Thermodynamics of an Ising model with random exchange interactions

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An Ising model with an arbitrary distribution \( P(J) \) of exchange interactions \( J \) is solved exactly for the annealed case in which the system is allowed to reach complete thermal equilibrium at each temperature. The solution is expressed in terms of an Ising model on the same lattice with a single exchange parameter, allowing an exact solution to be obtained in one and two dimensions. Some feeling for the effect of annealing can be found by examining correlations between exchange interactions on neighboring bonds. Some special distributions \( P(J) \) are examined in detail.

I. INTRODUCTION

In the past few years there has been considerable interest in the thermodynamics of phase transitions in random systems. As a contribution to this work, we have considered an Ising model with an arbitrary distribution \( P(J) \) of nearest-neighbor exchange interactions. The model can be solved exactly if the system is allowed to come into complete thermal equilibrium (both spins and bonds) at each temperature.

As first pointed out by Brout,\(^1\) random systems, such as the one considered here, can have two distinct kinds of thermodynamic behavior. In the first (quenched) case, the randomness is frozen in and does not change with temperature. In our case, this corresponds to the exchange interactions \( J \) on different bonds being chosen independently according to a probability distribution \( P(J) \).

In the second (annealed) case, the system is allowed to come into thermal equilibrium at each temperature. In our case this can be visualized as follows: Each bond has some exchange \( J \) associated with it, chosen so that the system as a whole has a temperature-independent distribution \( P(J) \). However, unlike the quenched case, the system is allowed to lower its free energy by choosing an optimal spatial arrangement of these bonds. This introduces correlations between neighboring bonds. We will show that these correlations are greatest in the vicinity of the critical point when the disorder is not too severe. The correlations are such that there is a tendency for like bonds to cluster together, and so in the critical region the system can be thought of as being partially phase separated. While this changes the nature of the phase transition, the overall thermodynamic behavior is probably very similar to the quenched case when the disorder is weak.\(^2\) However, when the disorder is strong and there is competition between ferromagnetic and antiferromagnetic bonds, there are important differences between the two cases. For example, when \( P(J) = P(-J) \), a spin-glass phase may occur in the quenched system\(^3\) but does not occur in the annealed system.

The annealed case is mathematically tractable because it involves averaging the partition function rather than the free energy. In the quenched case the free energy is proportional to \( \ln(Z) \), where \( Z \) is the partition function and \( c \) denotes a configuration average. In the annealed case the free energy is proportional to \( \ln(Z') \), where the prime on the partition function means that a chemical potential has been incorporated into the system in order to produce the required distribution \( P(J) \). There is a quite different mathematical structure in the quenched and annealed cases. For example, Griffiths\(^4\) has shown that the free energy of a quenched dilute ferromagnet is a nonanalytic function of magnetic field \( H \) at \( H = 0 \) for all temperatures below the transition temperature of the undiluted system. On the other hand, the analytic properties of the free energy of annealed systems seem to be similar to those of nonrandom systems.

In Sec. II we give the general solution for an arbitrary \( P(J) \) and derive general expressions for the energy, entropy, and specific heat. In Sec. III we discuss a number of special cases, the one-dimensional chain and the Bethe lattice, the dilute ferromagnet and a ferromagnetic-antiferromagnetic alloy, a rectangular distribution and a Gaussian distribution for \( P(J) \) on a two-dimensional square lattice, the case of a narrow distribution, the symmetric distribution \( P(J) = P(-J) \) and its relationship to the spin-glass problem, and finally the inclusion of an external field and some general properties in one dimension. In Sec. IV we discuss the correlations that the annealing produces among the bonds and show how these can be calculated.

II. GENERAL SOLUTION

The Hamiltonian for the system is written as a summation over all of the bonds
\[ H = \sum_{\{ij\}} H_{ij}, \]  

(1)

where

\[ H_{12} = -\sum_i J_{12} f_i \sigma_i \sigma_2 - \sum_i \xi_i f_i. \]  

(2)

The spin variables \( \sigma = \pm 1 \) and each bond has an exchange interaction \( J_i \) associated with it, as shown in Fig. 1. It is convenient to let \( J_i \) take on a discrete set of values and then go to the continuous distribution at the end of the calculation. In Eq. (2) we have summed over all possible \( J_i \) and included an indicator function \( f_i \) that is 1 if the interaction is \( J_i \) and zero otherwise. We have the operator identity

\[ \sum_i f_i = 1, \]  

(3)

so that only a single exchange interaction is associated with each bond. The chemical potential \( \xi_i \) couples to the \( f_i \) in (2) and will be chosen so as to make \( \langle f_i \rangle \) temperature independent. This will mean that the chemical potentials \( \xi_i \) will be temperature dependent. The angular brackets denote thermal average in the usual way.

The grand partition function \( \Xi \) involves a trace over both the spin variables and the \( f_i \),

\[ \Xi = \sum_{\{\sigma\}} \sum_{\{f\}} e^{-\beta H}, \]  

(4)

with \( \beta = 1/k_B T \), where \( k_B \) is Boltzmann's constant and \( T \) is the temperature of the system. The method of solution involves doing the partial trace over the \( f_i \) and expressing the result in terms of a regular Ising model on the same lattice.\(^6\) Rather than write out the complete expression for (4), let us concentrate on a single bond, as in Eq. (2). Doing the partial trace over \( f_i \) for this bond only, we get

\[ \sum_i \exp(\beta J_i \sigma_i \sigma_2 + \beta \xi_i) = A e^{\beta^2/2}, \]  

(5)

where

\[ e^{\beta^2} = \left( \sum_i e^{\beta J_i \sigma_i \sigma_2} \right) / \left( \sum_i e^{\beta J_i \sigma_i \sigma_2} \right), \]  

(6)

\[ A^2 = \left( \sum_i e^{\beta J_i \sigma_i \sigma_2} \right) / \left( \sum_i e^{\beta J_i \sigma_i \sigma_2} \right). \]

This method utilizing partial traces has been widely exploited by Syozzi and co-workers\(^7\) to discuss bond decorations in which extra spins are placed on the bonds. The right-hand side of Eq. (5) describes a bond in a regular Ising model. Doing the partial traces over the \( f_i \) for all the bonds we may write

\[ \Xi = A^{N/2} Z(K), \]  

(7)

where \( Z(K) \) is the partition function for a regular Ising model with interaction parameter \( K \), and \( \frac{1}{2} N_2 \) is the total number of bonds when each of the \( N \) atoms has \( z \) neighbors. The bond occupation factors \( \langle f_i \rangle \) are obtained from

\[ \beta \langle f_i \rangle = \frac{2}{N_2} \frac{\partial \ln \Xi}{\partial \xi_i} = \frac{\partial \ln A}{\partial \xi_i} + \epsilon(K) \frac{\partial K}{\partial \xi_i}, \]  

(8)

where \( \epsilon(K) \) is the two-spin-correlation function of the regular Ising model [i.e., \( \epsilon(K) = \langle \sigma_i \sigma_j \rangle \)]. From (6) and (8) we obtain

\[ e^{\beta T_i} / \sum_j e^{\beta T_i + \beta J_i} = 2\langle f_i \rangle / [1 + \epsilon(K)] e^{\beta T_i} / [1 - \epsilon(K)] e^{2\beta T_i} = 1. \]  

(9)

We can eliminate the unwanted chemical potentials by multiplying both sides of this equation by \( e^{\beta T_i} \) and summing over \( i \) to obtain

\[ \sum_i \langle f_i \rangle = 1. \]  

(10)

Noting that the operator equation (3) implies that

\[ \sum_i \langle f_i \rangle = 1, \]  

(11)

we can rewrite (9) as

\[ \sum_i \langle f_i \rangle = \coth(K - \beta J_i) - \epsilon(K) = 0. \]  

(12)

We now demand that the \( \langle f_i \rangle \) be temperature independent and go to a continuous distribution involving an integral over \( P(J) \).
\[
\int [\coth(K - \beta J) - \epsilon(K)]^{-1} P(J) \, dJ = 0. \tag{13}
\]

This result allows us to determine \( K(\beta) \) for any distribution \( P(J) \), and so provides the link between the random Ising model and the regular Ising model. An exact solution can be found whenever \( \epsilon(K) \) is known for the reference system, as it is in one and two-dimensional systems. In three dimensions good numerical approximations for \( \epsilon(K) \) exist and we use one in Sec. III E.

The energy per bond \( E \) can be found in a similar way from
\[
E = - \sum_i J_i \langle f_i \sigma_i \sigma_2 \rangle = \frac{2}{Nz} \beta \int \frac{\partial \ln Z}{\partial J_i}, \tag{14}
\]
\[
\beta E = \sum_i J_i \frac{\partial \ln A}{\partial J_i} + \epsilon(K) \sum_i J_i \frac{\partial K}{\partial J_i}. \tag{15}
\]

With some manipulation of (6), (9), and (15) we obtain the result
\[
E = \int \left[ \left(1 - \epsilon^2(K) \right) [\coth(K - \beta J) - \epsilon(K)]^{-1} - \epsilon(K) \right] J P(J) \, dJ. \tag{16}
\]

Note again that the expression for \( E \) does not contain the unwanted chemical potentials \( \epsilon_i \).

The specific heat per bond \( C \) is most easily obtained by differentiating (16) with respect to the temperature implicitly. The result is expressed in terms of the three integrals
\[
I_1 = \int \left[ \coth(K - \beta J) - \epsilon(K) \right]^2 P(J) \, dJ, \tag{17}
\]
\[
I_2 = \int \left[ \coth(K - \beta J) - \epsilon(K) \right]^2 \coth^2(K - \beta J) J P(J) \, dJ, \tag{18}
\]
\[
I_3 = \int \left[ \coth(K - \beta J) - \epsilon(K) \right]^2 \coth^2(K - \beta J) J^2 P(J) \, dJ. \tag{19}
\]

Differentiating (16) with respect to \( \beta \), we get
\[
\frac{C}{k_B} = \beta^2 \left[ I_3 \left(1 - \epsilon(K)\right) - I_2 \left(1 - \epsilon^2(K) - \frac{\partial \epsilon(K)}{\partial K} \right) \frac{\partial K}{\partial \beta} \right]. \tag{20}
\]

Differentiating (13), we find
\[
\frac{\partial K}{\partial \beta} = I_2 \left[1 - I_1 \left(1 - \epsilon^2(K) - \frac{\partial \epsilon(K)}{\partial K} \right) \right]^{-1}, \tag{21}
\]
and thus obtain the result
\[
\frac{C}{k_B} = \beta^2 \left[ I_3 \left(1 - \epsilon^2(K)\right) + I_2 \left[ \frac{\partial \epsilon(K)}{\partial K} \right]^{-1} \right]. \tag{22}
\]

The entropy per bond \( S \) can be obtained from the specific heat, but is most easily obtained from the thermodynamic potential \(-k_B T \ln \mathcal{Z}\).

\[
S = \frac{2}{Nz} \frac{\partial (k_B T \ln \mathcal{Z})}{\partial T}, \tag{23}
\]
where the differentiation is done keeping the chemical potentials \( \epsilon_i \) constant. From (6), (7), and (21) we get
\[
S = \frac{S(K)}{k_B} + K \epsilon(K) + \beta E + \sum_i \langle f_i \rangle \ln \left[ \cosh(K - \beta J_i) - \epsilon(K) \sinh(K - \beta J_i) \right] \tag{24}
\]
\[
- \sum_i \langle f_i \rangle \ln \langle f_i \rangle, \tag{25}
\]
where \( S(K) \) is the entropy of the reference system and the last temperature-independent term \(-\sum_i \langle f_i \rangle \ln \langle f_i \rangle\) goes to \( +\infty \) as we go to the continuous distribution \( P(J) \). This can be interpreted as an entropy of mixing. It is only possible to measure changes in the entropy so that the entropy of mixing is not a measureable quantity, and we shall neglect it. However, the remaining part of the entropy can become negative in some cases at low temperatures. There is no paradox, as the total entropy in (22) is always positive. A further discussion of this is given in Sec. IV. A similar problem (negative entropy) was found by Sherrington and Kirkpatrick in the spin-glass problem.\(^{11}\)

The critical behavior of this model is closely tied to that of the reference system. The critical exponents are renormalized because of a rescaling of the temperature given by \( K(\beta) \) in the form of Eq. (13). From Eq. (19) we can see that near the critical point \( \partial \epsilon(K)/\partial K \) becomes large; then
\[
\beta - \beta_c = \frac{I_1}{I_2} \left[S(K) - S(K_c)\right], \tag{26}
\]
where \( I_1 \) and \( I_2 \) are evaluated at the critical point. This relation is obtained if there is no disorder so that \( I_1 \neq 0 \). Equation (23) shows how the temperature rescales between the disordered system and the reference system close to the critical point. If the specific heat in the reference system diverges with an exponent \( \alpha \), then
\[
\beta - \beta_c \sim (K - K_c)^{-\alpha}. \tag{27}
\]
From (20) we see that the specific heat has a cusp at the critical point. Near the critical point, the specific heat is given approximately by
\[
\frac{C}{k_B} = \beta^2 \left[ I_3 (1 - \epsilon^2) + \frac{I_2}{I_1} \left( \frac{I_2}{I_1} \right)^2 \frac{\partial \epsilon(K)}{\partial K} \right], \tag{28}
\]
where \( I_1, I_2 \), and \( I_3 \) are evaluated at the critical point. Using a subscript \( d \) for the disordered sys-
tem, we have

\[ \alpha = -\alpha/(1 - \alpha). \]  
\[ (26) \]

Other exponents that involve a temperature derivative have a similar renormalization, but without a minus sign in the numerator,

\[ \beta = \beta/(1 - \alpha), \quad \gamma = \gamma/(1 - \alpha), \]  
\[ (27) \]

and of course we have similar relations for the primed indices where they are defined. Those critical indices that do not involve a temperature derivative such as \( \delta \), are unchanged.\(^{13}\) These results are a special case of critical exponent renormalization discussed by Fisher\(^{14}\) for systems with “hidden variables” subject to constraints. For most of this paper we shall be concerned with the two-dimensional Ising model, where the specific heat diverges logarithmically so that \( \alpha = 0 \) and the exponents in (27) are unaltered.

We note that Harris\(^{15}\) has recently performed a coherent-potential-approximation (CPA) type of approximation on the quenched version of the model discussed in this paper. It is interesting that he obtains our expression (13), which shows that the annealed model with a distribution \( P(J) \) forms an approximation to the quenched model with the same \( P(J) \). This is discussed further in Sec. IV.

III. SOME SPECIAL CASES

In this section we will examine some applications of the general results obtained in Sec. II to a number of different distributions in one, two, and three dimensions.

A. One-dimensional and Bethe lattices

The regular Ising model is easy to solve in one dimension\(^{8}\) and the energy is given by

\[ \epsilon(K) = \tanh K. \]  
\[ (28) \]

Inserting this into Eq. (13), we find

\[ (1 + e^{-2K})^{-1} = \int (1 + e^{-2\beta J})^{-1} P(J) dJ, \]  
\[ (29) \]

which gives the \( K(\beta) \) relationship explicitly for a given \( P(J) \). The energy [Eq. (16)] is given by

\[ E = -\int J \tanh(\beta J) P(J) dJ, \]  
\[ (30) \]

where the \( K \) dependence drops out. This is because annealing makes no difference, as all bond arrangements have the same energy associated with them.\(^{16}\)

The Bethe lattice is a treelike structure that contains no closed rings of bonds.\(^{17}\) It is sometimes called a pseudolattice. The regular Ising model has an exact solution for this lattice with critical parameters given by\(^{17}\)

\[ \epsilon(K_c) = \tanh K_c = (q - 1)^{-1}, \]  
\[ (31) \]

where \( q \) is the number of bonds at each vertex \( (q = 2 \) in one dimension). Inserting this result into (13) we find, after some rearrangement, that the transition temperature \( \beta_c \) in the random model is given by

\[ \int \tanh(\beta_c J) P(J) dJ = (q - 1)^{-1}, \]  
\[ (32) \]

which agrees with the result of Matsubara\(^{18}\) for the quenched case if there are no antiferromagnetic interactions present.\(^{19}\)

We note that the mean-field result for the reference system \( \epsilon_0 = K_c = 0 \) can be obtained from the Bethe solution [Eq. (31)] as \( q \to \infty \). This is a useful limit that we will use later.

B. Dilute Ising model

For the dilute Ising model we put

\[ P(J) = \rho \delta(J - J_0) + (1 - \rho) \delta(J) \]  
\[ (33) \]

into Eq. (13) to obtain

\[ e^{2\beta J_0} = \frac{2\rho + [1 - \epsilon(K)] e^{2K} - 1}{2\rho - [1 + \epsilon(K)] (1 - e^{-2K})}. \]  
\[ (34) \]

This result has previously been obtained by Rapaport.\(^{2} \) The transition temperature is reduced by dilution and goes to zero at the critical concentration \( \rho_c \) given by

\[ \rho_c = \frac{1}{2} \frac{1}{1 + \epsilon} (1 - e^{-2K_c}). \]  
\[ (35) \]

The critical concentrations for the triangular net, square net, and honeycomb lattices are 0.3522, 0.5000, and 0.6478, which are very close to the bond percolation concentrations of 0.3473, 0.5000, and 0.6527, respectively.\(^{20}\) The bond percolation concentration is where the transition temperature of the quenched dilute bond Ising model goes to zero. The Szyoz model,\(^{31} \) in which a spin at the center of each bond can be either present or absent, leads to the same value of \( \rho_c \) as (35). The phase diagram from (34) for the two-dimensional square net \( \epsilon = 1/\sqrt{2}, e^{2K} = 1 + \sqrt{2} \) is shown in Fig. 2. The energy can be found from (16) and is given by\(^{2}\)

\[ E = J \rho_c - \frac{2 J \rho_c}{1 + \epsilon(K)} + \frac{e^{2K} - 2K \epsilon_0}{e^{2K_0} - 2K \epsilon_0}. \]  
\[ (36) \]

The specific heat can be obtained from (20). The expression is complicated, but the height of the cusp at the critical point of the two-dimensional square net is given by the simple expression
we put $F = p$, $D = 1 - p$, and $A = 0$, and Eq. (40) results with $F = p$, $D = 0$, and $A = 1 - p$. It is interesting that only the quantities $F$, $D$, and $A$ determine (41), so that it is irrelevant how strong the bonds are—only their sign (+, −, or 0) is important.

C. Rectangular distribution

We examine the rectangular distribution

$$P(J) = \begin{cases} \frac{\delta}{2}, & \text{if } J_0 - \delta < J < J_0 + \delta \\ 0, & \text{otherwise} \end{cases}$$  \hspace{1cm} (43)

This distribution is sketched in Fig. 3 for various values of $\delta/J_0$. We see that when $\delta > J_0$ there are both ferromagnetic and antiferromagnetic bonds. For this distribution, the integral in (13) can be done explicitly to give

$$e^{2K - 2\delta J_0} = \frac{1 + \epsilon(K) \sinh[\delta \epsilon(K)]}{1 - \epsilon(K) \sinh[\delta \epsilon(K)]},$$  \hspace{1cm} (44)

allowing the temperature ($1/J_0$) in the random system to be related to the temperature in the regular system ($1/K$). This is plotted in Fig. 4 for several values of $\delta/J_0$. The horizontal line at $1/K = 2.269$ represents the critical point; below this line the system is ferromagnetic, while above it the system is paramagnetic. The phase boundary as a function of $\delta/J_0$ is shown in Fig. 5. We see that as the width of the distribution $\delta/J_0$ increases from zero, the transition temperature is only slightly depressed for $\delta/J_0 < 1$. When $\delta/J_0 = 1$ all of the bonds are still ferromagnetic, but for $\delta/J_0 > 1$ there is a competition between the ferromagnetic and antiferromagnetic bonds and the phase transition rapidly disappears. However there is an interesting region $1.4 < \delta/J_0 < 1.7$, where there are two transition temperatures and the system is not ordered at zero temperature. Of course, the total order in the system (negative entropy) decreases monotonically with temperature. At low temperatures, in this regime, the order is predominantly associated with the bond arrangements rather than the spins. We note that for $0 < \delta/J_0 < 1$, the system is fully aligned at zero temperature ($1/K = 0$).

![Rectangular distribution for $P(J)$ [Eq. (43)] with $\delta/J_0 = 0.5, 1.0, 2.0$.](image)
FIG. 4. Relationship between the temperature (1/\(\beta J_0\)) in the square lattice with a rectangular distribution and the reference temperature (1/\(K\)) in the regular lattice for several values of \(\delta/J_0\).

However, this is not true for \(\delta/J_0 > 1\), where \(K\) is given by the solution to

\[
\epsilon(K) = J_0/\delta.
\]

Thus as \(\delta/J_0\) becomes larger the system becomes progressively more disordered at zero temperature, because of the competition between the ferromagnetic and antiferromagnetic interactions. The specific heat is plotted in Fig. 6 [from Eq. (20)] and the magnetization is obtained from the formula

\[
M = (1 - \sinh^{-1}(2K))^{1/6}
\]

and is shown in Fig. 7 for various values of \(\delta/J_0\).

FIG. 5. Phase diagram for the rectangular distribution [Eq. (43)] and the Gaussian distribution [Eq. (48)] in a square lattice (\(\epsilon_c = 1/\sqrt{2}\), \(\epsilon_c = 1 + \sqrt{2}\)). Also shown as a dashed line is the transition temperature corrected by the second moment [Eq. (49)].

FIG. 6. Specific heat \(C/k_B\) vs temperature (1/\(\beta J_0\)) for various values of \(\delta/J_0\) for the rectangular distribution on a square net. The arrow marks the position of the second transition temperature for \(\delta/J_0 = 1.5\), where the cusp in the specific heat is too small to show up. For \(\delta/J_0 = 0.5\) and 1.0, the height of the cusps are off the figure at 10.87 and 1.92, respectively.

It can be seen that as \(\delta/J_0\) increases, the magnetization becomes unsaturated at zero temperature, and then a second critical point develops at low temperatures. Finally, these two critical points come together and there is no phase transition.

The point where the phase boundary crosses zero temperature can be obtained using the discussion of Sec. III B and Eqs. (41) and (42) and is given by

\[
F = \int_0^\infty P(J) dJ = \frac{1 + \epsilon_c}{2}.
\]

For the square net this point occurs at \(\delta/J_0 = 1/\epsilon_c = 1.414\), as can be seen in Fig. 5. Note that the

FIG. 7. Spontaneous magnetization vs temperature (1/\(\beta J_0\)) on the horizontal axis for various values of \(\delta/J_0\) for the rectangular distribution on a square net.
mean-field result ($\epsilon_c = K_c = 0$) would give a horizontal line for the phase boundary in Fig. 5. In this approximation there would be a phase transition as long as there is a nonzero average of $J$.

D. Gaussian distribution and weak disorder

In order to see how important the shape of the distribution $P(J)$ is, we have also calculated the phase boundary for the Gaussian distribution

$$P(J) = \left(\frac{3}{2\pi \delta^2}\right)^{1/2} \exp \left[-\frac{3}{2} \frac{(J - \bar{J})^2}{\delta^2}\right],$$

which has the same second moment about its center $\frac{1}{2} \delta^2$ as the rectangular distribution [Eq. (43)]. This phase boundary is also shown in Fig. 5. The overall shape is very similar to that obtained from the rectangular distribution with the boundary crossing the zero temperature axis, as given by Eq. (47), at $\delta/\bar{J}_o = \sqrt{\frac{3}{2}} \exp^{-1}(\epsilon) = 1.647$. It is striking that the two distributions lead to indistinguishable phase boundaries for $0 < \delta/\bar{J}_o < 1$. By examining Eq. (13) for narrow distributions $P(J)$, it is easy to show that

$$T_c^T = T_c^R \left[1 - \epsilon_c K_c (M_N/M_1^2 - 1)\epsilon^2 \right],$$

where the transition temperature in the disordered system $T_c^T$ is shown by a dashed line in Fig. 5. The $m$th moment of the distribution $P(J)$ about $J = 0$ is denoted by $M_n$, so that $M_n/M_1^2 = 1$ is a measure of the width of the distribution. It can be seen that Eq. (49) works extremely well for $0 < \delta/\bar{J}_o < 1$, but breaks down rapidly as $\delta/\bar{J}_o > 1$ and competition develops between the ferromagnetic and antiferromagnetic bonds. The result (49) has also been obtained by Harris by an approximate calculation in the quenched case. There is probably very little difference between the annealed and quenched cases for distributions where all the interactions have the same sign. However, we expect substantial differences when both ferromagnetic and antiferromagnetic interactions are present.

The specific heat [Eq. (20)] takes a particularly simple form in the case of weak disorder

$$C_{\bar{K}_{\bar{J}}} = K^2 \left\{ \frac{1 - \epsilon^2(K)}{3J_0^2} \left[1 - \epsilon^2(K) - \frac{\epsilon(K)}{\delta K}\right]^{-1}\right\},$$

It can be seen that the specific heat is unaffected by the disorder unless

$$\frac{K^2 \epsilon^2}{3J_0^2} \approx \left(\frac{\epsilon(K)}{\delta K}\right)^{-1},$$

which occurs only in the critical region. Thus for weak disorder there is a crossover type of behavior and the randomness is manifested only in a small region around the critical point. Indeed it is easy to show from Eqs. (23) and (51) that if $\alpha$ is positive, the randomness is important only in the region

$$\frac{(\beta - \beta_c)}{\beta_c} \approx (\delta/\bar{J}_o)^{1/(1-\alpha)},$$

which can be made arbitrarily small by choosing $\delta/\bar{J}_o$ to be small (note that $\alpha > 1$, as the specific heat must be integrable). In two dimensions we have the special case of $\alpha = 0$ corresponding to a logarithmic divergence in the specific heat, and the region defined by Eq. (52) becomes exponentially small.

E. Spin glass

There has been a considerable amount of theoretical work and speculation recently on the possibility of forming a spin-glass state in which the spins are frozen into random positions. While it is clear that quenching is necessary to form such a phase, it is nevertheless interesting to ask what would happen in the corresponding annealed case. We therefore consider the case of a distribution that is symmetric about the origin,

$$P(J) = P(-J),$$

Equation (13) can be rewritten

$$\int_0^\infty \kappa(J)P(J)\,dJ = 0,$$

where the kernel $\kappa(J)$ is positive definite. There are therefore no nontrivial solutions, and we have $K = 0$ for all $\beta$. There is no phase transition and the energy is given by the same expression as for the one-dimensional chain [Eq. (30)], and the susceptibility is Curie-like at all temperatures.

In order to understand the situation a little better we have computed the phase boundary for a fcc lattice ($\epsilon_c = 0.2474$, $e^{2\epsilon_c} = 1.227$ based on good numerical approximations). This is shown in the upper part of Fig. 8. Also shown in the figure as a dashed line is the mean-field result corresponding to $\epsilon_c = K_c = 0$ in the reference system. When $J_0/\delta$ is large the two results are similar, although the mean-field transition temperature is always higher by a factor of 1.225. This phase diagram is qualitatively the same for all lattices, although deviations from the mean-field result are smallest for the fcc lattice because of the large number (12) of nearest neighbors. Nevertheless, we see that these deviations are important, particularly when $J_0/\delta$ is small. In the lower half of the figure we show the phase diagram for the same Hamiltonian in the quenched case and in the mean-field limit


The free energy \( F \) of a regular Ising model in one dimension with interaction parameter \( K \) and with an external field term \( -H \sum_i \sigma_i \) added to the Hamiltonian is given by

$$ -\beta F = K + \ln \left[ \cosh \beta H + (\sinh \beta H + e^{-4K})^{1/2} \right]. $$

From this it is easy to obtain the magnetization \( M \),

$$ M = \langle \sigma \rangle = \left[ 1 + (e^{2K} \sinh \beta H)^{-2} \right]^{-1/2}, $$

and the susceptibility \( \chi(H) = \partial M/\partial H \),

$$ \chi(H) = \beta e^{-4K} (\cosh \beta H/\sinh \beta H) \left[ 1 + (e^{2K} \sinh \beta H)^{-2} \right]^{-3/2}. $$

It is now possible to calculate magnetic-field-dependent quantities in the disordered system. The susceptibility in the disordered system \( \chi^D(H) \) is obtained from Eqs. (29) and (57) and is conveniently written

$$ \chi^D(H)/\chi^D(0) = \cosh(\beta H) \left[ 1 + [\chi^D(0) \sinh(\beta H)/\beta]^2 \right]^{-3/2}, $$

where

$$ \chi^D(0) = \beta \int \frac{P(J) dJ}{1 + e^{-2\beta J}} / \int \frac{P(J) dJ}{1 + e^{2\beta J}}, $$

and we have the interesting result that the disorder only enters into the magnetic-field-dependent susceptibility through \( \chi^D(0) \). This is also true for the magnetization \( M^D \) in the disordered system,

$$ M^D = \left[ 1 + [\chi^D(0) \sinh(\beta H)/\beta]^2 \right]^{-1/2}. $$

A knowledge of \( \chi^D(0) \) is therefore sufficient to determine all of the magnetic-field-dependent quantities in one dimension. This is of course not true in higher dimensions.

For the dilute ferromagnet [Eq. (33)], the susceptibility [Eq. (59)] becomes

$$ \chi^D(0) = \beta(1 + p \tanh \beta H)/(1 - p \tanh \beta H), $$

a result previously obtained by Wortis and by Cabib and Mahanti. For the symmetric case \( P(J) = P(-J) \) we have \( K = 0 \) for all \( \beta \), so that the magnetization and susceptibility are as for free spins. This situation has recently been studied in a computer calculation for the quenched case. The results show that the largest differences between the annealed and quenched cases occur at low temperatures—a conclusion that is consistent with the discussion in Sec. IV.

IV. CORRELATIONS AMONG THE BONDS

We have obtained a number of results for annealed systems, and it is important to understand more about the annealing process itself in which both the spins and the exchange interactions \( J \) are allowed to come into equilibrium at each tem-
perature. We included a chemical potential, so that the probability of a single bond being \( J_i \) is determined by the temperature-independent distribution \( P(J_i) \). However, if we ask for the joint probability distribution \( P(J_i, J_j) \) that different bonds have exchange interactions \( J_i \) and \( J_j \), it is not \( P(J_i)P(J_j) \). That is, the system can lower its free energy by choosing a nonrandom arrangement of bonds. It is again convenient to work out these correlations for a discrete distribution of the \( J_i \) and then go to the continuous distribution.

The expectation value of any product of operators including an \( f_i \) may be written
\[
\langle f_i \cdots \rangle = \frac{\text{Tr}(f_i \cdots \exp^{-\beta H})}{\text{Tr} \exp^{-\beta H}}, \tag{62}
\]
where the trace is over both the spin operators \( (\sigma) \) and the indicator functions \( (f_i) \) for each bond. The \( f_i \) operator in the numerator of Eq. (62) introduces an extra factor
\[
\exp(\beta f_i + \beta J_i \sigma_i \sigma_2)/A e^{\sigma_1 \sigma_2} \tag{63}
\]
when the partial trace over the \( f_i \) is done. Using Eqs. (6) and (9), we arrive at the operator equivalence
\[
f_i \sim \langle f_i \rangle \left[ \frac{\coth(K - \beta J_i) - \sigma_i \sigma_2}{\coth(K - \beta J_i) - \epsilon(K)} \right], \tag{64}
\]
where \( f_i \) is an operator in the disordered system, and on the right-hand side of the equation we have \( \sigma_i \sigma_2 \), which is an operator in the reference system. Of course the operator \( f_i \) refers to the bond with spins \( \sigma_i \) and \( \sigma_2 \) at either end, but we have suppressed the bond labels for clarity. The interpretation of Eq. (64) is that the operator \( f_i \) in the disordered system has an operator equivalent which is a function of \( \sigma_i \sigma_2 \) in the reference system (the regular Ising model). If we take expectation values of both sides of Eq. (64) we get the necessary result \( \langle f_i \rangle = \langle f_i \rangle \). The energy can be found from the operator \( f_i \sigma_i \sigma_2 \), which, using Eq. (64), becomes
\[
f_i \sigma_i \sigma_2 
\sim \langle f_i \rangle \left[ \frac{\epsilon(K) \coth(K - \beta J_i) - 1}{\coth(K - \beta J_i) - \epsilon(K)} \right], \tag{65}
\]
so that
\[
\langle f_i \sigma_i \sigma_2 \rangle = \langle f_i \rangle \left[ \frac{\epsilon(K) \coth(K - \beta J_i) - 1}{\coth(K - \beta J_i) - \epsilon(K)} \right], \tag{66}
\]
using Eq. (14) we get the result for the energy [Eq. (16)] as we go to the continuous distribution.

We want the expectation value of \( f_i f_j \), where \( f_i \) refers to a bond with associated spins \( \sigma_i \) and \( \sigma_{i+1} \). Using the operator equivalent from Eq. (64) we find that
\[
\langle f_i f_j \rangle = \langle f_i \rangle \langle f_j \rangle (1 + c), \tag{67}
\]
where \( c \) is a measure of the correlation between the bonds and is given by
\[
c = \frac{\langle \sigma_i \sigma_2 \sigma_j \sigma_{j+1} \rangle - \langle \sigma_i \sigma_2 \rangle \langle \sigma_j \sigma_{j+1} \rangle}{\left[ \frac{\coth(K - \beta J_i) - \epsilon(K)}{\coth(K - \beta J_j) - \epsilon(K)} \right]} - 1. \tag{68}
\]
We see that the bond correlations in the disordered system are proportional to the four spin-correlation functions of the regular Ising model. These functions \( \omega(r) \) have been calculated for the two-dimensional Ising model by Stephenson\textsuperscript{28} for spins on the same row, and are shown in Fig. 9, where
\[
\omega(r) = \langle \sigma_i \sigma_2 \sigma_{i+1} \rangle - \langle \sigma_i \sigma_2 \rangle \langle \sigma_{i+1} \rangle. \tag{69}
\]
For the nearest neighbors [\{1\} and \{2\} in Fig. 9] this reduces to a two-spin-correlation function and may be obtained from Kaufman and Onsager\textsuperscript{29}. We see that these correlations are greatest in the vicinity of the critical point. If we sum the correlations over all distinct pairs of bonds we get
\[
\sum_i \omega(r) = -1 + \epsilon^2(K), \tag{70}
\]

![Fig. 9. Four-spin-correlation function \( \omega(r) \) [Eq. (69)] for the reference system (square lattice, Refs. 28 and 29). The sites involved are indicated in the upper left-hand part of the figure. The dashed line is the sum of these correlations over all pairs of sites [Eq. (70)] on a vertical scale increased by a factor of 50.](image-url)
which is essentially the specific heat of the reference system and is also shown in Fig. 9.

The information in Fig. 9 is the input information necessary to determine bond correlations in the disordered system. In Fig. 10 we show the correlation $c$ between adjacent bonds in the dilute ferromagnet. It can be seen that this correlation is never very large, but is greatest in the critical region. It is negligible at high temperatures but not always negligible at low temperatures. It is also positive, which means that like bonds tend to cluster. This can be regarded as a tendency to partially phase separate. Indeed from Eq. (68) with $J_i = J_j$ we can see that $c$ is always positive for like bonds as the four-spin-correlation function in the numerator is positive.\(^3\)

This tendency for like bonds to cluster that is most pronounced in the critical region may be regarded as a tendency for the system to phase separate.

For a continuous distribution, the result (67) must be rewritten in terms of the joint probability distribution $P(J_i, J_j)$,

$$P(J_i, J_j) = P(J_i)P(J_j)(1 + c),$$  \hspace{1cm} (71)

with the same expression (68) for $c$. In Fig. 11 we show the probability distribution on a bond when its neighbor has a particular $J$ associated with it. The tendency for like bonds to attract can again be clearly seen. Finally, in Fig. 12 we show how these correlations behave as functions of temperature. Notice that the correlations are negative, because the two bonds are at the extreme ends of the rectangular distribution and so tend to avoid each other.

Although these correlations give some idea of the effect of annealing, they do not tell the whole story. Even if there was no correlation between pairs of bonds, this would not imply that there was no difference between the annealed and quenched cases. The converse is true. In the one-dimensional chain, discussed in Sec. IIIA, the four-spin-correlation function factorizes so that $\omega(r) = c = 0$. In the case of a symmetric distribution

\hspace{1cm} FIG. 10. Bond-bond correlation [$c$ from Eq. (67)] for neighboring bonds [marked (2) in Fig. 9] for the dilute ferromagnet at concentrations of 0.5, 0.75, and 0.90 (see Fig. 2). The transition temperatures are shown by arrows.

\hspace{1cm} FIG. 11. Probability distribution of exchange interactions on a two-dimensional square net for a pair of neighboring bonds [marked (2) in Fig. 9] when one of the bonds has $J/J_0 = 0.0$ (solid line), $J/J_0 = 1.0$ (long dashed line), and $J/J_0 = 2.0$ (short dashed line) for the case $\delta/J_0 = 1.0$. All three cases are at the transition temperature. Using Eq. (13), (67), and (68), it can easily be shown that there is unit area under each of the three curves.
FIG. 12. Correlation [c in Eq. (71)] between the exchange interactions on neighboring bonds as a function of temperature ($1/\beta J_0$) for various values of $\delta / J_0$ when one bond has an exchange $\delta_0 + \delta$ and the other $\delta_0 - \delta$. The dashed line refers to bonds marked (1) and the solid line to bonds marked (2) in Fig. 9. The correlation for $\delta_0 = 0.5$ (not shown) has a maximum magnitude of 0.0076.

$P(J) = P(-J)$, we have $K = 0$ for all $\beta$ and the operator equivalence [Eq. (64)] becomes

$$f_i \rightarrow \langle f_i \rangle (1 - \sigma_i \sigma_j \tanh \beta J_i).$$  \hspace{1cm} (72)

Products of $f_i$ operators factorize unless they go around a closed loop, so that the spin operators in (72) can be paired off. In the fcc lattice, there are triangles of bonds, thus

$$\langle f_i f_j f_k \rangle = \langle f_i \rangle \langle f_j \rangle \langle f_k \rangle \times \langle 1 - \tanh \beta J_i \tanh \beta J_j \tanh \beta J_k \rangle,$$  \hspace{1cm} (73)

where $i$, $j$, and $k$ refer to the three bonds with exchange interactions $J_i$, $J_j$, and $J_k$. One might imagine that higher-order correlations such as (73) are of little consequence—in fact, they are responsible for the nonoccurrence of the spin-glass phase.

It is instructive to examine the expression for the entropy per bond [Eq. (22)] at zero and infinite temperature. If we neglect the entropy of mixing terms, at very high temperatures ($\beta \rightarrow 0$) we have

$$S/k_B = (2/\pi) \ln 2,$$  \hspace{1cm} (74)

where $(2/\pi) \ln 2$ is just the entropy per bond of

the reference system at $K = 0$ [as $\beta \rightarrow 0$, we always have $K \rightarrow 0$ for any $P(J)$]. At very low temperatures (again neglecting the entropy of mixing) we have ($\beta \rightarrow \infty$)

$$S/k_B = S(k)/k_B + \frac{1}{2} [1 + \epsilon(K)] \ln [1 + \epsilon(K)]$$

$$+ \frac{1}{2} [1 - \epsilon(K)] \ln [1 - \epsilon(K)],$$  \hspace{1cm} (75)

where we have to compute the value of $K$ for $\beta \rightarrow \infty$ appropriate to a given $P(J)$. This entropy can become negative. For example, in the dilute ferromagnet at the critical concentration for the square net ($\rho_c = 1/2$) the entropy at zero temperature can be obtained from the critical values for the regular Ising model ($S_c/k_B = 0.1532$, $\epsilon_c = 1/\sqrt{2}$); thus for $\beta \rightarrow \infty$

$$S/k_B = -0.2633,$$  \hspace{1cm} (76)

which we see is negative. This apparent paradox disappears if we add the entropy of mixing $\ln(2) = 0.6931$ to both (74) and (76).

V. CONCLUSION

We have discussed the thermodynamics of an Ising model with a distribution $P(J)$ of exchange interactions in the annealed limit in which the complete system (spins and bonds) is allowed to come into thermal equilibrium. Although the system is well defined thermodynamically, actual physical situations are difficult, although not impossible, to imagine. For example, if the exchange goes through a ligand it might be possible to put the ligand into an excited state optically and get a different exchange which might be mobile via exciton hopping.

Annealed-bond systems also approximate quenched-bond systems which are more easily realized (e.g., an alloy with one kind of magnetic ion but two kinds of ligands). Available evidence suggests the annealed- and quenched-bond problems have similar thermodynamic behavior when the disorder is not too strong, except in the critical region.

Kasai and Syozai have used similar reasoning to obtain Eqs. (13) and (16) and have discussed phase diagrams for a number of distributions. Also, Falk has rederived Eq. (10) in a slightly more general form using a very elegant technique that utilizes probability distribution functions rather than chemical potentials. His technique provides some useful insights into the relationship between the quenched and annealed models.

Note added in proof. Recently H. Au-Yang, R. E. Fisher, and A. E. Ferdinand [Phys. Rev. B 13, 1238 (1976)] have studied the properties of two-
dimensional Ising models with a superlattice of point defects. For the case when \( P(x) = (1 - c) \times \delta(J - x) + c \delta(J' - x) \) we find from Eq. (13) that the transition temperature is reduced by a factor 1 + \( c/K_x \left[ (\varepsilon - \coth(K_x - \beta_0 J'))^{1/4} \right] \) for small \( c \) which agrees with the result of Au-Yang et al. [see Eqs. (4.13) and (4.17)] if the appropriate parameters for the square net are used (\( \varepsilon_c = 1/\sqrt{2} \), \( e^{2\varepsilon} = 1 + \sqrt{2} \)). It is probably generally true that the leading correction to the transition temperature is the same for quenched and annealed systems.

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5P. A. P. Moran, An Introduction to Probability Theory (Oxford U. P., Oxford, 1968). We would like to thank Professor H. Falk for pointing out this reference to us.
6A preliminary account of this work was given by M. F. Thorpe and D. Beeman, Bull. Am. Phys. Soc. 21, 231 (1976).
13All of the formalism of this section goes through if a magnetic field term \(-H \sum f_i q_i\) is added to the Hamiltonian, because the operator \( f_i \) is not involved in this additional term. This is not very helpful in general, as no exact solutions are known for Ising models in a field outside of one dimension—a case that is discussed in Sec. III F.

15A. B. Harris, J. Phys. C (to be published).
19We would like to thank Dr. A. P. Young for pointing out that the result of Matsubara (Ref. 18) for the transition temperature in the quenched case \( \int \tan(\beta_0 J') \int dJ \) only agrees with the annealed result [Eq. (32)] if \( P(J) = 0 \) for \( J < 0 \).
31J. W. Halley (private communication).