

positive maxima near both Curie temperature of about $4.9 \times 10^8 \text{ J/m}^3 \text{ deg}$ ($2.7 \times 10^{-8} \text{ J/g deg}$). This value is only 0.3% of C_P and would be difficult to observe. Positive values for ΔC at both Curie temperatures suggest that cooling through either transition produces a more ordered state, a conclusion that is consistent with some of the proposed models of ferroelectric Rochelle salt.^{17,18}

The agreement between the electrocaloric data and the susceptibility data is regarded as good, in particular, the values for the Curie temperatures, -19.2 and

¹⁷ E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, New Jersey, 1952).

¹⁸ P. W. Forsbergh, Jr., *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XVII.

25.2°C . This ferroelectric range is somewhat larger than the range ordinarily cited, but it agrees well with the extrapolated reciprocal susceptibility values of Mueller.²

There are discontinuities in the values of the slope dX_0/dT at both Curie temperatures which are possibly caused by ignoring the correction terms of higher order. These discontinuities are similar to those observed by Mueller² for dielectric, elastic, and piezoelectric properties. The slope, dX_0/dT , determined from the electrocaloric measurements near the upper Curie temperature is in excellent agreement with the values of $-1/(2\chi_r)$ determined from Mueller's susceptibility measurements¹¹ and in reasonable agreement with Hablützel's susceptibility measurements.¹²

Properties of Ising Models Containing Dilute Impurities

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The coupling-parameter equations for spin-pair correlation functions are examined for field-free Ising models with coordination number four (including both two- and three-dimensional cases). By means of sets of identities discovered by Fisher, it proves possible to eliminate exactly all higher order correlation functions from the equations, in the event that only nearest-neighbor sites interact. As a result, one can rigorously show for this class of Ising models that each spin-pair correlation function (one spin partially coupled) is a linear combination of two independent functions of the coupling parameter, and that spatial dependence occurs only through their multiplicative factors. Only one relation between these spatial factors is available for each site-pair separation distance, so that the Ising problem in its usual interpretation (coupling-parameter unity) is not yet rigorously soluble by this approach. However, by using the correlation function for the fully coupled case itself as a second set of constraints, exact results can be obtained explicitly for the pair correlation function, and hence the solution thermodynamics, for dilute impurities coupled with arbitrary strength to their nearest neighbors.

I. INTRODUCTION

IN a previous paper,¹ the functional equations for the spin-pair correlation functions $\langle \mu_1 \mu_2 \rangle$ in field-free Ising models with arbitrary scalar interactions were derived by means of the single-site variable coupling scheme. The resulting formalism is the order-disorder analog of Kirkwood's^{2,3} coupling-parameter theory for liquid state molecular distribution functions. It has become traditionally expected in liquid theory, as developed by the coupling-parameter method, that the determining equation for the pair correlation function involves unknown higher order correlation functions. Also, it has tacitly been assumed that, if a closed exact expression for these higher order functions were available in terms of the desired pair function, the corresponding substitution would yield an equation that

should uniquely and exactly determine the important pair correlation function. The example provided below seems, however, to contradict this hope.

The "higher order functions" which arise in the coupling parameter (λ) analysis of order-disorder theory, are spin quadruplet correlations $\langle \mu_1 \mu_2 \mu_3 \mu_4 \rangle$. If only nearest neighbors in the lattice interact, then the quadruplet configurations are considerably restricted: Two sites must be nearest neighbors of a third.

The following section shows that the remaining quadruplet functions may exactly be replaced by pair correlation functions when the lattice has coordination number 4. This further restriction nevertheless still allows both two-dimensional (square) and three-dimensional (diamond, ice) lattices to be considered. The key element in this reduction is the relevant set of Fisher identities⁴ for these lattices, which are exhibited in detail below [Eqs. (8)–(14)].

¹ F. H. Stillinger, Jr., *Phys. Rev.* **126**, 1239 (1962).

² J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

³ T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

⁴ M. E. Fisher, *Phys. Rev.* **113**, 969 (1959).

After the required reductions are performed, one finds that the λ dependence of each $\langle \mu_1 \mu_2 \rangle$ (μ_1 is the partially coupled spin) is described by a second-order, nonlinear, homogeneous differential equation in λ , in which there is no explicit appearance of the pair separation \mathbf{r}_{12} . Both solutions of the equation are admissible, so the general $\langle \mu_1 \mu_2 \rangle$ is a linear combination of them. The necessary pair of multiplicative factors for these two solutions varies as the separation between sites \mathbf{r}_{12} changes; it is in this variation alone that the spatial dependence of $\langle \mu_1 \mu_2 \rangle$ arises. For complete determination of the spin-pair correlation function, therefore, one requires two conditions for each \mathbf{r}_{12} .

The present theory, unfortunately, can provide only one condition (for each \mathbf{r}_{12}).⁵ Therefore, the problem of determining the pair correlation function (specifically for the fully coupled situation, $\lambda=1$) remains indeterminate. On the other hand, if one is willing to regard the $\lambda=1$ pair correlation as known, this function may itself act as the second set in determination of $\langle \mu_1 \mu_2 \rangle$ for $\lambda \neq 1$. Since a single site with arbitrary coupling parameter amounts to an impurity dissolved in an otherwise pure Ising host lattice, this somewhat less ambitious point of view allows one to obtain the excess thermodynamic behavior of such a "doped" Ising model in the limit of infinite dilution. The relevant partially coupled pair correlation function is obtained in the last section in closed form.

The Fisher identities are sufficiently powerful tools in the context of the coupling-parameter formalism that the type of analysis presented here is apparently limited neither by coordination number equal to four, nor to the absence of external fields. The algebraic manipulations for each case, however, are quite tedious and, furthermore, seem not to be trivial transcriptions of one another. For these reasons, it was elected to present here this single exploratory example.

II. ELIMINATION OF QUADRUPLET CORRELATIONS

Our system comprises N classical spins $\mu_1 \cdots \mu_N$ which have values ± 1 , and which are arranged on a regular lattice. These spins normally interact in pairs through a potential energy

$$v(\mathbf{r}_{ij})\mu_i\mu_j; \quad (1)$$

periodic boundary conditions will apply. As in Ref. 1, a coupling parameter λ will be attached to the site numbered 1, so for a pair of spins one of which is μ_1 , (1) is replaced by

$$\lambda v(\mathbf{r}_{1j})\mu_1\mu_j. \quad (2)$$

When the thermal behavior of the system is represented by a canonical ensemble, the spin-pair correlation $\langle \mu_1 \mu_2 \rangle$ is by definition equal to

$$\begin{aligned} \langle \mu_1 \mu_2 \rangle &\equiv \psi(12, \lambda) \\ &= \frac{\sum_{\mu_1 \cdots \mu_N = \pm 1} \mu_1 \mu_2 \exp\{-\beta[\lambda \mu_1 \sum_{j=2}^N v(1j)\mu_j + \sum_{j < k=2}^N v(jk)\mu_j\mu_k]\}}{\sum_{\mu_1 \cdots \mu_N = \pm 1} \exp\{-\beta[\lambda \mu_1 \sum_{j=2}^N v(1j)\mu_j + \sum_{j < k=2}^N v(jk)\mu_j\mu_k]\}}, \\ \beta &= (kT)^{-1}. \end{aligned} \quad (3)$$

For a pair of sites j and 2, neither of which is partially coupled, the spin-pair correlation $\langle \mu_j \mu_2 \rangle$ is obviously also equal to an expression of type (3); since, however, its λ dependence differs from that of $\psi(12, \lambda)$, we denote it by

$$\langle \mu_j \mu_2 \rangle = \psi(j2 | \lambda). \quad (4)$$

It is well to remember that when $\lambda \neq 1$, $\psi(j2 | \lambda)$ depends not only on the relative distance \mathbf{r}_{j2} , but also on one of the distances to the partially coupled site 1, say, \mathbf{r}_{12} .

If Eq. (3) is subjected to a single λ differentiation, one

easily obtains⁶

$$\begin{aligned} \frac{d\psi(12, \lambda)}{d\lambda} &= -w(12) + F(\lambda)\psi(12, \lambda) \\ &\quad - \sum_{j=3}^N w(1j)\psi(j2 | \lambda), \end{aligned} \quad (5)$$

where w is the reduced interaction

$$w(ij) = \beta v(ij)$$

and $F(\lambda)$ is proportional to the mean energy of interaction of partially coupled site 1 with its surroundings

$$F(\lambda) = \sum_{j=2}^N w(1j)\psi(1j, \lambda). \quad (6)$$

⁵ The fact that the author has so far been unable to find a second set perhaps only means that if it exists, it is not utterly trivial. Indeed, the rich reward of obtaining an exact solution to a three-dimensional Ising model which would follow constitutes strong motivation for continuing the search.

⁶ Equation (19) in Ref. 1.

Another fundamental relation, along with (5), is similarly obtained by λ differentiation of the $\psi(j2|\lambda)$ analog of Eq. (3)⁷

$$\frac{d\psi(j2|\lambda)}{d\lambda} = -w(1j)\psi(12,\lambda) - w(12)\psi(1j,\lambda) + F(\lambda)\psi(j2|\lambda) - \sum_{l=3(\neq j)}^N w(1l)y(12jl,\lambda), \quad (7)$$

$$y(12jl,\lambda) = \langle \mu_1 \mu_2 \mu_j \mu_l \rangle,$$

where, as in Eq. (3), $\langle \rangle$ stands for an average in the partially coupled canonical ensemble. Thus, the necessity of having to distinguish two different ψ 's, and of having to obtain a functional equation for each, has injected the quadruplet correlations y .

In the event that $v(\mathbf{r})$ vanishes except for nearest neighbors, Eqs. (5) and (7) show that sites j and l must both be nearest neighbors of 1. The four-site configurations that must be considered, hence, are quite restricted. Fisher⁴ has shown that there exist simple relations between such restricted quadruplet correlation functions, and the correlation functions for the constituent pairs. Our first task is to establish how the Fisher identities may most effectively be exploited in the coupling parameter context.

In a spin-space average such as that exhibited in Eq. (3), the variable μ_1 occurs in the numerator summand both as μ_1 itself, as well as once in the exponential function for each nearest neighbor with which it interacts. Fisher notes that the former type of occurrence may generally be replaced by a suitable combination of products of μ 's from the nearest-neighbor shell. For the specific case of four nearest neighbors (denoted by $\mu_j, \mu_k, \mu_l, \mu_m$), the basic Fisher identity has the form

$$\sum_{\mu_1=\pm 1} \mu_1 \exp\{\beta J \lambda \mu_1 (\mu_j + \mu_k + \mu_l + \mu_m)\} = [A(\lambda)(\mu_j + \mu_k + \mu_l + \mu_m) + B(\lambda)(\mu_k \mu_l \mu_m + \mu_j \mu_l \mu_m + \mu_j \mu_k \mu_m + \mu_j \mu_k \mu_l)] \times \sum_{\mu_1=\pm 1} \exp\{\beta J \lambda \mu_1 (\mu_j + \mu_k + \mu_l + \mu_m)\}, \quad (8)$$

where $-J$ stands for the nearest-neighbor value of $v(\mathbf{r})$. $A(\lambda)$ and $B(\lambda)$ may easily be evaluated by picking various values for μ_j, μ_k, μ_l , and μ_m :

$$\begin{aligned} A(\lambda) &= \frac{1}{8} [\tanh(4\beta J \lambda) + 2 \tanh(2\beta J \lambda)], \\ B(\lambda) &= \frac{1}{8} [\tanh(4\beta J \lambda) - 2 \tanh(2\beta J \lambda)]. \end{aligned} \quad (9)$$

Since $v(\mathbf{r})$ is assumed to be isotropic, only sums of products of nearest-neighbor spins which are completely symmetrical will occur in the identity (8).

In applying the basic Fisher identity to elimination of the y 's in Eq. (7), one must distinguish two possibilities: (a) Sites 1 and 2 are nearest neighbors; (b) sites 1 and 2 are not nearest neighbors. In the former case, we may

⁷ Equation (44) in Ref. 1.

let $m=2$ in Eq. (8) and substitute this relation into the definition of $y(1j2,\lambda)$:

$$\begin{aligned} y(12jl,\lambda) &= \langle \mu_1 \mu_j \mu_l \mu_2 \rangle \\ &= \langle [A(\mu_j + \mu_k + \mu_l + \mu_2) + B(\mu_k \mu_l \mu_2 + \mu_j \mu_l \mu_2 + \mu_j \mu_k \mu_2 + \mu_j \mu_k \mu_l)] \mu_j \mu_l \mu_2 \rangle, \\ &= A[\langle \mu_l \mu_2 \rangle + \langle \mu_k \mu_j \mu_l \mu_2 \rangle + \langle \mu_j \mu_2 \rangle + \langle \mu_j \mu_l \rangle] \\ &\quad + B[\langle \mu_k \mu_j \rangle + 1 + \langle \mu_k \mu_l \rangle + \langle \mu_k \mu_2 \rangle], \end{aligned} \quad (10)$$

where we have used the fact that the square of any spin is always +1. The remaining quadruplet spin average involves the entire shell of neighbors surrounding 1; it may be eliminated by performing the same substitution operation on $\langle \mu_1 \mu_2 \rangle$:

$$\begin{aligned} \langle \mu_1 \mu_2 \rangle &= \langle [A(\mu_j + \mu_k + \mu_l + \mu_2) + B(\mu_k \mu_l \mu_2 + \mu_j \mu_l \mu_2 + \mu_j \mu_k \mu_2 + \mu_j \mu_k \mu_l)] \mu_2 \rangle, \\ &= A[\langle \mu_j \mu_2 \rangle + \langle \mu_k \mu_2 \rangle + \langle \mu_l \mu_2 \rangle + 1] \\ &\quad + B[\langle \mu_k \mu_l \rangle + \langle \mu_j \mu_l \rangle + \langle \mu_j \mu_k \rangle + \langle \mu_j \mu_k \mu_l \mu_2 \rangle]. \end{aligned} \quad (11)$$

Combining Eqs. (10) and (11), one finds (1 and 2 nearest neighbors)

$$\begin{aligned} y(1j2,\lambda) &= (B^2 - A^2)/B + (A/B)\langle \mu_1 \mu_2 \rangle \\ &\quad + [A(B-A)/B][\langle \mu_j \mu_2 \rangle + \langle \mu_l \mu_2 \rangle] \\ &\quad + [(B^2 - A^2)/B]\langle \mu_k \mu_2 \rangle \\ &\quad + (B-A)[\langle \mu_k \mu_j \rangle + \langle \mu_k \mu_l \rangle], \end{aligned} \quad (12)$$

so that at least for this first case, the quadruplet functions may be rigorously supplanted by pair functions.

In the other case, none of the four neighbors of site 1 (j, k, l, m) is the site numbered 2, so Eq. (10) must be modified to read

$$\begin{aligned} y(12jl,\lambda) &= \langle [A(\mu_j + \mu_k + \mu_l + \mu_m) + B(\mu_k \mu_l \mu_m + \mu_j \mu_l \mu_m + \mu_j \mu_k \mu_m + \mu_j \mu_k \mu_l)] \mu_2 \mu_j \mu_l \rangle, \\ &= A[\langle \mu_l \mu_2 \rangle + \langle \mu_k \mu_j \mu_l \mu_2 \rangle + \langle \mu_j \mu_2 \rangle + \langle \mu_m \mu_j \mu_l \mu_2 \rangle] + B[\langle \mu_k \mu_m \mu_j \mu_2 \rangle + \langle \mu_m \mu_2 \rangle + \langle \mu_k \mu_m \mu_l \mu_2 \rangle + \langle \mu_k \mu_2 \rangle]. \end{aligned} \quad (13)$$

Thus, a greater number of quadruplet averages arises than before. In place of Eq. (11), in addition, one calculates

$$\begin{aligned} \langle \mu_1 \mu_2 \rangle &= \langle [A(\mu_j + \mu_k + \mu_l + \mu_m) + B(\mu_k \mu_l \mu_m + \mu_j \mu_l \mu_m + \mu_j \mu_k \mu_m + \mu_j \mu_k \mu_l)] \mu_2 \rangle, \\ &= A[\langle \mu_j \mu_2 \rangle + \langle \mu_k \mu_2 \rangle + \langle \mu_l \mu_2 \rangle + \langle \mu_m \mu_2 \rangle] \\ &\quad + B[\langle \mu_k \mu_l \mu_m \mu_2 \rangle + \langle \mu_j \mu_l \mu_m \mu_2 \rangle + \langle \mu_j \mu_k \mu_m \mu_2 \rangle + \langle \mu_j \mu_k \mu_l \mu_2 \rangle]. \end{aligned} \quad (14)$$

Consistent with the form of the basic Fisher identity, Eq. (8), the quadruplet averages in Eq. (14) occur only in a symmetrical combination, one term appearing for each way of selecting three spins out of the set of four nearest neighbors of the central partially coupled site 1. On the other hand, the quadruplet averages do not occur symmetrically in Eq. (13), so their elimination cannot immediately be effected. The situation, however, is very easily rectified, for the fundamental Eq. (5)

shows that when 2 is not next to 1 only a symmetrical sum of functions $\psi(j2|\lambda)$ over 1's nearest-neighbor shell is required. Finally, then, $y(12jl,\lambda)$ will be symmetrically summed over both j and l in this shell, and relation (14) should suffice for the desired reduction.

For this purpose, we define

$$\eta(12|\lambda) = \sum_{j=3}^N w(1j)\psi(j2|\lambda); \quad (15)$$

there are, of course, only four nonvanishing terms at most. Then differential Eqs. (5) and (7) may be rewritten

$$\frac{d\psi(12,\lambda)}{d\lambda} = -w(12) + F(\lambda)\psi(12,\lambda) - \eta(12|\lambda), \quad (16)$$

$$\begin{aligned} \frac{d\eta(12|\lambda)}{d\lambda} = & -\frac{1}{2}F(\lambda)w(12) - \theta^2\psi(12,\lambda) + F(\lambda)\eta(12|\lambda) \\ & - \sum_{j \neq l=3}^N w(1j)w(1l)y(12jl,\lambda); \end{aligned} \quad (17)$$

the quantity θ is defined by

$$\theta^2 = \sum_{j=2}^N w^2(1j) = 4\beta^2 J^2. \quad (18)$$

For the two cases (a) and (b) above, there are, respectively, six and twelve terms in the j, l summation in Eq. (17).

For (a), Eq. (12) may be applied to Eq. (17) to show that the last term reduces to

$$\begin{aligned} & - \sum_{j \neq l=3}^N w(1j)w(1l)y(12jl,\lambda) \\ & = (6/B)[A^2 - B^2 - A\psi(12,\lambda)](\beta J)^2 \\ & \quad + (6/B)(B^2 - A^2)\eta(12|\lambda)(\beta J). \end{aligned} \quad (19)$$

Furthermore, as anticipated, only symmetrical combinations of quadruplet averages occur for case (b) when Eq. (13) is inserted in Eq. (17). If subsequently Eq. (14) is utilized to eliminate them, the result is not quite the same as shown in Eq. (19), but the two cases may conveniently be combined into a single expression by exploiting the nearest-neighbor character of $w(12)$; one obtains

$$\begin{aligned} & - \sum_{j \neq l=3}^N w(1j)w(1l)y(12jl,\lambda) \\ & = (6/B)(A^2 - B^2)w^2(12) + (3/2)F(\lambda)w(12) \\ & \quad - (6/B)(A + B)(\beta J)^2\psi(12,\lambda) \\ & \quad + (6/B)(B^2 - A^2)(\beta J)\eta(12|\lambda). \end{aligned} \quad (20)$$

We are now able to rewrite Eq. (17) in the following

manner:

$$\begin{aligned} \frac{d\eta(12|\lambda)}{d\lambda} = & [F(\lambda) + 6\beta J(B^2 - A^2)/B]w(12) \\ & - [10 + (6A/B)](\beta J)^2\psi(12,\lambda) \\ & + [F(\lambda) + 6\beta J(B^2 - A^2)/B]\eta(12|\lambda). \end{aligned} \quad (21)$$

The function $\eta(12|\lambda)$ only occurs once in Eq. (16), undifferentiated. If this equation is then solved for $\eta(12|\lambda)$, we may eliminate that function entirely from Eq. (21) to leave a second-order homogeneous⁸ differential equation in the desired function ψ :

$$\begin{aligned} \frac{d^2\psi(12,\lambda)}{d\lambda^2} - 2\{F(\lambda) + 3\beta J[B^2(\lambda) - A^2(\lambda)]/B(\lambda)\} \frac{d\psi(12,\lambda)}{d\lambda} \\ + \{F^2(\lambda) - dF(\lambda)/d\lambda + 6\beta JF(\lambda)[B^2(\lambda) - A^2(\lambda)]/B(\lambda) \\ - [10 + (6A(\lambda)/B(\lambda))](\beta J)^2\}\psi(12,\lambda) = 0. \end{aligned} \quad (22)$$

Of course, this equation is not linear in view of the definition of $F(\lambda)$, Eq. (6), which under present restrictions is proportional to ψ at the nearest-neighbor separation,⁹

$$F(\lambda) = -4\beta J\psi(\text{n.n.}, \lambda). \quad (23)$$

Since the spin μ_1 has no way of correlating with any other spin when its interactions are turned off, the solution to (22) must satisfy

$$\psi(12, \lambda=0) = 0. \quad (24)$$

An interesting feature of differential equation (22) is the fact that the spatial coordinate \mathbf{r}_{12} appears only as an index in the unknown function $\psi(\mathbf{r}_{12}, \lambda)$. Consequently, we may immediately infer that for all pairs of sites the λ dependence has a common simple representation in terms of that equation's solutions. If one writes

$$\begin{aligned} F(\lambda) & = -\beta Jf(x), \\ \psi(12,\lambda) & = \varphi(x), \\ x & = \beta J\lambda, \end{aligned} \quad (25)$$

then Eq. (22) simplifies somewhat,

$$\begin{aligned} \frac{d^2\varphi(x)}{dx^2} + [2f(x) - 3(\tanh x + \coth x)] \frac{d\varphi(x)}{dx} \\ + \left[f^2(x) + \frac{df(x)}{dx} - 3(\tanh x + \coth x)f(x) \right. \\ \left. + 3(\tanh^2 x + \coth^2 x) + 2 \right] \varphi(x) = 0, \end{aligned} \quad (26)$$

⁸ The fact that differential Eq. (22) is homogeneous may be traced to the identity of the coefficients of $w(12)$ and $\eta(12|\lambda)$ in Eq. (21). This coincidence seems to be restricted to our choice of lattices with four neighbors. Both for the linear array (two nearest neighbors) and the planar honeycomb lattice (three nearest neighbors), the differential equations analogous to Eq. (22) have additional inhomogeneous terms proportional to $w(12)$. At least for the first of these other examples, where the exact pair correlation result is known from other considerations, it is possible to show that this inhomogeneous term vanishes. Whether the resulting ψ differential equation homogeneity is a general phenomenon or not is not clear.

⁹ We shall henceforth denote this (scalar) separation simply by "n.n."

the explicit expressions in Eq. (9) having been used for A and B .

One knows on physical grounds that $f(x)$ will be proportional to x for small values of that argument. The dominant nature of the coefficients of $d\varphi/dx$ and φ in Eq. (26) hence arise from the hyperbolic cotangents. Near $x=0$, therefore, this differential equation adopts the following limiting form:

$$\frac{d^2\varphi(x)}{dx^2} - \frac{3}{x} \frac{d\varphi(x)}{dx} + \frac{3}{x^2}\varphi(x) = 0. \quad (27)$$

From this, one establishes that the small- x behavior of solutions $\varphi(x)$ may either be linear or cubic in x . There are thus two independent solutions to the basic Eq. (26), which will be denoted by $\varphi_1(x)$ and $\varphi_3(x)$:

$$\begin{aligned} \varphi_1(x) &\sim x, \\ \varphi_3(x) &\sim x^3, \end{aligned}$$

where we choose the normalization to give unit coefficients to these leading terms.

Similarly, one finds the large- x differential equation form to be

$$\frac{d^2\varphi(x)}{dx^2} + 2\frac{d\varphi(x)}{dx} = 0, \quad (28)$$

with solutions $a \exp(-2x) + b$. Consequently, both φ_1 and φ_3 approach constants as x increases without bound.

Differential equation (26) may be integrated by standard methods to give¹⁰

$$\begin{aligned} \varphi_1(x) &= \exp\left[-\int_0^x f(x')dx'\right] \sinh x \cosh^3 x, \\ \varphi_3(x) &= \exp\left[-\int_0^x f(x')dx'\right] \sinh^3 x \cosh x. \end{aligned} \quad (29)$$

In the high-temperature limit, the reduced energy $f(x)$ becomes

$$f(x) \cong 4 \tanh x,$$

so the two fundamental solutions approach $\tanh x$ and $\tanh^3 x$, respectively.

In view of their small- and large- x properties, both $\varphi_1(x)$ and $\varphi_3(x)$ must be admitted as possible solutions in the physical problem at hand. The desired spin-pair correlation function, for all \mathbf{r}_{12} , will have the same type of representation in terms of a linear combination of φ_1 and φ_3 :

$$\psi(12, \lambda) = \alpha(12) \varphi_1(\beta J \lambda) + \beta(12) \varphi_3(\beta J \lambda). \quad (30)$$

The entire spatial dependence is carried in the set of multiplicative constants α and β . It is nonetheless interesting, and heretofore unanticipated, that the λ variation of *all* pair correlations involving the partially

coupled spin μ_1 should be constrained (at a given temperature) to a two-parameter family of functions.

Complete solution to the over-all problem of determination of the pair correlation functions consequently now amounts to formulation of a sufficient set of "boundary" conditions on the coupling-parameter variation problem. Since two parameters are required for each \mathbf{r}_{12} , two conditions are required for each value of this separation. Unfortunately, only one seems to be available. It stems from the fact that, when $\lambda=1$,

$$\psi(\mathbf{r}, \lambda=1) = \psi(\mathbf{r} | \lambda=1), \quad (31)$$

reflecting the complete translational invariance of the lattice when all its spins are coupled to the same degree. For this value of λ , Eq. (5) becomes

$$\begin{aligned} \frac{d\psi(12, \lambda=1)}{d\lambda} &= -w(12) + F(\lambda=1)\psi(12, \lambda=1) \\ &\quad - \sum_{j=3}^N w(1j)\psi(j2, \lambda=1). \end{aligned} \quad (32)$$

If only one of the independent solutions, say, $\varphi_1(x)$, had been physically admissible, so that only the first term would have appeared in Eq. (30), then the constraints (32), which are in the form of a finite-difference equation, would completely determine $\psi(12, \lambda)$. The resulting expression would be proportional to the Green's function for the difference equation,¹ and would be very similar to the pair correlation that has been calculated for the spherical model.¹¹ However, the much more complicated behavior of the actual model, especially near its critical point,¹² must arise out of a delicately balanced competition between $\alpha(12)$ and $\beta(12)$, which cannot be determined with present incomplete information.

III. DILUTE IMPURITIES

In spite of the fact that the λ coupling scheme does not seem capable of producing a solution to the Ising problem as ordinarily construed, it does allow exact deduction of a less ambitious result. If one is willing to regard the pair correlation function of the fully coupled ($\lambda=1$) model as known information,¹³ then this¹⁴ $\psi(12)$ may itself be taken as the second set of conditions necessary to determine $\alpha(12)$ and $\beta(12)$, for out of the entire set of choices for these quantities which satisfy Eq. (32), only one choice will reproduce the correct $\psi(12)$. Once $\alpha(12)$ and $\beta(12)$ have been determined, Eq. (30) immediately yields the mean spin distribution around an isolated impurity spin which couples with

¹¹ T. H. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).

¹² M. E. Fisher, Physica **28**, 172 (1962).

¹³ For the two-dimensional square lattice, certain of the spin-pair correlations have already been calculated exactly; see B. Kaufman and L. Onsager, Phys. Rev. **76**, 1244 (1949).

¹⁴ In the following it will be understood that if λ is suppressed as a variable in $\psi(12, \lambda)$, $\eta(12 | \lambda)$, or $A(\lambda)$ and $B(\lambda)$, its value should be taken to be unity.

¹⁰ The author is indebted to Dr. L. R. Walker for first pointing out this solution.

anomalous strength ($\lambda \neq 1$) to its four neighbors. Because such impurities will individually behave as though isolated if they are dissolved in a host Ising lattice with sufficient dilution, we therefore have, in principle, a means for determining the low concentration statistical-thermodynamic behavior of impure Ising models. The explicit connections between the $\lambda \neq 1$ pair correlation function, and excess susceptibilities, free energy, etc., follow in a sufficiently straightforward way from classical theories of solutions, so that reiteration is not required here.^{2,15,16}

This program may be carried to explicit completion by rewriting the definition (3) in a somewhat modified way:

$$\psi(12, \lambda) = \frac{\langle \mu_1 \mu_2 \exp\{-(\lambda-1)\mu_1 \sum_{j=2}^N w(1j)\mu_j\} \rangle_{\lambda=1}}{\langle \exp\{-(\lambda-1)\mu_1 \sum_{j=2}^N w(1j)\mu_j\} \rangle_{\lambda=1}}. \quad (33)$$

Both numerator and denominator are averages of λ -dependent functions in the fully coupled ($\lambda=1$) canonical ensemble, as denoted by subscripts on the angular brackets. Since each spin is restricted to values ± 1 , it follows that

$$\exp\{-(\lambda-1)w(1j)\mu_1\mu_j\} = \cosh[(\lambda-1)w(1j)] \times \{1 + \mu_1\mu_j \tanh[-(\lambda-1)w(1j)]\}.$$

Equation (33), therefore, may be transformed to

$$\psi(12, \lambda) = \frac{\langle \mu_1 \mu_2 \prod_{j=2}^N \{1 + \mu_1\mu_j \tanh[-(\lambda-1)w(1j)]\} \rangle_{\lambda=1}}{\langle \prod_{j=2}^N \{1 + \mu_1\mu_j \tanh[-(\lambda-1)w(1j)]\} \rangle_{\lambda=1}} = \frac{N(12, \lambda)}{D(\lambda)}. \quad (34)$$

The nearest-neighbor interaction ensures that only four factors in the j products in both numerator and denominator of (34) need be considered. If these finite products are expanded, they lead to sums of averaged spin products in the $\lambda=1$ ensemble. The spin-pair averages, of course, are the function $\psi(12)$, which we treat as known. The spin-quadruplet averages may be reduced to $\psi(12)$ and $\eta(12)$ by exactly the same techniques as employed in the preceding section. The only

novel point worth acknowledging is that once, in the numerator, there is generated the sextuplet spin correlation

$$\langle \mu_1 \mu_j \mu_i \mu_l \mu_m \mu_2 \rangle,$$

when sites 1 and 2 are not nearest neighbors. By means of Eq. (8), though, it may ultimately also be reduced to ψ and η functions in the $\lambda=1$ ensemble, in standard fashion.

We shall not reproduce the very tiresome details of the reduction here, since the procedure is straightforward and uninteresting. If

$$T(\lambda) = \tanh[\beta J(\lambda-1)], \quad \nu(12) = -v(12)/J,$$

then the result is

$$\begin{aligned} N(12, \lambda) = & [\nu(12)/B] \\ & \times [BT(\lambda) + 3(B^2 - A^2)T^2(\lambda) - AT^3(\lambda) \\ & + (B^2 - A^2)T^4(\lambda)] + \psi(12) - T(\lambda) \\ & \times [\eta(12)/\beta J] + [3T^3(\lambda)/B][(B+A)\psi(12) \\ & - (B^2 - A^2)\eta(12)/\beta J] + [T^3(\lambda)/B] \\ & \times [\psi(12) + A\eta(12)/\beta J] + [T^4(\lambda)/B] \\ & \times [A\psi(12) - (B^2 - A^2)\eta(12)/\beta J]; \quad (35) \end{aligned}$$

$$\begin{aligned} D(\lambda) = & 1 + 4T(\lambda)\psi(\text{n.n.}) - 2T^2(\lambda)\eta(\text{n.n.})/\beta J \\ & + [4T^3(\lambda)/B][B^2 - A^2 + A\psi(\text{n.n.}) \\ & - (B^2 - A^2)\eta(\text{n.n.})/\beta J] + [T^4(\lambda)/B] \\ & \times [-A + \psi(\text{n.n.}) + (B+A)\eta(\text{n.n.})/\beta J]. \quad (36) \end{aligned}$$

The ratio of these expressions, by Eq. (34), amounts to the exact transformation of the fully coupled ensemble pair correlation function to that with arbitrary λ . Naturally, it reduces to an identity as λ approaches unity. This constitutes rigorous solution of the impurity problem in terms of the pure Ising problem.

If one were willing to accept the pair correlation functions ψ and η at some other value of the coupling parameter $\lambda = \lambda_0$ as being known, rather than at $\lambda=1$, then it is clear that a simple modification of the manipulations in this section could be developed. The result generally is equivalent to a transformation law for pair correlation functions displaced by a finite amount, $\lambda - \lambda_0$, in their coupling parameters. As this difference becomes infinitesimal, the transformation law reduces to differential equation (16). In spite of the fact that the expressions utilized in this section might superficially seem quite unrelated to the differential formulation of Sec. II, they are equivalent only to an integrated form of Eq. (16). They contain no more nor less physical information, and this latter approach was selected solely on the basis of expedience in obtaining the closed solution (35)-(36).

¹⁵ W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

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