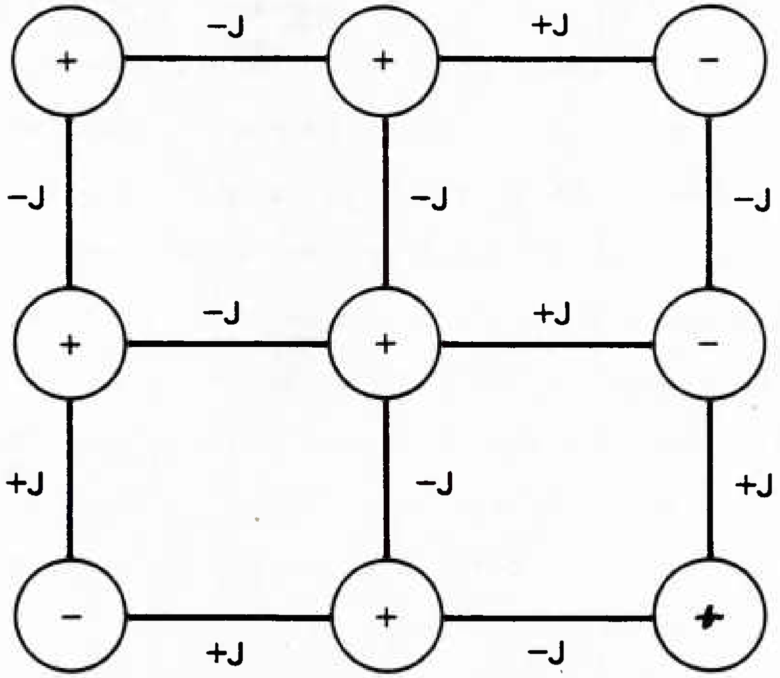
Ising studied this model in one dimension; his exact results showed that spontaneous magnetization did not occur at any temperature. This result is correct. He extended the one dimensional results to higher dimensions, incorrectly, and did not find any phase change in two or three dimensions. This result is incorrect. Subsequent calculations by others has shown that there is not a phase transition in one dimension as correctly shown by Ising, but for two or more dimensions, spontaneous magnetization does occur below a critical temperature. It was unfortunate that Ising's results in two and three dimensions were incorrect since it caused the model to be discarded for many years. The model was later rediscovered and solved exactly, in zero magnetic field, for two dimensions by Onsager in 1944[13,14].

Lenz - Ising Model

Further work has shown that by a change of names the Lenz-Ising model can be made to simulate various systems [15,16]. Examples of such systems are (1) magnets, in which each molecule has a "spin" that can be oriented up or down relative to the direction of an external applied field; (2) binary alloys such as Cu-Sn; (3) liquids which can be represented by molecules and "holes" (i.e. empty spaces) on a lattice (this is called a "lattice fluid") and there are more examples. These physical systems can all be represented abstractly by the same model which can be described in the following way. We assign a two-valued variable (+1 or -1) to each node of a regular space lattice to represent the spin μ_i, associated with each node i of the lattice. For a magnet μ corresponds to an electron spin state. For an alloy μ corresponds to an ion type (say Cu vs. Sn). For a "lattice fluid" μ corresponds to the presence or absence of an atom. A configuration of the lattice is a particular set of values of all the spins, and for N nodes there are 2^N different configurations. An example of a configuration is shown in Fig.2.

In this model it is assumed that the forces between molecules are only short range i.e., only nearest neighbor (n.n.). When neighboring spins are the same (both +1 or both -1) the energy is -J and when they are different (one is +1, the other is -1) the energy is +J[12].

The interaction tends to align the n.n. spins as parallel and to give aligned spins the lower energy state. Heisenberg in 1926 was the first one to describe the reason for this interaction between spins. It is an electrostatic interaction, a Coulombic type force that causes the spins to align. And so the spin couplings which manifest themselves as magnetic effects are in fact due to electrical forces which cause the spins to be parallel and antiparallel. The symmetric or anti-symmetric wave functions that the electron spins are part of must of course satisfy the rules of quantum mechanics. For the three physical systems described above, this interaction could result in (1) spontaneous magnetization, with most spins in the same direction, even with $B = 0$; (2) transition between an ordered superlattice and a lattice with random arrangement of atoms on the lattice points; (3) condensation of molecules in one region



THE ENERGY OF THE CONFIGURATION IS,

$$H = -\mu_B B \sum_i \mu_i - J \sum_{i,j} \mu_j \mu_i$$
(n.n. PAIRS)

$$H = -\mu_B B (+6-3) + (-7J + 5J)$$

$$H = -3\mu_B B - 2J$$

Fig. 2. A POSSIBLE CONFIGURATION OF A FINITE SQUARE LATTICE.

of space (clustering), leaving empty space in the rest of the container[11].

For ferromagnetism the total internal energy is the sum of the interaction energy and a magnetic energy term $-\mu_0 B \mu_i$ for each lattice point. For magnetic systems, μ_0 is a characteristic value of a magnetic moment (such as the Bohr magneton) and B is an external magnetic field (see figure 2). For other physical systems this term $-\mu_0 B \mu_i$ may be any parameter which plays the role of a "chemical potential" in determining the average number of up and down spins, or average composition of a mixture, or average density of a molecule-hole system.

For ferromagnetic materials we calculate the mean value of electron magnetic moment as[10],

$$M = N\mu_0 \tanh \Omega$$

where N = number of atoms per unit volume, μ_0 is the magnetic moment per atom, and Ω represents $\mu B_a / k_B T$ where B_a is the mean field acting on the atom, and $k_B T$ is the Boltzmann energy and μ is the magnetic moment per electron equal to q/2m times its g-factor, times its angular momentum $\vec{J}$. To calculate the internal energy of the material, we note that the energy of an electron is exactly proportional to the magnetic moment. We replace μ_0 with $-\mu_0 B$ to calculate energy and B can be written as $(H + \tau M/\epsilon_0 c^2)$ where H is the magnetizing field and τ has been called the "exchange" force and is due to the exclusion principle in quantum mechanics. (Note: we are using τ for the "exchange" force in this discussion to avoid confusion with $\vec{J}$ the angular momentum. In the rest of this work J will represent the "exchange" force). Theoretical predictions for the value of τ are failures. The most recent calculations of the energy between the two electron spins in iron-assuming that the interaction is a direct one between the two electrons in neighboring atoms-not only do not give the correct value but even give the wrong sign. With these substitutions the mean energy of the material can be written as,

$$\langle U\rangle = N\mu_0[H+\tau M/2\epsilon_0 c^2]\tanh\Omega$$

The "2" is inserted to correct for overcounting. The term $\tau M/\epsilon_0 c^2$ represents interactions of all possible pairs of atoms, and we must count each pair only once. With H = 0 we can rewrite this equation as,

$$M/M_{sat} = \tanh[(T_c/T)(M/M_{sat})]$$

where $M_{sat} = N\mu$ and $T_c = \mu\tau M_{sat}/k\epsilon_0 c^2$.

The solution to this equation is shown in Fig.3. For the energy of the spontaneous magnetization below the Curie point, we can set H=0, and note that $\tanh\Omega = M/M_{sat}$. The mean energy is proportional to M^2, and can be written as

$$\langle U\rangle_{av} = -N\mu\tau M^2/[2\epsilon_0 c^2 M_{sat}].$$

If we plot the energy due to the magnetism as a function of temperature, we get a curve which is the negative of the square of curve of Fig.3, and is drawn in Fig.4a. If we were

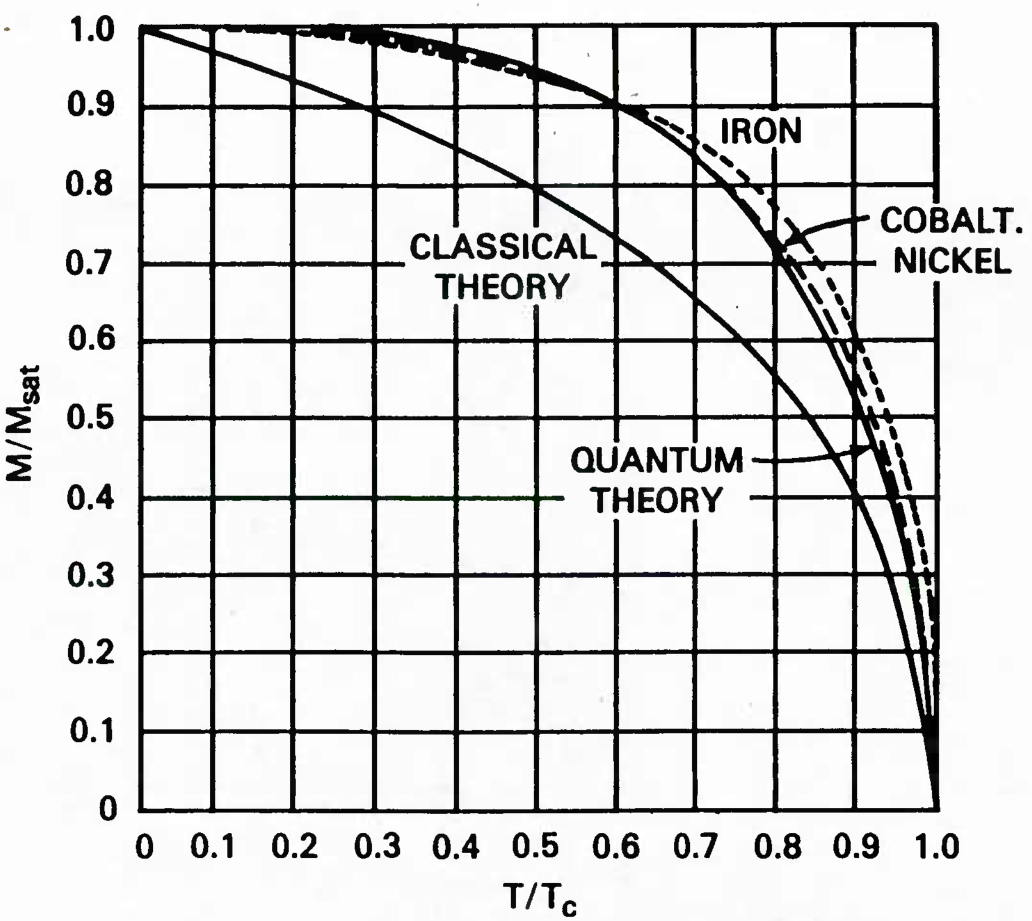


Fig. 3. THE SPONTANEOUS MAGNETIZATION (B=0) OF FERROMAGNETIC CRYSTALS AS A FUNCTION OF TEMPERATURE R. FEYNMAN, <u>THE FEYNMAN LECTURES ON PHYSICS</u>, <u>2</u>, 34-4, (1964)

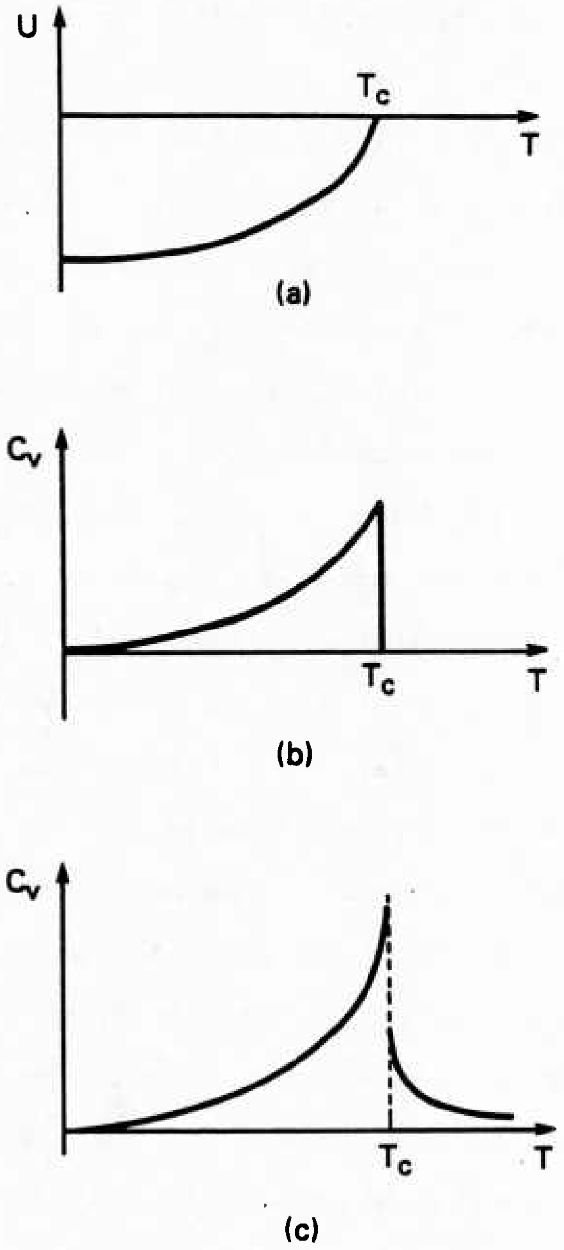


Fig. 4. THE ENERGY PER UNIT VOLUME AND SPECIFIC HEAT OF A FERROMAGNETIC CRYSTAL. SOURCE: SEE Figure 3, Page 34

to measure the specific heat of such a material we would obtain a curve which is the derivative of Fig.4a, and is shown in Fig.4b. The true situation is more complicated and both experiment and improved theory suggest the curve should be more like that shown in Fig.4c. The curve goes higher at the peak and falls to zero somewhat slowly.

In Fig.5 several specific heat curves are summarized for a two dimensional Lenz-Ising model calculated with various methods of approximation [17]. Onsager's exact solution for B = 0 is shown for comparison[13]. Approximate methods [18,19] have attempted to reproduce the singularity in the specific heat and other thermodynamic functions at the transition point. Methods such as using Pade's approximants [11] to extrapolate series expansions of the partition functions and thermodynamic properties have been used in the past twenty years. The more recent renormalization group work has given the most accurate results at the critical point [20].We are using a different approach to understanding the behavior of the model over a range of temperatures and magnetic fields: we are expressing the free energy of the Lenz-Ising model using the Morita cluster expansion and then minimizing the free energy expansion to obtain the equilibrium macrostate P_0 and then studying the resulting approximation to the thermal behavior.

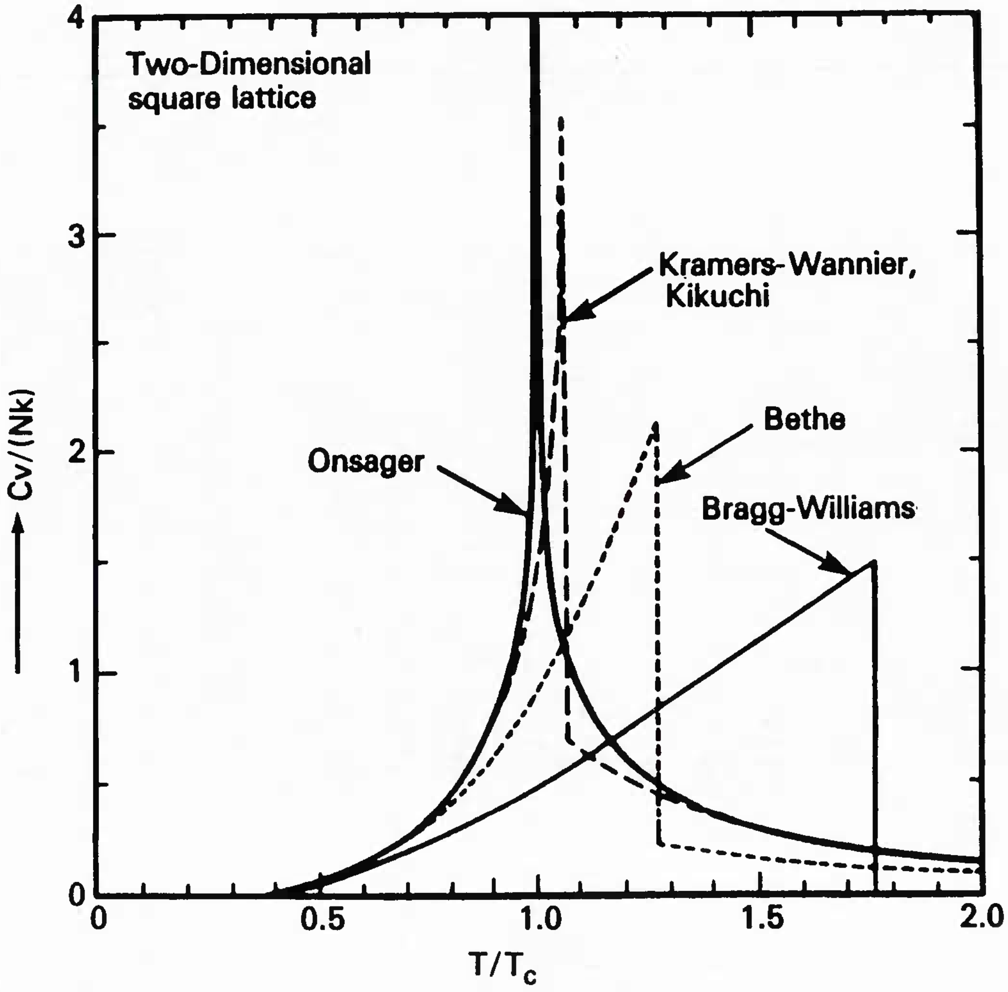


Fig. 5. SEVERAL SPECIFIC HEAT CURVES FOR A TWO DIMENSIONAL (SQUARE) ISING SPIN LATTICE CALCULATED WITH VARIOUS METHODS OF APPROXIMATION. THE EXACT TREATMENT FOR B=0 IS ALSO SHOWN. R. KUBO, STATISTICAL MECHANICS, 321, (1965)

Diagramatically this method can be outlined as shown in Fig.6. The last step shown in Fig.6, to "study F_0", means to study these behaviors:[21,22]

"Study F_0"

$U = F - TS = F + T(\delta F/\delta T)_B$ i.e. U can be obtained from F and its derivatives.

$-M = (\delta F/\delta B)_T$ $\qquad C_B = (\delta S/\delta T)_B$

$-S = (\delta F/\delta T)_B$ $\qquad x = (\delta M/\delta B)_T$

---

where M is the magnetization

S is the entropy

F is the Helmholtz free energy

T is the temperature

B is the external magnetic field

U is the internal energy

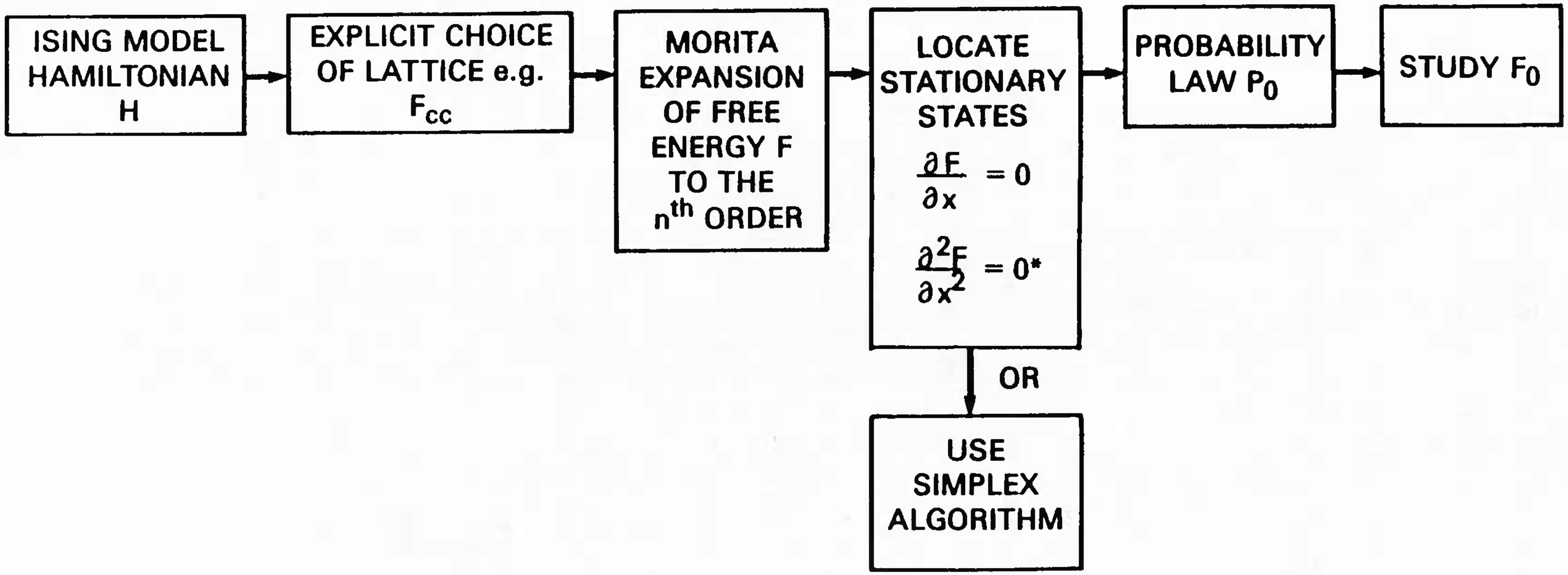
C_B is the specific heat at constant magnetic field

x is the magnetization/particle

In this work we also use Φ, the free energy in reduced units:

$$\Phi = F/NJ,$$

where N is the number of particles in the system and J is the interaction energy.



*TO SHOW THAT $\frac{\partial F}{\partial x} = 0$ IS A STABLE POINT.

Fig. 6. DIAGRAMATIC OUTLINE OF METHOD USED IN THE MORITA CLUSTER EXPANSION OF THE FREE ENERGY.

CHAPTER III

EXACT SOLUTION OF THE LENZ-ISING MODEL FOR SMALL SYSTEMS

Exact Solution for A System of One Particle

The Cluster Expansion Method used in this work involves approximating the behavior of systems of many particles as a concatination of simpler systems: systems of one particle, systems of two particles, and so on. In order to introduce the notations and methods used here in a simple and exact context, we begin by studying small systems. Because these small systems can be studied exactly, their behavior serves as a measure of the consequences of the approximations used in the Cluster Expansion Method.

The equilibrium behavior of the Lenz-Ising system of N particles for fixed temperature T and magnetic field B is given by Gibbs' canonical prescription:

$Z(T,B,N) = \Sigma_{\mu} \exp(-\beta H(\mu))$
is the canonical partition function,

$F(T,B,N) = -k_B T \ln Z$
is the equilibrium free energy,

$P^{(N)}(\mu;T,B) = \exp(-\beta H(\mu))/Z$,
is the equlibrium macrostate

which follows exactly from minimization of $F(P^N)$ versis $P^{(N)}$. Since there are 2^N distinct microstates, Z(T,B,N) has

2^N terms, before any combining of similar terms is effected; hence, Z can be explicitly calculated for small enough values of N. When N = 10, $2^N = 1024$; direct computation of Z is feasible, particularly if a computer is used. When N = 20, $2^N \approx 10^6$; direct computation of Z is just within the bounds of feasibility with current large computers. When N = 30, $2^N \approx 10^9$; direct computation of Z is currently infeasible.

In order to introduce the notations and methods used we shall discuss the cases N = 1,2,3,and 4.

Microstate:

The microstate for this one particle system is a two-column

$$\mu = \begin{pmatrix} +1 \\ -1 \end{pmatrix} ;$$

at any instant, the system is either spin-up ($\mu = +1$) or spin-down ($\mu = -1$).

Energy:

The energy H is $H = H(\mu) = -\mu_0 B \mu$

where,

μ is the microstate,

μ_0 is the magnetic moment of the particle,

and B is the magnetic field,

The exchange term $-J\mu_i\mu_j$ does not exist here, since there can be no pair interaction when there is one particle. The system is an ideal paramagnet which is a trivial case to study.

Macrostate:

The macrostate is the probability law for the microstate,

$$P = P^{(1)}(\mu) = P^{(1)}\begin{pmatrix}+1\\-1\end{pmatrix} = \begin{pmatrix}a\\b\end{pmatrix},$$

where "a" is the probability that the system is spin-up,and "b" is the probability that the system is spin-down. Since "a" and "b" are probabilities,

$a \geq 0$ constraint 1
and $b \geq 0$

and
$a + b = 1$ constraint 2.

It is more convenient to express $P(\mu)$ in terms of a single number controlled by a single constant, mainly the average magnetization

$$x = \langle\mu\rangle = a - b\ ,$$
$$-1 \leq x \leq 1\ ,$$

with

$$a = (1 + x)/2$$
$$b = (1 - x)/2\ ;$$

$$P = \tfrac{1}{2}\begin{pmatrix}1 + x\\1 - x\end{pmatrix} \text{ with } -1 \leq x \leq 1\ .$$

Internal Energy:

The internal energy of this spin is

$$U = \langle H\rangle = \Sigma^{1}_{\mu=-1}[H(\mu=+1)P^{(1)}(\mu=+1)+H(\mu=-1)P^{(1)}(\mu=-1)]$$
$$= H(\mu=+1)P^{(1)}(\mu=1) + H(\mu=-1)P^{(1)}(\mu=-1)$$
$$= (-\mu_0 B)a + (\mu_0 B)b$$
$$= (-\mu_0 B)[\tfrac{1}{2}(1+x)] + (\mu_0 B)[\tfrac{1}{2}(1-x)]$$
$$= (\mu_0 B)[(-\tfrac{1}{2})(1+x) + \tfrac{1}{2}(1-x)]$$
$$= -(\mu_0 B)x\ .$$

Entropy:

The entropy of this spin is

$$-S/k_B = \langle \ln P\rangle = \Sigma^{1}_{\mu=-1}P^{(1)}(\mu)\ln P^{(1)}(\mu)$$

$$= P^{(1)}(-1)\ln P^{(1)}(-1) + P^{(1)}(1)\ln P^{(1)}(1)$$

$$= a*\ln(a) + b*\ln(b)$$

$$= \tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x) \ .$$

Free Energy:

The same term "free energy" is used for two distinct properties: On the one hand, it is used for the function

$$F(P) = U(P) - TS(P),$$

where P is any macrostate at all, not necessarily one corresponding to any kind of equilibrium. On the other hand, it is used for the function

$$F(T,B) = F(P_{eq}(T,B))$$

where $P_{eq} = P_{eq}(T,B)$ is the unique macrostate describing the system in equilibruim at a temperature T and in a magnetic field B. The context of use will always make clear which function is meant.

The free energy for any macrostate P(x) is

$$F(x) = U(x) - TS(x)$$

$$= -\mu_0 Bx + k_B T[\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)] \ .$$

We now vary x to locate the value that makes F a minimum:

$$0 = (\delta F/\delta x)$$

$$= -\mu_0 B + k_B T[\tfrac{1}{2}\ln\tfrac{1}{2}(1+x) - \tfrac{1}{2}\ln\tfrac{1}{2}(1-x)] \ .$$

The solution of this equation is

$$x_{min} = \tanh(\mu_0 B/k_B T) = \tanh(\beta\mu_0 B),$$

where $\beta = 1/k_B T$

The minimum value of F is

$$\begin{aligned} F_{min} = F(x_{min}) = -\mu_0 B\tanh[\beta\mu_0 B] &+ k_B T\{\tfrac{1}{2}[1+\tanh(\beta\mu_0 B)]\ln\tfrac{1}{2}[1+\tanh(\beta\mu_0 B)] \\ &+ \tfrac{1}{2}[1-\tanh(\beta\mu_0 B)]\ln\tfrac{1}{2}[1-\tanh(\beta\mu_0 B)]\} \ . \end{aligned}$$

Examination of $(\delta^2 F/\delta x^2)$ shows that this is actually a minimum of the free energy, and consequently x_{min} and F_{min} are the equilibrium values:

$$\begin{aligned} F &= F_{min} \\ x &= x_{min} . \end{aligned}$$

Other Quantities:

With the equilibrium value of the free energy F known, we can find the equilibrium value of other properties:

$$S = -(\delta F/\delta T) = -k_B[\tfrac{1}{2}(1\pm x)\ln\tfrac{1}{2}(1\pm x)] \ .$$

$$U = F + TS = \langle H\rangle = -\mu_0 Bx \ .$$

Specific Heat: $C_B = T(\delta S/\delta T) = \delta U/\delta T$.

Magnetization: $M = \delta F/\delta B = Nx\mu_0 = N\mu_0 \tanh(\mu_0 B/k_B T)$.

Suspectibility: $\text{chi} = (\delta M/\delta B)_T$.

$$= [N\mu_B^2/k_B T]\text{sech}^2(\mu_B B/k_B T) \ .$$

For $\mu_B B << k_B T$,

$$\text{chi} = C_P/T$$

where $C_P = N\mu_B^2/k_B$

is the Curie constant.

A System of Two Particles

We derive exactly the equilibrium free energy F and the equilibrium macrostate $P^{(2)}$ for the Lenz-Ising model with two particles as a function of the external magnetic field B and the temperature T. These exact results will be obtained using the approach of the cluster expansion method in order to illustrate this method in a simple case; the method of Gibbs ensemble is also used. Comparison will be made between these exact results and an approximate solution which estimates the probability distribution as the product of single particle probability functions.

Cluster Expansion

We first derive the exact results using the free energy minimization method. The free energy for an arbitrary macrostate $P^{(2)}$ is given by

$$F(P^{(2)}) = U(P^{(2)}) - TS(P^{(2)})$$

where U is the internal energy,

and S is the entropy.

For a specified temperature T and magnetic field B, a unique macrostate $P^{(2)}_{min}$ minimizes this free energy F; this macrostate is the equilibrium state for the specified T and B, and $F_{min} = F(P^{(2)}_{min}) = F(T,B)$ contains all the system's equilibrium behaviors.

Microstate:

The microstate of the system is $\mu = (\mu_1, \mu_2)$ where μ_i is the microstate of the i^{th} particle.

Energy:

The hamiltonian H is

$$H = \mu_0 B(\mu_1 + \mu_2) - J\mu_1\mu_2 ,$$

where

B is the external magnetic field
μ_0 is the magnetic moment of each particle
and J is the exchange integral .

Macrostate:

The macrostate of the system is $P^{(2)}$

$$P^{(2)}(\mu) = P^{(2)}\begin{bmatrix} 1 & 1 \\ 1 & -1 \\ -1 & 1 \\ -1 & -1 \end{bmatrix} = \tfrac{1}{4}\begin{bmatrix} 1+x_1+x_2+y \\ 1+x_1-x_2-y \\ 1-x_1+x_2-y \\ 1-x_1-x_2+y \end{bmatrix}$$

where $x_i = \langle\mu_i\rangle$ for $i = 1,2$
and $y = \langle\mu_1\mu_2\rangle$.

Note that $-1 \leq x_i \leq +1$ and that $-1 \leq y \leq +1$.

This system is now assumed to be unchanged under exchange of its particles.

Because the magnetic field B is uniform in space, so that it acts equally on each particle, and because all particles have the same properties, then all equilibrium properties must be unchanged under exchange of x_1 and x_2. Hence, the equlibrium macrostate can depend only on a common value

$$x = x_1 = x_2 :$$

$$P^{(2)} = \tfrac{1}{4}\begin{bmatrix} 1+2x+y \\ 1 \quad -y \\ 1 \quad -y \\ 1-2x+y \end{bmatrix}$$

and this simpler expression will be used below.

Internal Energy:

The internal energy U is

$$U = \langle H\rangle = -(\mu_0 B)(\mu_1 + \mu_2) - J\mu_1\mu_2$$

$$= -2\mu_0 Bx - Jy.$$

Entropy:

The entropy S is

$$S = -k_B\Sigma_{\text{all states}} P^{(2)}(\mu)\ln P^{(2)}(\mu)$$

$$= -k_B[\tfrac{1}{4}(1+2x+y)\ln(\tfrac{1}{4})(.) + 2*\tfrac{1}{4}(1-y)\ln(\tfrac{1}{4})(.)$$

$$+\tfrac{1}{4}(1-2x+y)\ln(\tfrac{1}{4})(.)]$$

Free Energy:

The free energy F is,

$$F = U - TS = -2\mu_o Bx - Jy + k_B T\{[\tfrac{1}{4}(1+2x+y)]\ln[.]$$
$$+2[(\tfrac{1}{4})(1-y)]\ln[.] + [\tfrac{1}{4}(1-2x+y)]\ln[.]\} .$$

Note: The notation [.] means the quantity which precedes the logarithm is repeated as the argument of the logarthim; that is,

$$[A]\ln[.] \equiv [A]\ln[A] .$$

We vary x and y in the free energy to (1) locate those values of x and y which minimize F, and (2) to locate the corresponding minimum value of F.

(x-eqn.)

$$0 = (\delta F/\delta x)_{y,B,T}$$
$$= -2\mu_o B + k_B T[(\tfrac{1}{4})2\ln(\tfrac{1}{4})(1+2x+y) - (\tfrac{1}{4})2\ln(\tfrac{1}{4})(1-2x+y)]$$

or $$4\beta\mu_o B = \ln[(1+2x+y)/(1-2x+y)] .$$

(y-eqn.)

$$0 = (\delta F/\delta y)_{x,B,T}$$
$$= -J + k_B T[\tfrac{1}{4}\ln(\tfrac{1}{4})(1+2x+y)$$
$$- 2(\tfrac{1}{4})\ln(\tfrac{1}{4})(1-y) + (\tfrac{1}{4})\ln(\tfrac{1}{4})(1-2x+y)]$$

or $$4\beta J = \ln\left[\frac{(1+2x+y)(1-2x+y)}{(1-y)^{(2)}}\right] .$$

These are two simultaneous, non-linear equations in the two unknowns x and y. Their solution gives the minimizing expressions for x and y:

$$y = \tanh\{\beta J+(\tfrac{1}{2})\ln[\cosh(2\beta\mu_o B)]\}$$

$$x = \tfrac{1}{2}(1+y)\tanh(2\beta\mu_0 B) \quad . \qquad (1)$$

Note that this solution has the correct behavior under a "mirror reflection" of the magnet. Such a reflection causes these changes:

$$\begin{array}{lcl} x & \text{-->} & -x \\ y & \text{-->} & y \\ B & \text{-->} & -B \\ T & \text{-->} & T \\ J & \text{-->} & J \ ; \end{array}$$

These are compatible with equations (1).

When J = 0, this system becomes simply a pair of uncoupled particles, that is, a pair of the systems studied in the previous section. Indeed, when J = 0, equations (1) become

$$y = x^2 ,$$

i.e., the particles are uncorrelated, and

$$x = \tanh\beta\mu_0 B \ ,$$

as shown in the previous section.

To calculate the minimum value of the free energy we substitute $(x,y)_{min}$ into $F(x,y,;T,B)$, obtaining $F(T,B)$.

Gibbs Ensemble:

Following the suggestion of Dr. J. Goldman we next derive the same exact results for a Lenz-Ising model of two particles using the Gibbs ensemble method.

The equilibrium free energy is given by

$$F = -k_B T \ln Z$$

where the partition function Z,is expressed by,

$$Z = \Sigma_\mu \exp[-\beta H(\mu)_\mu)]; \quad \beta = 1/k_B T$$

H(μ) is the energy per each microstate

$$= -\mu_0 B(\mu_1 + \mu_2) - J\mu_1\mu_2 \quad .$$

The macrostate is

$$P(\mu) = \exp[-\beta H(\mu)]/Z \ .$$

For the Lenz-Ising model with N = 2, the microstates are

$$\mu = \begin{pmatrix} +1 & +1 \\ +1 & -1 \\ -1 & +1 \\ -1 & -1 \end{pmatrix} ,$$

and $E(\mu) = E\begin{pmatrix} +1 & +1 \\ +1 & -1 \\ -1 & +1 \\ -1 & -1 \end{pmatrix} = \begin{pmatrix} -2\mu_0 B & -J \\ & +J \\ & +J \\ +2\mu_0 B & -J \end{pmatrix}$,

Using these values, we calculate Z and then F:

$$F = k_B T \ln[4\exp(\Gamma)\cosh(\Gamma+\beta J)]$$

where $\qquad \Gamma = \frac{1}{2}\ln[\cosh(2\beta\mu_0 B)] \ .$

The macrostate is

$$P^{(2)}\begin{pmatrix} +1 & +1 \\ +1 & -1 \\ -1 & +1 \\ -1 & -1 \end{pmatrix} = \frac{1}{4}\begin{Bmatrix} 1+2x+y \\ 1 \quad -y \\ 1 \quad -y \\ 1-2x+y \end{Bmatrix} = 1/Z \begin{Bmatrix} \exp[-\beta E(+1,+1)] \\ \exp[-\beta E(+1,-1)] \\ \exp[-\beta E(-1,+1)] \\ \exp[-\beta E(-1,-1)] \end{Bmatrix} .$$

By direct comparison we find

$$\frac{1}{4}(1 - y) = \exp[-\beta E(+1,-1)]/Z \ ;$$

hence, $\qquad y = \tanh\{\beta J+\frac{1}{2}\ln[\cosh(2\beta\mu_0 B)]\}$,

which is the same expression for y as obtained previously using the cluster expansion.

Further, by direct comparison, we find

$$1+2x+y = 4\exp[\beta(2\mu_0 B+J)]/Z$$

and $\qquad 1-2x+y = 4\exp[\beta(-2\mu_0 B+J)]/Z$

hence, $\qquad x_G = \{\exp[\beta(2\mu_0 B+J)]-\exp[\beta(-2\mu_0 B+J)]\}/Z$

or,

$$x_G = x_{cluster} = \frac{1}{2}(1+y)\tanh 2\beta\mu_0 B$$

as previously obtained.

Magnetization:

$$\text{Magnetization} = M = \mu_0(\mu_1+\mu_2) = 2\mu_0 x$$

$$= (2\mu_0/2)(1+y)\tanh 2\beta\mu_0 B\ .$$

Magnetic Suspectibility:

$$\text{Susceptibility} = \text{chi} = (\delta M/\delta B)_{(B=0)}$$

$$= (2\mu_0/2)[(\delta y/\delta B)_{(B=0)}]\tanh(2\beta\mu_0 B) + (2\mu_0/2)(1+y)(\operatorname{sech}^2 2\beta\mu_0 B)2\beta\mu_0$$

$$= (2\beta\mu_0{}^2)(1+\tanh\beta J)$$

Comparison of Exact $P^{(2)}$ with the Macrostate for Two Uncorrelated Paticles:

This system has two particles, and the behavior of these is correlated by the exchange term $-J\mu_1\mu_2$. To measure the extent of the correlations between the particles one computes the macrostate which

(1) is consistent with the exact one-particle macrostates $P^{(1)}{}_{(1)}$ and $P^{(1)}{}_{(2)}$,

and (2) has <u>no</u> correlation between their particles:

$$[P^{(2)}(\mu_1\mu_2]_{\text{uncorrelated}} = P^{(1)}{}_{\text{exact}}\mu_1 P^{(1)}{}_{\text{exact}}\mu_2\ .$$

This uncorrelated macrostate is

$$[P^{(2)}(\mu_1\mu_2)]_{\text{uncorrelated}} = \tfrac{1}{2}\begin{array}{c}1+x_1\\1-x_1\end{array} *\tfrac{1}{2}\begin{array}{c}1+x_2\\1-x_2\end{array}$$

$$= \tfrac{1}{4}\begin{array}{c}(1+x_1)\begin{array}{c}1+x_2\\1-x_2\end{array}\\ \text{----------}\\ (1-x_1)\begin{array}{c}1+x_2\\1-x_2\end{array}\end{array}$$

$$= \tfrac{1}{4}\begin{array}{c}(1+x_1)(1+x_2)\\(1+x_1)(1-x_2)\\ \text{----------}\\(1-x_1)(1+x_2)\\(1-x_1)(1-x_2)\end{array} = \tfrac{1}{4}\begin{array}{c}1+x_1+x_2+x_1x_2\\1+x_1-x_2-x_1x_2\\ \text{-----------}\\1-x_1+x_2-x_1x_2\\1-x_1-x_2+x_1x_2\end{array}\ .$$

For the systems of interest in this work, $x_1 = x_2 = x$; hence,

$$P^{(2)}_{\text{uncorrelated}} = \tfrac{1}{4}\begin{Bmatrix} 1+2x+x^2 \\ 1 \quad -x^2 \\ 1 \quad -x^2 \\ 1-2x+x^2 \end{Bmatrix} = \tfrac{1}{4}\begin{Bmatrix} (1+x)^2 \\ (1+x)(1-x) \\ (1-x)(1+x) \\ (1-x)^2 \end{Bmatrix} .$$

On the other hand, the exact case is

$$P^{(2)}_{\text{exact}} = \tfrac{1}{4}\begin{Bmatrix} 1+2x+y \\ 1 \quad -y \\ 1 \quad -y \\ 1-2x+y \end{Bmatrix} .$$

If the two particles were uncorrelated (i.e., $J \ll k_B T$), then

$$P^{(2)}_{\text{uncorrelated}} = P^{(1)}_{\text{exact}} * P^{(1)}_{\text{exact}} ,\text{ and so}$$

$$y = \langle\mu_1\mu_2\rangle_{\text{exact}} = \langle\mu_1\rangle\langle\mu_2\rangle = x_1 x_2 = x^2 .$$

Hence one measure of the extent of correlation is the size of the difference $\langle\mu_1\mu_2\rangle - \langle\mu_1\rangle\langle\mu_2 = y - x^2$; this difference is zero for uncorrelated particles.

Other Results:

Other results for uncorrelated particles are as follows:

$$\begin{aligned} U_{\text{uncorrelated}} &= H_{av} = -\mu_0 B(x_1+x_2) - J\langle\mu_1\mu_2\rangle \\ &= \mu_0 B(x_1+x_2) - Jy_{12} \\ &= -2\mu_0 Bx - Jx^2 , \end{aligned}$$

$$\begin{aligned} -(S/k_B)_{\text{uncorrelated}} &= P^{(2)}(++)\ln P^{(2)}(++) + P^{(2)}(+-)\ln P^{(2)}(+-) \\ &\quad + P^{(2)}(-+)\ln P^{(2)}(-+) + P^{(2)}(--)\ln P^{(2)}(--) \\ &= \tfrac{1}{4}(1+x)^2\ln(.) + 2(\tfrac{1}{4})(1-x^2)\ln\tfrac{1}{4}(1-x^2) \\ &\qquad + \tfrac{1}{4}(1-x)^2\ln(.) \\ &= 2(\tfrac{1}{4})(1+x)^2\ln\tfrac{1}{2}(1+x) + 2(\tfrac{1}{4})(1-x^2)\ln\tfrac{1}{4}(1-x^2) \\ &\qquad + 2(\tfrac{1}{4})(1-x)^2\ln\tfrac{1}{2}(1-x) \\ &= \tfrac{1}{2}(1+x)^2 + \tfrac{1}{2}(1-x^2)\ln\tfrac{1}{2}(1+x) \\ &\qquad + \tfrac{1}{2}(1-x)^2 + \tfrac{1}{2}(1-x^2)\ln\tfrac{1}{2}(1-x) \end{aligned}$$

$= 2[\frac{1}{2}(1+x)\ln\frac{1}{2}(1+x) + \frac{1}{2}(1-x)\ln\frac{1}{2}(1-x))$.

$= -(S_1 + S_2)/k_B$,

or $S^{(2)}_{uncorrelated} = S_1^{(1)} + S_2^{(1)}$.

The approximate free energy is given by,

$F_{uncorrelated} = -2\mu_0 Bx - Jx^2 + 2kT[\frac{1}{2}(1+x)\ln\frac{1}{2}(1+x) + \frac{1}{2}(1-x)\ln\frac{1}{2}(1-x)]$

$= F^{(1)}_1 + F^{(1)}_2 - Jx^2$. (2)

This equation for the free energy can be minimized versis changes in x:

(x-eqn) $0 = \delta F/\delta x = -2\mu_0 B - 2Jx + 2kT[\frac{1}{2}\ln\frac{1}{2}(1+x) - \frac{1}{2}\ln\frac{1}{2}(1-x)]$

$(\mu_0 B + Jx)kT = \frac{1}{2}\ln[(1+x)/(1+x)] = \tanh(-1)x$,

or $x = \tanh[(\mu_0 B)/k_B T + (J/k_B T)x]$

$= \tanh(\beta\mu_0 B + \beta Jx)$ (3)

where $\beta = 1/k_B T$.

When J = 0, the two particles are independent, and hence they are uncorrelated; intensive properties are exactly the sum as in the N=1 case studied above, while extensive properties are exactly the sum of the extensive properties of the individual particles. When J > 0, then the two particles interact, and there is correlation. However, <u>one can retain the interaction but ignore the correlation</u>, by, for example, using Eq. (2) for the free energy.

The result for x, Eq. (3), is an approximation to the correct results; this approximate result for x can be used to obtain approximate results for other quantities, including U, S, and F.

Summary

The same exact results have been derived for N = 2 Lenz-Ising model using either the cluster expansion or the Gibbs ensemble method. The Gibbs ensemble can only be used for exact calculations, whereas the cluster expansion can be used for either exact or approximate calculations. We found that for the minimum free energy the agreement between exact and approximate results was good.

It is noted that for N = 2 the results for B = 0 are quite different than those for B =/ 0, whether the results are obtained by exact or approximate methods. Since many of the published calculations for the Lenz-Ising model are for the case B = 0 then it will be important to see if this tendency for non-zero B-field results to be different than zero B-field results continues for larger number of particles.

A System of Three Particles

We derive the exact results,for a Lenz-Ising model with only three particles using the cluster expansion. There are several possible configurations for three particles; Case I- three particles on a straight line, Case II- an equilateral triangle (all J's equal), Case III-a right triangle. We begin with Case II, and consider an equilateral triangle.

Microstate:

The microstate of this system is $\mu = (\mu_1\mu_2\mu_3)$ where

μ_i is the microstate of the i<u>th</u> particle.

Energy:

The hamiltonian for this system is,

$$H = -\mu_0 B(\mu_1+\mu_2+\mu_3) - J(\mu_1\mu_2+\mu_2\mu_3+\mu_1\mu_3)$$

where

μ_1, μ_2, μ_3 are the 1-particle microstates for particle 1,2,3 respectively,

B is the external magnetic field

and J is the interaction term for pairs of particles.

Macrostate:

There are three particles and initially we do not treat them as similar. Later we will let them be the same. The microstates are:

μ_1	μ_2	μ_3
1	1	1
1	1	-1
1	-1	1
1	-1	-1
-1	1	1
-1	1	-1
-1	-1	1
-1	-1	-1

This is an exact configuration.

Each macrostate is a probability law for these 8 microstates. The macrostate $P^{(3)}$ is

$$P^{(3)}(\mu_1\mu_2\mu_3) = P^{(3)} \begin{array}{ccc} \mu_1 & \mu_2 & \mu_3 \\ 1 & 1 & 1 \\ 1 & 1 & -1 \\ 1 & -1 & 1 \\ 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & -1 \\ -1 & -1 & 1 \\ -1 & -1 & -1 \end{array} = \begin{array}{c} \\ g \\ h \\ i \\ j \\ k \\ l \\ m \\ n \end{array}$$

Note the following constraints: $g,h,i,j,k,l,m,n >= 0$.

The quantities g -> n, are just numbers. We can either describe probability functions in terms of numbers such as these, or in terms of physical quantities x,y,z. The advantage of working with g -> n is that they do not mean anything. They are just numbers, and only mean the probability of being up or the probability of being down. For example, the probability for the microstate with all three particles being up, is given by "g". The physical quantities, such as "x", mean something - it is the probability of spin up minus the probability of spin down: i.e. x = p(^) - p( ).

The macrostate for this three particle system is,

$P^{(3)}(\mu_1, \mu_2, \mu_3)$

$$= 1/8 \left\{ \begin{array}{cccccccc} & x_1 & x_2 & x_3 & y_{12} & y_{13} & y_{23} & z_{123} \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & 1 & -1 & -1 & -1 \\ 1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 \\ 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 \end{array} \right\}$$

where x,y,z, have been previously defined. Note that the individual y entries are products of x's (y_{12} is the product of x_1, x_2 etc.) and z_{123} is the product of x_1, x_2, x_3. For example in the second row $y_{23} = (x_2)(x_3) = (1)(-1) = -1$, and in the third row $z_{123} = (1)(-1)(1) = -1$.

How can we check this arrangement? Use normalization and add up the g,h,...m,n's. For example,

$$g = 1/8 \left[\begin{array}{cccc} 1 & x,s & y's & z's \\ - & & & \\ \overline{8} & \overline{0} & \overline{0} & \overline{0} \end{array} \right] \qquad 1/8(8) = 1$$

For the Lenz-Ising model these three particles will be similar, and we can add up the x's and the y's. For example, $3x = x_1 + x_2 + x_3$ and all three spins are pointing up. Then $P^{(3)}$ can be written as,

$$P^{(3)} = 1/8 \left\{ \begin{array}{cccc} 1 & +3x & +3y & +z \\ 1 & +x & -y & -z \\ 1 & +x & -y & -z \\ 1 & -x & -y & +z \\ 1 & +x & -y & -z \\ 1 & -x & -y & +z \\ 1 & -x & -y & +z \\ 1 & -3x & +3y & -z \end{array} \right\}$$

Remember that the x and y entries above are sums, e.g. $3y = y_{12} + y_{13} + y_{23}$ (the sum for all three entries) and the value for z is a product of the three x values.

Internal Energy:

The internal energy is the the average value of the hamiltonian, i.e. the expectation value of H,

$$\begin{aligned} U = \langle H \rangle = &- \mu_0 B[\langle\mu_1\rangle+\langle\mu_2\rangle+\langle\mu_3\rangle] \\ &- J[\langle\mu_1\mu_2\rangle+\langle\mu_2\mu_3\rangle+\langle\mu_1\mu_3\rangle] \end{aligned}$$

Recall the N=1 case. We defined the average value or the expectation of the spin-state, μ, as

$$\begin{aligned} x &= \langle\mu\rangle = \Sigma_{\mu -1}^{1} P^{(1)}(\mu) \\ &= (\mu=+1)(P^{(1)}(+1)) + (\mu=-1)(P^{(1)}(-1)) \end{aligned}$$

We recognize symmetries in the crystal lattice,

$$\langle\mu_1\rangle = \langle\mu_2\rangle = \langle\mu_3\rangle = x$$

the average value of μ, i.e. the average value of the spin state, and

$$\langle\mu_1\mu_2\rangle = \langle\mu_2\mu_3\rangle = \langle\mu_1\mu_3\rangle = y$$

the average value of the product of μ.

The internal energy can then be written as,

$$U = -3\mu_o Bx - 3Jy$$

where x is the average value of the magnetization of the particle. It is the probability of spin up minus the probability of spin down: i.e. x=p(^)-p( ). The quantity y is the (average value) probability of finding a pair being parallel.

Entropy:

The entropy for this system is,

$$-S/k_B = \langle \ln P^{(3)} \rangle$$

$$-S/k_B = [\Sigma, \text{all states}] P^{(3)}(\mu_1\mu_2\mu_3) \ln P^{(3)}(\mu_1\mu_2\mu_3).$$

The exact configuration for the microstatees is a 3x8 array (see p.54). We wrote the macrostate in terms of the numbers g --> n. To write this macrostate in the form we use with x_1, x_2, y_{12}, z we need to evaluate the numbers g --> n as we evaluated the analogous numbers c,d,e,f for $P^{(2)}$. For the N=3 case the new quantity is $z = \langle\mu_1\mu_2\mu_3\rangle$ i.e. the product of all three microstates. The quantities x and y are the same as in macrostate $P^{(2)}$.

REDUCING

Is it the case that if I sum $P^{(3)}$ over any one of these three particles I get the $P^{(2)}$ of the other 2 particles. We do this in the following way, by extracting the behavior of 2 particles from the known behavior of 3 particles. We do this by adding up over all possible states of the third particle. This is known as reducing. (reducing the marginal probability)

$P^{(2)}(\mu_1\mu_2) = \Sigma_{\mu_3=-1}{}^{1} P^{(3)}(\mu_1\mu_2\mu_3)$
$P^{(2)}(\mu_1\mu_3) = \Sigma_{\mu_2=-1}{}^{1} P^{(3)}(\mu_1\mu_2\mu_3)$
$P^{(2)}(\mu_2\mu_3) = \Sigma_{\mu_1=-1}{}^{1}]P^{(3)}(\mu_1\mu_2\mu_3)$

$$P^{(2)}(\mu_1\mu_2) = P^{(2)} \begin{array}{rr} 1 & 1 \\ 1 & -1 \\ -1 & 1 \\ -1 & -1 \end{array} = P^{(3)} \underset{\mu_3=1}{\begin{array}{rrr} 1 & 1 & 1 \\ -1 & 1 & 1 \\ -1 & 1 & 1 \\ -1 & -1 & 1 \end{array}} + P^{(3)} \underset{\mu_3=-1}{\begin{array}{rrr} 1 & 1 & -1 \\ 1 & -1 & -1 \\ -1 & 1 & -1 \\ -1 & -1 & -1 \end{array}}$$

$$P^{(2)}(\mu_1\mu_2) = \begin{array}{lll} \overset{(1\ 1\ 1)}{1/8(1+3x+3y+z)} & \overset{(1\ 1\ -1)}{+1/8(1+x-y-z)} & \longrightarrow 1/8(2+4x+2y) \\ \overset{(-1\ 1\ 1)}{1/8(1+x-y-z)} & \overset{(1\ -1\ -1)}{+1/8(1-x-y+z)} & \longrightarrow 1/8(2 \quad -2y) \\ \overset{(-1\ 1\ 1)}{1/8(1+x-y-z)} & \overset{(-1\ 1\ -1)}{+1/8(1-x-y+z)} & \longrightarrow 1/8(2 \quad -2y) \\ \overset{(-1 -1\ 1)}{1/8(1-x-y+z)} & \overset{(-1 -1 -1)}{+1/8(1-3x+3y-z)} & \longrightarrow 1/8(2\ -4x+2y) \end{array}$$

$$= \frac{1}{4} \begin{array}{l} 1+2x+y \\ 1 - y \\ 1 - y \\ 1-2+y \end{array}$$

This is the same $P^{(2)}$ as derived earlier - this time by a reduction method.

Entropy:

$$-S/k = \Sigma_{\mu_1\mu_2\mu_3} P^{(3)} \ln P^{(3)}$$

$$\begin{aligned} = & (1/8)(1+3x+3y+z)\ln(1/8)(1+3x+3y+z) \\ & +(3/8)(1+x-y-z)\ln(1/8)(1+x-y-z) \\ & +(3/8)(1-x-y+z)\ln(1/8)(1-x-y+z) \\ & +(1/8)(1-3x+3y-z)\ln(1/8)(1-3x+3y-z) \end{aligned}$$

Energy:

$$\begin{aligned} F &= U - TS \\ &= -3\mu_0 Bx - 3Jy \\ & \quad +(k_B T/8)[(1+3x+3y+z)\ln(1/8)(1+3x+3y+z) \\ & \qquad +3\{(1+x-y-z)\ln(1/8)(1+x-y-z)\} \\ & \qquad +3(1-x-y+z)\ln(1/8)(1-x-y+z) \\ & \qquad +(1-3x+3y-z)\ln(1/8)(1-3x+3y-z)] \end{aligned}$$

We now MINIMIZE

$$\begin{aligned} 0 = \delta F/\delta x = -3\mu_0 B + (k_B T/8)[& 3\ln(1/8)(1+3x+3y+z) \\ & +3\ln(1/8)(1+x-y-z) \\ & -3\ln(1/8)(1-x-y+z) \\ & -3\ln(1/8)(1-3x+3y-z)] \end{aligned}$$

$$
\begin{aligned}
0 = \delta F/\delta y = -3J + (k_B T/8)[&3\ln(1/8)(1+3x+3y+z) \\
&-3\ln(1/8)(1+x-y-z) \\
&-3\ln(1/8)(1-x-y+z) \\
&+3\ln(1/8)(1-3x+3y-z)]
\end{aligned}
$$

$$
\begin{aligned}
0 = \delta F/\delta z = (k_B T)[&\ln(1/8)(1+3x+3y+z) \\
&-3\ln(1/8)(1+x-y-z) \\
&3\ln(1/8)(1-x-y+z) \\
&-\ln(1/8)(1-3x+3y-z)]
\end{aligned}
$$

Suppose B=0, so we can study (x,y,z) with B=0.

[x eqn] $$\frac{(1+3x+3y+z)(1+x-y-z)}{(1-3x+3y-z)(1-x-y+z)} = 1$$

$$\longrightarrow (1+3x+3y+z)(1+x-y-z) = (1-3x+3y-z)(1-x-y+z)$$

[z eqn] $$\frac{(1+3x+3y+z)(1-x-y+z)^3}{(1-3x+3y-z)(1+x-y-z)^3} = 1$$

$$\longrightarrow (1+3x+3y+z)(1-x-y+z)^3 = (1-3x+3y-z)(1+x-y-z)^3$$

From [x], we know

$$\frac{(1+3x+3y+z)}{(1-3x+3y-z)} = \frac{(1-x-y+z)}{(1+x-y-z)}$$

From [z], we know

$$\frac{(1+3x+3y+z)}{(1-3x+3y-z)} = \frac{(1+x-y-z)^3}{(1-x-y+z)^3}$$

Hence

$$\frac{(1-x-y+z)}{(1+x-y-z)} = \frac{(1+x-y-z)^3}{(1-x-y+z)^3}$$

$$
\begin{aligned}
(1-x-y+z)^4 &= (1+x-y-z)^4 \\
1-x-y+z &= 1+x-y-z \\
-x+z &= x-z \\
[x &= z]
\end{aligned}
$$

Return to [x], with (x = z)

$$
\begin{aligned}
(1+4x+3y)/(1-4x+3y) &= (1-y)/(1-y) = 1 \\
\longrightarrow \quad 1+4x+3y &= 1-4x+3y \\
\longrightarrow \quad [x &= 0]
\end{aligned}
$$

Hence, $(B = 0) \dashrightarrow [x = z = 0]$

We continue, $B = 0$ with [y eqn]

$$3J = 2k_BT/8[3\ln(1/8)(1+3y)-3\ln(1/8)(1-y)]$$

$$\dashrightarrow \quad J = (k_BT/4)\ln[(1+3y)/(1-y)]$$

$$4J/k_BT = \ln[(1+3y)/(1-y)] \qquad \alpha = 4J/k_BT = 4\beta J$$

$$\alpha = \ln[(1+3y)/(1-y)] \dashrightarrow \exp(\alpha) = (1+3y)/(1-y)$$

$$\dashrightarrow \quad \exp(\alpha) - \exp(\alpha)y = 1+3y$$
$$\dashrightarrow \quad \exp(\alpha) - 1 = y[3 + \exp(\alpha)]$$

$$y = [\exp(\alpha) - 1]/[3+\exp(\alpha)]$$

$$y = [\exp(4\beta J) - 1]/[\exp(4\beta J) + 3]$$

Case I

We have been examing case II for triangle arrangements. There are two other possibilities for a three particle Lenz-Ising lattice models: the triangle and straight line. We now examine case I for 3 particles in a straight line.

For a straight line we have $J_{12}=J_{23}=J$ and $J_{13} \approx 0$ Then $y_{12}=y_{23}=y_1$ and $y_{13}=y_2$. The microstates are as before,

$$P(3) = \left\{\begin{array}{rrr} 1 & 1 & 1 \\ 1 & 1 & -1 \\ 1 & -1 & 1 \\ 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & -1 \\ -1 & -1 & 1 \\ -1 & -1 & -1 \end{array}\right\}$$

The new macrostate is,

$$P(3) = 1/8 \left\{\begin{array}{lllllllll} 1 & + & 3x & + & 2y_1 & + & y_2 & + & z \\ 1 & + & x & - & & & y_2 & - & z \\ 1 & + & x & - & 2y_1 & + & y_2 & - & z \\ 1 & - & x & - & & & y_2 & + & z \\ 1 & + & x & - & & & y_2 & - & z \\ 1 & - & x & - & 2y_1 & + & y_2 & + & z \\ 1 & - & x & - & & & y_2 & + & z \\ 1 & - & 3x & + & 2y_1 & + & y_2 & - & z \end{array}\right\}$$

Free Energy:

$$U = -3\mu_0 Bx - 2Jy_1$$

$$\begin{aligned} F = {} & -3\mu_0 Bx - 2Jy_1 \\ & +k_B T\{(1/8)(1 + 3x + 2y_1 + y_2 + z)\ln(1/8)(.) \\ & \quad +(2/8)(1 + x - y_2 - z)\ln(1/8)(.) \\ & \quad +(1/8)(1 + x - 2y_1 + y_2 - z)\ln(1/8)(.) \\ & \quad +(2/8)(1 - x - y_2 + z)\ln(1/8)(.) \\ & \quad +(1/8)(1 - x - 2y_1 + y_2 + z)\ln(1/8)(.) \\ & \quad +(1/8)(1 - 3x + 2y_1 + y_2 - z)\ln(1/8)(.)\} \end{aligned}$$

Minimize: Suppose $B = 0$. Then $x = z = 0$.

[y_1]

$$\begin{aligned} 0 = \delta F/\delta y_1 = -2J + (k_B T/8)[& 2\ln(1/8)(1+2y_1+y_2) \\ & -2\ln(1/8)(1-2y_1+y_2) \\ & -2\ln(1/8)(1-2y_1+y_2) \\ & +2\ln(1/8)(1+2y_1+y_2)] \end{aligned}$$

[y_2]

$$\begin{aligned} 0 = \delta F/\delta y_2 = (kT/8)[& \ln(1/8)(1+2y_1+y_2) \\ & -2\ln(1/8)(1-y_2) \\ & + \ln(1/8)(1-2y_1+y_2) \\ & -2\ln(1/8)(1-y_2) \\ & + \ln(1/8)(1-2y_1+y_2) \\ & + \ln(1/8)(1+2y_1+y_2)] \end{aligned}$$

Solve [y_1] and [y_2]:

[y_1]

$$J = (k_B T/4)\ln[(1+2y_1+y_2)/(1-2y_1+y_2)]$$

$$\text{-->} \quad 4J/k_B T = \ln[(1+2y_1+y_2)/(1-2y_1+y_2)]$$

[y_2]

$$0 = \ln[(1+2y_1+y_2)^2(1-2y_1+y_2)^2/(1-y_2)^4]$$

$$\text{-->} \quad 1 = (1+2y_1+y_2)(1-2y_1+y_2)/(1-y_2)^2$$

$$(1+y_2+2y_1)(1+y_2-2y_1) = (1-y_2)^2$$

$$(1+y_2)^2 - 4y_1^2 = (1-y_2)^2$$

$$1 + 2y_2 + y_2^2 - 4y_1^2 = 1 - 2y_2 + y_2^2$$

$$4y_2 = 4y_1^2$$

$$[y_2 = y_1^2]$$

Substitute this result into [y_1]

[y_1] $$4J/k_B T = \ln[(1+2y_1+y_1^2)/(1-2y_1+y_1^2)]$$

$$2(J/k_B T) = \ln[(1+y_1)/(1-y_1)]$$

Results:

$y_1 = \tanh(\beta J)$

$y_2 = [\tanh(\beta J)]^2$

For $B = 0$ and

$x = 0$

$z = 0$

straight line case $\qquad \tanh(x) = [1-\exp(-2x)]/[1+\exp(-2x)]$

A System of Four Particles

This will be a 4-body exact calculation for an equi-everything pyramid. In these exact calculations it will be the first time that we have encountered a three dimensional Lenz-Ising model. For this pyramid all sides, faces and angles are equal.

We have,

$$x = \langle\mu_1\rangle = \langle\mu_2\rangle = \langle\mu_3\rangle = \langle\mu_4\rangle$$

Which is the average behavior of each particle separately.

$$y = \langle\mu_1\mu_2\rangle = \langle\mu_1\mu_3\rangle = \langle\mu_1\mu_4\rangle$$
$$= \langle\mu_2\mu_3\rangle = \langle\mu_2\mu_4\rangle = \langle\mu_3\mu_4\rangle$$

i.e. the average correlation for each pair of particles.

$$z = \langle\mu_1\mu_2\mu_3\rangle = \langle\mu_1\mu_2\mu_4\rangle = \langle\mu_1\mu_3\mu_4\rangle$$
$$= \langle\mu_2\mu_3\mu_4\rangle$$

$$w = \langle\mu_1\mu_2\mu_3\mu_4\rangle$$

Macrostate:

The behavior of a single particle is given by the macrostate $P^{(1)}$

$$P^{(1)}(\mu) = \tfrac{1}{2}\begin{bmatrix} 1+x \\ 1-x \end{bmatrix} = P^{(1)}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

The behavior of one particle with another is given by the macrostate $P^{(2)}$

$$P^{(2)}(\mu\ \mu') = \tfrac{1}{4}\begin{bmatrix} 1+2x+y \\ 1-y \\ 1-y \\ 1-2x+y \end{bmatrix} = P^{(2)}\begin{bmatrix} 1 & 1 \\ 1 & -1 \\ -1 & 1 \\ -1 & -1 \end{bmatrix}$$

$P^{(2)}(\mu\ \mu') = P^{(2)}(\mu_{i1}\ \mu_{i2})$. This is an alternative way of writing $P^{(2)}$ by using the Morita notation.

For three particles, the macrostate $P^{(3)}$ is

$$P^{(3)}(\mu,\mu',\mu'') = 1/8 \begin{bmatrix} 1+3x+3y+z \\ 1+x-y-z \\ 1+x-y-z \\ 1-x-y+z \\ 1+x-y-z \\ 1-x-y+z \\ 1-x-y+z \\ 1-3x+3y-z \end{bmatrix} = P^{(3)} \underbrace{\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \\ 1 & -1 & 1 \\ 1 & -1 & -1 \\ -1 & 1 & 1 \\ -1 & 1 & -1 \\ -1 & -1 & 1 \\ -1 & -1 & -1 \end{bmatrix}}_{\text{microstates}}$$

For four particles, the macrostate $P^{(4)}$ is

$$P^{(4)}(\mu,\mu',\mu'',\mu''')$$

$$= P^{(4)} \underbrace{\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 \\ 1 & 1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & -1 & -1 \\ -1 & 1 & 1 & 1 \\ -1 & 1 & 1 & -1 \\ -1 & 1 & -1 & 1 \\ -1 & 1 & -1 & -1 \\ -1 & -1 & 1 & 1 \\ -1 & -1 & 1 & -1 \\ -1 & -1 & -1 & 1 \\ -1 & -1 & -1 & -1 \end{bmatrix}}_{\text{microstates of the four particles.}} = 1/16 \begin{bmatrix} 1+4x+6y+4z+w \\ 1+2x+0y-2z-w \\ 1+2x+0y-2z-w \\ 1+0x-2y+0z+w \\ 1+2x+0y-2z-w \\ 1+0x-2y+0z+w \\ 1+0x-2y+0z+w \\ 1-2x+0y+2z-w \\ 1+2x+0y-2z-w \\ 1+0x-2y+0z+w \\ 1+0x-2y+0z+w \\ 1-2x+0y+2z-w \\ 1+0x-2y+0z+w \\ 1-2x+0y+2z-w \\ 1-2x+0y+2z-w \\ 1-4x+6y-4z+w \end{bmatrix}$$

$$\overline{16}\quad \overline{0}\quad \overline{0}\quad \overline{0}\quad \overline{0}$$

Internal Energy:

$$U = \langle H\rangle = -(\mu_0 B)(4x) - (J)(6)(y)$$
$$U = -\ 4\mu_0 Bx - 6Jy$$

Entropy:

$$\begin{aligned} -\ S/k_B &= \Sigma_\mu P^{(4)} \ln P^{(4)} \\ &= (1/16)(1+4x+6y+4z+w)\ln(1/16)(.) \\ &\quad +4(1/16)(1+2x-2z-w)\ln(1/16)(.) \\ &\quad +6(1/16)(1-2y+w)\ln(1/16)(.) \\ &\quad +4(1/16)(1-2x+2z-w)\ln(.) \\ &\quad +(1/16)(1-4x+6y-4z+w)\ln(1/16)(.) \end{aligned}$$

Free Energy:

$$\begin{aligned} F = &- 4\mu_o Bx - 6Jy \\ &+ (k_B T/16)[(1+4x+6y+4z+w)\ln(1/16)(.) \\ &\quad +4(1+2x-2z-w)\ln(1/16)(.) \\ &\quad +6(1-2y+w)\ln(1/16)(.) \\ &\quad +4(1-2x+2z-w)\ln(1/16)(.) \\ &\quad +(1-4x+6y-4z+w)\ln(1/16)(.)] \end{aligned}$$

Minimization:

[x]
$$\begin{aligned} 0 &= \delta F/\delta x \\ &= -4\mu_o B + (k_B T/16)[4\ln(1/16)(1+4x+6y+4z+w) \\ &\quad +8\ln(1/16)(1+2x-2z-w) \\ &\quad -8\ln(1/16)(1-2x+2z-w \\ &\quad -4\ln(1/16)(1-4x+6y-4z+w)] \end{aligned}$$

-->
$$4\mu_o B/k_B T = \tfrac{1}{4}\ln\left[\frac{(1+4x+6y+4z+w)(1+2x-2z-w)^2}{(1-4x+6y-4z+w)(1-2x+2z-w)^2} \right]$$

[y]
$$\begin{aligned} 0 &= \delta F/\delta y \\ &= -6J + (k_B T/16)[6\ln(1/16)(1+4x+6y+4z+w) \\ &\quad -12\ln(1/16)(1-2y+w) \\ &\quad +6\ln(1/16)(1-4x+6y-4z+w)] \end{aligned}$$

-->
$$16J/k_B T = \ln\left[\frac{(1+4x+6y+4z+w)(1-4x+6y-4z+w)}{(1-2y+w)^2} \right]$$

[z]
$$\begin{aligned} 0 &= \delta F/\delta z \\ &= (k_B T/16)[4\ln(1/16)(1+4x+6y+z+w) \\ &\quad -8\ln(1/16)(1+2x-2z-w) \\ &\quad +8\ln(1/16)(1-2x+2z-w) \\ &\quad -4\ln(1/16)(1-4x+6y-4z+w)] \end{aligned}$$

-->
$$0 = \ln\left[\frac{(1+4x+6y+4z+w)(1-2x+2z-w)^2}{(1-4x+6y-4z+w)(1+2x-2z-w)^2} \right]$$

-->
$$1 = \frac{(1+4x+6y+4z+w)(1-2x+2z-w)^2}{(1-4x+6y-4z+w)(1+2x-2z-w)^2}$$

[w]
$$\begin{aligned} 0 &= \delta F/\delta w \\ &= (k_B T/16)[\ln(1/16)(1+4x+6y+4z+w) \\ &\quad -4\ln(1/16)(1+2x-2z-w) \\ &\quad +6\ln(1/16)(1-2y+w) \\ &\quad -4\ln(1/16)(1-2x+2z-w) \\ &\quad +\ln(1/16)(1-4x+6y-4z+w)] \end{aligned}$$

-->
$$0 = \ln\left[\frac{(1+4x+6y+4z+w)(1-4x+6y-4z+w)(1-2y+w)^6}{(1+2x-2z-w)^4(1-2x+2z-w)^4} \right]$$

$$\longrightarrow \qquad 1 = \frac{(1+4x+6y+4z+w)(1-4x+6y-4z+w)(1-2y+w)^6}{(1+2x-2z-w)^4(1-2x+2z-w)^4}$$

Suppose B = 0.

$$[x] \qquad \frac{(1+4x+6y+4z+w)(1+2x-2z-w)^2}{(1-4x+6y-4z+w)(1-2x+2z-w)^2} = 1$$

$$[z] \qquad \frac{(1+4x+6y+4z+w)(1-2x+2z-w)^2}{(1-4x+6y-4z+w)(1+2x-2z-w)^2} = 1$$

$$\frac{(1+4x+6y+4z+w)}{(1-4x+6y-4z+w)} = \frac{(1-2x+2z-w)^2}{(1+2x-2z-w)^2} \qquad \text{(from [x])}$$

$$\text{ditto} = \frac{(1+2x-2z-w)^2}{(1-2x+2z-w)^2} \qquad \text{(from [z])}$$

$$\longrightarrow \quad (1+2x-2z-w) = (1-2x+2z-w)$$

$$\longrightarrow \quad 4x = 4z$$

$$\longrightarrow \quad [\ x = z\ ]$$

Using this result in the [x] equation:

$$\frac{1+8x+6y+w}{1-8x+6y+w} = 1$$

$$\longrightarrow \quad 1+8x+6y+w = 1-8x+6y+w$$

$$\longrightarrow \quad 16x = 0$$

$$\longrightarrow \quad x = 0$$

Hence, $(\ B = 0\ ) \longrightarrow (\ x = z = 0\ )$

Using $x = z = 0$, return to the original equation for [x].

$$[x] \qquad 16\mu_0 B/k_B T = \ln \left[\frac{(1+6y+w)(1-w)^2}{(1+6y+w)(1-w)^2}\right]$$

$$0 = \ln 1 \qquad \text{since } B=0$$
$$0 = 0$$

i.e., the x-eqn is automaticaly satisfied.

[y] $$16\beta J = \ln \left[\frac{(1+6y+w)^2}{(1-2y+w)^2}\right]$$

$$8\beta J = \ln \left(\frac{1+6y+w}{1-2y+w}\right) \qquad (4)$$

[z] is automatically satisfied, (1=1)

[w] $(1+6y+w)^2(1-2y+w)^6 = (1-w)^8$

--> $(1+6y+w)(1-2y+w)^3 = (1-w)^4$

--> $$1+6y+w = \frac{(1-w)^4}{(1-2y+w)^3} \qquad (5)$$

The above two equations (4) and (5) for y and w are two simultaneous equations in two unknowns. Substitute for 1+6y+w in the eqn. for [y].

$$8\beta J = \ln \left[\frac{(1-w)^4}{(1-2y+w)^4}\right]$$

$$2\beta J = \ln \left(\frac{1-w}{1-2y}\right)$$

--> $\alpha = \exp(2\beta) = (1-w)/(1-2y+w)$

--> $\alpha - 2\alpha y + \alpha w = 1 - w$

--> $\alpha - 1 - 2\alpha y + (\alpha + 1)w = 0$

--> $(\alpha + 1)w = 1 - \alpha + 2\alpha y$

--> $w = (1 - \alpha)/(1 + \alpha) + (2\alpha y)/(1 - \alpha)$

Hence, the Free Energy is for B = 0

$$\begin{aligned} F = -6Jy + (k_B T/16)[&2(1+6y+w)\ln(1/16)(.) \\ &+ 8(1-w)\ln(1/16)(.) \\ &+ 6(1-2y+w)\ln(1/16)(.)] \end{aligned}$$

with w as above.

Write,

$$\begin{aligned}\Phi = \beta F = -\ 6\beta Jy + (1/8)[&(1+6y+w)\ln(1/16)(.)\\ &+4(1-w)\ln(1/16)(.)\\ &+3(1-2y+w)\ln(1/16)(.)]\end{aligned}$$

In the Morita 1-cluster approximation,

$y = \langle \mu\mu' \rangle \approx \langle \mu \rangle\langle \mu' \rangle = \langle \mu \rangle\langle \mu \rangle = x^2 = 0;\ B = 0$

$z = \langle \mu\ \mu'\mu'' \rangle \approx \langle \mu \rangle\langle \mu' \rangle\langle \mu'' \rangle = x^3$

$w = \langle \mu\ \mu'\mu''\mu''' \rangle \approx \langle\mu\rangle\langle\mu'\rangle\langle\mu''\rangle\langle\mu'''\rangle = x^4$

In the Morita 2-cluster approximation,

$y = \langle \mu\mu' \rangle$ is treated exactly.

$z = \langle \mu\mu'\mu'' \rangle = \langle \mu \rangle\langle\mu'\mu''\rangle = xy = 0;\quad B = 0$

$w = \langle\mu\mu'\mu''\mu'''\rangle = \langle\mu\mu'\rangle\langle\mu''\mu'''\rangle = y^2$.

In the Morita 3-cluster approximation,

y,z are treated exactly,

$w = \langle \mu\mu' \rangle\langle \mu''\mu''' \rangle + \langle \mu \rangle\langle \mu\ \mu'\mu'' \rangle$

CHAPTER IV

APPLICATION OF THE CLUSTER VARIATIONAL METHOD TO THE LENZ-ISING MODEL

First Order Approximation: Mean Field Theory (One Cluster Approximation)

Internal Energy:

The internal energy of the Lenz-Ising model is, in the first approximation,

$$U = \langle H\rangle = -\mu_0 B\Sigma_i\langle\mu_i\rangle - \tfrac{1}{2}J\Sigma_{ij(n.n.)}\langle\mu_i\mu_j\rangle$$

$$= -\mu_0 BNx - \tfrac{1}{2}JNZx^2$$

where

$x = x_1{}^1$ and $Z = Z_1{}^{(2)}$ is the number of nearest neighbors.

y = pair correlation coefficent = x^2 in this 1-cluster approximation for independent clusters.

Entropy:

The entropy is

$$S = S\hat{}^{(1)} = \Sigma_i S\hat{}_i{}^{(1)} = NS\hat{}_.{}^{(1)}$$

$$S = -Nk_B[\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)]$$

Free Energy:

The Helmholtz free energy is

$$F = U - TS$$

$$F = -\mu_0 BNx - \tfrac{1}{2}JNZx^2 + Nk_B T[\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)]$$

It is convenient to work with a dimensionless version of the free energy:

$$\Phi = (F/NJ) = -B_r x - \tfrac{1}{2}Zx^2 + T_r[\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)] \qquad (6)$$

where $B_r = \mu_0 B/J$ and $T_r = k_B T/J$ are dimensionless versions of the magnetic field and the temperature.

The values of Φ given by Eq. (6),as a function of x, are shown in Fig. 7 for $T_r = 3,6,9,12,24,36$. The critical temperature for this first approximation is $T_{r,c}{}^{I}$ which is the same as the pair coordination number in this approximation, (see Eq. (8)). The values selected in this figure are multiples of $T_{r,c}$. The external magnetic field B_r,is zero in Fig. 7.

The units used in all figures for Φ, B_r, and T_r are called "reduced" units and are dimensionless. They are given in equation (6).

Similar results are given in Fig. 8 when the external magnetic field, B_r, is equal to 10. This is a very strong field and is equal to about 10^7 gauss for ferromagnetic systems. The minimum free energy here is close to saturation (x=1), as compared to Fig. 7, where B_r was zero.

Minimization:

The equilibrium state of this system is found by differentiating F, or Φ, with respect to x:

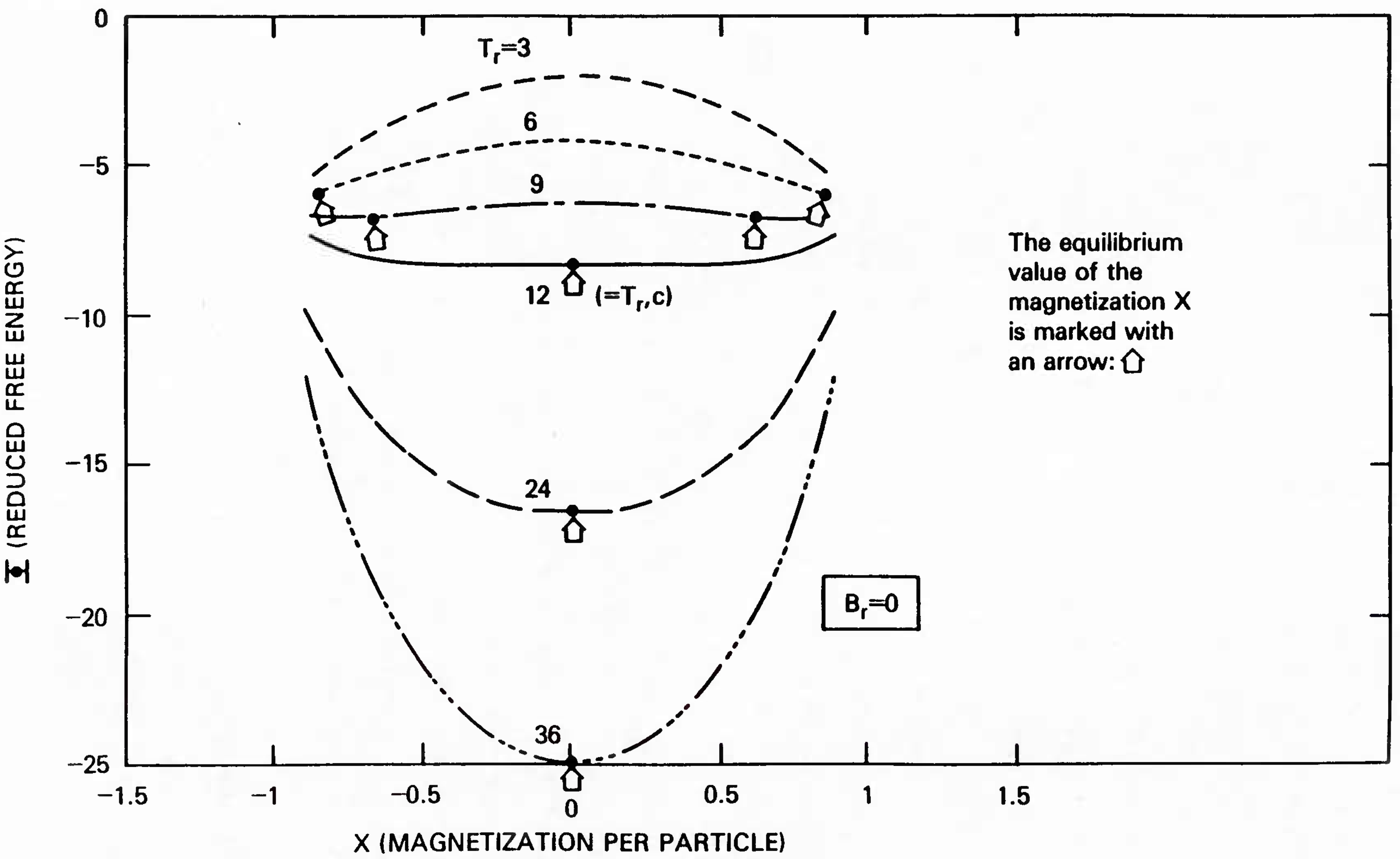


Fig. 7. FREE ENERGY PHI vs. MAGNETIZATION X, FOR FIXED VALUES OF TEMPERATURE T_r AND MAGNETIC FIELD B_r

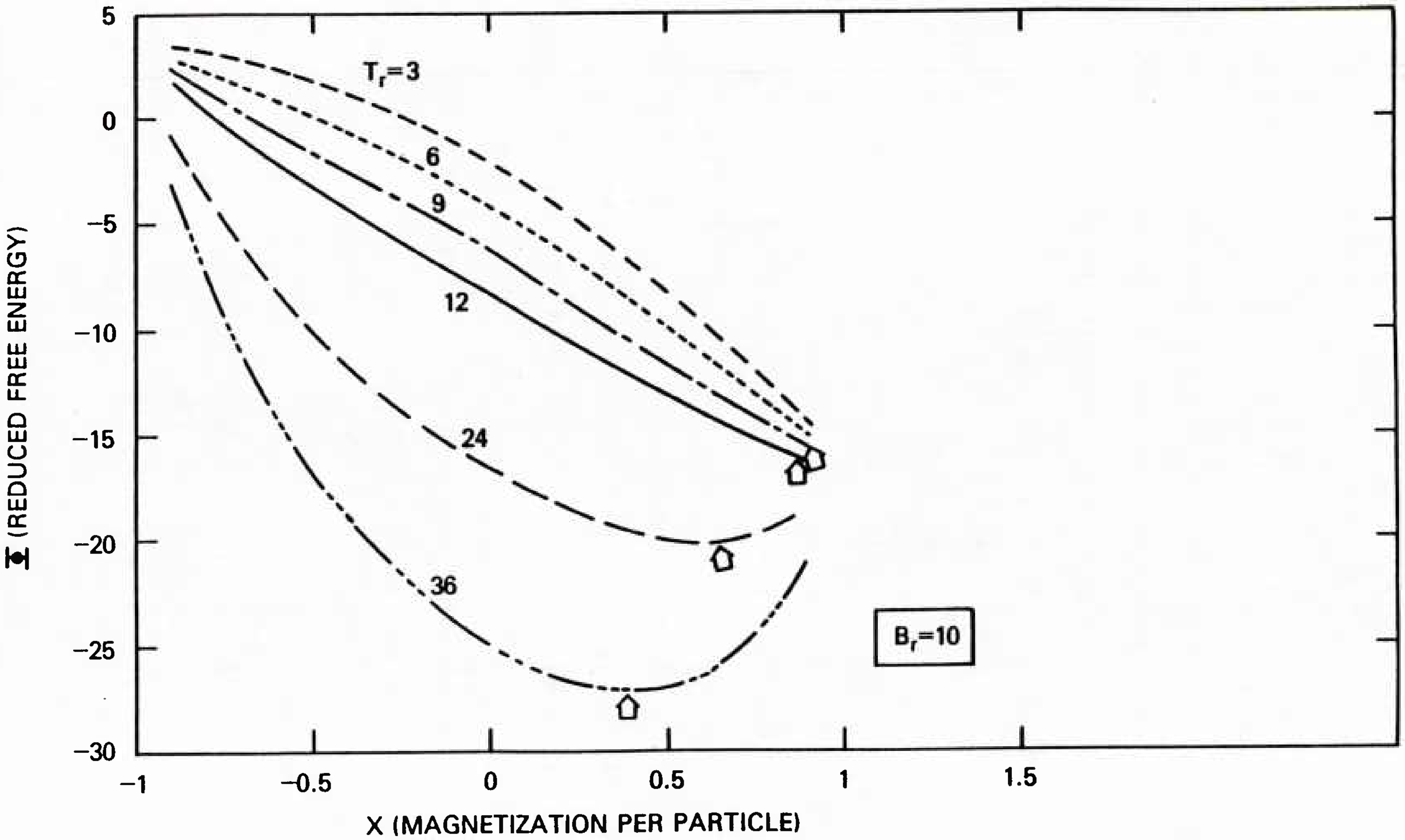


Fig. 8. FREE ENERGY PHI vs. MAGNETIZATION X, FOR FIXED VALUES OF TEMPERATURE T_r AND MAGNETIC FIELD B_r

[x eqn]

$$0 = (d\Phi/dx) = - B_r - Zx + T_r\,[\tfrac{1}{2}\ln\tfrac{1}{2}(1+x) - \tfrac{1}{2}\ln\tfrac{1}{2}(1-x)]$$

Hence:

$$B_r + Zx = \tfrac{1}{2}T_r \ln[(1+x)/(1-x)]$$

Considered as an equation determining $x = x(T_r, B_r)$, this is **transcendental** ,that is,the methods of algebra cannot solve this equation for $x(T_r, B_r)$. However, an explicit result is possible for $T_r = T_r(B_r, x)$:

$$T_r = \frac{2(B_r + Zx)}{\ln[(1+x)/(1-x)]} \tag{7}$$

Tables and graphs for $T_r = T_r(B_r, x)$ can be inverted to give $x = x(T_r, B_r)$.

The equilibrium free energy in this first approximation is calculated by solving Eq. (7) for T_r and x when B_r is kept at a constant value. These values are used in Eq. (6) to calculate the minimum free energy. The results are given in Fig. 9 for several different values of B_r.

There is a critical temperature in this case, which we can determine by the conditions that

$$B=0$$

and

$$x \approx 0 \ \& \ x \leq\geq 0$$

Equation (7) becomes

$$T_{r,c}^{1} = \frac{2Zx}{\ln[(1+x)/(1-x)]} = \frac{2Zx}{2x} = Z \tag{8}$$

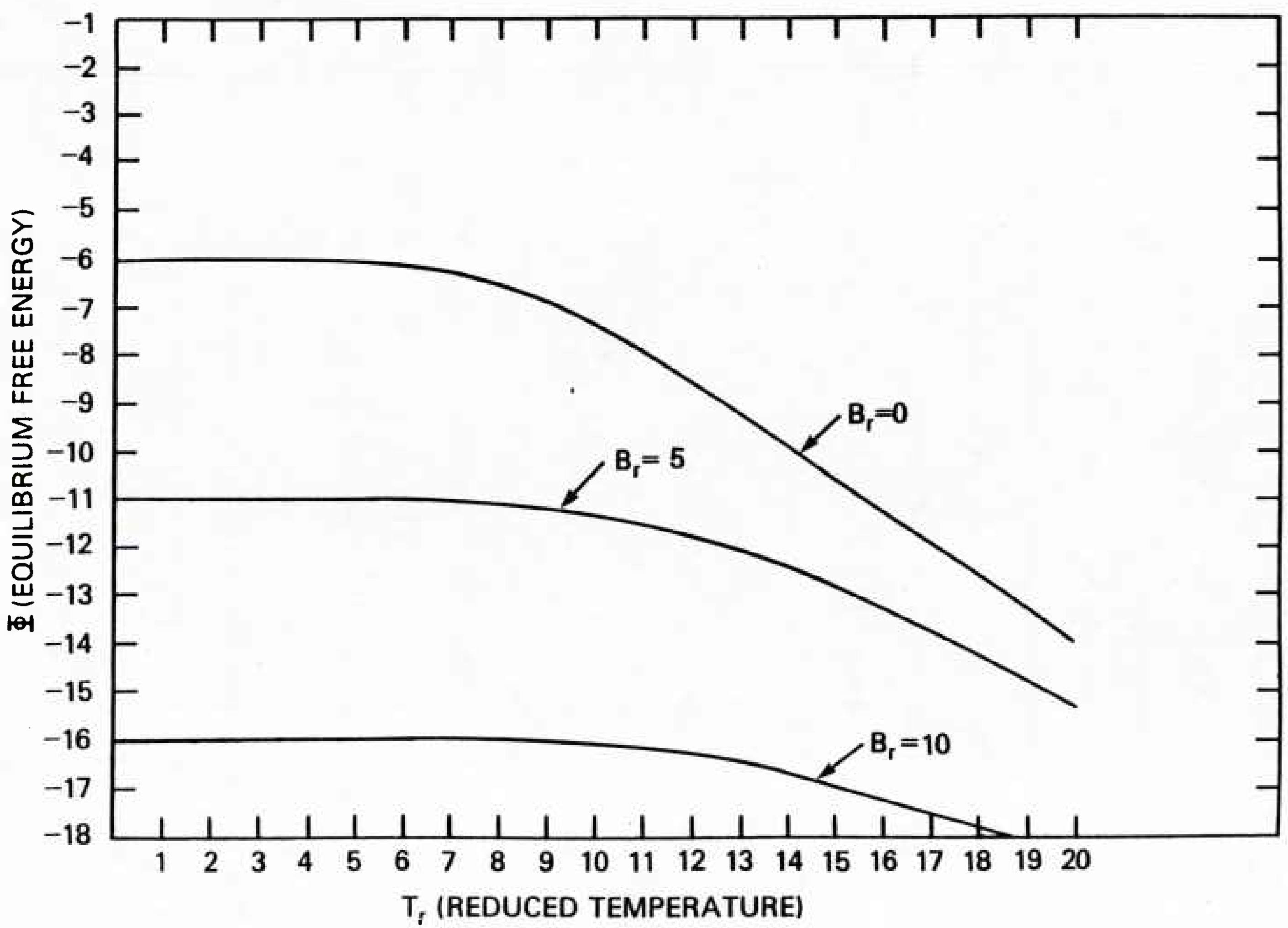


Fig. 9. EQUILIBRIUM FREE ENERGY Φ vs. TEMPERATURE T_r FOR VARIOUS VALUES OF MAGNETIC FIELD B_r (1 CLUSTER)

There are two branches for $x = x(T_r, 0)$ when $T_r < T_{r,c}^{1}$. $\mathfrak{F}$ is a minimum on one of these and is a maximum on the other. We use $d^2\mathfrak{F}/dx^2$ to determine which is which:

$$d^2\mathfrak{F}/dx^2 = -Z + T_r\{\tfrac{1}{2}[1/(1+x)] + \tfrac{1}{2}[1/(1-x)]\}$$

$$= -Z + \tfrac{1}{2}T_r[1/(1+x) + 1/(1-x)]$$

See Fig. 7. We observe that for $B_r = 0$, the branch $(x = 0)$ is always a solution of $(d\mathfrak{F}/dx) = 0$. However, this solution makes $\mathfrak{F}(x; T_r, B_r = 0)$ a minimum only for $T_r > T_{r,c}^{I} = Z$. For $T_r < T_{r,c}^{I}$, this branch makes $\mathfrak{F}(x; T_r, B_r = 0)$ a <u>maximum</u> (i.e., $d^2\mathfrak{F}/dx^2 < 0$). Thermostatic equilibrium occurs only when F is a minimum <u>vs.</u> changes in x. So, we select x-branches accordingly.

Magnetization x is compared in Fig. 10, to T_r for various values of the magnetic field B_r. Complete saturation is indicated by ±1, with all the spins up or down. A change of phase occurs when $B_r = 0$, and this is shown to occur in the figure for $T_{r,c}^{I} = 12$, and also derived in Eq. (8). The curve for $B_r = 0$ approaches the $x = 0$ line from either side, and almost crosses the line, before turning and becoming parallel with this line for values of $T_r > 12$.

The entropy for one particle clusters is presented in Fig. 11, as a function of the reduced temperature, for various values of the magnetic field. The entropy in bits per particle is calculated by dividing the entropy (joules/°K) by ln(2).

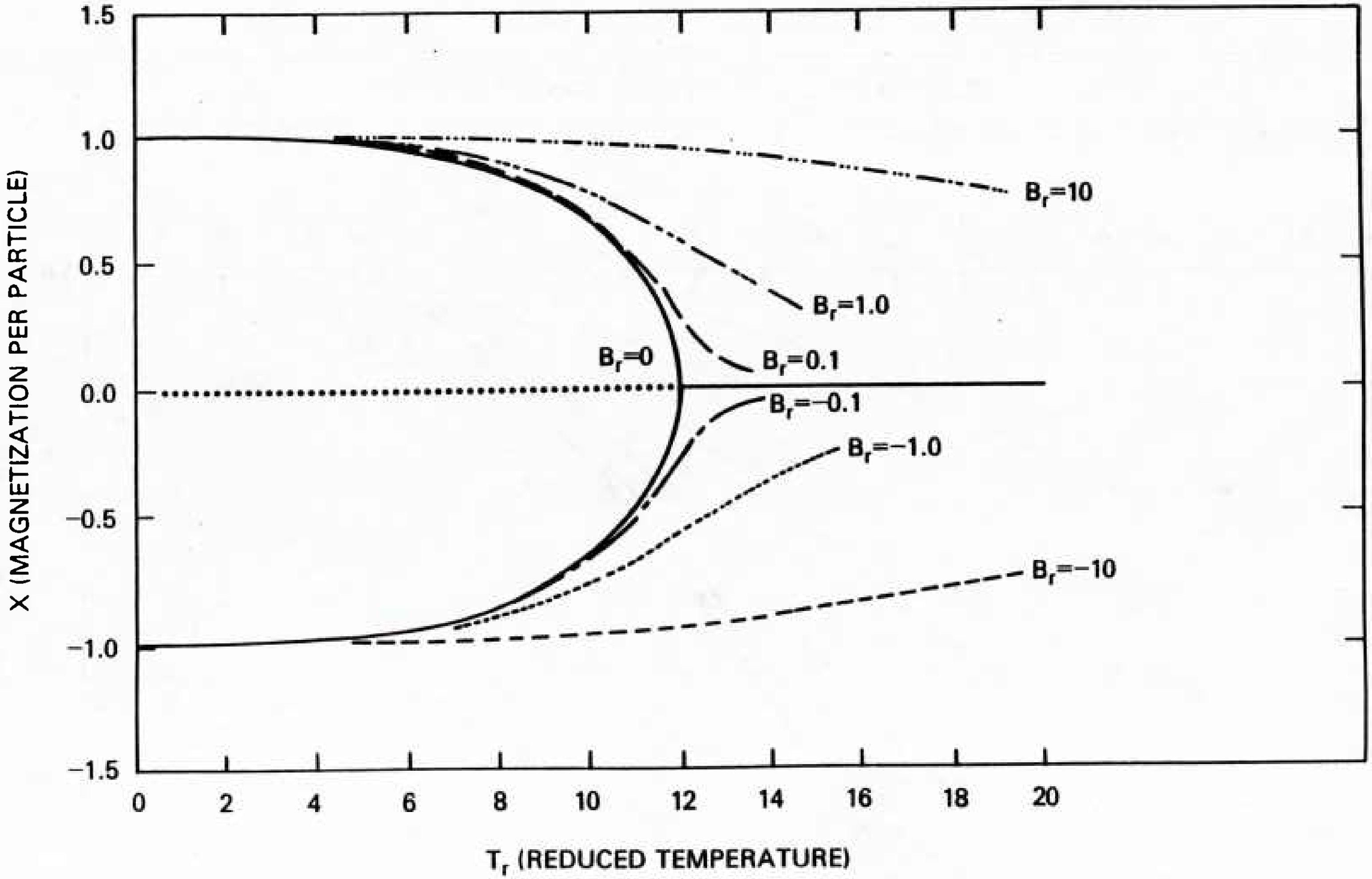


Fig. 10. MAGNETIZATION X vs. TEMPERATURE T_r FOR VARIOUS VALUES OF MAGNETIC FIELD B_r

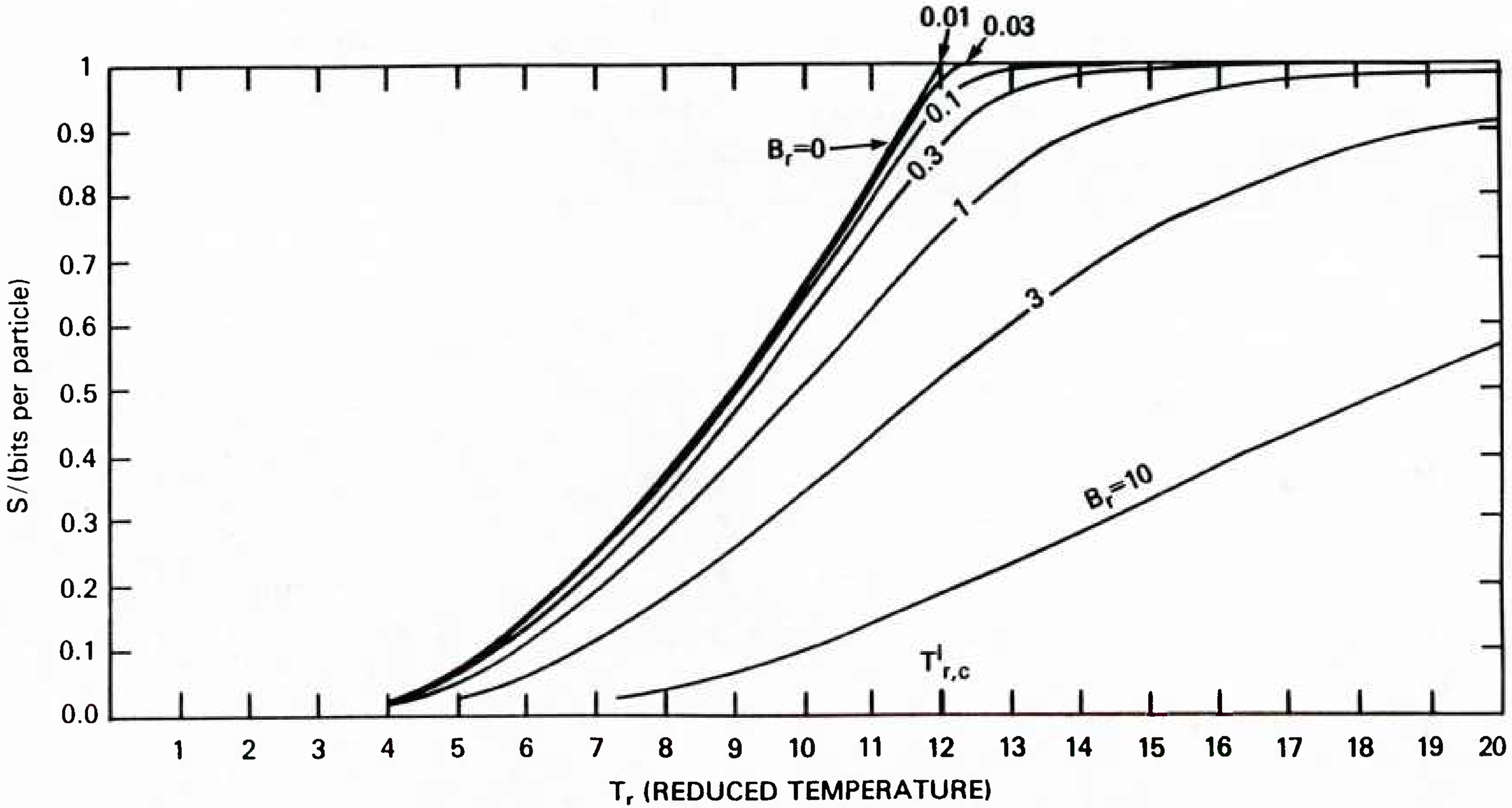


Fig. 11. ENTROPY FOR 1-PARTICLE CLUSTERS IN BITS PER PARTICLE vs. TEMPERATURE T_r AND FIXED MAGNETIC FIELD B_r. z=12

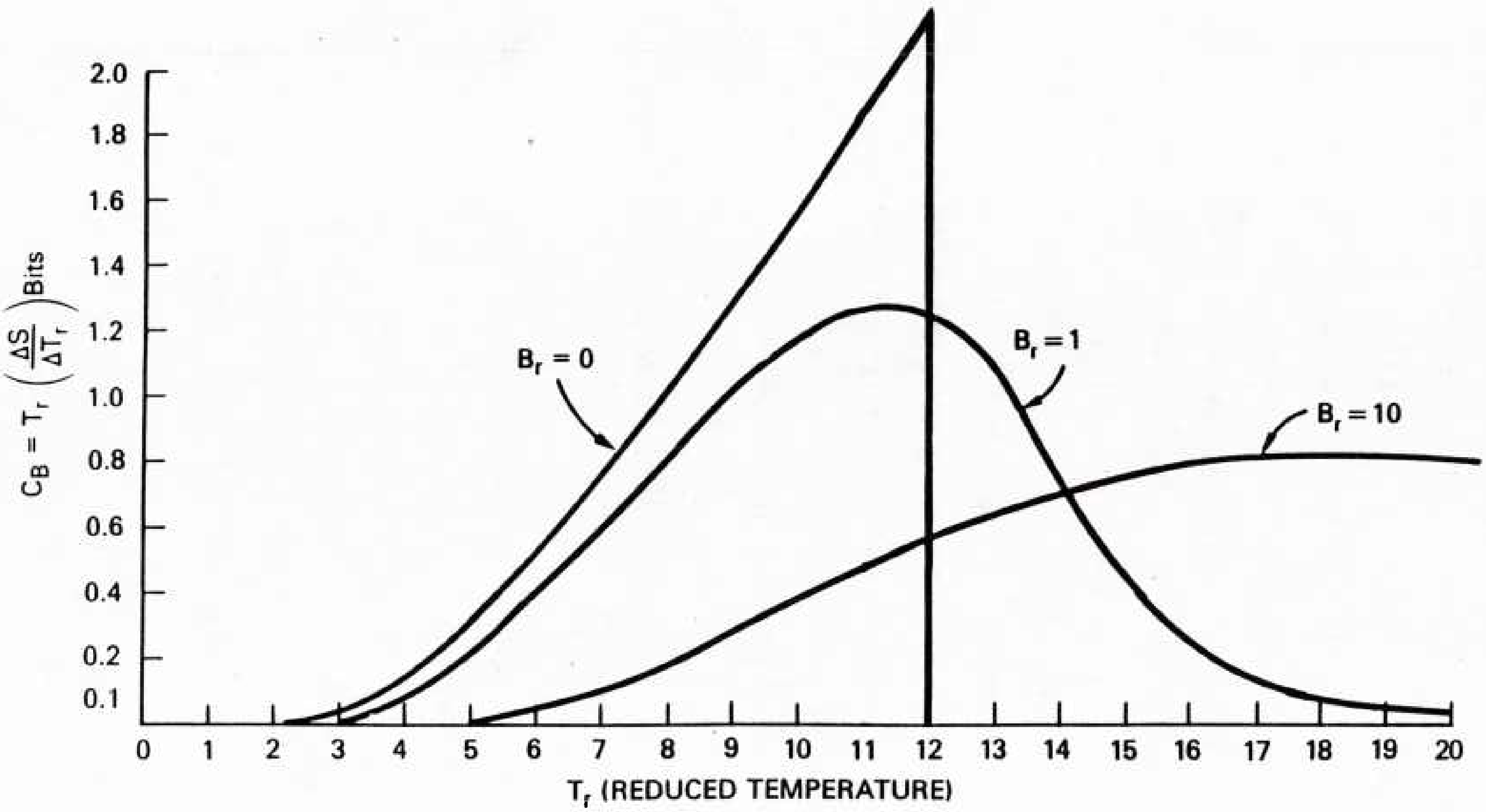


Fig. 12. SPECIFIC HEAT vs. REDUCED TEMPERATURE FOR AN FCC LATTICE (1-CLUSTER APPROXIMATION) (See Bragg - Williams Fig. 5).

The specific heat C_B is compared in Fig. 12 with T_r and different magnetic fields. These results can be compared directly with Fig. 5 from reference (17). The results in the first approximation, using the Morita expansion of the free energy, and truncating the series after the first term, are the same as the Weiss calculation for one particle systems using self-consistent field theory. In Fig. 5 (Ch. II) these results are labeled as Bragg - Williams, which is a refinement of Weiss's calculations.

A contour plot of the entropy in "bits" is presented in Fig. 13. This is only the entropy part of the free energy in Eq. (6) and all values are positive and above the x,y plane as they should be. This plot of the entropy will be referred to in subsequent approximations.

Second Order Approximation: Bethe-Peirels Theory (Two - Cluster Approximation)

Internal Energy:

The internal energy of the Lenz-Ising model is, in the second approximation,

$$U = \langle H \rangle = -\mu_0 BNx - \tfrac{1}{2}JNZy_1 \qquad (9)$$

where $x = x_i^{(1)}$, $y_p = x_{i,i+p}^{(2)}$,

and the interaction energy is represented by $\tfrac{1}{2}JNZy_1$.

Compare to U in the first approximation where $y = x^2$.

Entropy:

The entropy is

$S = S^{\hat{}(1)} + S^{\hat{}(2)}$

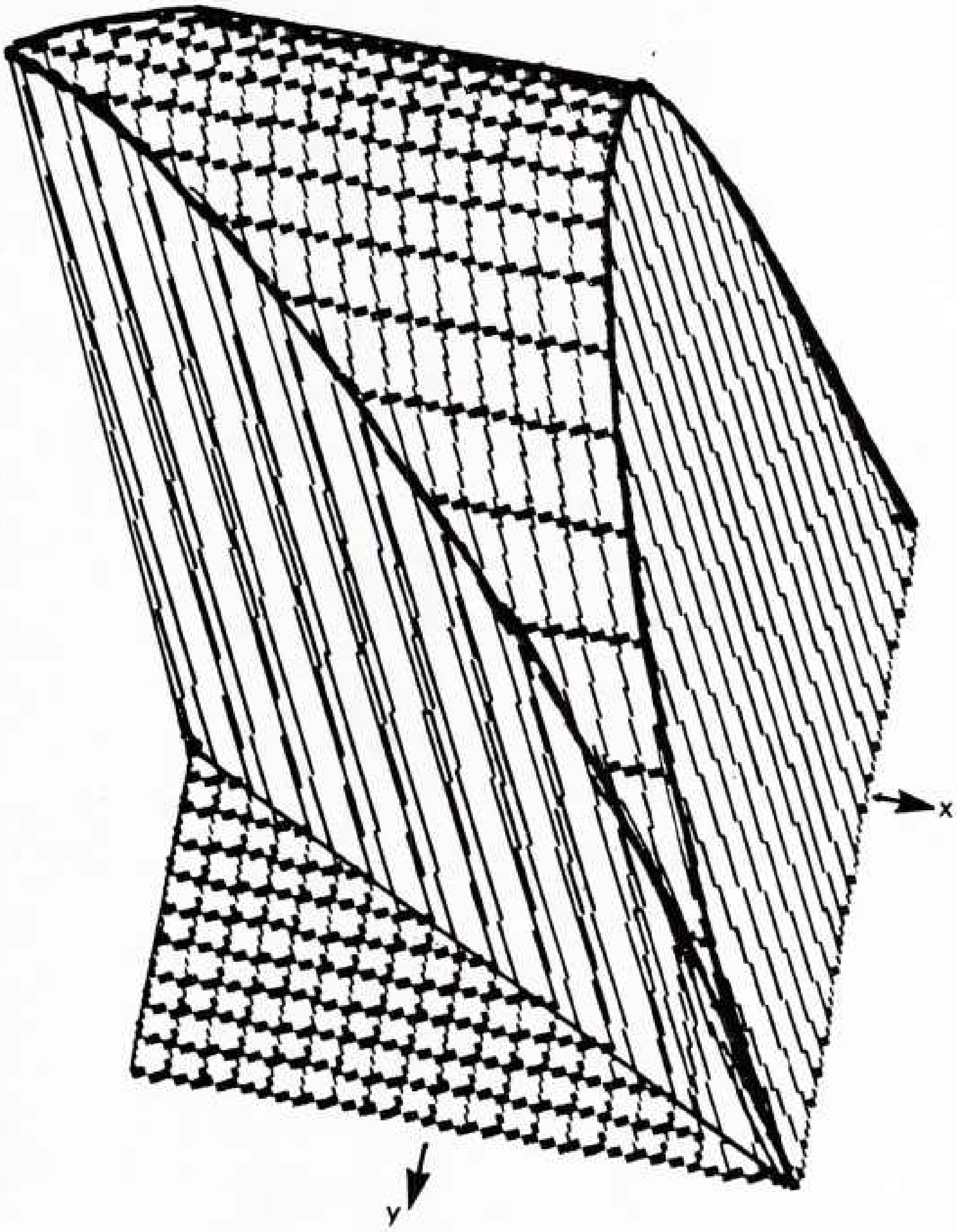


Fig. 13. ENTROPY FOR 1-PARTICLE CLUSTERS (UNITS ARE BITS) vs. x,y.

i.e. for the first two terms of the free energy expansion where

$$\hat{S}^{(1)} = \Sigma_{i=1}^{N} \hat{S}_i^{(1)} = N\hat{S}^{(1)}$$

$$\hat{S}^{(1)} = - Nk_B[\tfrac{1}{2}(1+x)\ln(.) + \tfrac{1}{2}(1-x)\ln(.)]$$

$$\hat{S}^{(2)} = \Sigma_{(i,j)}[S_{ij}^{(2)} - S_i^{(1)} - S_j^{(1)}]$$

$$\hat{S}^{(2)} = \tfrac{1}{2}Nk_B\Sigma_p Z_p[S^{(2)}_{i,i+p} - 2S^{(1)}_i]$$

$\hat{S}^{(1)}$ is all the entropy for 1-particle clusters and $\hat{S}^{(2)}$ is all the entropy for 2-particle clusters.

where p = spacing of a pair of particles

Z_p = pair coordination number

= number of pairs of spacing p.

$$\hat{S}^{(2)} = -\tfrac{1}{2}Nk_B\Sigma_p Z_p\{[\tfrac{1}{4}(1+2x+y_p)\ln(.)$$
$$+2(\tfrac{1}{4})(1-y_p)\ln(.) + \tfrac{1}{4}(1-2x+y_p)\ln(.)]$$
$$-2[\tfrac{1}{2}(1+x)\ln(.) + \tfrac{1}{2}(1-x)\ln(.)]\}$$

Free Energy:

The Helmholtz free energy is

$$F = U - TS$$

$$\Phi = F/NJ = (U - TS)/NJ$$

$$\Phi = -B_r x - \tfrac{1}{2}Zy_1 + T_r\{\tfrac{1}{2}(1+x)\ln(.) + \tfrac{1}{2}(1-x)\ln(.)$$
$$+ \tfrac{1}{2}\Sigma_p Z_p\{[\tfrac{1}{4}(1+2x+y_p)\ln(.) + 2(\tfrac{1}{4})(1-y_p)\ln(.)$$
$$+ \tfrac{1}{4}(1-2x+y_p)\ln(.)]$$
$$- 2[\tfrac{1}{2}(1+x)\ln(.) + \tfrac{1}{2}(1-x)\ln(.)]\}\} \qquad (10)$$

The equilibrium state of this system is found by differentating Φ with respect to x and y_1:

[x eqn]

$$0 = (\delta\Phi/\delta x)$$

$$0 = -B_r + T_r\{\tfrac{1}{2}\ln\tfrac{1}{2}(1+x) - \tfrac{1}{2}\ln\tfrac{1}{2}(1-x)$$

$$+ \tfrac{1}{2}\Sigma_p Z_p \{[2(\tfrac{1}{4})\ln\tfrac{1}{4}(1+2x+y_p)$$

$$- 2(\tfrac{1}{4})\ln\tfrac{1}{4}(1-2x+y_p)]$$

$$- 2[\tfrac{1}{2}\ln\tfrac{1}{2}(1+x) - \tfrac{1}{2}\ln\tfrac{1}{2}(1-x)]\}.$$

$$2B_r/T_r = \ln \frac{1+x}{1-x} + \tfrac{1}{2}\Sigma_p Z_p [\ln \frac{1+2x+y_p}{1-2x+y_p} - 2\ln \frac{1+x}{1-x}]$$

[y_p eqn]

$$0 = (\delta\Phi/\delta y_p)$$

$$0 = -\tfrac{1}{2}Z\delta_{p1} + \tfrac{1}{2}T_r\{Z_p[\tfrac{1}{4}\ln\tfrac{1}{4}(1+2x+y_p)$$

$$-\tfrac{1}{2}\ln\tfrac{1}{4}(1-y_p) + \tfrac{1}{4}\ln\tfrac{1}{4}\ln(1-2x+y_p)]\}$$

Hence:

$$4Z_1\delta_{p1} = T_r Z_p \ln[\frac{(1+2x+y_p)(1-2x+y_p)}{(1-y_p)^2}]$$

We must solve these two simultaneous equations.

Let p>1. Then the [y_p equation] is (for $T_r > 0$)

$$0 = \ln \left[\frac{(1+2x+y_p)(1-2x+y_p)}{(1-y_p)^2}\right]$$

since Z_p =/0 for any p. Hence,

$$\frac{(1+2x+y_p)(1-2x+y_p)}{(1-y_p)^2} = 1$$

$$(1+2x+y_p)(1-2x+y_p) = (1-y_p)^2$$

$$(1+2x)(1-2x) + [(1+2x)+(1-2x)]y_p + y_p^2 = 1-2y_p+y_p^2$$

$$4x^2+2y_p = -2y_p$$

from which we find

$$y_p = x^2 \quad , \quad p>1$$

That is, in the "2-cluster approximation", spin-correlation extends exactly as far as spin-interaction, which is "nearest - neighbor" in this case.

We can now simplify the [x] equation:

$$\Sigma_{p>1} Z_p \left[\ln \frac{1+2x+y_p}{1-2x+y_p} - 2\ln \frac{1+x}{1-x}\right]$$

$$= \Sigma_{p>1} Z_p \left[\ln \frac{1+2x+x^2}{1-2x+x^2} - 2\ln \frac{1+x}{1-x}\right]$$

$$= \Sigma_{p>1} Z_p \left[\ln \left(\frac{1+x}{1-x}\right)^2 - 2\ln \frac{1+x}{1-x}\right] = 0$$

Hence, the equations become:

$$[x] \quad 2B_r/T_r = \ln \frac{1+x}{1-x} + \tfrac{1}{2}Z_1 \left[\ln \frac{1+2x+y_1}{1-2x+y_1} - 2\ln \frac{1+x}{1-x}\right]$$

$$[y] \quad 4/T_r = \ln\left[\frac{(1+2x+y_1)(1-2x+y_1)}{(1-y_1)^2}\right] \qquad (11)$$

These are transendental when regarded as determining x & y as functions of T_r & B_r.

Certain results can be extracted from $[x]$ & $[y_1]$:

1. When $B_r = 0$, inspection shows that $(x = 0)$ is always a solution of $[x]$. We then use $[y_1]$ to determine $y_1 = y_1(T_r, 0)$:

$$4/Tr = \ln \frac{(1+y_1)^2}{(1-y_1)^2}$$

implies $$2/Tr = \ln \frac{1+y_1}{1-y_1} = 2\operatorname{arctanh} y_1$$

$$y_1 = \tanh 1/T_r$$

See the following derivation for this result.

$$[\text{Let } a = \ln \frac{1+y}{1-y} \text{ , } \frac{1+y}{1-y} = \exp(a) = b \text{ , } 1+y = b-by \text{ ,}$$

$$by+y = b-1 \text{ , } (1+b)y = b-1 \text{ , } y = \frac{b-1}{b+1} = \frac{\exp(a)-1}{\exp(a)+1} \text{ ,}$$

$$y = \frac{\exp(a/2)-\exp(a/2)}{\exp(a/2)+\exp(a/2)} = \tanh(a/2)$$

$$a = 2\operatorname{arctanh} y$$

See figure 14 and 15 for a plot of x vs. T_r and y vs. T_r.

An alternative method was actually used to generate the results plotted in figure 14 and 15. This is the Simplex method of minimization, and does not use the methods of calculus to achieve a minimum value for a function[6]. In this approximation it is used as a convenient method to obtain the results shown in these figures. The same results would be obtained by solving the minimum equations for [x] and [y] given by Eq. (11). It will be shown in later approximations that it is necessary to use the Simplex method to mimimize the free energy equations that are obtained by truncating the Morita expansion of the free energy. It will be shown in these higher approximations that the mimima occur on the boundary of the function, and minimization using the methods of calculus will not work in these situations. The Simplex program for this second approximation is listed in Appendix E.

The equilibrium free energy is given in Fig. 16 as a function of T_r for various values of B_r. If this result is compared with Fig. 9 in the 1-cluster result it will show that the equilibrium free energy results are the same in both cases, at least to the accuracy of the grid size used

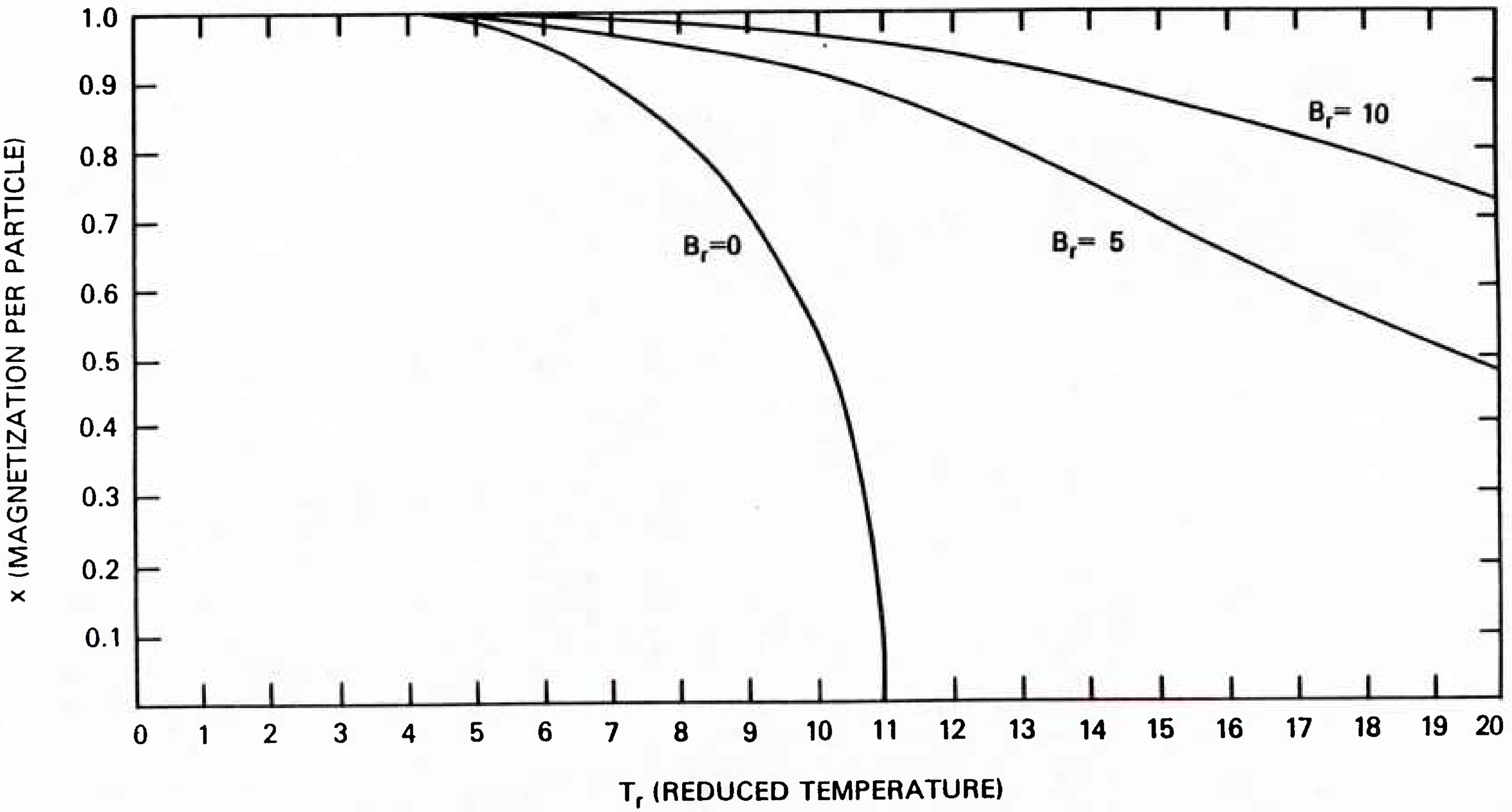


Fig. 14. MAGNETIZATION x vs. TEMPERATURE T_r FOR VARIOUS VALUES OF MAGNETIC FIELD B_r (1,2-CLUSTER APPROXIMATION)

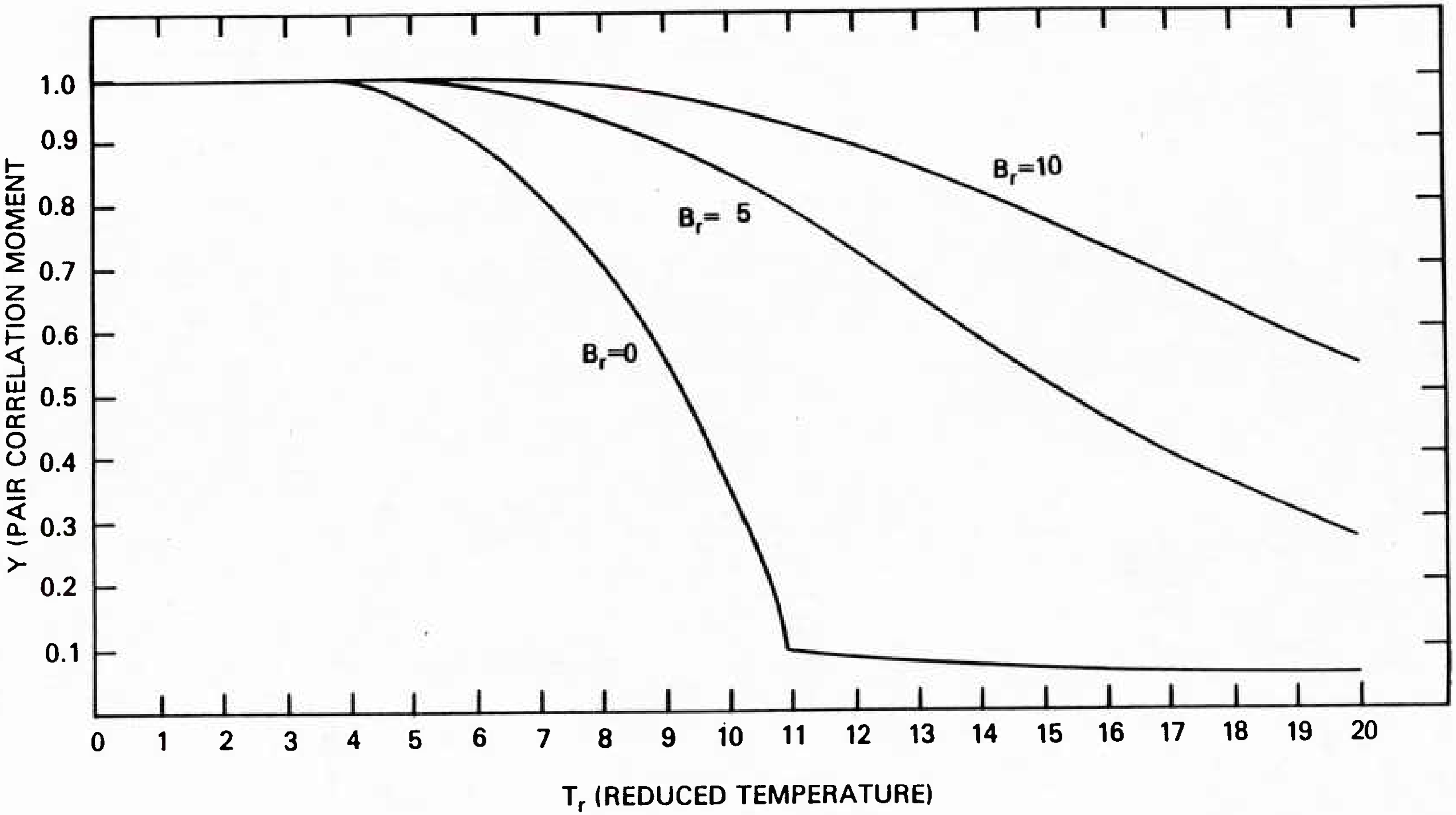


Fig. 15. PAIR CORRELATION MOMENT y vs. TEMPERATURE T_r FOR VARIOUS VALUES OF MAGNETIC FIELD B_r (1,2-CLUSTER APPROXIMATION)

to plot these results. See Appendix G, Table 2 for the actual values of the equilibrium free energy.

2. There is a critical temperature. We can deterrmine it as we did for the 1-cluster approximation, by setting the conditions

$$B_r = 0 \text{ and } (x \approx 0 \;\&\; x \neq 0)$$

[x]
$$0 = 2x + \tfrac{1}{2}Z_1 \left[\frac{4x}{1+y_1} - 4x \right]$$

implies $y_1 = \dfrac{1}{(Z_1 - 1)}$

as can be shown below.

$$0 = 1 + Z_1 \left[\frac{1}{1+y_1} - 1 \right]$$

$$\frac{1}{Z_1} = 1 - \frac{1}{1+y_1} = \frac{(1+y_1) - 1}{1+y_1} = \frac{y_1}{1+y_1}$$

$$Z_1 = \frac{y_1 + 1}{y_1} = 1 + \frac{1}{y_1}$$

$$Z_1 - 1 = \frac{1}{y_1}, \quad y_1 = \frac{1}{Z_1 - 1}$$

That is, at $T_{r,c}^{II}$, $y_1 = (Z_1 - 1)^{-1}$. We use this in [y_1] to determine $T_{r,c}$:

$$T_{r,c}^{II} = \frac{2}{\ln \dfrac{1+y_1}{1-y_1}} = \frac{2}{\ln\left[\left(1+\dfrac{1}{Z_1-1}\right)\left(1-\dfrac{1}{Z_1-1}\right)^{-1}\right]} = \frac{2}{\ln \dfrac{Z_1-1+1}{Z_1-1-1}}$$

$$= \frac{2}{\ln \dfrac{Z_1}{Z_1 - 2}} = \frac{2}{\ln \dfrac{1}{1 - 2(Z_1)^{-1}}}$$

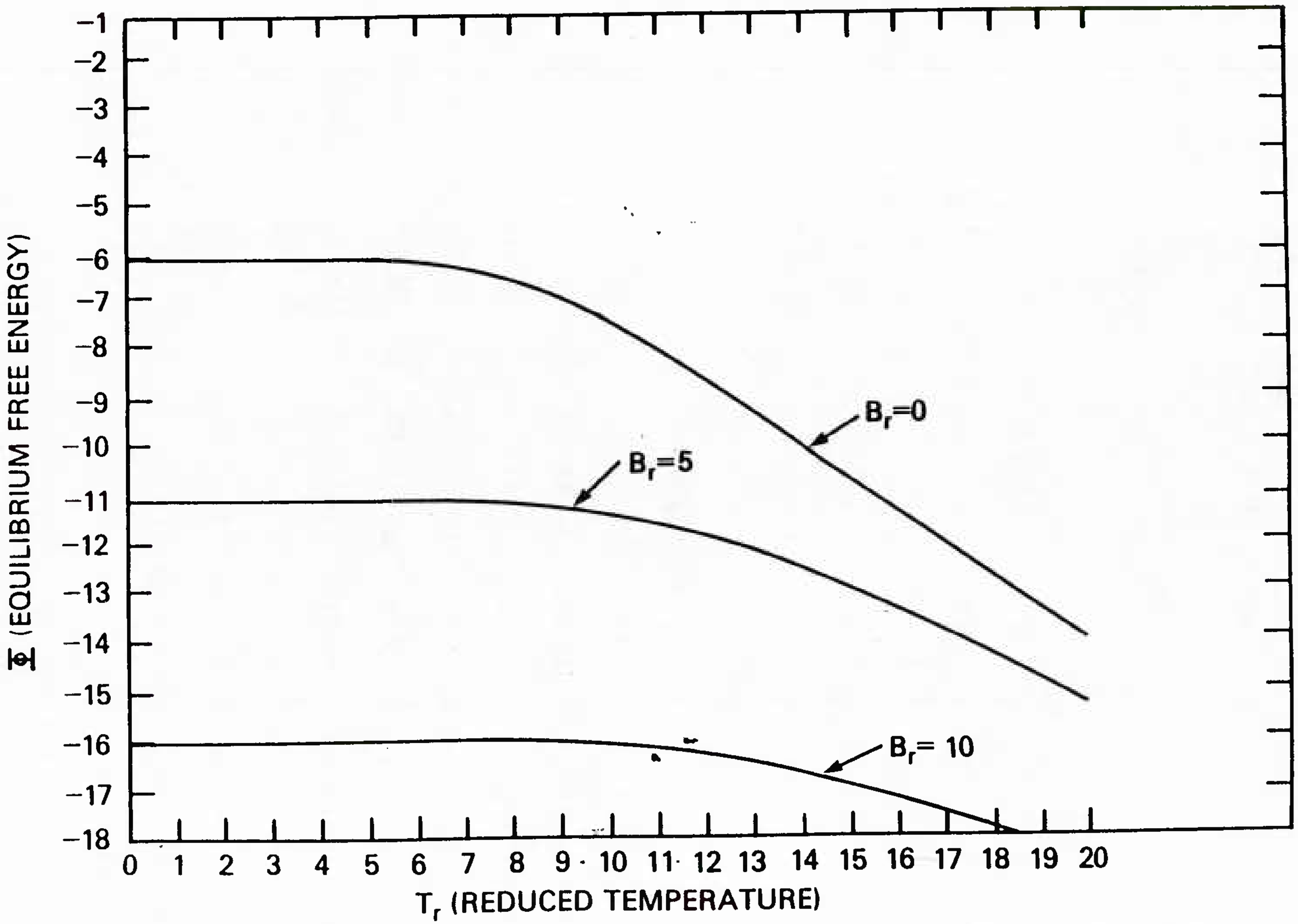


Fig. 16. EQUILIBRIUM FREE ENERGY Φ vs. TEMPERATURE T_r FOR VARIOUS VALUES OF MAGNETIC FIELD B_r (1,2-CLUSTER APPROXIMATION)

Expanding this as a series in $1/Z_1$ allows convenient comparison with $T_{r,c}{}^{I}$:

$$T_{r,c}{}^{II} = -\frac{2}{-2/Z_1 - \tfrac{1}{2}(2/Z_1)^2 - 1/3(2/Z_1)^3 + \ldots}$$

$$= -\frac{2}{(-2/Z_1)[1 + \tfrac{1}{2}(2/Z_1) + 1/3(2/Z_1)^2 + \ldots]}$$

$$= -\frac{Z_1}{1 + \tfrac{1}{2}(2/Z_1) + 1/3(2/Z_1)^2 + \ldots}$$

$$= Z_1\{1 - [\tfrac{1}{2}(2/Z_1) + 1/3(2/Z_1)^2 + \ldots]$$

$$+[\tfrac{1}{2}(2/Z_1) + \ldots]^2 + \ldots\}$$

$$= Z_1\{1 - \tfrac{1}{2}(2/Z_1) + (-1/3 + 1/4)(2/Z_1)^2 + \ldots\}$$

$$= Z_1\{1 - 1/Z_1 - (1/3)(1/Z_1)^2 - \ldots\}$$

$$= Z_1 - 1 - (1/3)(1/Z_1) + \ldots$$

$$= T_{r,c}{}^{I} - 1 - (1/3)(1/T_{r,c}{}^{I}) + \ldots$$

$$= T_{r,c}{}^{I}[1 - 1/Z_1 - (1/3)(1/(Z_1)^2 - \ldots]$$

As in the "1-cluster" approximation, the critical temperature depends on the crystal lattice structure -- including its dimension -- only through Z_1 = the number of nearest neighbors, 12 (See Fig. 1, Ch. I). So, for example, the two dimensional hexagonal lattice has the same behavior as the three dimensional cubic, in this approximation. Since exact calculations show that their behaviors are different, we note that a dependence on only Z_1 is a failing of this approximation.

It is well-know that these sorts of approximations become more exact as $Z_1 \to \infty$ (i.e., as dimension --> ∞), and becomes very bad as $Z_1 \to 2$ (i.e., as dimension $\to 1$).

We now examine the stability of the solutions :

$$\Phi_{xx} = \frac{\delta^2\Phi}{\delta x^2} = \frac{T_r}{2}\left[\frac{1}{1+x} + \frac{1}{1-x} + \Sigma_p Z_p\left(\frac{1}{1+2x+y_p} + \frac{1}{1-2x+y_p} - \frac{1}{1+x} - \frac{1}{1-x}\right)\right]$$

$$\Phi_{y_p x} = \frac{\delta^2\Phi}{\delta y_p \delta x} = \frac{T_r}{4}\Sigma_p Z_p\left(\frac{1}{1+2x+y_p} - \frac{1}{1-2x+y_p}\right)$$

$$\Phi_{x y_p} = \frac{\delta^2\Phi}{\delta x \delta y_p} = \frac{T_r}{4} Z_p\left(\frac{1}{1+2x+y_p} - \frac{1}{1-2x+y_p}\right)$$

$$\Phi_{y_p y_p} = \frac{\delta^2\Phi}{\delta y_p^2} = \frac{T_r}{8} Z_p\left(\frac{1}{1+2x+y_p} + \frac{2}{1-y_p} + \frac{1}{1-2x+y_p}\right)$$

Evaluating these on the branch :

$$B_r = 0, \quad x = 0 \quad \& \quad y_1 = \tanh 1/T_r, \quad y_{p>1} = 0$$

gives:

$$\frac{\delta^2\Phi}{\delta x^2} = \frac{T_r}{2}\left[2 + Z_1\left(\frac{2}{1+y_1} - 2\right) + \Sigma_{p>1} Z_p(0)\right] = T_r\left[1 + Z_1\left(\frac{1}{1+y_1} - 1\right)\right]$$

$$\frac{\delta^2\Phi}{\delta x \delta y_p} = \frac{T_r}{4} Z_p(0) = 0$$

$$\frac{\delta^2\Phi}{\delta y_p^2} = \frac{T_r Z_p}{4}\left[\begin{array}{ll} 1(1+y_1)^{-1} + 1(1-y_1)^{-1} & p=1 \\ 0 & p>1 \end{array}\right]$$

Inspection shows that the branch $B_r = 0$, $x = 0$, $y_p = \begin{cases} \tanh 1/T_r & p=1 \\ 0 & p>1 \end{cases}$

is stable ($\Phi'' > 0$) for $T_r > T_{r,c}^{II}$, but is unstable

($\Phi_{xx} < 0$) for $T_r < T_{r,c}^{II}$.

There is another branch for $B_r = 0$ & $x \neq 0$;

it is stable for $T_r < T_{r,c}^{II}$. We now study it ...

Equation [x] can be solved for $y_1 = y_1(x; B_r/T_r)$:

$$[\ln \frac{1+2x+y_1}{1-2x+y_1} - 2\ln \frac{1+x}{1-x}] = (\frac{2B_r}{T_r} - \ln \frac{1+x}{1-x})(Z_1/2)^{-1}$$

$$\ln \frac{1+2x+y_1}{1-2x+y_1} = 2[\frac{1}{Z_1}(\frac{2B_r}{T_r} - \ln \frac{1+x}{1-x}) + \ln \frac{1+x}{1-x}]$$

$$\ln \frac{1+2x+y_1}{1-2x+y_1} = 2[\frac{2B_r}{Z_1 T_r} + (1 - \frac{1}{Z_1})\ln \frac{1+x}{1-x}] = a$$

$$\longrightarrow (1+2x+y_1)/(1-2x+y_1) = \exp a = b$$

$$\longrightarrow 1+2x+y_1 = b-2bx+by_1$$

$$y_1 - by_1 = b-2bx-1-2x$$

$$(1-b)y_1 = (b-1)-2x(1+b)$$

$$\longrightarrow y_1 = -1-2x[(1+b)/(1-b)] = -1 +2x[(1+\exp a)/(-1+\exp a)]$$

$$y_1 = -1 +2x[(\exp a+1)/(\exp a-1)]$$

$$y_1 = -1 + 2x/(\tanh\{2B_r/Z_1 T_r + (1-1/Z_1)\ln[(1+x)/(1-x)]\})^{-1}$$

Suppose $B_r = 0$ and $Z_1 \longrightarrow \infty$. Then

$$y_1 = -1 + 2x/(\tanh\{\ln[(1+x)/(1-x)]\})^{-1}$$

$$= -1 +2x/[4x/(2+2x2)] =-1 + 1 + x^2 = x^2$$

as we would expect.

Suppose $B_r = 0$. Then

$$y_1 = -1 + 2x/(\tanh\{(1-1/Z_1)\ln[(1+x)/(1-x)]\})^{-1}$$

Also for $x \sim 0$, we find:

$$y_1 = -1 + 2x/\tanh[(1-1/Z_1)(2x)]$$

$$= -1 + 2x/(1-1/Z_1)2x$$

$$= -1 + 1/(1-Z_1) = (-1 + 1/Z_1 + 1)/(1 - 1/Z_1)$$

$$= 1/(Z_1 - 1)$$, as expected.

These results are plotted in Fig. 17, with y_1 vs x.

We observe a deviation from the 1-cluster result, $y = x^2$, as a result of including pair-correlation effects.

This result for $y_1 = y_1(x;B_r/T_r)$ can be used in the $[y_1]$-eqn,

$$[y_1] \qquad 4/T_r = \ln \frac{(1+2x+y_1)(1-2x+y_1)}{(1-y_1)^2}$$

to calculate Tr as a function of x & Br/Tr. The results,

$$y_1 = y_1(x;B_r/T_r)$$

$$T_r = T_r(x;B_r/T_r)$$

can be inverted to give

$$x = x(T_r,B_r)$$

$$y_1 = y_1(T_r,B_r) \; .$$

of course, $y_{p>1} = x^2$.

[Results ... in the same pattern as for 1-cluster case.]

Although the results in this 1- and 2-cluster approximation seem to be reasonable e.g. a real critical temperature is calculated, it was discovered that already at this level of approximation there is a problem with truncating the free energy expansion. The results of this difficulty will show up very clearly in the next higher cluster, i.e. the 3-cluster approximation, where for example, a complex value is obtained for the critical temperature. The following figures will illustrate the roots of the problem.

In Fig. 18 we plot only the internal energy part of

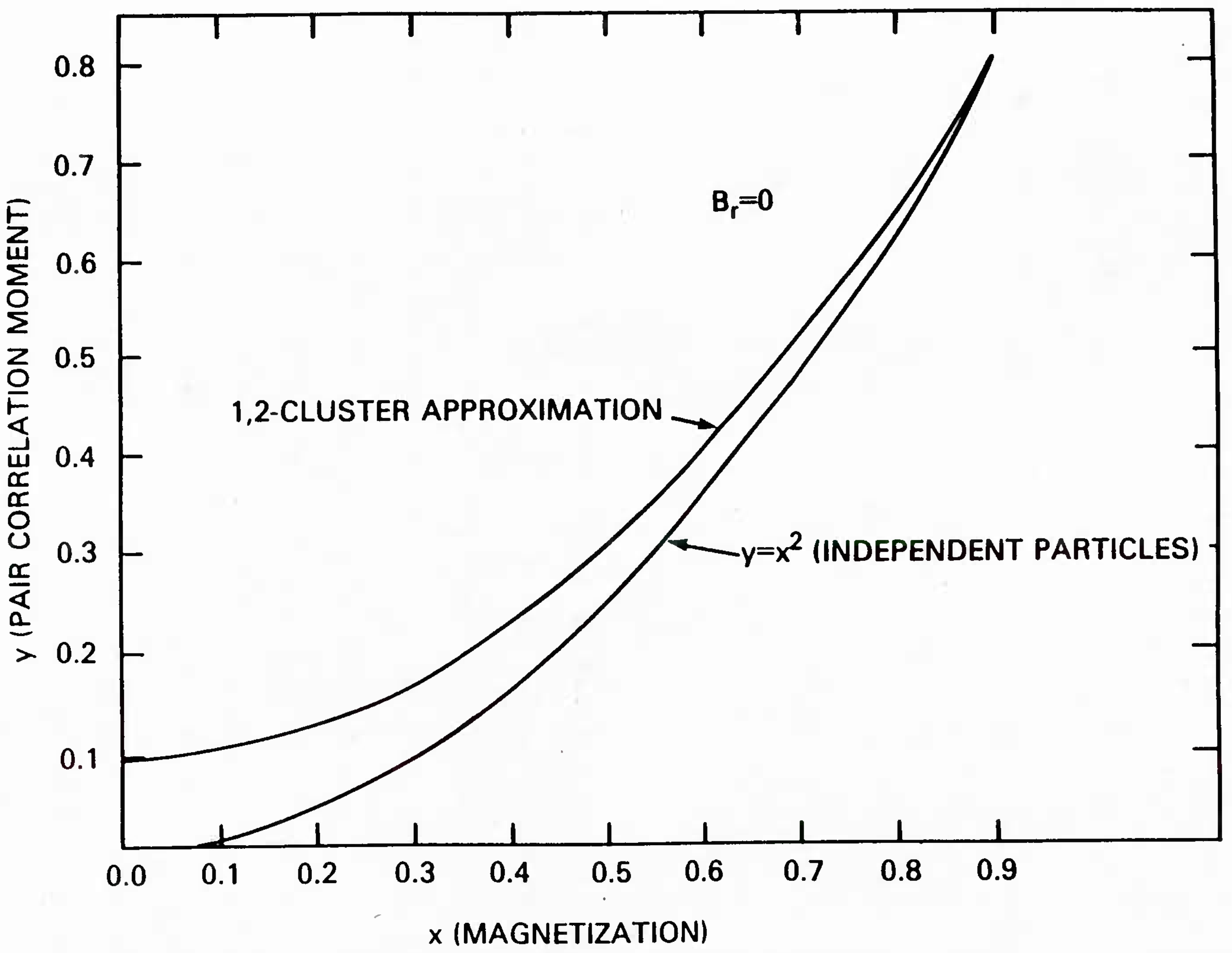


Fig. 17. 1,2-CLUSTER APPROXIMATION FOR y COMPARED TO 1 CLUSTER ($y=x^2$)

Eq. 10 for the free energy, which is the same as given by Eq. 9. The contour plotting method used in these results is similar to those discussed in [23],[24],[25]. In Fig. 19 only the entropy part of the free energy is plotted. This shows some very unphysical behavior where the entropy becomes negative for some regions of the x,y plane. This of course is physically impossible, and will be a particular problem in the next higher approximations.

Figures 20 and 21 show the entire free energy given by Eq. 10. It shows two minima, and the illustrates the distortion in the free energy surface due to the behavior of the entropy. This distortion will become worse with the third approximation, and the minima will occur on the boundary, where the methods of calculus cannot be used to find a minimum. This 2-cluster approximation has illustrated the effect of truncating the free energy expansion, although the difficulties resulting from this truncation are more evident in the 3-cluster results. A listing of the program HIDDEN6 used in this contour plotting is given in Fig. 33 of Appendix E.

Third Order Approximation: Limited 3-Cluster

We will restrict ourselves to a "square" lattice and include only nearest neighbor and next-nearest neighbor pairs and retain only the most compact triplet and ignore all other n-clusters ($n \geq 2$).

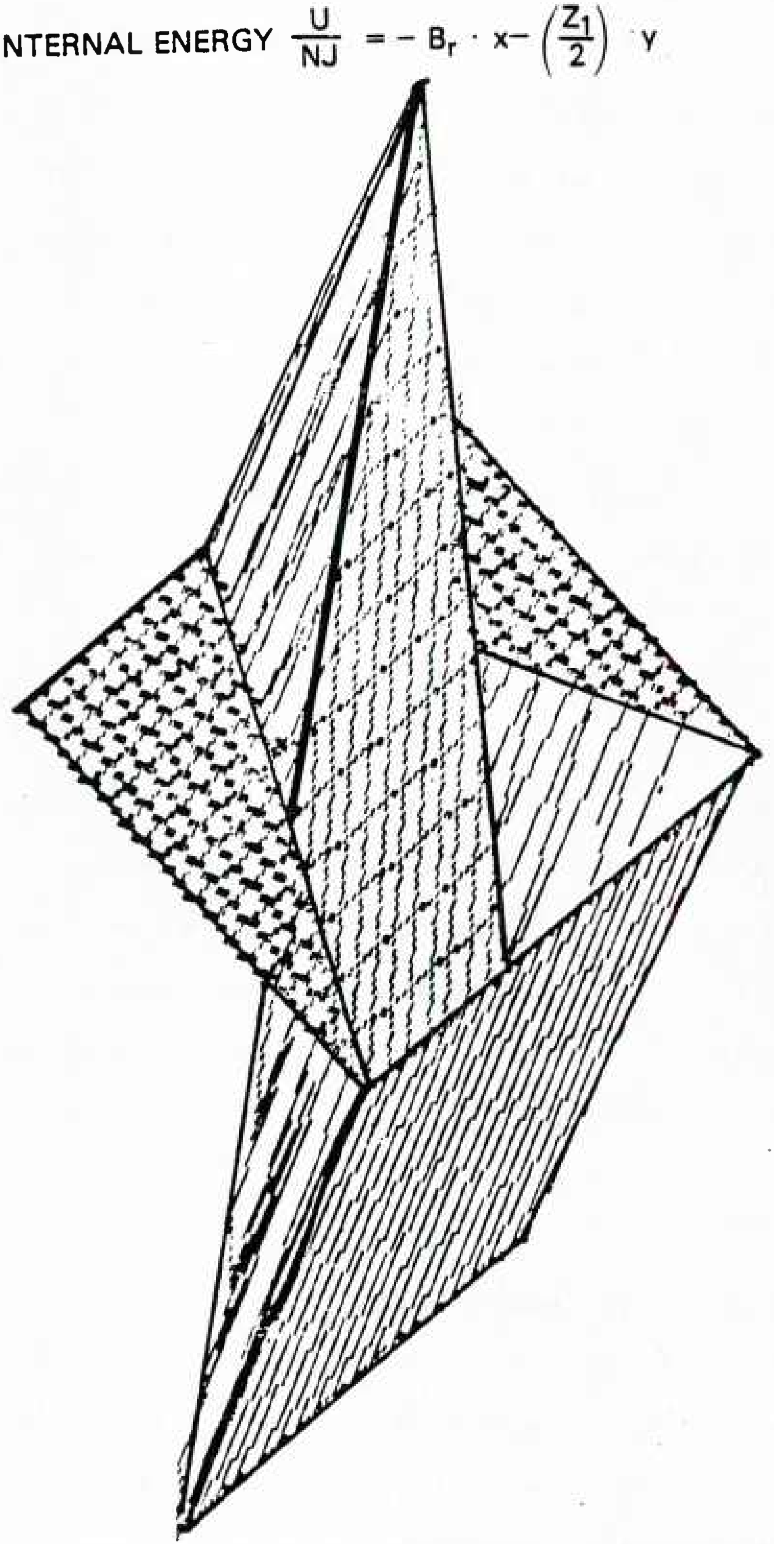


Fig. 18. INTERNAL ENERGY ONLY FOR 1,2-PARTICLE CLUSTERS vs. x,y WITH B_r=0.

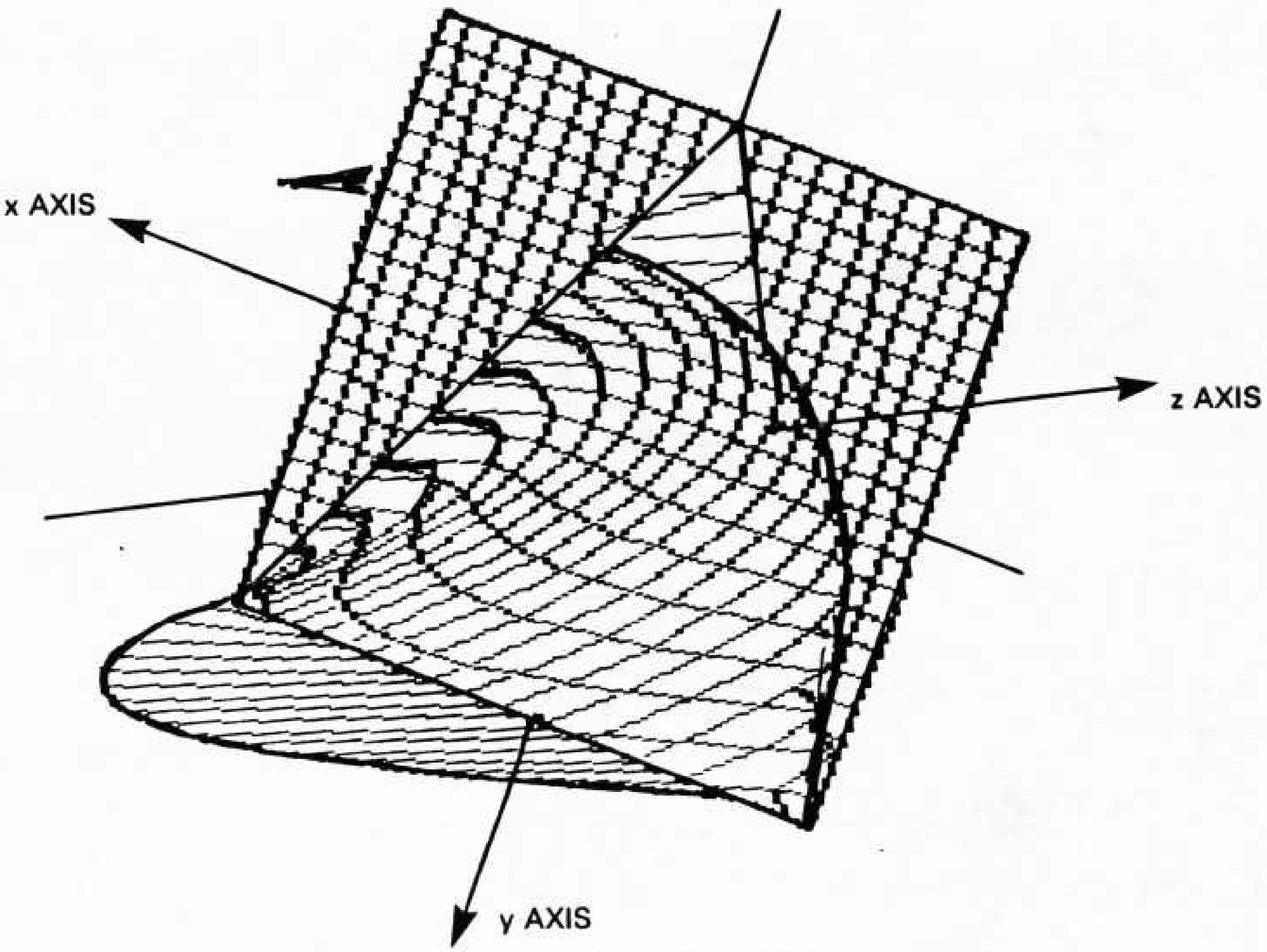


Fig. 19. ENTROPY (IN BITS) FOR 1,2-PARTICLE CLUSTERS vs. x,y

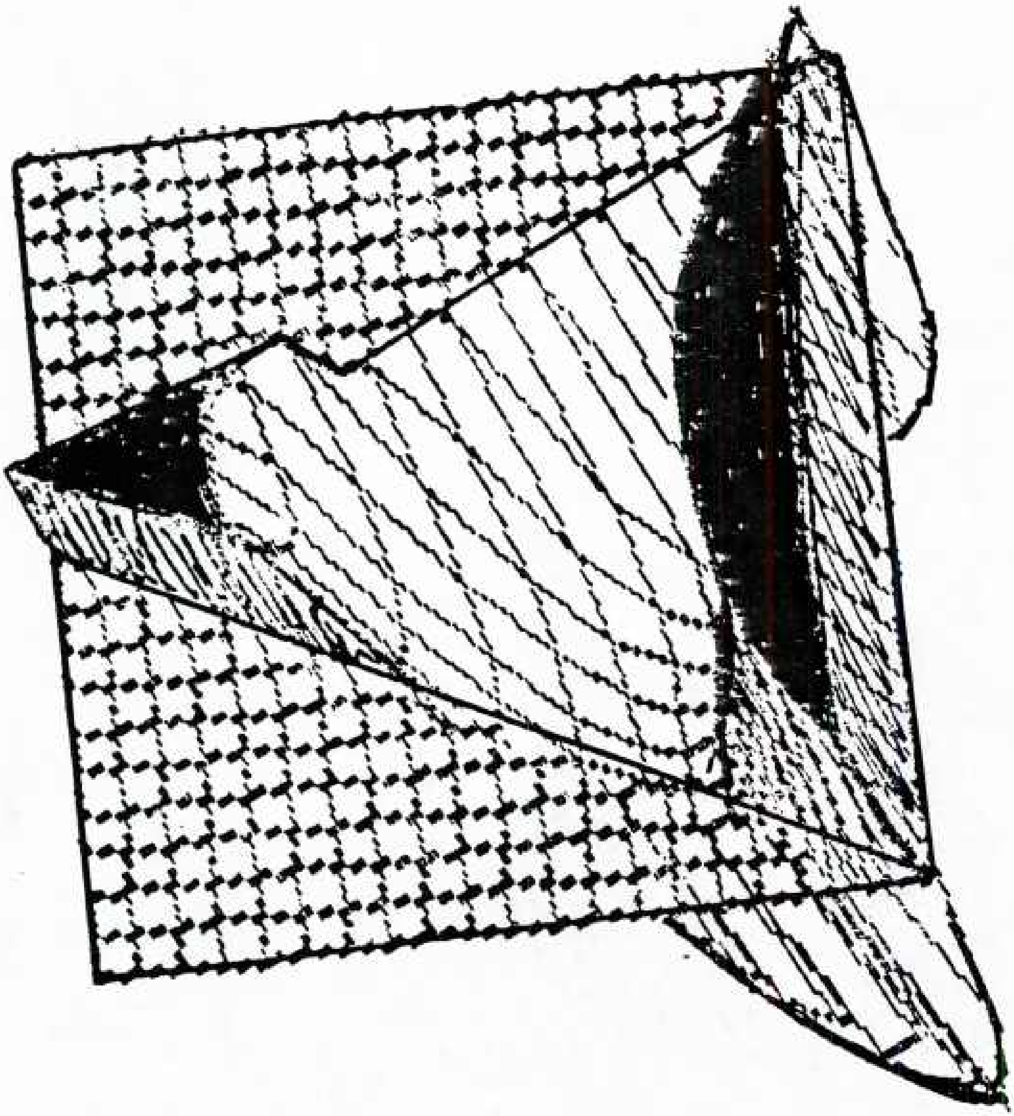


Fig. 20. Φ (INTERNAL ENERGY & ENTROPY) FOR 1,2-PARTICLE CLUSTERS vs. x,y FOR $B_r=0$, $T_r=10$. (Φ CLIPPED AT $\Phi \geqq 2$)

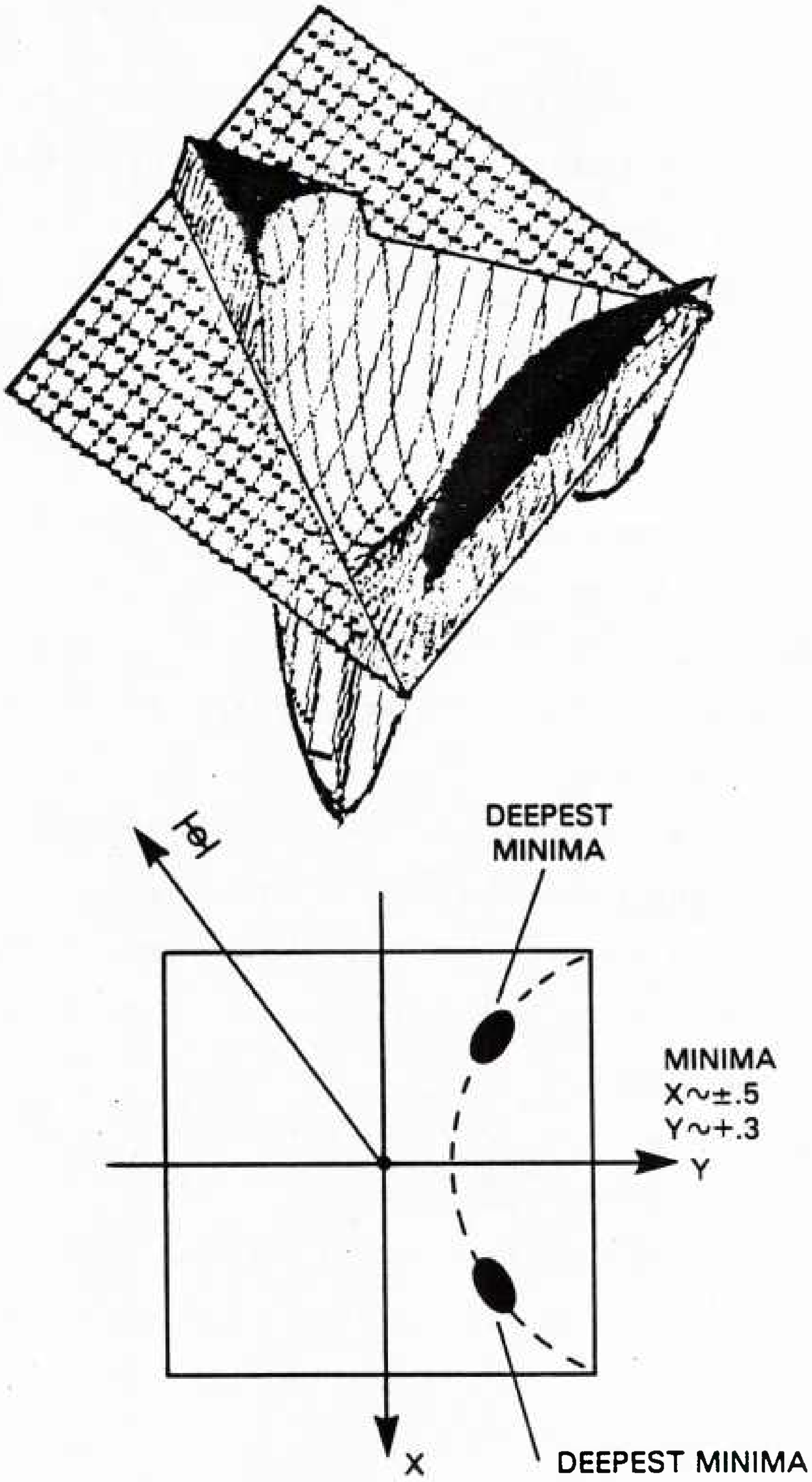


Fig. 21. Φ FOR 1,2-PARTICLE CLUSTERS vs. x,y FOR $B_r=0$, $T_r=10$. (Φ CLIPPED AT $\Phi \geqq 2$)

In this restricted view we have the following "square" lattices:

In one dimension, the lattice is linear, and the retained pairs are given by p=1 and p=2. The quantities p,q,r are the distances between particles. The retained triangle is described by p=1, q=1, r=2. The coordination numbers in 1-dimension are:

pairs---> Z_p; $Z^{(2)}_1 = 2$, $Z^{(2)}_2 = 2$

compact triplet---> Z_{pqr}; $Z^{(3)}_{112} = 6$.

In two dimensions, the lattice is square and the retained pairs are p=1,and p=2 (or strictely, $p=\surd 2$ but we have retained p as an "index" of distance). The retained triangle is given by p=1, q=1,r=2(actually $r=\surd 2$. The coordination numbers are:

pairs---> Z_p; $Z^{(2)}_1 = 4$, $Z^{(2)}_2 = 4$

triplet---> Z_{pqr}; $Z^{(3)}_{112} = 24$

In three dimensions the lattice is cubic. The retained clusters are like those in the square case, and the coordination numbers are:

pairs---> Z_p; $Z^{(2)}_1 = 6$, $Z^{(2)}_2 = 12$

triplet---> Z_{pqr}; $Z^{(3)}_{112} = 72$

These results can also be obtained arithmetically, using the rule that particles are located at lattice sites according to

$$\vec{r}_{i_1,i_2\ldots i_d} = a\Sigma^{D}_{\alpha=1} n_{i\alpha}\hat{b}_{\alpha}$$

where the $\hat{b}_{\alpha}$ are orthogonal unit vectors for "square" lattices, a is the lattice constant, and the $n_{i\alpha}$ are integers.

We select the particle "." at $\vec{r} = \vec{0}$, and vary it to locate other particles. The distance between "." and any other particle is $|\mathbf{1n}|^{(2)} = \Sigma_{i=1}^{D} n_i^{2}$. We calculate the coordination numbers of each particular sort of n-cluster by counting the number of 1n's that generate n-clusters of that particular sort.

In one dimension , D=1, and we have:

{n=+1, n=-1} <--> smallest 2-cluster

<--> $Z^{(2)}_{1} = 2$

{n=+2, n=-2} <--> next smallest 2-cluster

<--> $Z^{(2)}_{1} = 2$

n	n'	p	q	r
1	2	1	2	1
2	1	2	1	1
-1	+1	1	1	2
+1	-1	1	1	2
-1	-2	1	2	1
-2	-1	2	1	1

$Z^{(3)}_{112} = 6$

In two dimensions, D = 2, and we have

nx	ny	||n||
0	1	1
0	-1	1
1	0	1
-1	0	1

$Z^{(2)}_{1} = 4$

nx	ny	||n||
1	1	$\sqrt{2}$
1	-1	$\sqrt{2}$
-1	1	$\sqrt{2}$
-1	-1	$\sqrt{2}$

$Z^{(2)}_{2} = 4$

nx	ny	nx'	ny'	p= ||1n||	q= ||1n'||	r= ||1n-1n'||
0	1	1	0	1	1	$\sqrt{2}$
0	-1	-1	0	1	1	$\sqrt{}$

We continue in a similar way as in the first two approximations.

Internal Energy:

The internal energy is,

$$U = \langle H \rangle = -\mu_0 BNx - \tfrac{1}{2} JNZ_1 y_1$$

Entropy:

The entropy is,

$$S = \hat{S}^{(1)} + \hat{S}^{(2)\prime} + \hat{S}^{(3)\prime}$$

(where the prime notation reminds us that we are restricting our attention to n.n. pairs and the n.n.n. pairs and only to triangles for the triplets.)

The intrinsic entropy for 1-clusters is,

$$\hat{S}^{(1)} = \Sigma_i \hat{S}^{(1)}_i = N\hat{S}^{(1)} = -Nk_b\{\tfrac{1}{2}(1 \pm x)\ln.\}$$

(The notation "ln." means that, the quantity that immediately precedes the function "ln" is repeated as its argument.)

For pairs the intrinsic entropy is,

$$\hat{S}^{(2)\prime} = \hat{S}^{(2)}_{.,.+1} + \hat{S}^{(2)}_{.,.+2}$$
$$= -Nk_B\{Z_1\{[(1/4)(1+2x+y_1)\ln.+\text{etc}]-2[\,]\}$$
$$+ Z_2\{[(1/4)(1+2x+y_2)\ln.+\text{etc}]-2[\,]\}\}$$

For triangles the intrinsic entropy is,

$$\hat{S}^{(3)\prime} = \hat{S}^{(3)}_{.,.+1,.+2}$$
$$= -Nk_B Z_{112}\{[(1/8)(1+3x+2y_1+y_2+z_{112})\ln.+\text{etc}]-\text{etc}\}$$

(Note: In this description the "." used as a subscript, as in $\hat{S}_.$,is meant to replace the i usually used to represent a single particle. Also in the pair notation the i,j would be replaced by .,.+1 and n.n.n. pairs are written as .,.+2. For triangles we use .,.+1,.+2 instead of the usual i,j,k.)

Free Energy:

The Helmholtz free energy for this limited 3-cluster approximation is

$$
\begin{aligned}
\Phi = (F/NJ) = [-B_r x - 1/2 Z_1 Y_1] + T_r\{&[\tfrac{1}{2}(1+x)\ln. + (\tfrac{1}{2}(1-x)\ln.] \\
&+\tfrac{1}{2}\Sigma_{p=1,2} Z_p\{[\tfrac{1}{4}(1+2x+y_p)\ln. + 2*\tfrac{1}{4}(1-y_p)\ln. \\
&+\tfrac{1}{4}(1-2x+y_p)\ln.] - 2[\tfrac{1}{2}(1+x)\ln. + \tfrac{1}{2}(1-x)\ln.]\} \\
&+(1/6)Z_{112}\{[(1/8)(1+3x+2y_1+y_2+z_{112})\ln. \\
&\qquad +2*(1/8)(1+x-y_2-z_{112})\ln. \\
&\qquad +(1/8)(1-x-2y_1+y_2+z_{112})\ln. \\
&\qquad +(1/8)(1+x-2y_1+y_2-z_{112})\ln. \\
&\qquad +2*(1/8)(1-x-y_2+z_{112})\ln. \\
&\qquad +(1/8)(1-3x+2y_1+y_2-z_{112})\ln.] \\
&-2[\tfrac{1}{4}(1+2x+y_1)\ln. + 2*\tfrac{1}{4}(1-y_1)\ln. + \tfrac{1}{4}(1-2x+y_1)\ln.] \\
&- [\tfrac{1}{4}(1+2x+y_2)\ln. + 2*\tfrac{1}{4}(1-y_2)\ln. + \tfrac{1}{4}(1-2x+y_2)\ln.] \\
&+3[\tfrac{1}{2}(1+x)\ln. + \tfrac{1}{2}(1-x)]\}\}
\end{aligned}
$$

Minimization:

We will minimize the free energy using calculus minima and also with the Simplex algorithm, reference (6).

The equilibrium state of this system is determined by finding the minimum values for x, y_1, y_2, z_{112} which are obtained by calculating the derivative of Φ first wrp. to x, and then y_1, etc., setting the eqns. equal to zero, and solving for x, y_1, y_2, z_{112}.

Calculating the derivative of Φ wrp. x, and setting the result equal to zero, is called the [x] eqn.

[x] $0 = (\delta\Phi/\delta x)$

$$= -B_r + T_r\{\tfrac{1}{2}\ln\frac{1+x}{1-x}$$

$$+\tfrac{1}{2}(\Sigma_{p=1,2})Z_p[\tfrac{1}{2}\ln\frac{1+2x+y_p}{1-2x+y_p} - \ln\frac{1+x}{1-x}]$$

$$+(1/6)Z_{112}\ [(3/8)\ln\frac{1+3x+2y_1+y_2+z_{112}}{1-3x+2y_1+y_2-z_{112}} + (2/8)\ln\frac{1+x-y_2-z_{112}}{1-x-y_2+z_{112}}$$

$$(1/8)\ln\frac{(1+x-2y_1+y_2-z_{112})}{(1-x-2y_1+y_2+z_{112})} - \ln\frac{1+2x+y_1}{1-2x+y_1}$$

$$-\tfrac{1}{2}\ln\frac{1+2x+y_2}{1-2x+y_2} + (3/2)\ln\frac{1+x}{1-x}]\}$$

$$2*B_r/T_r = \ln\frac{1+x}{1-x} + \tfrac{1}{2}(\Sigma_{p=1,2})Z_p[\ln\frac{1+2x+y_p}{1-2x+y_p} - 2\ln\frac{1+x}{1-x}]$$

$$+\frac{Z_{112}}{24}[3\ln\frac{1+3x+2y_1+y_2+z_{112}}{1-3x+2y_1+y_2-z_{112}} + 2\ln\frac{1+x-y_2-z_{112}}{1-x-y_2+z_{112}}$$

$$+\ln\frac{1+x-2y_1+y_2-z_{112}}{1-x-2y_1+y_2+z_{112}} - 8\ln\frac{1+2x+y_1}{1-2x+y_1}$$

$$-4\ln\frac{1+2x+y_2}{1-2x+y_2} + 12\ln\frac{1+x}{1-x}]$$

[y1]

$0 = (\delta\Phi/\delta y_1)$

$$= -4Z_1 + T_r\{Z_1[\ln\tfrac{1}{4}(1+2x+y_1) - 2\ln\tfrac{1}{4}(1-y_1) + \ln\tfrac{1}{4}(1-2x+y_1)]$$

$$+ 2(4/6)Z_{112}\{[(2/8)\ln(1/8)(1+3x+2y_1+y_2+z_{112})$$

$$- 2(1/8)\ln(1/8)(1-x-2y_1+y_2+z_{112})$$

$$- 2(1/8)\ln(1/8)(1+x-2y_1+y_2-z_{112})$$

$$+ (2/8)\ln(1/8)(1-3x+2y_1+y_2-z_{112})]$$

$$- \tfrac{1}{2}[\ln\tfrac{1}{4}(1+2x+y_1) - 2\ln\tfrac{1}{4}(1-y_1) + \ln\tfrac{1}{4}(1-2x+y_1)]\}\}$$

$$4/Tr = \ln \frac{(1+2x+y_1)(1-2x+y_1)}{(1-y_1)^2}$$

$$+ \frac{Z_{112}}{3Z_1} [\ln \frac{(1+3x+2y_1+y_2+z_{112})(1-3x+2y_1+y_2-z_{112})}{(1-x-2y_1+y_2+z_{112})(1+x-2y_1+y_2-z_{112})}$$

$$- 2\ln \frac{(1+2x+y_1)(1-2x+y_1)}{(1-y_2)^2}]$$

$[y_2]$

$$0 = (\delta\Phi/\delta y_2)$$

$$= Tr\{\tfrac{1}{2}Z_2\ [\tfrac{1}{4}\ln\ \tfrac{1}{4}(1+2x+y_2)-2*\tfrac{1}{4}\ln\tfrac{1}{4}(1-y_2)+\tfrac{1}{4}\ln\tfrac{1}{4}(1-2x+y_2)]$$

$$+(1/6)Z_{112}[(1/8)\ln(1/8)(1+3x+2y_1+y_2+z_{112})$$

$$-2(1/8)\ln(1/8)(1+x-y_2-z_{112})$$

$$+(1/8)\ln(1/8)(1-x-2y_1+y_2+z_{112})$$

$$+(1/8)\ln(1/8)(1+x-2y_1+y_2-z_{112})$$

$$-2(1/8)\ln(1/8)(1-x-y_2+z_{112})$$

$$+(1/8)\ln(1/8)(1-3x+2y_1+y_2-z_{112})]$$

$$-[\tfrac{1}{4}\ln\tfrac{1}{4}(1+2x+y_2)-2\tfrac{1}{4}\ln\tfrac{1}{4}(1-y_2)+\tfrac{1}{4}\ln\tfrac{1}{4}(1-2x+y_2)]\}$$

$$\dashrightarrow\quad 0=(\tfrac{1}{2})(\tfrac{1}{4})Z_2\ln \frac{(1+2x+y_2)(1-2x+y_2)}{(1-y_2)^2}$$

$$+ \frac{Z_{112}}{6*8} [\ln \frac{(1+3x+2y_1+y_2+z_{112})(1-x-2y_1+y_2+z_{112})}{(1+x-y_2-z_{112})^2(1-x-y_2+z_{112})^2}$$

$$* \frac{(1+x-2y_1+y_2-z_{112})(1-3x+2y_1+y_2-z_{112})}{(1+x-y_2-z_{112})^2(1-x-y_2+z_{112})^2}$$

$$-2\ln \frac{(1+2x+y_2)(1-2x+y_2)}{(1-y_2)^2}\ ]$$

$$\dashrightarrow\quad 0 = \ln \frac{(1+2x+y_2)(1-2x+y_2)}{(1-y_2)^2}$$

$$+\frac{Z_{112}}{6Z_2}\left[\ln\frac{(1+3x+2y_1+y_2+z_{112})(1-3x+2y_1+y_2-z_{112})}{(1+x-y_2-z_{112})^2(1-x-y_2+z_{112})^2}\right.$$

$$*\frac{(1-x-2y_1+y_2+z_{112})(1+x-2y_1+y_2-z_{112})}{(1+x-y_2-z_{112})^2(1-x-y_2+z_{112})^2}$$

$$\left.-2\ln\frac{(1+2x+y_2)(1-2x+y_2)}{(1-y_2)^2}\right]$$

$[z_{112}]$

$$0=(\delta\Phi/\delta z_{112})$$

$$=\mathrm{Tr}\{(1/6)Z_{112}[(1/8)\ln(1/8)(1+3x+2y_1+y_2+z_{112})$$

$$-2(1/8)\ln(1/8)(1+x-y_2-z_{112})$$

$$+(1/8)\ln(1/8)(1-x-2y_1+y_2+z_{112})$$

$$-(1/8)\ln(1/8)(1+x-2y_1+y_2-z_{112})$$

$$+2(1/8)\ln(1/8)(1-x-y_2+z_{112})$$

$$-(1/8)\ln(1/8)(1-3x+2y_1+y_2-z_{112}]\}$$

$$1=\frac{(1+3x+2y_1+y_2+z_{112})(1-x-2y_1+y_2+z_{112})(1-x-y_2+z_{112})^2}{(1-3x+2y_1+y_2-z_{112})(1+x-2y_1+y_2-z_{112})(1+x-y_2-z_{112})^2}$$

We begin the study of these by supposing that $B_r = 0$. By inspection, we find that ($x=0, z_{112}=0$) then satisfy $[x]$, $[z_{112}]$ identically:

$$[x]\quad 0=\ln 1+½(\Sigma_{p=1,2})Z_p\left[\ln\frac{1+y_p}{1+y_p}-2\ln 1\right]$$

$$+\frac{Z_{112}}{24}\left[3\ln\frac{1+2y_1+y_2}{1+2y_1+y_2}+2\ln\frac{1-y_2}{1-y_2}\ln\frac{1-2y_1+y_2}{1-2y_1+y_2}\right.$$

$$\left.-8\ln\frac{1+y_1}{1+y_1}-4\ln\frac{1+y_2}{1+y_2}+6\ln 1\right]$$

$[z_{112}]$

$$\frac{(1+2y_1+y_2)(1-2y_1+y_2)(1-y_2)^2}{(1+2y_1+y_2)(1-2y_1+y_2)(1-y_2)^2} = 1$$

Equations [y_1] & [y_2] become:

[y_1]
$$\frac{4}{T_r} = 2\ln\frac{1+y_1}{1-y_1} + \frac{Z_{112}}{3Z_1}[2\ln\frac{(1+2y_1+y_2)}{(1-2y_1+y_2)} - 4\ln\frac{1+y_1}{1-y_1}]$$

$$\frac{2}{T_r} = \ln\frac{1+y_1}{1-y_1} + \frac{Z_{112}}{3Z_1}[\ln\frac{1+2y_1+y_2}{1-2y_1+y_2} - 2\ln\frac{1+y_1}{1-y_1}]$$

[y_2]
$$0=2\ln\frac{1+y_2}{1-y_2} + \frac{Z_{112}}{6Z_2}[2\ln\frac{(1+2y_1+y_2)(1-2y_1+y_2)}{(1-y_2)^2} - 4\ln\frac{1+y_2}{1-y_2}]$$

$$0=\ln\frac{1+y_2}{1-y_2} + \frac{Z_{112}}{6Z_2}[\ln\frac{(1+2y_1+y_2)(1-2y_1+y_2)}{(1-y_2)^2} - 2\ln\frac{1+y_2}{1-y_2}]$$

We will now solve [y_2] for $y_1 = y_1(y_2;Z_{112}/Z_2)$, and use the result in [y_1] to obtain $T_r = T_r(y_2;Z_{112}/Z_1;$and $Z_{112}/Z_2)$.

[y_2]

$$\frac{6Z_2}{Z_{112}}[-\ln\frac{1+y_2}{1-y_2}] = \ln\frac{(1+2y_1+y_2)(1-2y_1+y_2)}{(1-y_2)^2} - 2\ln\frac{1+y_2}{1-y_2}$$

$$\ln\frac{(1+2y_1+y_2)(1-2y_1+y_2)}{(1-y_2)^2} = [2-\frac{6Z_2}{Z_{112}}][\ln\frac{1+y_2}{1-y_2}]$$

$$\frac{(1+2y_1+y_2)(1-2y_1+y_2)}{(1-y_2)^2} = \exp\{[2-\frac{6Z_2}{Z_{112}}][\ln\frac{1+y_2}{1-y_2}]\} = b$$

$$(1+2y_1+y_2)(1-2y_1+y_2) = (1-y_2)^2 b$$

$$(1+2y_1)(1-2y_1) + [(1+2y_1)+(1-2y_1)]y_2 + y_2^2 = b(1-y_2)^2$$

$$1 - 4y_1^2 + 2y_2 + y_2^2 = b(1-2y_2 + y_2^2)$$

$$-4y_1^2 = [1-2y_2+y_2^2]b - 1 - 2y_2 - y_2^2$$

$$y_1^2 = \tfrac{1}{4}[1 + 2y_2 + y_2^2 - b + 2by_2 - by_2^2]$$

$$y_1^2 = \tfrac{1}{4}[(1-b) + 2(1+b)y_2 + (1-b)y_2^2]$$

$$y_1^2 = \tfrac{1}{4}[1-b][1+y_2^2+2[(1+b)/(1-b)]y_2]$$

We have now derived the equations for b and y_1^2.

To evaluate b and y_1^2 we have the following calculations in one and two dimensions.

In One Dimension $Z_2 = 2$ and $Z_{112} = 6$. Hence

$$b = \exp\{[2-6*2/6]\ln[(1+y_2)/(1-y_2)]\}$$

$$= \exp\{[\ 0\ ]$$

$$= 1 \qquad \text{and}$$

$$y_1^2 = (1/4)[\ 0 + 2*2y_2 + 0*y_2^2]$$

$$y_1^2 = y_2$$

Summarizing: $b = 1$

$$y_2 = y_1^2$$

In Two Dimensions $Z_2 = 12$ and $Z_{112} = 24$. Hence

$$b = \exp\{[2-6*12/24]\ln[(1+y_2)/(1-y_2)\ \}$$

$$= \exp\{[2-3]\ln[(1+y_2)/(1-y_2)]$$

$$= \exp\{-\ln[(1+y_2)/(1-y_2)]\}$$

$$= [(1+y_2)/(1-y_2)](-1)$$

$$= [(1-y_2)/(1+y_2)]$$

and the relation between y_1 and y_2 is,

$$y_1^2 = \tfrac{1}{4}[(1-b) + (1-b)y_2^2 + 2(1+b)y_2\ ]$$

$$= \tfrac{1}{4}\{(1-[(1-y_2)/(1+y_2)]) + 2(1+[(1-y_2)/(1+y_2)])y_2 + (1-[(1-y_2)/(1+y_2)])\ \}$$

$$= \tfrac{1}{4}\{\ (2y_2)/(1+y_2) + 2(2/(1+y_2))y_2 + (2y_2/(1+y_2))y_2^2\ \}$$

$$= \tfrac{1}{4}[2y_2/(1+y_2)][3+y_2^2]$$

$$= \tfrac{1}{2}[y_2/(1+y_2)][3+y_2^2]$$

Summarizing: $b = [(1-y_2)/(1+y_2)]$

$y_1^2 = \tfrac{1}{2}[y_2/(1+y_2)][3+y_2^2]$

We use these results in $[y_1]$ to obtain T_r.

$[y_1]$

$$\frac{2}{T_r} = \ln\frac{1+y_1}{1-y_1} + \frac{Z_{112}}{3Z_1}\left[\ln\frac{1+2y_1+y_2}{1-2y_1+y_2} - 2\ln\frac{1+y_1}{1-y_1}\right]$$

We derived the result for y_1^2 as:

$$y_1^2 = \tfrac{1}{4}\{(1-b)+2(1+b)y_2+(1-b)y_2^2\}$$

where $b = \exp\{[2-\frac{6Z_2}{Z_{112}}]\ln\frac{1+y_2}{1-y_2}\}$ (from p.105)

Using these equations we found in ONE dimension that $y_2 = y_1^2$.

In ONE dimension, if we use this result in $[y_1]$ above and recall that $Z_{112} = 6, Z_1 = 2$ then we derive y_1 as:

$$\frac{2}{T_r} = \ln\frac{1+y_1}{1-y_1} + \frac{6}{6}\left[\ln\frac{1+2y_1+y_1^2}{1-2y_1+y_1^2} - 2\ln\frac{1+y_1}{1-y_1}\right]$$

$$= \ln\frac{1+y_1}{1-y_1} + 2\ln\frac{1+y_1}{1-y_1} - 2\ln\frac{1+y_1}{1-y_1}$$

$$= \ln\frac{1+y_1}{1-y_1} + 0$$

--> $2/T_r = \ln[(1+y_1)/(1-y_1) = a$

--> $(1+y_1)/(1-y_1) = \exp(a) = b$

--> $1+y_1 = b - by_1$

--> $(1+b)y_1 = b - 1$

$$\longrightarrow \qquad y_1 = \frac{b-1}{b+1} = \frac{\exp(a)-1}{\exp(a)+1}$$

$$\longrightarrow \qquad = \frac{\exp(a/2)-\exp(-a/2)}{\exp(a/2)+\exp(-a/2)}$$

$$\longrightarrow \qquad = \tanh(a/2)$$

$$\longrightarrow \qquad = \tanh(1/T_r)$$

We know that this is the same result as in the 2-cluster case.

$$y_1^2 = (1/4)[-(\ )2y_2 + 2(2)y_2 -(\ )y_2^2]$$

$$= (1/4)[4(1+1/2(\ )y_2 -(\ )y_2^2]$$

$$\text{since } (\ )y_2^2 = 0$$

$$y_1^2 = (1/4)[4(1+1/2(\ )y_2]$$

$$= [1+1/2(2-6Z_2/Z_{112})]y_2$$

$$= [2 -3Z_2/Z_{112}]y_2 = [2-(3*2)/6]y_2$$

In one dimension, we found $y_1^2 = y_2$, and we find it again from this result.

Hence, in one dimension, $y_1 = \tanh(1/T_r)$ ...same as in the 2-cluster approximation.

Summary

For any dimension, we find, for $B_r=0$

$$b = \exp\{[2 - \frac{6Z_2}{Z_{112}}][\ln \frac{1+y_2}{1-y_2}]\}$$

$$y_1 = \tfrac{1}{2}\sqrt{\{(1-b)[1+2(\frac{1+b}{1-b})y_2+y_2^2]\}}$$

$$\frac{2}{T_r} = \ln \frac{1+y_1}{1-y_1} + \frac{Z_{112}}{3Z_1} [\ln \frac{1+2y_1+y_2}{1-2y_1+y_2} - 2\ln \frac{1+y_1}{1-y_1}]$$

$$x = z_{112} = 0$$

The existence of negative values for the entropy in the truncated free energy was illustrated in the previous section, see Fig. 19. The effect on the free energy surface was shown in Figs. 20 and 21. In the third approximation these negative values of the entropy have severe effects on the derived results. If a critical temperature is derived from these minimized equations it will have a complex value [23]. To examine the entropy values resulting from truncating the expansion after the third term the values are shown in Figs. 22 and 23 for two different values of z, the triple correlation moment . In Fig. 22 the value of the entropy values are given as a function of magnetization, x, and the pair correlation, y, for a constant value of z = 0.2. Similar results are given in Fig. 23 for z = 0. The entropy values shown in the upper half of both figures are negative in some cases and greater than unity for some values. Neither of these kind numerical are physically realistic: the entropy must be ≤ 1 and can never be negative for this system. The entropy values where obtained with the program GRID 6 and the listing is given in Appendix E.

An attempt at reducing the magnitude of these non-physical results is shown in the lower half of figures 22 and 23. This reduction is suggested by numerical techniques which only use ½ of the value of the last term in a series in order to speed-up convergence. We have used only ½ of

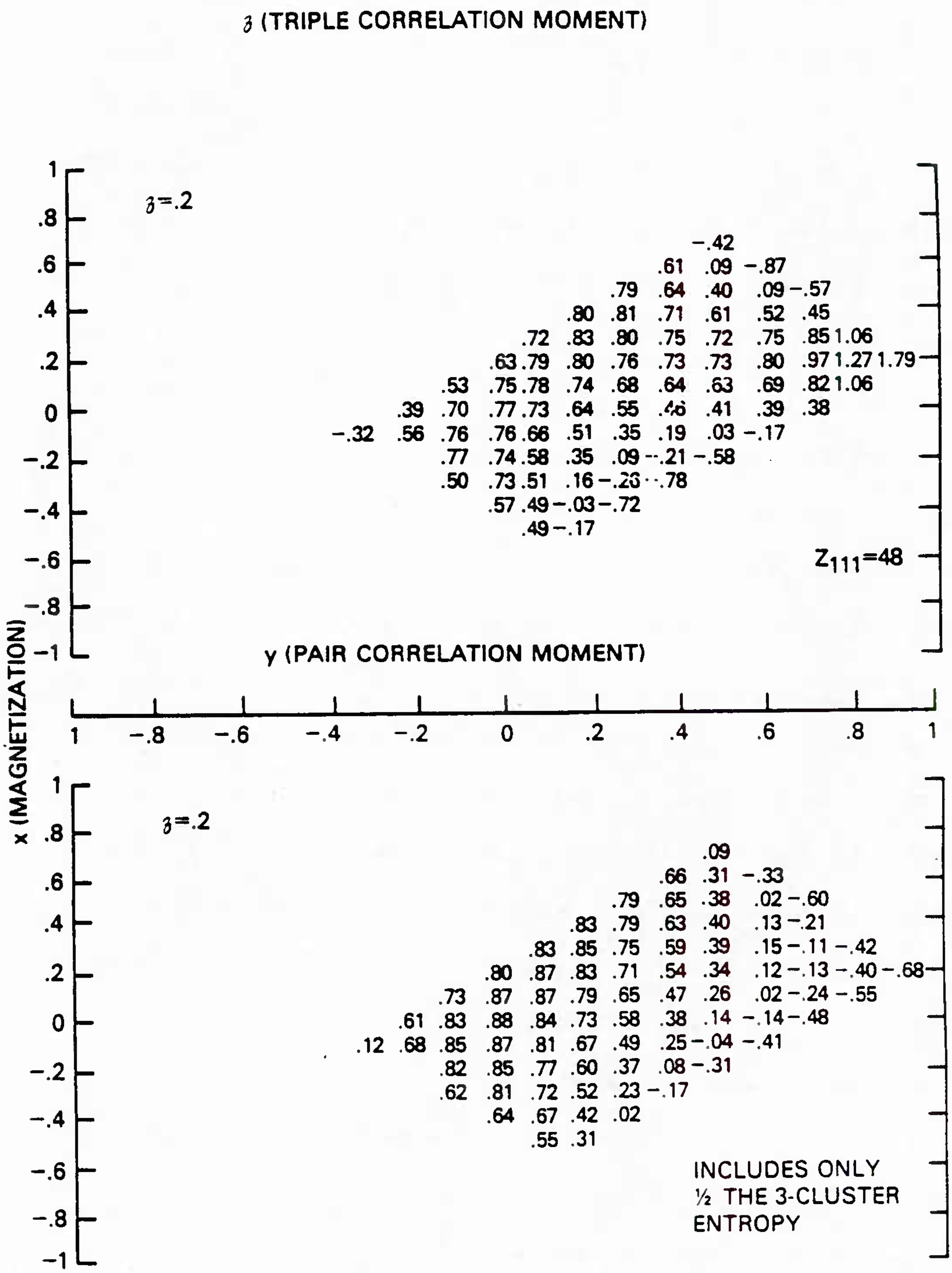


Fig. 22. ENTROPY FOR 1,2,3-PARTICLE CLUSTERS vs. x,y WITH z=.2

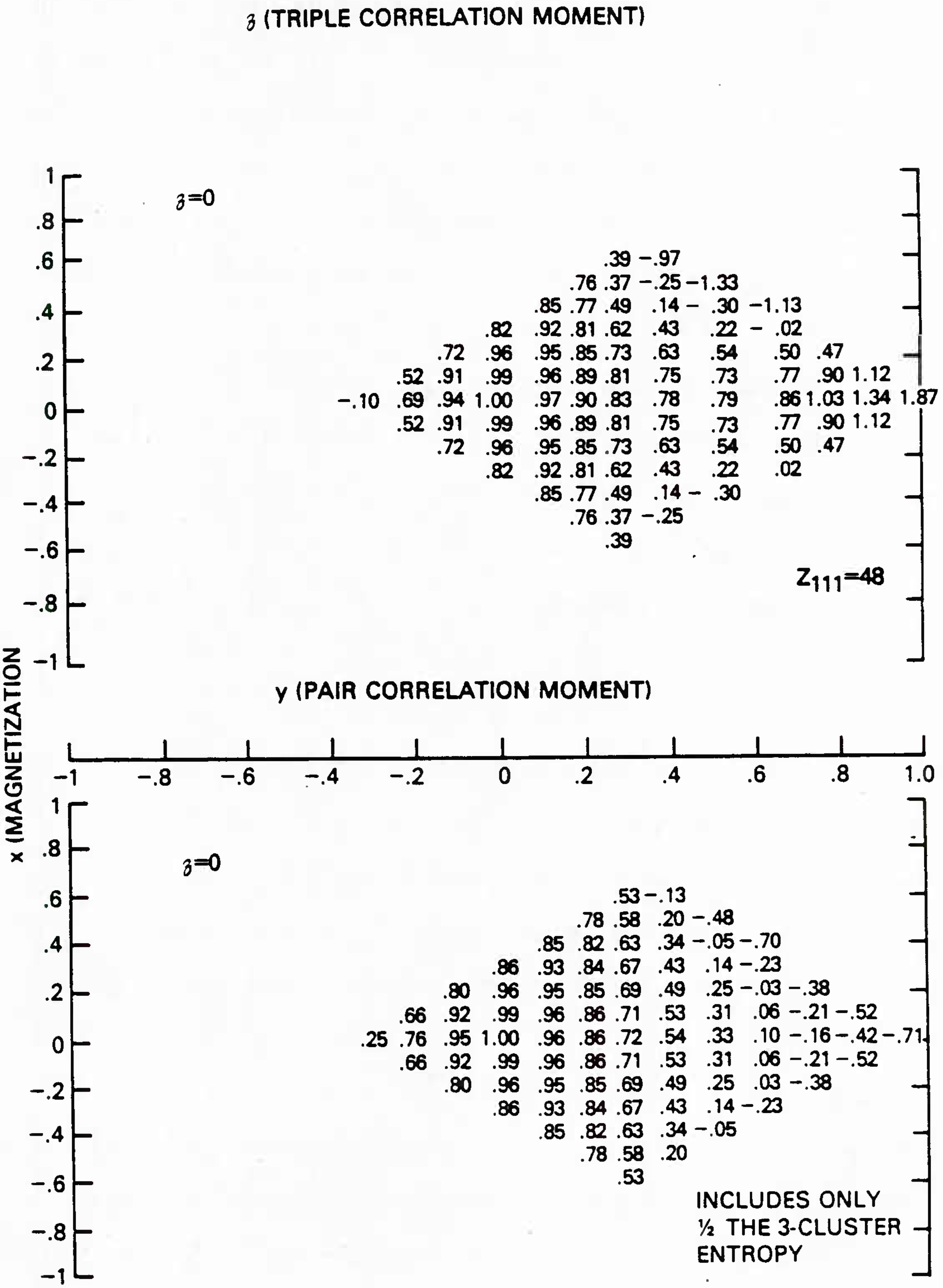


Fig. 23. ENTROPY FOR 1,2,3-PARTICLE CLUSTERS vs. x,y WITH ȝ=0

the entropy contributon from the three particle cluster (the last custer term in the truncated series) and re-calculated the total entropy for the 1,2,3-particle clusters. The results do show an improvement in the entropy values: some become less negative and all are ≤ 1. In Fig. 23 the entropy value is unity for $z = y = x = 0$, as it should be for both calculations.

The equilibrium free energy is plotted in Fig. 24 for the third approximation as a function of T_r. The values were determined by the Simplex minimization algorithm. A listing of the Simplex program is give in Appendix E, and the essential steps are given in reference [6].

As mentioned in the previous section (4.1) the minimum occur on the boundary and the calculus minimazation will not work. We have used the Simplex algorithm to minimize the truncated free energy equation. This minimization technique is not a calculus type minimization method and can be used to obtain minima which are located on the boundary.

In Fig. 24 the equilibrium values are denoted by "X" for Φ when no correction is made to the entropy contribution of the third term in the truncated free energy. These values for Φ are very different than the solid curves which are the equilibrium values for the free energy that were

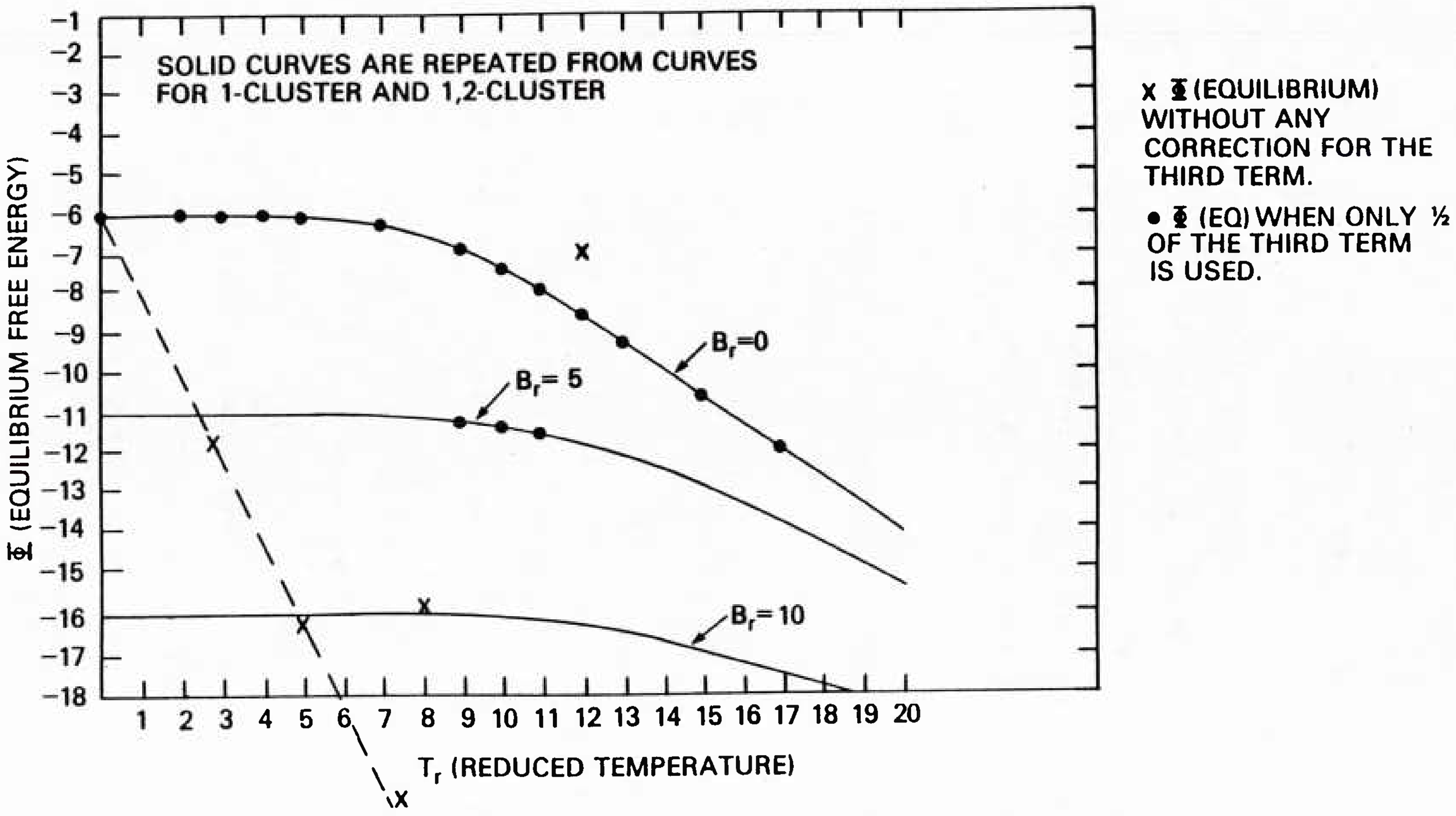


Fig. 24. EQUILIBRIUM FREE ENERGY Φ vs. TEMPERATURE T_r FOR VARIOUS VALUES OF MAGNETIC FIELD B_r (1,2,3-CLUSTER APPROXIMATION)

obtained in the earlier approximations and re-plotted in Fig. 24. It was noted previously that the numerical value of Φeq. would not change very much for the higher order approximations as compared to the approximations for 1,2-particle clusters. To evaluate the effect of only using ½ of the entropy contribution of the third term, as was done in Figs. 22 and 23, the values of Φ were re-calculated using only ½ of the third term. These results are denoted by the large black dots, and show good agreement with the earlier results.

Fourth Order Approximation:(4-Cluster)

The following is a list of the principal steps in this derivation.

The Helmholtz Free Energy is given as $F = U - TS$.

1. Calculate U.
2. Calculate S. ^ indicates intrinsic entropy.

$$S = S\hat{}(1) + S\hat{}(2) + S\hat{}(3) + S\hat{}(4) \qquad (11)$$

$S\hat{}(1)$ is the same as in the 1-c approximation.
$S\hat{}(2)$ " 2-c "
$S\hat{}(3)$ " 3-c "
$S\hat{}(4) = S(4) - 4S(3) + 6S(2) - 4S(1)$

$S(1), S(2), S(3)$ are known from the earlier approximations and are given as R1,R2,R3, respectively in the program SIM4,see the listing in Appendix E.

$S(4)$ is determined from $P(4)(\mu' \ldots \mu''')$ which is the probability distribution for only 4 particles. (See section 3.3). The equations for this distribution are denoted by R4 in SIM4, (see Appendix E). (Note that "R" is used to represent entropy in SIM4.) The total entropy, R, is given as follows

$$R = R1 + [Z1/2](R2-2R1) + [Z111/6](R3-3R2+3R1) + [Z111111/24](R4-4R3+6R2-4R1) \qquad (12)$$

Z1 is the pair coordination number
Z111 is the triplet coordination number
Z111111 is the 4-particle coordination number

Z1,Z111 are known from the previous approximations. Z111111 is the only new coordination number.

3. The Helmholtz free energy is given as,

$$\Phi = -B_r x - \tfrac{1}{2} Z_1 y + T_r (R) \qquad (13)$$

Φ, B_r and T_r are the reduced free energy, magnetic field and temperature respectively.

4. Minimize the free energy, and obtain the minimum value of Φ. The probabililty distribution associated with this minimum value of Φ is the equilibrium macrostate for this system. From this macrostate all quantities of thermodynamic interest can be derived by the standard formulas.

The following is a description of the 4-cluster approximation results for the FCC lattice.

Internal Energy:

$$U = \langle \text{Hamiltonian} \rangle = -\mu_0 BNx - \tfrac{1}{2} JNZ^{(1)} \langle \mu_1 \mu_2 \rangle$$

These quantities have been previously defined and the definitions are repeated here.

μ_0 is the magnetic moment of each particle

B is the external magnetic field

N is the number of particles in the system

x is the magnetization per particle

The interaction energy is given by the second term.

J is the exchange integral

Z1 is the pair coordination number

μ_1 is the microstate of one of the particles in the pair and μ_2 is the microstate of the other particle. This pair of particles are nearest neighbors (n.n.) and the average value of the product of the two microstates is called y_1, the pair correlation coefficient.

U can be written as,

$$U = N[-\mu_0 Bx - \tfrac{1}{2} J Z_1 y_1]$$

Entropy:

The entropy for this 4-cluster approximation is given by,

$$S = \hat{S}^{(1)} + \hat{S}^{(2)} + \hat{S}^{(3)} + \hat{S}^{(4)}$$

The intrinsic entropy for each cluster is represented by S with a superscript " ^ ", and each cluster approximation by a number, i.e. $\hat{S}^{(2)}$ is the intrinsic entropy for the second approximation. The intrinsic entropy for each approximation is written as follows.

$\hat{S}^{(1)} = S^{(1)}$ for the first approximation, since there is only one particle in each cluster and it is not necessary to correct for the prescence of any other clusters. $S^{(1)}$ is given by the entropy for the one-particle exact calculation, see section 3.0.

$$\hat{S}^{(1)} = S^{(1)} = -k_B[\tfrac{1}{2}(1+x)\ln\tfrac{1}{2}(1+x) + \tfrac{1}{2}(1-x)\ln\tfrac{1}{2}(1-x)] \quad (14)$$

The intrinsic entropy for the 2-cluster is written as,

$$\hat{S}^{(2)} = \Sigma_{i,j}[S^{(2)}_{i,j} - S^{(1)}_{i} - S^{(1)}_{j}]$$

$$\hat{S}^{(2)} = \tfrac{1}{2}N\Sigma_{p}Z_p[S^{(2)}_{i,i+p} - 2S^{(1)}_{i}]$$

$S^{(2)}_{i,i+p}$ is the entropy derived in the exact calculation for two particles, see section 3.1, and is given as,

$$S^{(2)} = -k_B[\tfrac{1}{4}(1+2x+y_p)\ln(.) + \tfrac{1}{2}(1-y_p)\ln(.) + \tfrac{1}{4}(1-2x+y_p)\ln(.)] \quad (15)$$

$S^{(1)}$ is the same as above. Then $\hat{S}^{(2)}$ is given as,

$$\hat{S}^{(2)} = -\tfrac{1}{2}Nk_B\Sigma_{p}Z_p\{[\tfrac{1}{4}(1+2x+y_p)\ln(.) + \tfrac{1}{2}(1-y_p)\ln(.) + \tfrac{1}{4}(1-2x+y_p)\ln(.)] - 2[\tfrac{1}{2}(1+x)\ln(.) + \tfrac{1}{2}(1-x)\ln(.)]\} .$$

The intrinsic entropy for the 3-cluster is written as,

$$\hat{S}^{(3)\prime} = S^{(3)} - 2S^{(2)}_{p=1} - S^{(2)}_{p=2} + 3S^{(1)}$$

$S^{(3)}$ is the entropy derived in the exact calculation for three particles, see section 3.2, and is given as,

$$S^{(3)} = -k_B[(1/8)(1+3x+2y_1+y_2+z_{112})\ln(.) + 2(1/8)(1+x-y_2-z_{112})\ln(.) + (1/8)(1-x-2y_1+y_2+z_{112})\ln(.) + (1/8)(1+x-2y_1+y_2-z_{112})\ln(.) + 2(1/8)(1-x-y_2+z_{112})\ln(.) + (1/8)(1-3x+2y_1+y_2-z_{112})\ln(.)] \quad (16)$$

$S^{(2)}$ and $S^{(1)}$ are the same as given above. The intrinsic $\hat{S}^{(3)}$ is given in the previous section.

The intrinsic entropy for the 4-cluster is

$$\hat{S}^{(4)} = S^{(4)} - 4S^{(3)} + 6S^{(2)} - 4S^{(1)}$$

All terms in this equation have been previously defined.

$S(4)$, the exact distribution for only 4 particles, is given in section 3.3. $S(1)$, $S(2)$, $S(3)$ are given by Eqs. (14),(15),(16) respectively.

The total entropy for the first, second, third and fourth cluster is given by Eqs. (11),(12). In SIM4 the total entropy for these four clusters is denoted by R.

Free Energy:

The free energy is given by Eq. (13) and is denoted by line 190 in SIM4 (Appendix E, Fig. 32).

Minimization:

The minimization of the free energy is calculated with SIM4 and the results presented in Fig. 26.

Discussion:

The entropy values for the first four clusters are shown in Fig. 25 in a similar way as the entropy values are given in Figs. 22 and 23 for the third order approximation. (These values were calculated with the program GRID6 that is listed in Appendix E as Fig. 34). The entropy as a function of x and y is given in Fig. 25 for $z = w = 0$ in the upper half of the figure, and for $z = w = 0.2$ in the lower half. In this case however it is not necessary to adjust these entropy values as was done in the third order approximation. The values are plausible and physically acceptable - none are >1 and none are negative. Note also that for $x = y = z = w = 0$ the entropy has a maximum value of unity as it should. The equilibrium free energy is given in Fig. 26 as a

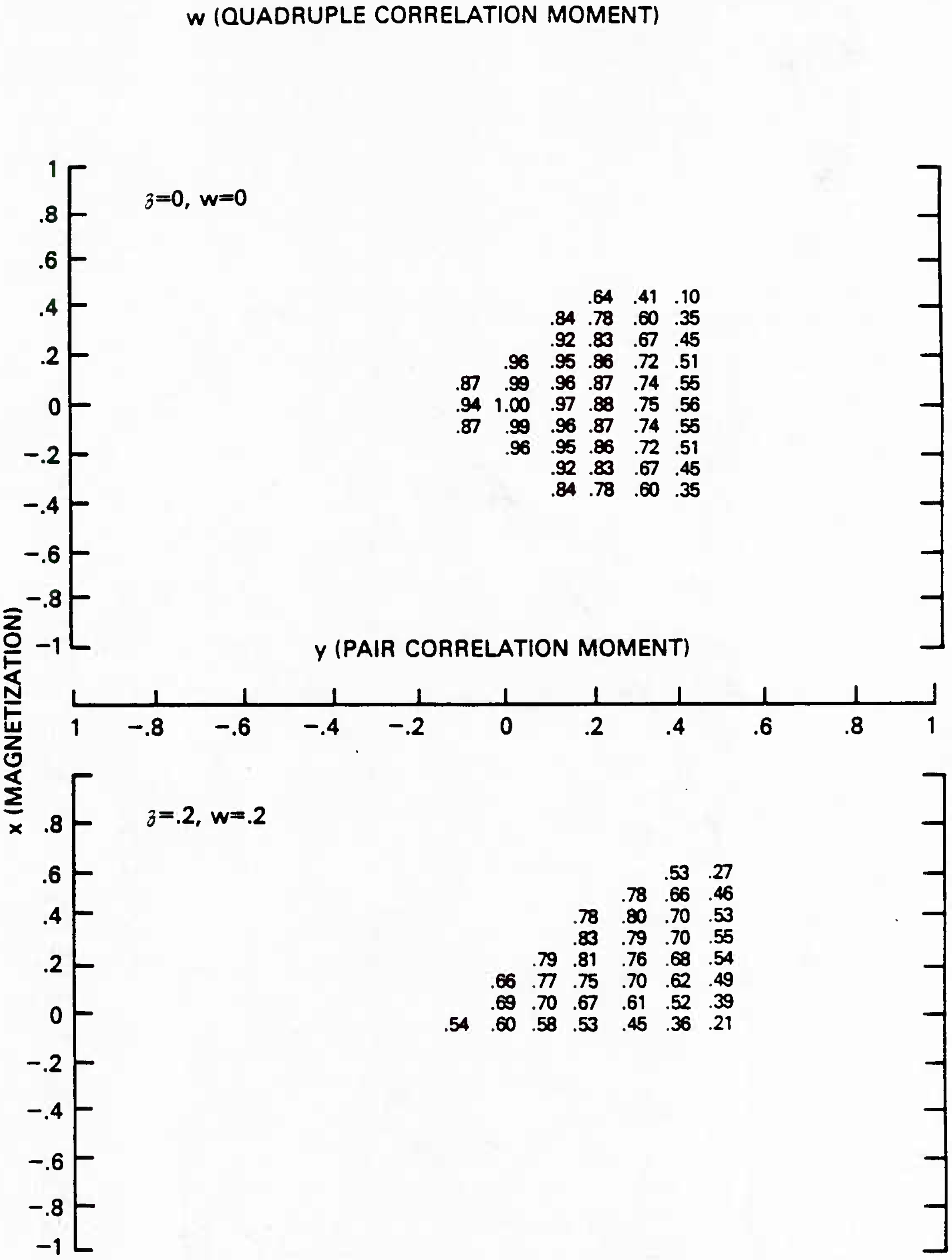


Fig. 25. ENTROPY FOR 1,2,3,4-PARTICLE CLUSTERS vs. x,y WITH $\mathfrak{z}$=0, w=0 AND $\mathfrak{z}$=.2, w=.2

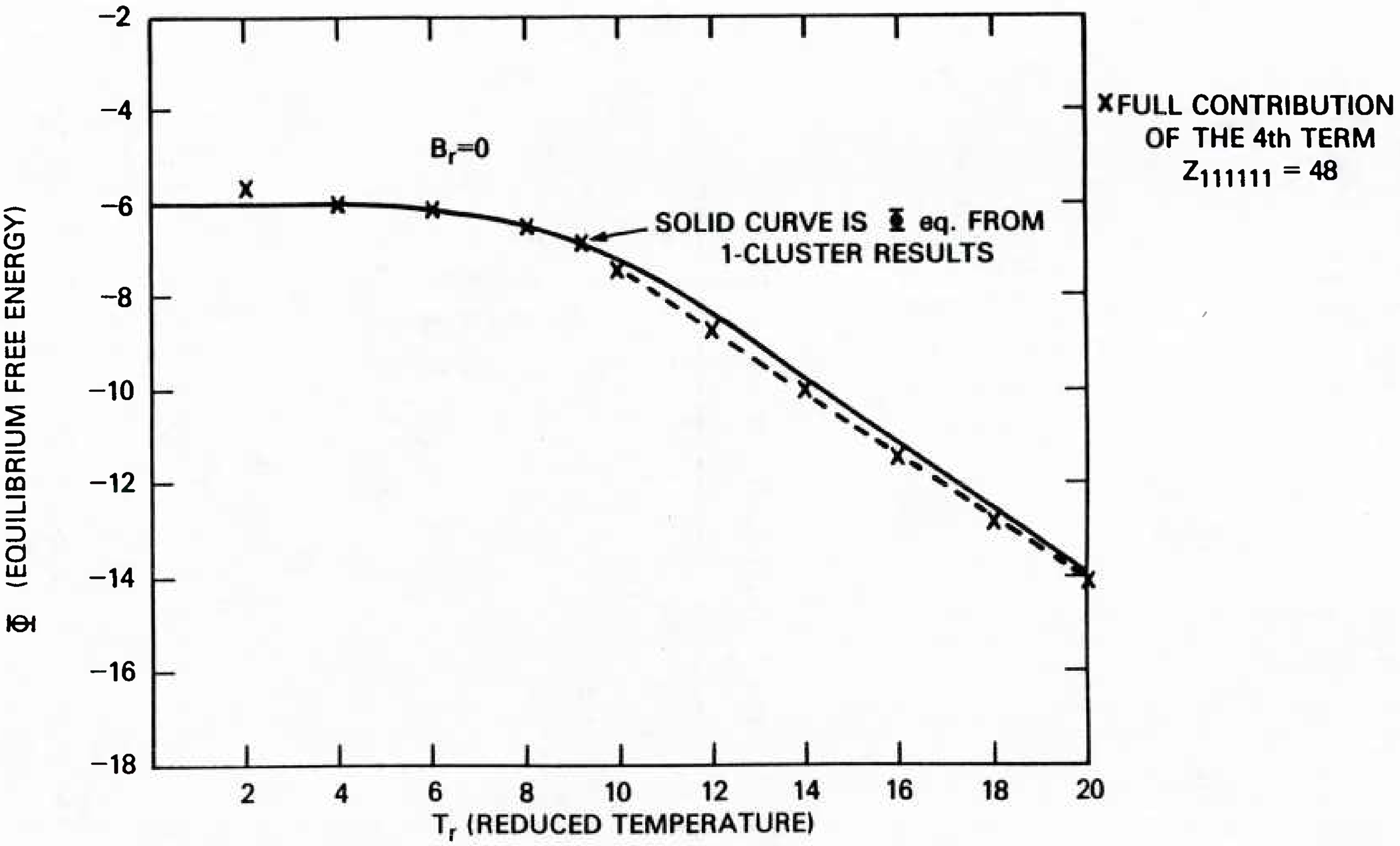


Fig. 26. EQUILIBRIUM FREE ENERGY Φ vs. TEMPERATURE T_r (4-CLUSTER)

function of the reduced temperature T_r and is denoted by "x". The reduced magnetic field is zero. The solid curve is the equilibrium free denergy for a 1-particle clusters and as previously noted these equilibrium vaues will not change very much with higher order approximations. The equilibrium values are also given in Table 1, Appendix G. For any value of T_r, the minimization program SIM4 may calculate values for equilibrium $\tilde{\Phi}$ which are more negative than those plotted in Fig. 26 and represented by "x". The correlation values x,y,z,w for these more negative $\tilde{\Phi}$ values will be less acceptable than the correlation values associated with the less negative value of $\tilde{\Phi}$. Table 2 in Appendix G gives values of x,y,z,w for T_r = 4,8,10,16. The values of $\tilde{\Phi}$ plotted in Fig. 26 also agree very closely with the equilibrium $\tilde{\Phi}$ values for the lower order approximations. The reason that other values are calculated for $\tilde{\Phi}$ is that these other equilibrium values are associated with the spurious minimum that are located on the boundary. These values of $\tilde{\Phi}$ are too low and the values of x,y,z,w associated with them are physically unacceptable. The entropy calculated for these $\tilde{\Phi}$ values will be negative. These were the criteria used in selecting the $\tilde{\Phi}$ values that are plotted in Fig. 26.

APPENDIX A

COORDINATION NUMBERS

Linear Lattice: Ising1.BAS

p	$Z^{(2)}_p$
1	2
2	2
3	2
4	2
5	2

P	Q	R	$Z^{(3)}_{pqr}$:Ising2.BAS
1	1	2	6
1	2	3	12
1	3	4	12

See Fig.27

Square Lattice:

Line#	$Z^{(2)}_p$	P
0	4	1
1	4	1.41421356
2	4	2
3	8	2.23606797
4	4	2.82842712
5	4	3
6	8	3.16227766
7	8	3.60555127
8	4	4
9	8	4.12310562
10	4	4.24264068
11	8	4.47213595
12	12	5

P	Q	R	$Z^{(3)}_{pqr}$
1	1	$\sqrt{2}$	24
1	1	2	12
1	$\sqrt{2}$	$\sqrt{5}$	48
1	2	$\sqrt{5}$	48
$\sqrt{2}$	$\sqrt{2}$	2	24

Cubic Lattice:

Line#	$Z^{(2)}_p$	p	√
0	6	1	1
1	12	1.41421356	2
2	8	1.7320508	3
3	6	2	4
4	24	2.23606797	5
5	24	2.44948974	6
6	12	2.82842712	8
7	30	3	9
8	24	3.16227766	10
9	24	3.31662479	
10	8	3.46410161	
11	24	3.60555127	
12	48	3.74165738	
13	6	4	
14	48	4.12310562	
15	36	4.24264068	
16	24	4.35889894	
17	24	4.47213595	
18	48	4.58257569	
19	24	4.69041576	
20	24	4.89897948	

P	Q	R	$Z^{(3)}_{pqr}$
1	1	√2	72
1	1	2	18
1	√2	√3	144
√2	√2	√2	48

"4-cube" Lattice:

Line#	$Z^{(2)}_p$	p
0	8	1
1	24	1.41421356
2	32	1.7320508
3	24	2
4	48	2.23606797
5	96	2.44948974
6	64	2.64575131
7	24	2.82842712
8	104	3

"5-cube" Lattice:

Line#	$Z^{(2)}_p$	p
0	10	1
1	40	1.41421
2	80	1.73205
3	90	2
4	112	2.23607
5	240	2.44949
6	320	2.64575
7	200	2.82843
8	250	3
9	-	-
10	-	-

"6-cube" Lattice:

Line#	$Z^{(2)}_p$	p
0	12	1
1	60	1.41421
2	160	1.73205
3	252	2
4	312	2.23607
5	544	2.44949
6	960	2.64575
7	1020	2.82843
8	876	3

Some General Results for "n-cube" lattices:

smallest clusters

D	Z_1	Z_{112}	Z_{112}/Z_1
1	2	6	3
2	4	24	6
3	6	72	12
4	8		
5	10		
6	12		

APPENDIX B

ISING1 PROGRAM

Regarding the program ISING1.BAS for computing $Z^{(2)}_p$--pair coordination numbers, we list the following rules. (See Fig. 27)

1. Put one particle at the origin of the lattice. Put the other particle at the location specified by the lattice numbers N1,N2,...,ND = ¦N (where D = dimension of the lattice).

Since the lattice is generated by the basis vectors $B1^{\to}$, $B2^{\to}$,...,$BD^{\to}$ = $¦B^{\to}$ by the rule

$$r^{\to} = \Sigma_I N_I B_I^{\to} ,$$

then the location (of the particle) specified by ¦N has cartesian coordinates

$$r = \Sigma_I N_I (B_I)^{\to}_j$$

where $(B_I)^{\to}_j$ are the cartesian coordinates of $¦B^{\to}$. This is the location rule.

The "n-cube" lattices are:

n	n - cube
1	linear lattice
2	square lattice
3	cubic lattice
4	hyper - cube lattice
5	who knows what it is called?
6	etc.

These lattices are generated by the "standard" orthonormal basis, whose cartesian components are $(B_I)_j^{\rightarrow} = \delta_{jI}$.

The distance rule is given by the following. The distance between the particle at the origin, and the one specified by ¦N is

$$\begin{aligned} P &= \|r^{\rightarrow} - 0^{\rightarrow}\| = \|r^{\rightarrow}\| \\ &= \Sigma_j [\Sigma_I N_I (B_I^{\rightarrow})_j]^2 \end{aligned}$$

For "n-cube" lattices, this is

$$\begin{aligned} P &= \surd[\Sigma_j (\Sigma_I N_I \delta_{jI})^2] \\ &= \surd[\Sigma_j N_j^2]. \end{aligned}$$

2. Step over all values of ¦N,

reject P if (a) P = 0 (we have accidentally put the roving particle at the origin)

(b) P > Pmax (we have an ¦N that puts the roving particle too far from the origin) .

3. We keep a list, P(I), of distinct values of P, always arranged in ascending order. We keep a second list, C(I), of the number of times the distance P(I) has been obtained. These lists are initialized to { C(I) = 0 }
{ P(I) = Pmax+1 } .

Upon moving the roving particle to each new location, and computing P, we scan the list P(I) starting from the smallest value (at the top). For each value of I (I=0 to Imax), we compare P with P(I):

(a) if P = P(I), then we increment the counter C(I), C(I)+1, and then quit the comparison.

(b) if P < P(I), then we recognize that we have encountered a new value of P, which we must insert into the list. So we pause to open up a space in the list, by moving all values from the current value P(I) to the top of the list P(Imax) down by one. And we also move the counters. (Of course, P(Imax) and (Imax) fall off the end of the lists.)

```
For J = Imax to I step-1
    P(J+1) = P(J)
    C(J+1) = C(J) .
Next J
```

We then insert P at location I, and set its counter to 1:

```
    P(I) = P
    C(I) = 1 .
```

We then quit the comparison.

(c) if P does not match any value on the list, we ignore it .

4. After the roving particle has moved over its entire domain, we print the results:

```
For I = 0 to Imax
    Print  I, P(I),C(I)
Next I
```

Of course, we can read this as

P, $Z^{(2)}P$.

```
150 REM N=2
160 REM
170 OPTION BASE 1
172 CLEAR
174 POKE 18,0:POKE 19,0:POKE 20,0:
180 DIM B(3,3)
200 REM DEFINITION OF BASIC VECTORS
210 REM B(I,X) is Xth component of Bi
220 B(1,1)=1 : B(1,2)=0 : B(1,3)=0
230 B(2,1)=0 : B(2,2)=1 : B(2,3)=0
240 B(3,1)=0 : B(3,2)=0 : B(3,3)=1
250 MAX=2:M2=MAX*MAX
260 DIM R(3),C(M2)
300 FOR I=-MAX TO MAX
310 FOR J=-MAX TO MAX
320 FOR K=-MAX TO MAX
330 FOR L=1 TO 3
340 R(L)=I*B(1,L)+J*B(2,L)+K*B(3,L)
350 NEXT L
360 D=R(1)*R(1)+R(2)*R(2)+R(3)*R(3)
370 IF (D=0) OR  (D>M2) THEN 400
380 C(D)=C(D)+1
400 NEXT K
410 NEXT J
412 PRINT "I=";I
420 NEXT I
490 OPEN #1,"P:" OUTPUT
500 PRINT #1,"D  ";"Z(D)"
510 FOR D=1 TO M2
520 PRINT #1,D;"  ";C(D)
522 PRINT D;"  ";C(D)
530 NEXT D
600 CLOSE #1
```

FIGURE 27. Program Ising1 for Calculating Coordination Numbers

APPENDIX C

ISING2 PROGRAM

Regarding the program ISING2.BAS for computing $Z^{(3)}_{pqr}$ ---triangle coordination number. Put one particle α at the origin of the lattice. Put another β at a location specified by ¦M and a third Γ at a location specified by ¦N. Then

$$r_{\alpha}\text{->} = 0\text{->}$$

$$r_{\beta}\text{->} = \Sigma_I N_I B_I\text{->}$$

$$r_{\Gamma}\text{->} = \Sigma_I N_I B_I\text{->}$$

The distances between the particles are

$$D_{\alpha\beta} = \|r_{\alpha}\text{->} - r_{\beta}\text{->}\| = \|r_{\beta}\text{->}\|$$

$$= \sqrt{\{\Sigma_j [\Sigma_I M_I (B_I\text{->})_j]^2\}}$$

$$D_{\alpha\Gamma} = \|r_{\alpha}\text{->} - r_{\Gamma}\text{->}\| = \|r_{\Gamma}\text{->}\|$$

$$= \sqrt{\{\Sigma_j [\Sigma_I N_I (B_I\text{->})_j]^2\}}$$

$$D_{\beta\Gamma} = \|r_{\beta}\text{->} - r_{\Gamma}\text{->}\|$$

$$= \sqrt{\{\Sigma_j [\Sigma_I (M_I - N_I)(B_I\text{-->})_j]^2\}}$$

For "n-cube" lattices these are:

$$D_{\alpha\beta} = \sqrt{(\Sigma_j M_j^2)}$$

$$D_{\alpha\Gamma} = \sqrt{(\Sigma_j N_j^2)}$$

$$D_{\beta\alpha} = \sqrt{[\Sigma_j (M_j - N_j)^2]}$$

2. Step β and Γ throughout the entire region surronding α. Arrange $D_{\alpha\beta}$, $D_{\alpha\Gamma}$,and $D_{\beta\Gamma}$

into ascending order:

$(D\alpha\beta, D\alpha\gamma, D\beta\gamma) \text{ --> } (P,Q,R)$

i.e. ascending order where $P < = Q < = R$.

At each pair of locations, compute $D\alpha\beta$, $D\alpha\gamma$, $D\beta\gamma$.

Go immediately to the next location if

(a) any of these are 0 (at least one particle has accidently been placed on top of another).

(b) any of these exceed Dmax (at least one particle has gotten too far away).

3. There are only certain possible distances between lattice points. We know what these are from the "$Z^2{}_p$" work. Call these possible distances, A,B,C,..., and arrange them in ascending order. Then the combinatorially possible 3-tuples are

AAA		
AAB	ABB	
AAC	ABC	ACC
AAD	ABD	ACD
AAE	ABE	ACE
-	-	-
-	-	-
-	-	-
BBB		
BBC	BCC	
BBD	BCD	BDD
BBE	BCE	BDE
-	-	-
-	-	-
-	-	-
CCC		
CCD	CDD	
CCE	CDE	CEE
-	-	-
-	-	-
-	-	-

Of course, not all of these combinatorially possible p-tuples is a possible triangle on a given lattice; for example, in 1-dimension, $D\alpha\beta + D\beta\gamma = D\alpha\gamma$. In practice we are only interested in "small" triangles. So in practice, we will cut off each sequence when the corresponding triangle is "too big". We can now assign each remaining 3-tuple a counting number I, and a counter C(I). We increment this counter whenever P,Q,R passes the appropriate entrance requirement.

For n-cube lattices, the possible distances are m, m=1,2,3,... . (Not all values of m occur for smaller n-cube lattices.)

So:

```
FOR J = 0 TO 4
    D(J) = SQR(J)
NEXT J
```

loads a more-than-adequate set into D(.). We might prefer to do this "by hand" for each explicit lattice, to ensure that only distances possible for that lattice occur. Anyway, D(.) is to contain the possible distances.

Here is a possible scheme, for n-cubic lattices, that cuts off.

TABLE 1

TRIANGLE COORDINATION NUMBER

I	P	Q	R
0	D(0)	D(0)	D(0)
1	D(0)	D(0)	D(1)
2	D(0)	D(0)	D(2)
3	D(0)	D(0)	D(3)
4	D(0)	D(1)	D(1)
5	D(0)	D(1)	D(2)
6	D(0)	D(0)	D(3)
7	D(0)	D(2)	D(2)
8	D(0)	D(2)	D(3)
9	D(0)	D(3)	D(3)
10	D(1)	D(1)	D(1)
11	D(1)	D(1)	D(2)
12	D(1)	D(2)	D(2)
13	D(2)	D(2)	D(2)

See figure 28.

```
100 REM THIS PROGRAM COMPUTES
110 REM N-COORDINATION NUMBERS (FCC)
130 REM  4 DEC 1985 (copied from ISING3.msb 16 feb 1985)
140 REM
150 REM N=3
160 REM
170 OPTION BASE 1
172 CLEAR
174 TIME=0
176 F$="scrn:"
178 OPEN F$ FOR OUTPUT AS #1
195 DEFINT A-Z
200 REM DEFINITION OF BASIS VECTORS
210 REM B(I,X) is the Xth component of Bi
212 DIM B(3,3)
214 REM FACE CENTERED CUBIC
220 B(1,1)=1 : B(1,2)=1 : B(1,3)=0
230 B(2,1)=0 : B(2,2)=1 : B(2,3)=1
240 B(3,1)=1 : B(3,2)=0 : B(3,3)=1
250 MAX=2
260 M2=MAX*MAX
270 DIM C(M2,M2)
280 DIM R1 (3),R2(3)
300 FOR I1=-MAX TO MAX
302 FOR J1=-MAX TO MAX
304 FOR K1=-MAX TO MAX
306 FOR L=1 TO 3
308 R1 (L)=I1*B(1,L)+J1*B(2,L)+K1*B(3,L)
310 NEXT L
312 D1=R1(1)*R1(1)+R1(2)*R1(2)+R1(3)*R1(3)
314 IF (D1=0) OR (D1>M2) THEN 450
320 FOR I2=-MAX TO MAX
322 FOR J2=-MAX TO MAX
324 FOR K2=-MAX TO MAX
326 FOR L=1 TO 3
328 R2(L)=I2*B(1,L)+J2*B(2,L)+K2*B(3,L)
330 NEXT L
332 D2=R2(1)*R2(1)+R2(2)*R2(2)+R2(3)*R2(3)
334 IF (D2=0) OR (D2>M2) THEN 400
338 D3=0
340 FOR L=1 TO 3
342 R3=R1(L)-R2(L):D3=D3+R3*R3
344 NEXT L
```

FIGURE 28. Program Ising2 for Calculating Coordination Numbers

```
346 IF (D3=0) OR (D3>M2) THEN 400
348 GOSUB 6000
400 NEXT K2
402 NEXT J2
404 NEXT I2
450 NEXT K1
460 NEXT J1
470 NEXT I1
500 PRINT #1,"D1,  D2,   Z(D1,D2)"
510 FOR D1=1 TO M2
512 FOR D2=1 TO M2
522 PRINT #1,D1;"  ";D2;"  ";C(D1,D2)
524 PRINT D1;"  ";D2;"  ";C(D1,D2)
530 NEXT D2,D1
534 PRINT #1, "This calculation took   ";TIME$;"."
536 PRINT #1:PRINT TIME$
600 CLOSE #1
5000 P=D1
5010 IF D1>D2 THEN T=D1:D1=D2:D2=T
5020 IF D2>D3 THEN T=D2:D2=D3:D3=T
5030 IF D1>D2 THEN T=D1:D1=D2:D2=T
5040 C(D1,D2,D3)=C(D1,D2,D3)+1
5050 D1=P
5060 RETURN
6000 D(1)=D1:D(2)=D2:D(3)=D3:P1=D1
6010 M=3
6020 FOR G=M-1 TO 1 STEP -1
6030 FOR F=1 TO G
6040 IF D(F)>D(F+1) THEN SWAP D(F),D(F+1)
6050 NEXT F
6060 NEXT G
6070 D1=D(1):D2=D(2):D3=D(3)
6080 C(D1,D2)=C(D1,D2)+1
6085 D1=P1
6090 RETURN
```

FIGURE.28 continued

APPENDIX D

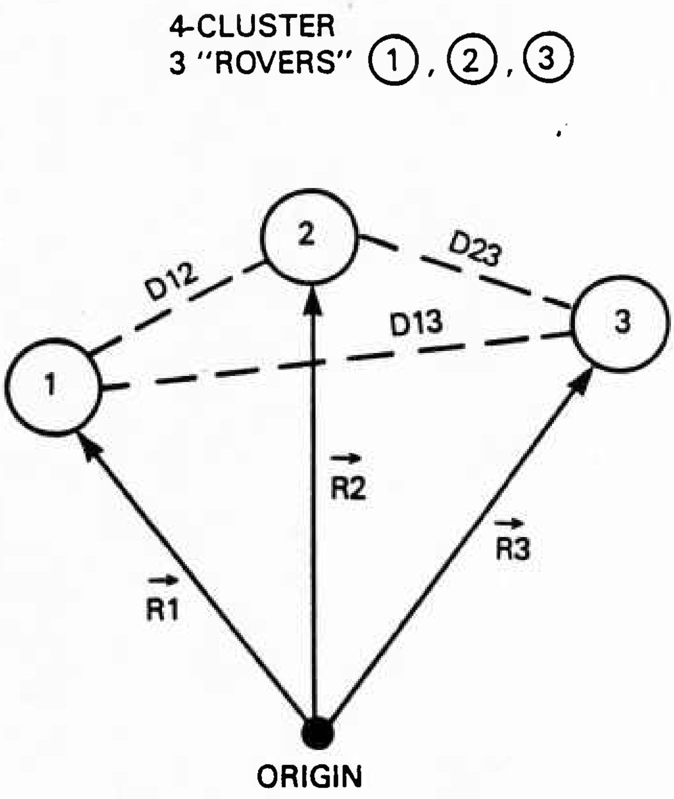
CLUSTERS OF 4-PARTICLES

This appendix describes the calculation of the coordination number for a cluster of four particles. Two pieces of information are obtained from the calculation: (1) the shape of the most compact figure for 4-particles and (2) the number of these most compact figures which is called the cordination number. The particles are fixed in position at the lattice sites of the crystal (see Fig. 1, Ch. I)

Fig. 29 is a diagram of the method used in ISING4F to calculate the distances between the particles. Use one of the particles as the origin and draw a vector to each of the other three particles which are called the "rovers" and labeled 1,2,3. Calculate the distances corresponding to these 3 vectors and the distances between each of the 3 "rovers". The vectors and the associated distances are labeled as shown in Fig. 29.

The calculation of the six distances are calculated and stored by ISING4F for each particle that is choosen as an origin. The distances are sorted and the number of similar figures are counted. The results for the 4-cluster case are given in Fig. 30 and show that the most compact figure is an equilateral pyramid with six sides equal and that there are 48 of them. The fact that all six sides are equal length is an important distinction. This has been true for the calculations in this study. It will not be true for higher order clusters e.g. 5-cluster and 6-cluster configurations. This means that the entropy calculation will be done in a different way than described in this work.

Fig. 31 is a listing of the steps in the program ISING4F to carry out this calculation for an FCC latice. Other lattices are possible by changing the values in lines 160 to 180 to represent other lattice sites.



$\vec{R1}$	D1
$\vec{R2}$	D2
$\vec{R3}$	D3
$\vec{R12}$	D12
$\vec{R13}$	D13
$\vec{R23}$	D23

Fig. 29. DIAGRAM OF A 4-PARTICLE CLUSTER SHOWING THE ORIGIN AND 3 "ROVERS". THE VECTORS $\vec{R1}$ THRU $\vec{R23}$ AND CORRESPONDING DISTANCES D1 THRU D23 ARE USED IN THE PROGRAM ISING 4F TO CALCULATE THE NUMBER OF THE MOST COMPACT FIGURES FOR AN FCC LATTICE.

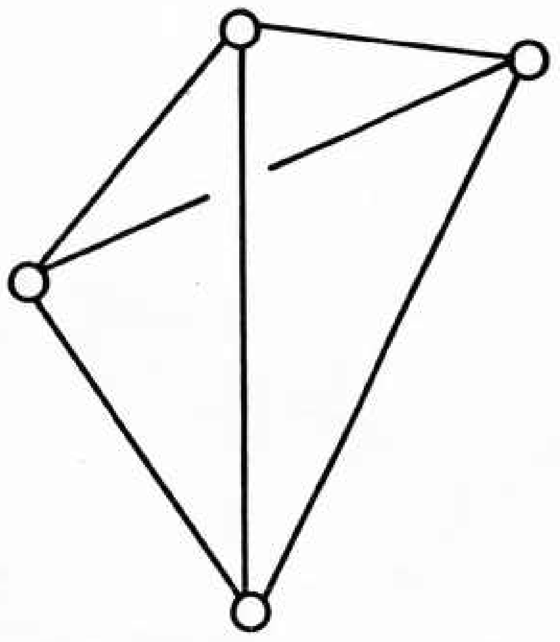


Fig. 30. AN EQUILATERAL PYRAMID WITH SIX EQUAL SIDES IS THE MOST COMPACT FIGURE FOR A 4-PARTICLE CLUSTER. THIS CONFIGURATION WAS OBTAINED USING ISING 4F AND 48 (CONFIGURATION NUMBER) OF THESE PYRAMIDS WERE COUNTED.

```
10 REM THIS PROGRAM COMPUTES
20 REM N-COORDINATION NUMBERS (FCC)
40 REM  4 DEC 1985 (converted from ISING3.msb 16 feb 1985)
50 REM  see pg. 18/VIII and
60 REM N=4
70 REM
80 OPTION BASE 1
90 CLEAR
100 TIME=0
102 F$="lpt1:"
104 OPEN F$ FOR OUTPUT AS #1
110 DEFINT A-Z
120 REM DEFINITION OF BASIS VECTORS
130 REM B(I,X) is the Xth component of Bi
140 DIM B(3,3)
150 REM FACE CENTERED CUBIC
160 B(1,1)=1 : B(1,2)=1 : B(1,3)=0
170 B(2,1)=0 : B(2,2)=1 : B(2,3)=1
180 B(3,1)=1 : B(3,2)=0 : B(3,3)=1
190 MAX=2
200 M2=MAX*MAX
210 DIM C(M2,M2,M2,M2,M2,M2)
220 DIM R1(3),R2(3),R3(3)
230 FOR I1=-MAX TO MAX
240 FOR J1=-MAX TO MAX
250 FOR K1=-MAX TO MAX
270 FOR L=1 TO 3
280 R1 (L)=I1*B(1,L)+J1*B(2,L)+K1*B(3,L)
290 NEXT L
300 D1=R1(1)*R1(1)+R1(2)*R1(2)+R1(3)*R1(3)
310 IF (D1=0) OR (D1>M2) THEN 710
320 FOR I2=-MAX TO MAX
330 FOR J2=-MAX TO MAX
340 FOR K2=-MAX TO MAX
350 FOR L=1 TO 3
360 R2(L)=I2*B(1,L)+J2*B(2,L)+K2*B(3,L)
370 NEXT L
380 D2=R2(1)*R2(1)+R2(2)*R2(2)+R2(3)*R2(3)
390 IF (D2=0) OR (D2>M2) THEN 700
400 FOR I3=-MAX TO MAX
410 FOR J3=-MAX TO MAX
420 FOR K3=-MAX TO MAX
430 FOR L=1 TO 3
440 R3(L)=I3*B(1,L)+J3*B(2,L)+K3*B(3,L)
```

FIGURE 31. Program Ising4f for Calculating Coordination Number for a 4-cluster

```
450 NEXT L
460 D3=R3(1)*R3(1)+R3(2)*R3(2)+R3(3)*R3(3)
470 IF (D3=0) OR (D3>M2) THEN 690
480 D12=0
490 FOR L=1 TO 3
500 R12=R1(L)-R2(L):D12=D12+R12*R12
510 NEXT L
520 IF (D12=0) OR (D12>M2) THEN 690
530 D13=0
540 FOR L=1 TO 3
550 R13=R1(L)-R3(L):D13=D13+R13*R13
560 NEXT L
570 IF (D13=0) OR (D13>M2) THEN 690
580 D23=0
590 FOR L=1 TO 3
600 R23=R2(L)-R3(L):D23=D23+R23*R23
610 NEXT L
620 IF (D23=0) OR (D23>M2) THEN 690
630 REM BUBBLE SORT
635 GOSUB 6000
690 NEXT K3,J3,I3
700 NEXT K2,J2,I2
710 NEXT K1,J1,I1
720 PRINT #1,"D1,  D2,  D3,  D12,  D13,  D23
                                   Z(D1,D2,D3,D12,D13,D23)"
730 FOR D1=1 TO M2
740 FOR D2=1 TO M2
750 FOR D3=1 TO M2
752 FOR D12=1 TO M2
754 FOR D13=1 TO M2
756 FOR D23=1 TO M2
760 PRINT #1,D1;"  ";D2;"  ";D3;"  ";D12;"  ";D13;"  ";
                             D23;"  ";C(D1,D2,D3,D12,D13,D23)
765 PRINT D1;"  ";D2;"  ";D3;"  ";D12;"  ";D13;"  ";
                             D23;"  ";C(D1,D2,D3,D12,D13,D23)
770 NEXT D23,D13,D12,D3,D2,D1
780 CLOSE #1
6000 D(1)=D1:D(2)=D2:D(3)=D3:D(4)=D12:D(5)=D13:
                                          D(6)=D23:P1=D1
6010 M=6
6020 FOR G=M-1 TO 1 STEP -1
6030 FOR F=1 TO G
6040 IF D(F)>D(F+1) THEN SWAP D(F),D(F+1)
6050 NEXT F
6060 NEXT G
6070 D1=D(1):D2=D(2):D3=D(3):D12=D(4):D13=D(5):D23=D(6)
6080 C(D1,D2,D3,D12,D13,D23)=C(D1,D2,D3,D12,D13,D23)+1
6085 D1=P1
6090 RETURN
```

FIGURE 31. continued

APPENDIX E

PROGRAM LISTINGS

There are three programs listed in this appendix. Fig. 32 is a listing of SIM4 used to obtain the equilibrium (minimum) free energy for the fourth approximation which is the sum of the first, second, third and fourth term of the Morita expansion. The minimization program for lower order approximations can be obtained by deleting the equations for the higher order clusters. The Simplex minimization that is used here is described in reference 6.

Fig. 33 is a listing of HIDDEN6 that is used for making the contour plots shown in the text. This program is described in reference [24-26].

The program GRID6 listed in Fig. 34 was used to calculate the entropy values in the third and fourth approximations that were plotted as a function of x,y. .

```
10 REM **PROGRAM NAME IS 'SIM4.BAS', BECAUSE IT DOES A
         'SIMPLEX' MINIMIZATION
20 REM **ON THE 4-CLUSTER ISING MODEL
30 REM **COPIED FROM 'SIM9.BAS' RUNNING ON HEN'S PDP-11
40 REM **21-MAR-1985
50 RANDOMIZE
60 Z1=12:Z111=48:Z111111=48
70 TR=2
80 BR=0
90 GOTO 330
99 REM **PUT THE FUNCTION TO-BE-MINIMIZED HERE...
100 ON ERROR GOTO 299
110 X=A(0)
120 Y=A(1)
122 Z=A(2)
124 W=A(3)
130 P1=(1+X)/2 : P2=(1-X)/2
140 R1=P1*LOG(P1)+P2*LOG(P2)
150 P21=(1+2*X+Y)/4:P22=(1-Y)/4:P23=(1-2*X+Y)/4
160 R2=P21*LOG(P21)+2*P22*LOG(P22)+P23*LOG(P23)
162 P31=(1+3*X+3*Y+Z)/8:P34=(1-3*X+3*Y-Z)/8
163 P32=(1+X-Y-Z)/8:P33=(1-X-Y+Z)/8
164 R3=P31*LOG(P31)+P34*LOG(P34)+3*P32*LOG(P32)
    +3*P33*LOG(P33)
170 P41=(1+4*X+6*Y+4*Z+W)/16:P43=(1+2*X-2*Z-W)/16
172 P42=(1-4*X+6*Y-4*Z+W)/16:P44=(1-2*X+2*Z-W)/16
174 P45=(1-2*Y+W)/16
176 R4=P41*LOG(P41)+P42*LOG(P42)+4*(P43*LOG(P43)
    +P44*LOG(P44))+6*P45*LOG(P45)
180 R=R1+(Z1/2)*(R2-2*R1)+(Z111/6)*(R3-3*R2+3*R1)
182 R=R+(Z111111/24)*(R4-4*R3+6*R2-4*R1)
190 F=-BR*X-(Z1/2)*Y+TR*R
298 ON ERROR GOTO 0:RETURN
299 F=1E+35:RESUME 298
330 N=4
340 I1=0
350 DIM X(5,5),M(5),V(5),R(5),E(5),C(5),A(5)
360 FOR I=0 TO N-1
370 READ M(I),V(I)
380 NEXT I
390 FOR J=0 TO N
400 FOR I=0 TO N-1
410 X(I,J)=M(I)+RND*V(I)
420 NEXT I
430 NEXT J
440 F7=1E+37 : F9=-F7
450 V7=-1 : V9=-1
460 FOR J=0 TO N
```

FIGURE 32. Program SIM4

```
470 FOR I=0 TO N-1
480 A(I)=X(I,J)
490 NEXT I
500 GOSUB 100:X(N,J)=F
510 IF F<F7 THEN F7=F : V7=J
520 IF F>F9 THEN F9=F : V9=J
530 NEXT J
540 IF V7=-1 THEN PRINT"F-MIN NOT FOUND" :STOP
550 IF V9=-1 THEN PRINT"F-MAX NOT FOUND" :STOP
560 IF V7=V9 THEN PRINT"F-MIN = F-MAX!!!":STOP
570 PRINT"ITTERATION #";I1:I1=I1+1
580 FOR J=0 TO N
590 PRINT J;" ";
600 FOR I=0 TO N
610 PRINT X(I,J);" ";
620 NEXT I
630 PRINT
640 NEXT J
650 PRINT
660 FOR I=0 TO N-1
670 S=0
680 FOR J=0 TO N
690 IF J<>V9 THEN S=S+X(I,J)
700 NEXT J
710 M(I)=S/N
720 V(I)=X(I,V9)-M(I)
730 R(I)=M(I)-V(I)
740 A(I)=R(I)
750 NEXT I
760 GOSUB 100 :F1=F
770 IF F1<=F7 THEN 910
780 IF F1<=F9 THEN 1020
790 FOR I=0 TO N-1
800 C(I)=M(I)+V(I)/2 : A(I)=C(I)
810 NEXT I
820 GOSUB 100 : F2=F
830 IF F2<=F9 THEN 1070
840 FOR I=0 TO N-1
850 FOR J=0 TO N
860 IF J<>V7 THEN X(I,J)=(X(I,J)+X(I,V7))/2
870 NEXT J
880 NEXT I
890 PRINT"CONTRACT ENTIRE SIMPLEX"
900 GOTO 1120
910 FOR I=0 TO N-1
920 E(I)=M(I)-2*V(I):A(I)=E(I)
930 NEXT I
940 GOSUB 100:F3=F
950 IF F3<=F7 THEN 970
960 GOTO 1020
```

FIGURE 32 continued

```
970 FOR I=0 TO N-1
980 X(I,V9)=E(I)
990 NEXT I
1000 PRINT"ACCEPT EXPANDED VERTEX"
1010 GOTO 1120
1020 FOR I=0 TO N-1
1030 X(I,V9)=R(I)
1040 NEXT I
1050 PRINT"ACCEPT REFLECTED VERTEX"
1060 GOTO 1120
1070 FOR I=0 TO N-1
1080 X(I,V9)=C(I)
1090 NEXT I
1100 PRINT"ACCEPT CONTRACTED VERTEX"
1110 GOTO 1120
1120 GOTO 440
1130 DATA .0,.3
1140 DATA .0,.3
1150 DATA .0,.3
1160 DATA .0,.3
```

FIGURE 32 continued

```
1 'From NIBBLE/Vol 4/No. 8/pp 61-71
2 'Xfered to Jack's COMPAQ on 3-27-86 by HL
3 '
4 CMAX=639:RMAX=199
5 Z1=12
6 TR=10
7 BR=0
90 DIM H(CMAX),L(CMAX)
100 MM=1E+10:UH=-MM:UL=MM:VH=-MM:VL=MM
110 FOR I=0 TO CMAX:L(I)=RMAX:NEXT
120 XE=2/2.5:YE=1/2.5:ZE=1/2.5
130 S1=XE*XE+YE*YE:S2=SQR(S1):S3=SQR(S1+ZE*ZE):S4=1/(S2*S3)
140 M=20:N=20
150 DIM X(M),Y(N),R(M,N,1)
160 XL=-1:XH=1:YL=-1:YH=1
170 DX=(XH-XL)/M:DY=(YH-YL)/N
180 X0=XH:IF XE<0 THEN DX=-DX:X0=XL
190 Y0=YH:IF YE<0 THEN DY=-DY:Y0=YL
200 CX=(CMAX+1)/2:CY=(RMAX+1)/2
210 FOR I=0 TO M:X(I)=X0-I*DX:NEXT
220 FOR J=0 TO N:Y(J)=Y0-J*DY:NEXT
230 FOR I=0 TO M:FOR J=0 TO N
240 X=X(I):Y=Y(J)
250 '
260 ' Replacable function
270 ' Z=F(X,Y)
272 '
278 P1=(1+X)/2:P2=(1-X)/2
280 IF P1<=0 OR P2<=0 THEN PHI=0:GOTO 300
283 SS1=P1*LOG(P1)+P2*LOG(P2)
284 P21=(1+2*X+Y)/4:P22=(1-Y)/4:P23=(1-2*X+Y)/4
285 IF P21<=0 OR P22<=0 OR P23<=0 THEN PHI=0:GOTO 300
286 SS2=P21*LOG(P21)+2*P22*LOG(P22)+P23*LOG(P23)
288 PHI=-BR*X-(Z1/2)*Y+TR*(SS1+(Z1/2)*(SS2-2*SS1))
300 IF PHI>2 THEN PHI=2
310 Z=PHI/20+.5
320 GOSUB 890
330 R(I,J,0)=U:R(I,J,1)=V:GOSUB 1420
340 NEXT J:PRINT "I=";I,"MAX=";M:NEXT I
350 'S is the scale factor
360 S=MM:IF UL=0 THEN 380
370 S0=CMAX/(2.1*ABS(UL)):IF S0<S THEN S=S0
380 IF UH=0 THEN 400
390 S0=CMAX/(2.1*ABS(UH)):IF S0<S THEN S=S0
400 IF VL=0 THEN 420
410 S0=RMAX/(2.1*ABS(VL)):IF S0<S THEN S=S0
420 IF VH=0 THEN 450
430 S0=RMAX/(2.1*ABS(VH)):IF S0<S THEN S=S0
440 'Locate in HGR2 coordinates
450 FOR I=0 TO M:FOR J=0 TO N
```

FIGURE 33. PROGRAM HIDDEN6

```
460 R(I,J,0)=INT(S*R(I,J,0)+CX):R(I,J,1)=INT(S*R(I,J,1)+CY)
470 NEXT J:NEXT I
480 'Start graphics
490 KEY OFF:SCREEN 2
492 CLS
500 IF ABS(XE)<ABS(YE) THEN 670
510 FOR I=0 TO M
520 'Draw fixed X-lines
530 FOR J=1 TO N
540 U1=R(I,J-1,0):V1=R(I,J-1,1):U2=R(I,J,0):V2=R(I,J,1)
550 GOSUB 950:'Test visibility, and plot...
560 GOSUB 1220:'Update H,L arraws
570 NEXT J
580 IF I=M THEN 650
590 'Draw fixed Y-line segments
600 FOR J=0 TO N
610 U1=R(I,J,0):V1=R(I,J,1):U2=R(I+1,J,0):V2=R(I+1,J,1)
620 GOSUB 950:'Test visibility, and plot...
630 GOSUB 1220:'Update H,L arrays
640 NEXT J
650 NEXT I
660 GOTO 820
670 FOR J=0 TO N
680 'Draw fixed Y-lines
690 FOR I=1 TO M
700 U1=R(I-1,J,0):V1=R(I-1,J,1):U2=R(I,J,0):V2=R(I,J,1)
710 GOSUB 950
720 GOSUB 1220
730 NEXT I
740 IF J=N THEN 810
750 'Draw fixed X-line segments
760 FOR I=0 TO M
770 U1=R(I,J,0):V1=R(I,J,1):U2=R(I,J+1,0):V2=R(I,J+1,1)
780 GOSUB 950
790 GOSUB 1220
800 NEXT I
810 NEXT J
820 PRINT CHR$(7):'Here is a chance to get printed output.
830 '
840 '
850 END
860 '
870 'Transformation subroutine
880 '
890 U=(XE*Y-YE*X)/S2
900 V=(ZE*(X*XE+Y*YE)-S1*Z)*S4
910 RETURN
920 '
930 'Wright's algorithm!!!
940 '
950 T1=0:T2=0:G1=0:G2=0
```

FIGURE 33. continued

```
960 IF V1>=H(U1) THEN T1=1
970 IF V2>=H(U2) THEN T2=1
980 IF V1<=L(U1) THEN G1=1
990 IF V2<=L(U2) THEN G2=1
1000 IF T1=1 AND T2=1 THEN LINE(U1,V1)-(U2,V2):RETURN
1010 IF G1=1 AND G2=1 THEN LINE(U1,V1)-(U2,V2):RETURN
1020 IF T1+T2+G1+G2=0 THEN RETURN
1030 GOSUB 1370
1040 IF KM=KX THEN 1160
1050 F1=0:F2=0
1060 FOR K=KM TO KX
1070 VK=VM+(VX-VM)*(K-KM)/(KX-KM)
1080 IF VK>H(K) OR VK<L(K) THEN U1=K:V1=VK:F1=1:K=KX
1090 NEXT
1100 FOR K=KX TO KM STEP -1
1110 VK=VM+(VX-VM)*(K-KM)/(KX-KM)
1120 IF VK>H(K) OR VK<L(K) THEN U2=K:V2=VK:F2=1:K=KM
1130 NEXT
1140 IF F1=1 AND F2=1 THEN LINE(U1,V1)-(U2,V2)
1150 RETURN
1160 IF VX>H(U1) THEN LINE(U1,H(U1))-(U1,VX):RETURN
1170 IF VM<L(U1) THEN LINE(U1,L(U1))-(U1,VM)
1180 RETURN
1190 '
1200 'Update H,L arrays
1210 '
1220 IF V1>H(U1) THEN H(U1)=V1
1230 IF V2>H(U2) THEN H(U2)=V2
1240 IF V1<L(U1) THEN L(U1)=V1
1250 IF V2<L(U2) THEN L(U2)=V2
1260 IF ABS(U1-U2)<1 THEN RETURN
1270 GOSUB 1370
1280 FOR K=KM+1 TO KX-1
1290 VK=VM+(VX-VM)*(K-KM)/(KX-KM)
1300 IF VK>H(K) THEN H(K)=VK
1310 IF VK<L(K) THEN L(K)=VK
1320 NEXT K
1330 RETURN
1340 '
1350 'Find left-most point of the line
1360 '
1370 KM=U1:KX=U2:VM=V1:VX=V2:IF KM>KX THEN KM=U2:KX=U1:
     VM=V2:VX=V1:RETURN
1380 RETURN
1390 '
1400 'Find extreme values in U,V coordinates before scaling
1410 '
1420 IF U>UH THEN UH=U
1430 IF U<UL THEN UL=U
1440 IF V>VH THEN VH=V
1450 IF V<VL THEN VL=V
1460 RETURN
```

FIGURE 33 continued

```
10 Z1=12
20 Z111=48
30 Z111111=48
100 OPEN "lpt1:" FOR OUTPUT AS #1
102 LG2=LOG(2)
105 FOR W=.8 TO 0 STEP -.2
106 FOR Z=.8 TO 0 STEP -.2
108 PRINT #1,"Z=";Z;"w=";W;
110 PRINT #1,"                    Y-AXIS"
112 PRINT #1,"      ";
120 FOR Y=-10 TO 10
122 PRINT #1, USING "###";Y;
124 NEXT Y
126 PRINT #1,
200 FOR X=1 TO -1 STEP -.1
202 PRINT #1,USING "#.#";X;:PRINT #1,"   ";
210 FOR Y=-1 TO 1.05 STEP .1
220 ON ERROR GOTO 800
300 P1=(1+X)/2
310 P2=(1-X)/2
320 R1=P1*LOG(P1)+P2*LOG(P2)
330 P21=(1+2*X+Y)/4
340 P22=(1-Y)/4
350 P23=(1-2*X+Y)/4
360 R2=P21*LOG(P21)+2*P22*LOG(P22)+P23*LOG(P23)
400 P31=(1+3*X+3*Y+Z)/8
410 P32=(1+X-Y-Z)/8
420 P33=(1-X-Y+Z)/8
430 P34=(1-3*X+3*Y-Z)/8
440 R3=P31*LOG(P31)+3*P32*LOG(P32)+3*P33*LOG(P33)
          +P34*LOG(P34)
445 P41=(1+4*X+6*Y+4*Z+W)/16:P43=(1+2*X-2*Z-W)/16
450 P42=(1-4*X+6*Y-4*Z+W)/16:P44=(1-2*X+2*Z-W)/16
453 P45=(1-2*Y+W)/16
455 R44=P41*LOG(P41)+P42*LOG(P42)+4*(P43*LOG(P43)
          +P44*LOG(P44))+6*P45*LOG(P45)
460 R4=R1+(Z1/2)*(R2-2*R1)+(Z111/6)*(R3-3*R2+3*R1)
465 R4=R4+(Z111111/24)*(R44-4*R3+6*R2-4*R1)
470 R4=-R4/(LG2)
600 R=INT(100*R4+.5)
610 PRINT #1,USING "###";R;
700 NEXT Y
710 PRINT #1,
720 NEXT X
730 NEXT Z
740 NEXT W
799 END
800 PRINT #1," **";
810 RESUME 700
```

FIGURE 34. PROGRAM GRID6

APPENDIX F

UNITS and NOTATION

The following "reduced" units are used in the text.

Φ = "reduced" free energy F = (F/NJ)

B_r = "reduced" magnetic field B = $(\mu_0 B/J)$

T_r = "reduced" temperature T = $(k_B T/J)$

J = the value of the exchange integral = $(k_B T_c/Z)$.

For a Curie temperature = T_c = 1056 °K (Fe) and Z = 12 for an FCC lattice: $J = 7.56\ (10^{-3})$e.v.

Entropy: $$\frac{S(\text{Joules}/{}^{\circ}K)}{\ln 2} = S \text{ in "bits"}$$

In the equations two notations have been used to represent the same quantites.

$\langle\mu\rangle$ = either x or $x^{(1)}$

$\langle\mu\mu\rangle$ = either y_{ij} or $x^{(2)}_{ij}$

$\langle\mu\mu\mu\rangle$ = either z_{ijk} or $x^{(3)}_{ijk}$

APPENDIX G

TABLE 2

EQUILIBRIUM FREE ENERGY $\tilde{\Omega}$

$B_r = 0$

T_r	Approximation			
	First	Second	Third(½)	Fourth
2	-6.000012	-6.xxxxxx	-5.991287	-5.734586
4	-6.010053	-6.010166	-6.043771	-6.009864
6	-6.118027	-6.122647	-6.118978	-6.123150
8	-6.466731	-6.500590	-6.503969	-6.449281
10	-7.172468	-7.298410	-7.319456	-7.375871
12	-8.317766	-8.567490	-8.599178	-8.653156
14	-9.704059	-9.918160	xxxxxxxxx	-9.975911
16	-11.09035	-11.27774	-11.21078	-11.31896
18	-12.47665	-12.64323	-12.65670	-12.67498
20	-13.86294	-14.01289	-14.02367	-14.03782
3	-	-6.001010	-	-
5	-	-6.043730	-	-
7	-	-6.268225	-6.269251	-
9	-	-6.838270	-6.847406	-
9.5	-	-7.052020	-	-
10.25	-	-7.434480	-	-
10.5	-	-7.579450	-	-
10.75	-	-7.733550	-	-
10.85	-	-7.797817	-	-
10.9	-	-7.805160	-	-
10.95	-	-7.863579	-	-
11	-	-7.896960	-7.935181	-
13	-	-9.241450	-9.268160	-
15	-	-10.59706	-10.61683	-
17	-	-11.95988	-11.97504	-

TABLE 3.

SOME CORRELATION COEFFICIENTS

$B_r = 0$

Cluster	Correlation Coefficients			
	x	y	z	w
	$T_r = 4$			
1-c	.9948288	-	-	-
2-c	.9947500	.9895800	-	-
3-c(½)	.9651874	.9330112	.9030889	-
4-c	.9945275	.9891984	.9839292	.9787838
	$T_r = 8$			
1-c	.8581825	-	-	-
2-c	.8325000	.7070200	-	-
3-c(½)	.8276450	.7017475	.6039199	-
4-c	.7032843	.5307391	.4117586	.3277481
	$T_r = 10$			
1-c	.6588523	-	-	-
2-c	.5350000	.3400000	-	-
3-c(½)	.4924544	.3144164	.2087749	-
4-c	.1001604	.2064547	.0430753	.08437848
	$T_r = 16$			
1-c	1.089163E-3	-	-	-
2-c	-1.298148E-3	6.244406E-2	-	-
3-c(½)	-.1772807	9.670085E-2	-2.161592E-2	-
4-c	9.9860E-5	8.6007E-2	-1.988E-4	1.8118E-2

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