

Random Spin Systems: Some Rigorous Results*

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Several general results are obtained for a system of spins on a lattice in which the various lattice sites are occupied at random, and the spins, if present, interact via a general Heisenberg or Ising interaction decreasing sufficiently rapidly with distance. It is shown that the free energy per site exists in the limit of an infinite system, is a continuous function of concentration, and has the usual convexity (stability) properties. For Ising systems with interactions of finite range, the free energy is an analytic function of concentration and magnetic field for a suitable range of these variables. The random Ising ferromagnet on a square lattice (or simple cubic lattice) with nearest-neighbor interactions is shown to exhibit a spontaneous magnetization at sufficiently high concentrations and low temperatures.

1. INTRODUCTION

The problem of idealized Heisenberg or Ising ferromagnets on regular lattices in which certain sites, chosen at random, are vacant has been extensively studied in connection with the problem of ferromagnetism in quenched dilute alloys.¹ Whereas the physical properties of such alloys require a more complex analysis than was first thought to be the case, the model calculations have provided at least a qualitative guide in interpreting experimental data.² Investigations of statistical properties of a random spin system should also yield insight into the effects of impurities on phase transitions and critical points, both in magnetic and nonmagnetic systems.³

We shall discuss here, from a rigorous point of view, certain mathematical properties of such systems associated with taking the infinite volume or "thermodynamic" limit. In essence, we wish to extend to at least a certain class of random systems some of the results already known to hold for regular systems.

The mathematical techniques are unfortunately not of much value in making good estimates of thermodynamic properties, transition temperatures, critical concentrations, etc. Nonetheless, in the absence of soluble models (except in one dimension), general or "rigorous" results may prove valuable as a guide to intuition and a check on the consistency of approximate calculations.

An outline of our paper is as follows. In Sec. 2, the random spin problem is defined and some notation essential to further developments is introduced. Section 3 contains a proof of the infinite-volume limit of the free energy under fairly general conditions on the Hamiltonian. In Sec. 4 we show that an Ising ferromagnet with nearest-neighbor interactions on a square lattice will exhibit a spontaneous magnetization over a certain range of temperatures and concentration. The Ising-model free energy for a system with interactions of finite range is an analytic function of concentration and magnetic field for suitable ranges of these variables; the proof is found in Sec. 5. Some additional results are stated without proof in Sec. 6.

In the main, our procedures are simply an adoption to the problem at hand of mathematical techniques already published and discussed at length in several different papers. For this reason our proofs are somewhat abbreviated and certain steps are omitted in the interests of brevity; we have tried to include a complete discussion of the modifications required and difficulties encountered in applying the "well-known" methods to random systems.

2. NOTATIONS AND DEFINITIONS

A finite system or crystal Ω (which we shall usually assume has a simple shape, for instance, a cube) consists of N_Ω sites lying on a regular lattice. (We

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¹ H. Sato, A. Arrott, and R. Kikuchi, *J. Phys. Chem. Solids* **10**, 19 (1959); R. J. Elliott, *ibid.* **16**, 165 (1960); J. S. Smart, *ibid.* **16**, 169 (1960); M. Coopersmith and R. Brout, *ibid.* **17**, 254 (1961); R. J. Elliott and B. R. Heap, *Proc. Roy. Soc. (London)* **A265**, 264 (1962); B. R. Heap, *Proc. Phys. Soc. (London)* **82**, 252 (1963); D. H. Lyons, *Phys. Rev.* **128**, 2022 (1962); G. S. Rushbrooke and D. J. Morgan, *Molecular Phys.* **4**, 1, 291 (1961); **6**, 477 (1963); P. J. Wojtowicz, *ibid.* **6**, 157 (1963); G. S. Rushbrooke, *J. Math. Phys.* **5**, 1106 (1964); T. Morita, *ibid.* **5**, 1401 (1964); R. Abe, *Progr. Theoret. Phys. (Kyoto)* **31**, 412 (1964); N. W. Dalton, C. Domb, and M. F. Sykes, *Proc. Phys. Soc. (London)* **83**, 496 (1964); S. Katsura and B. Tsujiyama, in *Critical Phenomena*, M. S. Green and J. V. Sengers, Eds. (National Bureau of Standards, Washington, D.C., 1966), p. 219. See also Refs. 2-5 below.

² See, for example, M. W. Klein and R. Brout, *Phys. Rev.* **132**, 2412 (1963); C. E. Violet and R. J. Borg, *ibid.* **149**, 540 (1966).

³ For some applications to nonmagnetic systems, see G. M. Bell, *Proc. Phys. Soc. (London)* **72**, 649 (1958).

shall omit the subscript on N when the system referred to is clear from context.) A *partition* is a subset θ of sites from Ω which are occupied by spins, the remaining sites being empty. The case $\theta = \Omega$, all sites occupied, we call a *regular* system as distinct from a *random* system for which, in general, θ is a proper subset.

For a given partition θ , we define a spin Hamiltonian

$$\mathcal{H}(\theta) = -2 \sum_{i \in \theta} \sum_{j \in \theta} J_{ij} [S_i^z S_j^z + \gamma (S_i^x S_j^x + S_i^y S_j^y)] - 2\mu H \sum_{i \in \theta} S_i^z, \quad (2.1)$$

where S_i is the quantum-mechanical spin operator on the i th site; $J_{ij} = J_{ji}$ is the "exchange integral," equal to zero for $i = j$; μ is the magnetic moment; H , the external magnetic field. The x component of S_i , S_i^x , has eigenvalues $S, S - 1, S - 2, \dots, -S$, and likewise the y and z components; S , the "total spin quantum number," is a positive integer or half-odd integer. For $\gamma = 0$, we have an "Ising model" and, for $\gamma = 1$, a "Heisenberg model." The J_{ij} in (2.1) are regarded as functions only of the relative location of sites i and j and are independent of the partition θ . Note that the sums in (2.1) extend only over occupied sites.

The free energy F , defined by

$$e^{-\beta F} = \text{Tr} [e^{-\beta \mathcal{H}}], \quad (2.2)$$

where $\beta = (kT)^{-1}$, the inverse temperature, is a function of θ through (2.1). If θ contains n sites, "Tr" stands for a trace over all the $(2S + 1)^n$ possible states or *configurations* of the n spins located on the occupied sites. The magnetization M and entropy S for the partition in question may be found, as usual, by differentiation:

$$M(\theta) = - \left(\frac{\partial F(\theta)}{\partial H} \right)_T, \quad (2.3)$$

$$S(\theta) = - \left(\frac{\partial F(\theta)}{\partial T} \right)_H. \quad (2.4)$$

In the *random spin problem* or *random impurity problem* one assigns to each partition a probability $P(\theta)$ and defines the free energy for the crystal as a whole by

$$F_\Omega = \sum_\theta P(\theta) F(\theta). \quad (2.5)$$

We shall henceforth assume that $P(\theta)$ is independent of temperature and magnetic field. Physically, this is the assumption that the random "impurities" are frozen in position; Brout⁴ has pointed out that it should not be an unreasonable model of a real

⁴ R. Brout, Phys. Rev. **115**, 824 (1959); R. R. Mazo, J. Chem. Phys. **39**, 1224 (1963).

magnetic crystal in which the motion of various impurities is relatively slow and the time required for them to come to some ultimate equilibrium is long compared with magnetic relaxation in the spin system itself and the time scale of ordinary magnetic experiments. (It is also possible to define models in which "impurity" equilibrium as well as magnetic equilibrium is assumed⁵; we shall not discuss these here.)

In comparison with regular magnetic systems, random systems (as we have defined them) possess additional complexity through the existence of two kinds of average. There is the ordinary thermal average of an operator \mathcal{O} in some partition θ defined by

$$\langle \mathcal{O} \rangle_\theta = \frac{\text{Tr} [\mathcal{O} e^{-\beta \mathcal{H}(\theta)}]}{\text{Tr} [e^{-\beta \mathcal{H}(\theta)}]} \quad (2.6)$$

and, in addition, the average over partitions of some function $g(\theta)$ (which could, for example, be $\langle \mathcal{O} \rangle_\theta$):

$$\langle \langle g \rangle \rangle_\Omega = \sum_\theta P(\theta) g(\theta). \quad (2.7)$$

We shall consider two possible forms for $P(\theta)$:

(a) For a fixed value of n ,

$$P = \begin{cases} \binom{N}{n}^{-1}, & \text{if } \theta \text{ contains } n \text{ sites,} \\ 0, & \text{otherwise.} \end{cases} \quad (2.8)$$

(b) Choose some p between 0 and 1, and let $q = 1 - p$. When θ contains n sites of a total of N in Ω ,

$$P(\theta) = p^n q^{N-n}. \quad (2.9)$$

Clearly, (b) is equivalent to the assumption that each individual site is occupied with probability p and vacant with probability q , and the occupation of different sites is statistically independent. It is an assumption frequently made in random spin calculations. The relationship of (a) to (b) is analogous to the relationship between canonical and grand canonical "ensembles" in the statistical mechanics of regular systems. The analogy should not be pressed too far, and the proof of asymptotic equivalence of (a) and (b) for large crystals (Sec. 3) is a bit different from standard arguments relating canonical and grand canonical ensembles.

3. EXISTENCE AND PROPERTIES OF THE ASYMPTOTIC FREE ENERGY

Let $P(\theta)$ be given by (2.9). The free energy for a given crystal Ω is [see Eq. (2.5)]

$$N_\Omega f_\Omega(p) = F_\Omega(p) = \sum_{\theta \subset \Omega} F(\theta) p^{v(\theta)} q^{N-v(\theta)}, \quad (3.1)$$

⁵ For example, G. M. Bell and W. M. Fairbairn, Phil. Mag. **6**, 907 (1961); G. M. Bell and D. A. Lavis, *ibid.* **11**, 937 (1965); I. Szyo and S. Miyazima, Progr. Theoret. Phys. (Kyoto) **36**, 1083 (1966).

where $\nu(\theta)$ is the number of occupied sites in Ω . Provided certain conditions are satisfied by the Hamiltonian (2.1) and by a sequence of crystals Ω of increasing volume, we shall show that

$$f = \lim_{N_\Omega \rightarrow \infty} f_\Omega \quad (3.2)$$

exists.

In several papers, the existence of the limit (3.2) or its analogs has been demonstrated for regular systems.^{6,7} The physical idea which underlies all the proofs (and is not always clear in the thicket of mathematical detail) is quite simple: If a large macroscopic system is split into a number of macroscopic parts, its free energy is the sum of the free energies of the different parts plus correction terms due to the interactions of adjacent systems across their common boundary. The correction terms, being (roughly) proportional to surface areas, become negligible for large systems as the surface-to-volume ratio approaches zero.

Consider two systems Ω_1 and Ω_2 with free energies F_1 and F_2 which together constitute a total system Ω with free energy F . The totality of sites in a pair of partitions θ_1, θ_2 in Ω_1, Ω_2 clearly constitute a partition θ_{12} for Ω with a probability

$$P(\theta_{12}) = P(\theta_1)P(\theta_2). \quad (3.3)$$

We may write

$$\mathcal{H}(\theta_{12}) = \mathcal{H}(\theta_1) + \mathcal{H}(\theta_2) + \mathcal{H}^*(\theta_1, \theta_2), \quad (3.4)$$

where \mathcal{H}^* contains the terms in the double sum (2.1) for which i lies in θ_1 and j in θ_2 or vice versa; that is, it represents a "surface term" involving in a significant way only spins fairly close to the boundary separating Ω_1 and Ω_2 .

In Ref. 6 it is shown that if \mathcal{H}_A and \mathcal{H}_B are two Hamiltonians in the same vector space (note that in the present context a Hamiltonian is a *finite*-dimensional Hermitian matrix), the associated free energies defined by (2.2) satisfy an inequality

$$|F(\mathcal{H}_A) - F(\mathcal{H}_B)| \leq |\mathcal{H}_A - \mathcal{H}_B|, \quad (3.5)$$

where the norm $|\mathcal{H}|$ of a Hermitian operator \mathcal{H} is simply the largest of the absolute values of its eigenvalues. We may apply (3.5) to (3.4) by letting \mathcal{H}_A be $\mathcal{H}(\theta_{12})$ and \mathcal{H}_B be $\mathcal{H}(\theta_1) + \mathcal{H}(\theta_2)$; note that \mathcal{H}_B is the Hamiltonian for two noninteracting systems. It follows that

$$|F(\theta_{12}) - [F(\theta_1) + F(\theta_2)]| \leq |\mathcal{H}^*(\theta_1, \theta_2)|. \quad (3.6)$$

⁶ R. B. Griffiths, *J. Math. Phys.* **5**, 1215 (1964).

⁷ The arguments for spin systems are closely analogous to those used for classical and quantum fluids; see C. N. Yang and T. D. Lee, *Phys. Rev.* **87**, 404 (1952); D. Ruelle, *Helv. Phys. Acta* **36**, 183, 789 (1963); M. E. Fisher, *Arch. Rational Mech. Anal.* **17**, 377 (1964).

To obtain a bound independent of θ_{12} we note that $|\mathcal{H}^*|$ is less than the sum of the norms of the individual terms making up \mathcal{H}^* , which sum will be a maximum for that partition in which all sites are occupied. That is, $|\mathcal{H}^*(\theta_1, \theta_2)|$ is bounded by the corresponding bound used in Ref. 6 for the case of a perfect crystal—all sites occupied in both systems 1 and 2,

$$|\mathcal{H}^*(\theta_{12})| \leq A_{12}. \quad (3.7)$$

Finally, noting that

$$\sum_{\theta_{12}} P(\theta_{12})[F(\theta_{12}) - F(\theta_1) - F(\theta_2)] = F - F_1 - F_2, \quad (3.8)$$

we obtain with the help of (3.6) and (3.7)

$$|F - F_1 - F_2| \leq A_{12}. \quad (3.9)$$

The inequality (3.9) is the rigorous counterpart of the intuitive arguments mentioned earlier. Its generalization to the case of several systems placed in contact is immediate, and once it has been obtained the proof of an infinite volume limit reduces to an exercise in geometry (see Refs. 6, 7) which we shall not repeat here. The final result is embodied in the following.

Theorem 1: The limit (3.2) exists provided two conditions are satisfied.

1. The J_{ij} in (2.1) depend only on the relative positions of sites i and j (translational invariance) and possess a bound

$$|J_{ij}| \leq C/r_{ij}^{d+\epsilon}, \quad (3.10)$$

where r_{ij} is the distance between sites i and j , d is the dimensionality of the lattice, C and ϵ are strictly positive numbers (it is essential to have $\epsilon > 0$), independent of the choice of i and j .

2. The sequence Ω is of crystals with sufficiently regular shape; for example, a d -dimensional parallelepiped with all d edges increasing to infinity.

Note that the thermodynamic limit f as a function of H, T is convex upwards, or concave, in both variables together. That is, if two points of the $f(H, T)$ surface are joined by a chord, the chord lies entirely on or below the surface. This follows from the observation that for any finite crystal Ω and specific partition θ , $F_\Omega(\theta, H, T)$ is concave,⁶ while averages (2.5) and limits (3.2) of concave functions inherit the same property. The convexity (concavity) property is equivalent to the "stability" conditions of positive susceptibilities and heat capacities. It also implies that f is a continuous function of both H and T in the range $0 < T < \infty$, $-\infty < H < \infty$.

The foregoing results have all been established with the assumption that p , the fraction of occupied sites,

is held constant. We now wish to examine the dependence of f in (3.1) on p , and also the “microcanonical” probability (2.8). In connection with the latter let us introduce the quantity

$$\hat{F}_\Omega(n) = \binom{N}{n}^{-1} \sum_{\nu(\theta)=n} F(\theta), \quad (3.11)$$

for a crystal Ω with N sites, where the summation is over all partitions θ having $\nu(\theta) = n$ sites. We shall need the following result:

Theorem 2: Provided the temperature is less than infinity, and n and m lie between 0 and N , there exists a finite constant D , depending on the Hamiltonian (2.1) and the temperature, but independent of Ω , N , n , and m , such that

$$|\hat{F}(m) - \hat{F}(n)| \leq D |n - m|. \quad (3.12)$$

The proof of this theorem depends on two lemmas, the first of which is an almost obvious combinatorial result. Given a partition θ with n occupied sites, let $\theta_1, \theta_2, \dots, \theta_{N-n}$ be the $N - n$ distinct partitions with $n + 1$ occupied sites obtained by adding to θ one additional site from Ω .

Lemma 1: Let g be any function defined on the partitions. Then

$$\sum_{\nu(\theta)=n+1} g(\theta) = \frac{1}{n+1} \sum_{\nu(\theta)=n} \sum_{j=1}^{N-n} g(\theta_j). \quad (3.13)$$

This result merely expresses the fact that every partition containing $n + 1$ sites appears in the double sum on the right side of (3.13) precisely $n + 1$ times, since this is the number of distinct partitions containing n sites from which it can be derived by the addition of one more site.

Lemma 2: Let θ_k be a partition containing $n + 1$ sites obtained from a partition θ of n sites by the addition of one site, say the site l . Then

$$|F(\theta_k) + \beta^{-1} \ln(2S + 1) - F(\theta)| \leq h, \quad (3.14)$$

where

$$h = 4 \sum_j |J_{lj} [S_l^z S_j^z + \gamma(S_l^x S_j^x + S_l^y S_j^y)] + 2\mu H |S_l^z|. \quad (3.15)$$

The sum over j in (3.15) extends over all lattice sites; (3.10) insures its convergence (note that $J_{ll} = 0$).

Proof: (Theorem 2) The comparison of $F(\theta)$ and $F(\theta_k)$ is conveniently carried out in two steps. The first is to add the site l to θ_l but set all the terms in (2.1) which involve S_l equal to zero. The resulting Hamiltonian $\mathcal{H}'(\theta_k)$ is formally identical to $\mathcal{H}(\theta)$ but is defined in a larger space, the $(2S + 1)^{n+1}$ configura-

tions of θ_k . Hence with each eigenstate of $\mathcal{H}(\theta)$ are associated $2S + 1$ eigenstates of $\mathcal{H}'(\theta_k)$ having the same eigenvalue, and the corresponding free energies are related by

$$F'(\theta_k) = F(\theta) - \beta^{-1} \ln(2S + 1). \quad (3.16)$$

As a second step, we employ (3.5)

$$|F(\theta_k) - F'(\theta_k)| \leq |\mathcal{H}(\theta_k) - \mathcal{H}'(\theta_k)|, \quad (3.17)$$

and note that the two Hamiltonians differ in that one lacks all terms involving S_l . The right side of (3.17) is bounded by the sum of the norms of these terms, which in turn is bounded by (3.15). Thus (3.16) and (3.17) together imply (3.14).

If we define

$$D = h + \beta^{-1} \ln(2S + 1), \quad (3.18)$$

(3.14) implies that

$$\left| \sum_{j=1}^{N-n} F(\theta_j) - (N - n)F(\theta) \right| \leq (N - n)D. \quad (3.19)$$

If we insert this result in (3.13) (with g replaced by F) and use the definition (3.11), we obtain

$$|\hat{F}(n + 1) - \hat{F}(n)| \leq D, \quad (3.20)$$

from which (3.12) follows by an obvious iteration. This completes the proof of Theorem 2.

By combining (3.1) and (3.11) one obtains

$$F(p) = \sum_{n=0}^N b(n; N, p) \hat{F}(n), \quad (3.21)$$

where

$$b(n; N, p) = \binom{N}{n} p^n q^{N-n} \quad (3.22)$$

is the binomial distribution. Let n_p be the nearest integer to pN . The inequality (3.12) yields the bound

$$\begin{aligned} |F(p) - \hat{F}(n_p)| &\leq D \sum_n |n - n_p| b(n; N, p) \\ &\leq DA \sum_{|n-n_p| \leq A} b(n; N, p) + DN \sum_{|n-n_p| > A} b(n; N, p). \end{aligned} \quad (3.23)$$

By setting $A = N^{\frac{1}{2}}$ and employing an elementary estimate for the tails of the binomial distribution,⁸ we find

$$|F(p) - \hat{F}(n_p)| \leq O(DN^{\frac{1}{2}}). \quad (3.24)$$

Let $\hat{f}_\Omega(p)$ be defined by linear interpolation between successive points where Np is an integer, $0 \leq p \leq 1$, and at these points by the relation

$$\hat{f}_\Omega(p) = \hat{F}_\Omega(pN_\Omega)/N_\Omega. \quad (3.25)$$

⁸ H. Cramer, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, N.J., 1946), p. 196.

Comparison with (3.1) and (3.24) shows that

$$|f_\Omega(p) - \hat{f}_\Omega(p)| \leq O(DN_\Omega^{-\frac{1}{2}}), \quad (3.26)$$

which implies that f_Ω and \hat{f}_Ω converge to the same thermodynamic limit $f(p)$. Theorem 2 combined with (3.25), (3.26), and (3.2) tell us that

$$|f(p_1) - f(p_2)| \leq D |p_1 - p_2|, \quad (3.27)$$

where D is a continuous function of T and H [see (3.18) and (3.15)]. Since $f(p, H, T)$ at fixed p is known to be a continuous function of H and T by convexity, (3.27) shows that it is a continuous function of all three variables together.

4. SPONTANEOUS MAGNETIZATION IN ISING FERROMAGNETS

A large amount of information is available on the phase transition and critical point behavior of Ising ferromagnets in two and three dimensions with nearest-neighbor interactions.⁹ It would be interesting to know what effect the addition of random non-magnetic impurities has on the phase transition. With the relatively unrefined tools available for an exact analysis, we are unable to make any statement about the modification of the critical point indices upon addition of impurities. However, we shall demonstrate, using the appropriate modifications of an argument originally due to Peierls,^{10,11} that at sufficiently high concentrations and sufficiently low temperatures, a specific random Ising ferromagnet exhibits a spontaneous magnetization; i.e., as the magnetic field is reduced to zero from positive values, the bulk magnetization m , defined as

$$m = - \left(\frac{\partial f}{\partial H} \right)_{T,p}, \quad (4.1)$$

approaches a positive limit. To be specific we shall consider a system with Hamiltonian

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i, \quad (4.2)$$

where $\sigma_i = 2S_i^z = \pm 1$, the sum in (4.2) is over nearest-neighbor pairs of sites, and the constant J is positive. For a random system we make the obvious modifications in accordance with (2.1); the second sum in (4.2) extends only over occupied sites and the first over pairs of nearest-neighbor sites both of which are occupied.

If \mathcal{N}_- is the number of "down" spins ($\sigma_i = -1$), \mathcal{N}_+ the number of "up" spins ($\sigma_i = +1$), the mag-

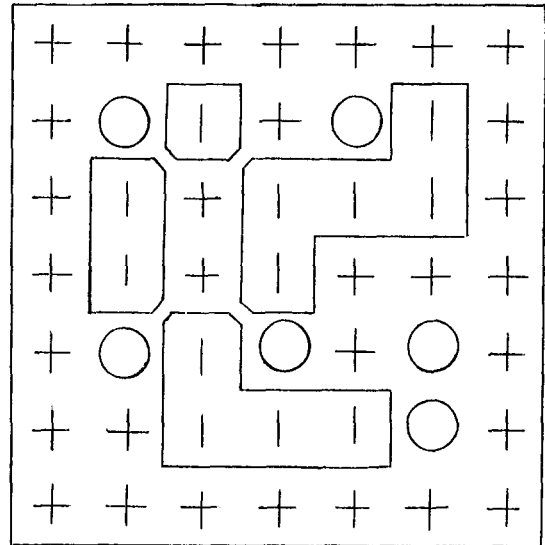


FIG. 1. A typical configuration on a square lattice of a random Ising system. The symbols +, - denote spins up and down, respectively, on occupied sites; 0 means the site is vacant. All boundary sites are occupied with + spins, and thus all - spins are enclosed within closed polygons (shown by the heavy lines).

netization operator \mathcal{M} is given by

$$\mathcal{M} = \mathcal{N}_+ - \mathcal{N}_-. \quad (4.3)$$

We shall establish an inequality of the form

$$\langle \langle \mathcal{N}_- \rangle \rangle_\Omega \leq \frac{1}{2}(p - \epsilon)N_\Omega, \quad (4.4)$$

with $\epsilon > 0$, for a series of crystals Ω with a special boundary condition but in zero magnetic field, $H = 0$ in (4.2). Here p is the fraction of sites occupied on the average, assuming $P(\theta)$ is given by (2.9). Since $\mathcal{N}_+ + \mathcal{N}_-$ is simply the number of occupied sites, with average value equal to pN_Ω , (4.4) implies that

$$\langle \langle \mathcal{M} \rangle \rangle_\Omega \geq \epsilon N_\Omega. \quad (4.5)$$

In turn, (4.5) implies that

$$\lim_{H \rightarrow 0^+} m(H) \geq \epsilon. \quad (4.6)$$

The connection between (4.5) and (4.6) is a trifle subtle, and is discussed for regular systems in Ref. 12. Identical considerations hold for random systems.

We shall consider a sequence of square crystals on a square lattice with the following special boundary conditions: The spins on all occupied sites on the edges of the squares are subjected to a magnetic field $J > 0$; alternatively, the sites just outside each edge are occupied with Ising spins for which $\sigma_i = +1$ (Fig. 1). Given any partition θ and any configuration for this partition, it is possible to enclose all spins with $\sigma_i = -1$ inside borders—nonself-intersecting polygons consisting of lines passing midway between lattice sites, as shown in Fig. 1.

¹² R. B. Griffiths, Phys. Rev. **152**, 240 (1966).

⁹ M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967).
¹⁰ R. Peierls, Proc. Cambridge Phil. Soc. **32**, 477 (1936).
¹¹ R. B. Griffiths, Phys. Rev. **136**, A437 (1964); see also R. L. Dobrushin, Teoriya Veroyatnostei Primeneniya **10**, 209 (1965) [Theory Probability Appl. **10**, 193 (1965)].

A particular site is *adjacent* to a border B —to the exterior or interior of B depending on whether the site lies outside or inside B —and has a *coordination number* z relative to B provided B passes between the site and $z \geq 1$ of its nearest neighbor. The border B is *realized* and the operator X_B assigned the value 1 provided (i) every site adjacent to the interior of B is occupied by a spin with $\sigma = -1$ and (ii) every site adjacent to the exterior of B is either unoccupied or occupied by a spin with $\sigma = +1$. Otherwise X_B has the value 0. The requirement that a border B not intersect itself has the consequence that z does not exceed three, except when B surrounds only one site (Fig. 1).

For a particular border B (fixed in position and orientation) and a given partition θ , let $r(B, \theta, z)$ be the number of occupied sites of coordination number z , relative to B , adjacent to the exterior of B . Define

$$\eta(B, \theta) = \sum_z z r(B, \theta, z). \tag{4.7}$$

When $X_B = 1$, η is the number of segments of B lying between pairs of nearest-neighbor occupied sites with $\sigma_i = +1$ and -1 on the site exterior and interior to B , respectively. The argument of Ref. 11 shows that

$$\langle X_B \rangle_\theta \leq y^{\eta(B, \theta)}, \tag{4.8}$$

where

$$y = e^{-2\beta J}. \tag{4.9}$$

[In essence, (4.8) is obtained by noting that for every configuration in which B is realized there is another, obtained by reversing every spin interior to B , which is lower in energy by $2\eta J$.] Note that (4.8) is satisfied even for partitions θ in which B cannot be realized because sites adjacent to its interior are vacant—for these $\langle X_B \rangle$ is necessarily zero.

Next, average (4.8) over partitions:

$$\langle \langle X_B \rangle \rangle \leq \sum_\theta P(\theta) y^{\eta(B, \theta)} = \sum_{r_1} \sum_{r_2} \sum_{r_3} P_B(r_1, r_2, r_3) y^{r_1 + 2r_2 + 3r_3}, \tag{4.10}$$

where $P_B(r_1, r_2, r_3)$ is the probability that precisely r_z occupied sites of coordination number z with respect to B are adjacent to the exterior of B . If k_z is the maximum possible value of r_z (given B), the value when all sites are occupied, then

$$P_B = \prod_{z=1}^3 \binom{k_z}{r_z} p^{r_z} q^{k_z - r_z}. \tag{4.11}$$

The insertion of (4.11) in (4.10) yields the estimate

$$\langle \langle X_B \rangle \rangle \leq (yp + q)^{k_1} (y^2p + q)^{k_2} (y^3p + q)^{k_3} \leq (y^3p + q)^{b/3}, \tag{4.12}$$

where

$$b = \sum_{z=1}^3 z k_z \tag{4.13}$$

is the length of the border B in units of the lattice constant. The final inequality in (4.12) is derived in the Appendix.

Since every minus spin is inside some realized border, and the number of occupied sites inside a border does not exceed $b^2/4$, we may write

$$\langle \langle N_- \rangle \rangle \leq \sum_b \nu(b) (b^2/4) (y^3p + q)^{b/3}. \tag{4.14}$$

If for $\nu(b)$, the number of different polygons of length b in a crystal Ω containing N_Ω sites, we use the generous estimate¹³

$$\nu(b) \leq 4N_\Omega 3^{b-2}/b, \tag{4.15}$$

and carry out the sum (4.14) over the values $b = 4, 6, 8, \dots$; the result is

$$\langle \langle N_- \rangle \rangle \leq \frac{2}{3} K^2 \frac{2 - K}{(1 - K)^2} N_\Omega, \tag{4.16}$$

where

$$K = 9(y^3p + q)^{\frac{2}{3}}. \tag{4.17}$$

Comparison with (4.4) shows that for sufficiently high concentrations and for y small enough (that is, at low enough temperatures), there will be a spontaneous magnetization. Due to the severe approximations involved, the estimate (4.16) is not very good. In particular, the concentration p must exceed approximately 0.985 before it will guarantee a spontaneous magnetization at a finite temperature. One actually expects that the concentration below which no spontaneous magnetization exists at any temperature will coincide with the critical concentration of the corresponding percolation problem,¹⁴ that is, approximately 0.59. Nonetheless, our argument shows that there is a finite range of concentrations for which vacancies in the lattice do not alter the qualitative nature of the phase transitions, in that the bulk magnetization still shows a discontinuity at zero magnetic field.

An argument analogous to that given above can also be carried out for, say, a three-dimensional Ising model on a simple cubic lattice. Or one may apply a general inequality for correlations in Ising ferromagnets in order to obtain a proof for three dimensions directly from the knowledge that a spontaneous magnetization exists for the two-dimensional case.

5. ANALYTIC PROPERTIES OF THE FREE ENERGY

A regular Ising spin system is isomorphic to a lattice gas, if an “up” spin indicates the presence, and a

¹³ See, for example, G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, Cambridge, England, 1959), p. 105. Note that there is no choice left in choosing the final step in a border, so we have reduced Wannier’s estimate by a factor of 3.

¹⁴ M. F. Sykes and T. W. Essam, *Phys. Rev.* **133**, A310 (1964).

“down” spin the absence, of a molecule at a particular site. In the analogous isomorphism for a random Ising spin system, one has two types of vacant sites. For a given partition θ , there are sites outside θ where gas molecules cannot be found because there is (in the spin language) no spin on the site. One may think of these sites as occupied by fixed impurity molecules whose presence excludes gas molecules. Then there are sites which belong to θ but at which, for a particular configuration, the spin is “down.” One may think of these as “vacuum” sites since there are other configurations (for the same θ) in which they may be occupied. Not only do the impurities exclude gas molecules from certain sites, they also interact with gas molecules on nearby sites. As the impurities are fixed in position, we treat this additional interaction as an “external” potential acting on the gas molecules. There is such an effect also in a “regular” system near the boundaries.

Carrying out explicitly the transformation from the spin variables $S_i^z = \pm \frac{1}{2}$ to the occupation number variable $\rho_i = S_i^z + \frac{1}{2} = (0, 1)$, we find, using (2.2),

$$\beta F(\theta) = \beta \sum_{i \in \theta} (\mu H + \frac{1}{4} \alpha_i) - \ln \Xi(\theta, z), \quad (5.1)$$

where $\Xi(\theta, z)$ is the grand partition function of a lattice gas, with fugacity $z = e^{2\beta\mu H}$, whose particles are confined to sites in θ and have a pair interaction potential between particles located at sites i and j :

$$\varphi_{ij} = \begin{cases} \infty, & i = j, \\ -4J_{ij}, & i \neq j, \end{cases} \quad (5.2)$$

and an external potential for a particle at site i equal to

$$-\alpha_i = 2 \sum_{j \in \theta} J_{ij} = 2 \sum_{j \in \Omega} J_{ij} - 2 \sum_{\substack{j \in \theta \\ j \neq i}} J_{ij}. \quad (5.3)$$

The first sum which is constant (except near the boundaries) amounts to a change in the fugacity while the second term corresponds formally to an external potential due to the impurities.

Continuing our transcription from spin system to lattice gas, we have from (3.1) and (3.2)

$$f_\Omega = p\mu H + p^2 \frac{1}{2N_\Omega} \sum_{j \in \Omega} \sum_{i \in \Omega} J_{ij} - \Pi_\Omega(p, z), \quad (5.4)$$

where

$$\Pi_\Omega(p, z) = \langle \langle \Pi(\theta, z) \rangle \rangle \equiv \beta^{-1} \frac{\langle \ln \Xi(\theta, z) \rangle}{N_\Omega}, \quad (5.5)$$

with $\Pi(\theta, z)$ the “pressure” of the lattice gas confined to θ . The existence of $f = \lim_{N_\Omega \rightarrow \infty} f_\Omega$ then implies the existence of $\Pi(p, z) = \lim_{\Omega \rightarrow \infty} \Pi_\Omega$ for $0 \leq z \leq \infty$, $0 \leq p \leq 1$. [We have suppressed here the dependence on β , $0 \leq \beta \leq \infty$. The second term on the right side

of (5.4) possesses a well defined limit as $N_\Omega \rightarrow \infty$ provided the J_{ij} satisfy (3.10).]

We shall now show, using methods developed for continuum systems and regular lattice systems,¹⁵ that $\Pi(p, z)$ is analytic in z and p for $|z| < R(\beta)$ and $|p| \leq 1$ in the case where the interactions have a finite range. [By the symmetry $H \rightarrow -H$, this is also true $|z| > R^{-1}(\beta)$.] For purely ferromagnetic interactions $J_{ij} \geq 0$, the Lee–Yang theorem¹⁶ guarantees analyticity in $|z|$ for $|z| < 1$, $H \neq 0$, and our results can be extended via a theorem due to Ruelle¹⁷ to give analyticity for real positive p , $0 \leq p \leq 1$, when $H \neq 0$. (Results on analyticity in β for “regular” systems, which can also be extended to random systems, will be discussed elsewhere.¹⁸)

We begin with the Mayer series

$$\beta \Pi(\theta, z) = \frac{1}{N_\Omega} \sum_{i=1}^{N_\Omega} \ln \left(\frac{1-z}{z_i(\theta)} \right) = \sum_{l=1}^{\infty} b'_l(\theta) z^l, \quad (5.6)$$

where the $z_i(\theta)$ are the zeros of the grand partition function $\Xi(\theta, z)$ and

$$b'_l(\theta) = \frac{1}{N_\Omega l!} \sum_{\mathbf{x}_1 \in \theta} \cdots \sum_{\mathbf{x}_l \in \theta} u_l(\mathbf{x}_1, \dots, \mathbf{x}_l) \left[\prod_{i=1}^l e^{\beta \alpha(\mathbf{x}_i)} \right], \quad (5.7)$$

where \mathbf{x}_i is the lattice vector of the i th site and the sum is over all lattice sites in θ , $\alpha(\mathbf{x}_i) = \alpha_i$, and u_l is the usual Mayer cluster function, $u_2(\mathbf{x}_1, \mathbf{x}_2) = \exp[-\beta\varphi(\mathbf{x}_1 - \mathbf{x}_2)] - 1$, etc. Taking the average, with $P(\theta)$, of $\Pi(\theta, z)$, we obtain

$$\beta \Pi_\Omega(p, z) = \sum_{l=1}^{\infty} b'_l(p, \Omega) z^l, \quad (5.8)$$

with

$$b'_l(p, \Omega) = \sum_{\theta} P(\theta) b'_l(\theta). \quad (5.9)$$

The averaging in (5.9) is facilitated by the fact that the probabilities of occupancy by impurities of different sites are independent and will be illustrated now for the case $l = 2$. Writing

$$\begin{aligned} b'_2(\theta) &= \frac{1}{2N_\Omega} \sum_{i \in \theta} \sum_{j \in \theta} u_2(\mathbf{x}_i, \mathbf{x}_j) \prod_{i \in \theta} e^{\beta J_{ij}} \\ &+ \frac{1}{2N_\Omega} \sum_{i \neq j, i, j \in \theta} u_2(\mathbf{x}_i, \mathbf{x}_j) e^{\beta J_{ij}} \prod_{\substack{k \in \theta \\ k \neq i, j}} e^{2\beta [J_{ik} + J_{jk}]}, \end{aligned} \quad (5.10)$$

¹⁵ See, for example, J. Groeneveld, *Proceedings of the I.U.P.A.P. Meeting, Copenhagen, 1966*, T. A. Bak, Ed. (W. A. Benjamin, Inc., N.Y., 1967), p. 110.

¹⁶ T. D. Lee and C. N. Yang, *Phys. Rev.* **87**, 410 (1952).

¹⁷ D. Ruelle (private communication).

¹⁸ J. L. Lebowitz and O. Penrose (to be published).

we have

$$b'_2(p, \Omega) = \frac{1}{2N_\Omega} p \sum_{i \in \Omega} u_2(\mathbf{x}_i, \mathbf{x}_i) \prod_{j \in \Omega} [pe^{A\beta J_{ij}} + (1-p)] + \frac{1}{2N_\Omega} p^2 \sum_{\substack{i \neq j \\ i, j \in \Omega}} u_2(\mathbf{x}_i, \mathbf{x}_j) e^{A\beta J_{ij}} \times \prod_{\substack{k \in \Omega \\ k \neq i, j}} [pe^{2\beta(J_{ik} + J_{jk})} + (1-p)]. \quad (5.11)$$

Restricting ourselves to finite-range interactions, we see that $b'_2(p, \Omega) \rightarrow b'_2(p)$ as $N_\Omega \rightarrow \infty$:

$$b'_2(p) = \frac{1}{2} p u_2(\mathbf{x}_1, \mathbf{x}_1) \prod_j [1 + p(e^{A\beta J_{1j}} - 1)] \cdot \frac{1}{2} p^2 \sum_{j=1} u_2(\mathbf{x}_1 - \mathbf{x}_j) e^{A\beta J_{1j}} \times \prod_{k \neq 1, j} [1 + p(e^{2\beta(J_{1k} + J_{jk})} - 1)], \quad (5.12)$$

the indices now running over the infinite lattice. Since J_{ij} has a finite range, only a finite number of the factors in the products in (5.12) are different from unity and thus $b'_2(p)$ is a polynomial. The same holds for every $b'_i(p)$. Further, for $|p| \leq 1$,

$$|b'_2(p, \Omega)| \leq \frac{1}{2N_\Omega} \sum_{i \in \Omega} |u_2(\mathbf{x}_i, \mathbf{x}_i)| \prod_{j \in \Omega} [1 + |e^{A\beta J_{ij}} - 1|] + \frac{1}{2N_\Omega} \sum_{\substack{i \neq j \\ i, j \in \Omega}} |u_2(\mathbf{x}_i, \mathbf{x}_j)| \times \prod_{\substack{k \in \Omega \\ k \neq i, j}} [1 + |e^{2\beta(J_{ik} + J_{jk})} - 1|] e^{A\beta J_{ij}} \leq \frac{1}{2N_\Omega} \sum_{i, j \in \Omega} |u_2(\mathbf{x}_i, \mathbf{x}_j)| e^{2\beta \sum_k (|J_{ik}| + |J_{jk}|)} \leq \frac{1}{2} \sum_j |u_2(\mathbf{x}_1 - \mathbf{x}_j)| e^{2\beta\Phi}, \quad (5.13)$$

where

$$\Phi = 2 \sum_k |J_{1k}| < \infty, \quad (5.14)$$

and the sum over j and k goes over the infinite lattices. Similarly,

$$|b'_i(p, \Omega)| \leq \frac{1}{l!} \sum_{\{\mathbf{x}_2, \dots, \mathbf{x}_l\}} |u_l(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_l)| e^{i\beta\Phi} \leq \frac{1}{l!} e^{2i\beta\Phi} l^{-2} B^{l-1}, \quad (5.15)$$

where

$$B = \sum_j |u_2(\mathbf{x}_1 - \mathbf{x}_j)|. \quad (5.16)$$

The last inequality in (5.15) is due to Penrose.¹⁹ It follows then from (5.15) that the power series (5.8), as well as the series

$$\beta \Pi(p, z) = \sum_{l=1}^{\infty} b'_l(p) z^l, \quad (5.17)$$

converge for $|p| \leq 1$:

$$|z| < R(\beta) = (B e^{2\beta\Phi + 1})^{-1}. \quad (5.18)$$

The convergence of (5.17) for $|z| < R$, $|p| \leq 1$ and the fact that the $b'_i(p)$ are analytic (polynomials) in p for finite-range potentials implies that $\Pi(p, z)$ and therefore f is analytic also in p for $|p| \leq 1$ and $|z| < R$.

For the case of purely ferromagnetic interactions, $J_{ij} \geq 0$ for all i, j , the Lee-Yang theorem¹⁶ states that the roots of the grand partition function $\Xi(\theta, z)$, all lie on the unit circle $|z_i(\theta)| = 1$, from which it follows that $\Pi(p, z)$ is analytic in z for $|z| < 1$ and p real positive $0 \leq p \leq 1$. Hence there exists some K such that

$$|b'_i(p)| < K, \quad \text{for } 0 \leq p \leq 1, \quad (5.19)$$

and

$$|b'_i(p)| < K/R^l, \quad \text{for } |p| \leq 1, \quad (5.20)$$

where (5.20) follows from our previous results. Combining (5.19), (5.20), and the fact that $b'_i(p)$ is analytic in p , it is possible to show that $\Pi(p, z)$ are analytic in p along the real axis $0 \leq p \leq 1$ for all $|z| < 1$, for systems where $J_{ij} > 0$.

6. ADDITIONAL RESULTS

In addition to the results established in this paper, there are many questions relating to random spin systems which we have not touched on at all. These concern the dependence of the correlation functions, magnetization, including spontaneous magnetization, and the critical point indices on p . There are several results which can be established easily for random Ising spin systems, which we shall state here without proof.

(1) The existence and analyticity of the correlation functions for $|z| \leq R$, $|p| \leq 1$.

For systems with purely ferromagnetic interactions we also have:

(2) The average magnetization per spin is a monotonically increasing function of p (as well as of β and H).

(3) It follows from (2) that the critical temperature $T_c(p)$ (onset of spontaneous magnetization) is also a monotonic function of p .

(4) If T_0 is the critical temperature obtained from mean field theory for a "regular" system, then $T_c(p) \leq pT_0$.

(5) For nearest-neighbor interactions, the concentration p_0 at which spontaneous magnetization occurs at $T = 0$ is greater than or equal to the critical percolation concentration p_0 .

¹⁹ O. Penrose, *Statistical Mechanics, Foundations and Applications*, T. A. Bak, Ed. (W. A. Benjamin, Inc., N.Y., 1967), p. 101.

APPENDIX: INEQUALITY USED IN
EQUATION (4.12)

Let z be a random variable which takes two possible values W and 1, with probability p and $q = 1 - p$, respectively. We assume that W is nonnegative. For $\alpha \geq 1$,

$$f_\alpha(z) = z^\alpha \quad (\text{A1})$$

is a convex function for positive z ; hence²⁰

$$(W^\alpha p) + q = \langle f_\alpha(z) \rangle \geq f_\alpha(\langle z \rangle) = (Wp + q)^\alpha. \quad (\text{A2})$$

Thus, for any $\gamma > 0$,

$$(W^\alpha p + q)^\gamma \geq (Wp + q)^{\alpha\gamma}. \quad (\text{A3})$$

We use (A3) twice in obtaining the second inequality in (4.12): first with $\alpha = 3$, $\gamma = k_1/3$, and $W = y$; next with $\alpha = \frac{3}{2}$, $\gamma = 2k_2/3$, and $W = y^2$.

²⁰ G. H. Hardy, J. E. Littlewood, and G. Polya, *Inequalities* (Cambridge University Press, Cambridge, England, 1964), Chap. III.

Two-Center Coulomb and Hybrid Integrals*

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Coulomb and hybrid integrals are shown to be related to overlap integrals. They are expressed by an integral whose integrand is an overlap integral plus a finite sum of overlap integrals.

INTRODUCTION

Three general numerical methods for the calculation of two-center Coulomb and hybrid integrals are: (1) the application of the exchange integral method based on the Neumann expansion,¹ (2) the numerical integrations on the second electron after the integration over the first electron has been carried out analytically,² and (3) the expression for Coulomb integrals based on the Fourier convolution theorem.³

For the Coulomb integrals a general analytical method has recently been developed by O-Ohata and Ruedenberg. An essential feature of their approach is the reduction of the Coulomb integrals to an integration over overlap integrals.⁴

In the present note, it is shown that there exists yet another way of expressing the Coulomb and hybrid integrals by integration over overlap integrals.

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¹ K. Ruedenberg, *Molecular Orbitals in Chemistry, Physics, and Biology*, B. Pullman and P. O. Löwdin, Eds. (Academic Press Inc., New York, 1964), p. 215.

² A. C. Wahl, P. E. Cade, and C. C. J. Roothaan, *J. Chem. Phys.* **41**, 2578 (1964); see also R. Christoffersen and K. Ruedenberg, *J. Chem. Phys.* **47**, 1855 (1967).

³ M. Geller, *J. Chem. Phys.* **41**, 4006 (1964).

⁴ K. O-Ohata and K. Ruedenberg, *J. Math. Phys.* **7**, 547 (1966).

ATOMIC ORBITALS AND CHARGE DISTRIBUTIONS

A normalized Slater-type atomic orbital on center A for electron i is given by

$$(Anlm, \zeta, i) = N_n (2\zeta)^{n+\frac{1}{2}} r_{Ai}^{n-1} \times \exp(-\zeta r_{Ai}) Y_{lm}(\theta_{Ai}, \phi_{Ai}), \quad (1)$$

$$N_n = (2n!)^{-\frac{1}{2}}, \quad (1')$$

where Y_{lm} may be either a real or complex spherical harmonic.⁵ While overlap integrals usually occur between such atomic orbitals, two-center Coulomb integrals are commonly defined between certain standard "charge distributions"

$$[Anlm, \zeta, i] = (M_{ni}/N_n)(Anlm, \zeta, i), \quad (2)$$

which differ from the orbitals of Eq. (1) by certain constants. Since several conventions have been employed for the factors M_{ni} , its specific form will not be used in the sequel.⁶ The electron index i may be omitted for convenience.

⁵ The real spherical harmonics used are those defined by C. C. J. Roothaan, *J. Chem. Phys.* **19**, 1445 (1951).

⁶ For example, C. C. J. Roothaan [*J. Chem. Phys.* **19**, 1445 (1951)] uses

$$M_{ni} = [(2l+1)/\pi]^{\frac{1}{2}} \zeta^{\frac{1}{2}} / [(n+l+1)! 2^{n-l-1}],$$

and K. O-Ohata and K. Ruedenberg (Ref. 4) use

$$M_{ni} = [(2l+1)/\pi]^{\frac{1}{2}} \zeta^{\frac{1}{2}} / [(n+1)! 2^{2n}].$$

Also, ζ_0 is replaced by 2ζ in both references.