Some Remarks on Correlations in Classical Order-Disorder Phenomena

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By means of a spin-magnitude variation parameter, equations are derived for spin-pair correlation functions in classical lattice theories. Specifically, the case of two spin states present in equal average numbers is considered, but with arbitrary scalar interaction between pairs of spin sites. It is pointed out that in this case the spin-triplet correlation functions which occur in the theory, as well as all higher odd-order correlation functions, may be reduced exactly to linear combinations of lower-order correlation functions. The nature of spin-quadruplet correlations, which are also required in this method for rigorous determination of the pair functions, unfortunately have no corresponding reduction, but their character is discussed qualitatively. The approximate theory resulting from use of a simple closure relation for quadruplets is examined, with particular attention to the position of the critical temperature for ferromagnetic coupling of varying range. It is remarked, on the basis of the approximate theory, that spin-pair correlations at large distance tend to become independent of direction (relative to the fundamental axes of the lattice) as the critical temperature is approached, when the interaction satisfies a certain second-moment isotropy condition.

An alternative, and apparently more accurate, closure relation for determination of spin-quadruplet correlation functions is proposed with a view toward possible application to modern computing techniques.

I.

PERHAPS the most central quantity in classical order-disorder problems is the distribution of pairs of spins (or "particles" in lattice gas terminology) separated by a given distance in the lattice of interest. Not only does this pair distribution lead to the mean energy of the system (by multiplying by the site-site interaction, and summing over all pairs of positions in the lattice) and subsequently to the other thermodynamic properties, but its Fourier transform yields the response of the system to small, externally applied, periodic force fields. Likewise, one may obtain as well from this pair distribution the scattering character of the lattice for incident radiation.

There have been previous proposals[1,2] for determination of spin-pair distribution functions. These techniques tended, however, to rely upon Bethe's[3,4] notions of average local fields acting on clusters of one or more sites, these fields being independent of the state of the chosen set of sites. As a result, the local configurational free energy changes associated with change in state of the chosen small set of spins are unfortunately oversimplified, in the sense that one disregards the rather complicated back reaction of the surrounding set of spins on the chosen small cluster, due to the fact that they are "polarized" by the state of this cluster.

In the following, we have attempted to provide an alternative discussion of spin-pair correlation functions based upon a systematic development of classical order-disorder theory (where each lattice site has two possible states with equal *a priori* probability), from the fundamentals of Gibbsian statistical mechanics. In the event that interactions are restricted solely to nearest neighbors, our considerations apply then to the resulting Ising model in vanishing external field. The many well-known techniques applicable to the nearest-neighbor models are not discussed below at any length, in view of the available standard reviews on the subject.[5,6] We are interested here, however, in developing techniques applicable to the general case of arbitrary scalar interactions. It is in fact possible to exhibit an estimate of the manner in which ferromagnetic Curie temperatures depend upon range and isotropy of the interaction potential [Eq. (35)], so that the following analysis has the capacity to describe those often more realistic lattice theories that have not received the intensive study devoted to the Ising model. We do not, however, consider at all in this paper the case of finite external fields, which produce a preference of one spin state over the other.

Section II defines the spin correlation functions, and states their elementary properties. For the purposes of later development, the spin-magnitude coupling parameter is introduced *ab initio*. Section III is devoted to derivation of a fundamental relation satisfied by pair correlation functions, and it is shown how the spin-triplet correlation functions arising in the course of this derivation may exactly be eliminated in favor of pair functions. As an application of this fundamental relation, Sec. III also indicates its solution for the one-dimensional field-free Ising model.

In Sec. IV, a second fundamental equation is obtained for the effect of a nearby partially coupled site on the spin correlation for a chosen pair of lattice sites. The occurrence of irreducible quadruplet correlation functions in this latter expression, however, necessitates use of a closure relation for deduction of distribution of spin pairs (except in certain special situations, as the one-dimensional Ising model). Such a closure relation is suggested, and the resulting approximate theory is developed. In particular, one then easily establishes the aforementioned ferromagnetic Curie point relation.

[1] F. Zernike, Physica **7**, 565 (1940).
[2] R. J. Elliott and W. Marshall, Revs. Modern Phys. **30**, 75 (1958).
[3] H. A. Bethe, Proc. Roy. Soc. (London) **A150**, 522 (1935).
[4] P. I. Richards, *Manual of Mathematical Physics* (Pergamon Press, New York, 1959), pp. 219–20.
[5] G. F. Newell and E. W. Montroll, Revs. Modern Phys. **25**, 353 (1953).
[6] C. Domb, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, pp. 149–361.

Furthermore, it is pointed out that pair correlations at large distance are predicted to become isotropic as the critical point T_c is approached from above, if the interaction satisfies certain second moment conditions (Appendix B).

Section V discusses the nature of the pair correlations below T_c, in the case that two ferromagnetic phases may coexist, and it is remarked that solution of the fundamental equations (at zero external field) would allow the boundary of the two-phase region to be plotted in the relevant temperature-composition diagram (Fig. 1).

Finally, Sec. VI presents an alternative closure relation to the rather crude one whose consequences were developed in Sec. IV. This second procedure, though somewhat awkward to apply, is argued to be more accurate on the basis of certain limit properties.

It should be remarked that the following analysis was largely prompted by a desire ultimately to understand the relation between the well-known integral equation methods[7] in the theory of dense fluid distribution functions, and the standard approaches to the Ising theory. For proper comparison, it was necessary to generate a method not specially restricted to nearest-neighbor interactions.

The approach outlined below admittedly has much in common with certain aspects of the continuum fluid theories, for example, the use of a coupling parameter,[8] as well as stress given to distribution functions for small sets of spins. In this connection, it seemed important to examine the lattice analog of the traditional liquid theory superposition approximation.[8] The fact that lattice triplet distributions (at zero external field) have a nearly trivially demonstrable reduction to a linear combination of pair functions rather than a superposition-like product is worthy of future attempted clarification, especially since an inverted order of precision can be exhibited for ordinary fluids.[9]

II.

We consider a regular lattice of N sites, with periodic boundary conditions imposed at the surface of the lattice. Each site i has two possible states which may be characterized by a "spin" parameter μ_i, having values ± 1. The total interaction energy V for the lattice has the form:

$$V(\mu_1\cdots\mu_N)=\sum_{i<j=1}^{N} v(ij)\mu_i\mu_j, \qquad v(ij)\equiv v(\mathbf{r}_{ij}). \tag{1}$$

The absence of terms linear in the μ's reflects our initial assumption of no external fields acting on the "spins" $\mu_1\cdots\mu_N$. The interaction potential $v(\mathbf{r})$ will, for our general remarks, be arbitrary, and its range may thus span many nearest-neighbor spacings in the lattice; imposition of the periodic boundary condition however demands that the displacement $\mathbf{r}_{ij}$ for a given pair of sites refer to the shortest such vector connecting the respective sites to one another or to their images.

If the interacting system of spins is brought into thermal contact with a heat reservoir at absolute temperature T, then the probability for spin configurations may be taken as the canonical density,

$$P^{(N)}(\mu_1\cdots\mu_N)=[Z(T)]^{-1}\exp[-V(\mu_1\cdots\mu_N)/kT], \qquad Z(T)=\sum_{\mu_1\cdots\mu_N=\pm 1}\exp[-V(\mu_1\cdots\mu_N)/kT], \tag{2}$$

where k is Boltzmann's constant.

Although the two physically significant site states are specified by the discrete values ± 1 for the μ_i, we shall follow a convenient artifice that has found widespread application in liquid state theory,[8] and therefore introduce a coupling parameter λ, attached arbitrarily to the site numbered 1; this parameterization is accomplished by replacing μ_1 with $\lambda\mu_1$. The corresponding modification of the potential energy V is just

$$V(\mu_1\cdots\mu_N,\lambda)=\lambda\sum_{j=2}^{N} v(1j)\mu_1\mu_j+\sum_{i<j=2}^{N} v(ij)\mu_i\mu_j. \tag{3}$$

The configuration probability density $P^{(N)}$ and partition function Z have obvious generalizations appropriate to inclusion of the coupling parameter λ.

The effect of λ is quite clear. Setting $\lambda=\pm 1$ reproduces the original fully coupled physical situation. As λ is allowed to decrease to zero, however, the extent to which site 1 can interact with its neighbors diminishes continuously until this site's state is entirely independent of the surroundings, when $\lambda=0$.

In view of the fact that our model is free of external fields acting to bias the spin population at any given site i, the fraction of members of a representative ensemble of identical lattice systems which have either $\mu_i=+1$ or $\mu_i=-1$ is just $\frac{1}{2}$. The probability, $P^{(n)}$, that a given subset of all the N sites (specifically we choose $1\cdots n$) has a given set of spins $\mu_1\cdots\mu_n$, irrespective of the value of the remaining $N-n$ μ's, may be found by summing $P^{(N)}$ over this latter extraneous set of spins:

$$P^{(n)}(\mu_1\cdots\mu_n,\lambda)=\sum_{\mu_{n+1}\cdots\mu_N=\pm 1} P^{(N)}(\mu_1\cdots\mu_N,\lambda). \tag{4}$$

Although the chosen set $\mu_1\cdots\mu_n$ includes the partially coupled spin μ_1, a similar relation can be utilized for any set of spins not including μ_1; the resulting λ dependence of the $P^{(n)}$ obtained, however, would generally differ from that of Eq. (4).

If the temperature is sufficiently high, the set of spins will exhibit no long-range order. Under this circumstance, a set of n sites selected far from one another by comparison with the range of $v(\mathbf{r})$, will have independent spins, so $P^{(n)}$ must equal $(\frac{1}{2})^n$, for any values of $\mu_1\cdots\mu_n$

[7] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.
[8] J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).
[9] F. H. Stillinger, J. Fluid Phys. **3**, 725 (1960).

and λ. By way of stressing the nonrandom joint spin probability for sites which are close enough to interact statistically, we define "n-spin correlation functions," $p_{\alpha\beta\cdots\nu}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda)$, by factoring the *a priori* individual spin probabilities out of $P^{(n)}$:

$$P^{(n)}(\mu_1\cdots\mu_n,\lambda)=(\tfrac{1}{2})^n p_{\alpha\beta\cdots\nu}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda). \quad (5)$$

The subscript α stands, respectively, for $+$ or $-$ if spin μ_1 on the site at $\mathbf{r}_1$ has value $+1$ or -1. Subscripts $\beta\cdots\nu$ are assigned accordingly, from the values $\mu_2\cdots\mu_n$.

Certain general properties of the $p^{(n)}$ are immediately obvious:

(a) Vanishing of external fields along with imposition of periodic boundary conditions implies that all local properties of the spin system, and in particular each $p^{(n)}$, are translation invariant when $\lambda=+1$. Furthermore, the $p^{(n)}$ must also exhibit rotational symmetry appropriate to the regular lattice considered.

(b) Above the transition temperature T_c to any possible long-range ordered state, the $p^{(n)}$ exhibit a factorization property: If $\mathbf{r}_1\cdots\mathbf{r}_n$ separate into two sets of positions, with all members of one set much farther from all members of the other set than the range of $v(\mathbf{r})$, than $p^{(n)}$ reduces to the product of the two lower-order p's appropriate to those sets.

(c) By virtue of the lack of external fields, one recognizes that our model has complete symmetry with respect to $+$ and $-$ spins. As a result, each $p_{\alpha\beta\cdots\nu}{}^{(n)}$ is unchanged if all $+$'s in its set of subscripts are changed to $-$'s, and *vice versa*.

(d) The single-spin correlation function is trivial:

$$p_\alpha{}^{(1)}(\mathbf{r}_1,\lambda)\equiv 1. \quad (6)$$

(e) When λ vanishes, $p_{\alpha\beta\cdots\nu}{}^{(n)}$ is independent of α:

$$p_{+\beta\cdots\nu}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda=0)=p_{-\beta\cdots\nu}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda=0). \quad (7)$$

(f) Finally, notice should be given to a set of normalization conditions satisfied by the spin correlation functions which follows from Eqs. (4) and (5). Upon summing over any subscript in $p^{(n)}$, the next lower-order spin correlation function is obtained:

$$p_{\alpha\beta\cdots\mu+}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda)+p_{\alpha\beta\cdots\mu-}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda) =2p_{\alpha\beta\cdots\mu}{}^{(n-1)}(\mathbf{r}_1\cdots\mathbf{r}_{n-1},\lambda). \quad (8)$$

The result of these considerations for the spin-pair correlation functions $p_{\alpha\beta}{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\lambda)$ is that one may write:

$$\begin{aligned} p_{++}{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\lambda)&=p_{--}{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\lambda)=1+\psi(\mathbf{r}_{12},\lambda),\\ p_{+-}{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\lambda)&=p_{-+}{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\lambda)=1-\psi(\mathbf{r}_{12},\lambda). \end{aligned} \quad (9)$$

Thus, a single function ψ of relative position suffices to describe the average distribution of spin pairs in the lattice, one member of which is partially coupled. The probabilistic definition of the spin-pair correlation functions demands that for $T>0$,

$$-1<\psi(\mathbf{r},\lambda)<+1. \quad (10)$$

III.

The major task of the statistical theory of field-free classical lattices thus amounts to determination of the single function ψ. It is the purpose of the following discussion to indicate the nature of a possible calculation procedure.

For this reason, we set μ_1 and μ_2 in Eq. (2) equal to $+1$, and compute the λ derivative of the result, when $n=2$. One finds, after some straightforward manipulation

$$\begin{aligned} \frac{\partial\psi(12,\lambda)}{\partial\lambda}=&-w(12)[1+\psi(12,\lambda)]\\ &-\frac{1}{2}\sum_{j=3}^{N} w(1j)[p_{+++}{}^{(3)}(12j,\lambda)-p_{++-}{}^{(3)}(12j,\lambda)]\\ &+[1+\psi(12,\lambda)]\sum_{j=2}^{N} w(1j)\psi(1j,\lambda), \end{aligned} \quad (11)$$

where $w(1j)=v(1j)/kT$. Notice that the first summation exempts both sites 1 and 2, but the second exempts only 1. As usual, we adhere to the simplifying convention of replacing $\mathbf{r}_1\cdots\mathbf{r}_N$ by $1\cdots N$ when they appear as arguments of v,w,ψ, etc. It is understood that differential Eq. (11) is ultimately to be solved subject to the boundary condition

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

reflecting the fact that a completely decoupled spin can in no way correlate with its neighbors.

The appearance of the spin-triplet functions $p^{(3)}$ in Eq. (11) is typical in derivation of pair-function relations for interacting systems. Obviously, it is necessary to have some information regarding their behavior before Eq. (11) may be considered useful for prediction of the basic quantity ψ. We therefore examine the entire set of normalization conditions (8) for spin-triplet correlation functions; written out in detail, they are:

$$\begin{aligned} p_{+++}{}^{(3)}(123,\lambda)+p_{-++}{}^{(3)}(123,\lambda)&=2p_{++}{}^{(2)}(23|\lambda)\\ p_{++-}{}^{(3)}(123,\lambda)+p_{-+-}{}^{(3)}(123,\lambda)&=2p_{+-}{}^{(2)}(23|\lambda)\\ p_{+-+}{}^{(3)}(123,\lambda)+p_{--+}{}^{(3)}(123,\lambda)&=2p_{-+}{}^{(2)}(23|\lambda)\\ p_{+--}{}^{(3)}(123,\lambda)+p_{---}{}^{(3)}(123,\lambda)&=2p_{--}{}^{(2)}(23|\lambda); \end{aligned} \quad (13)$$

$$\begin{aligned} p_{+++}{}^{(3)}(123,\lambda)+p_{+-+}{}^{(3)}(123,\lambda)&=2p_{++}{}^{(2)}(13,\lambda)\\ p_{++-}{}^{(3)}(123,\lambda)+p_{+--}{}^{(3)}(123,\lambda)&=2p_{+-}{}^{(2)}(13,\lambda)\\ p_{-++}{}^{(3)}(123,\lambda)+p_{--+}{}^{(3)}(123,\lambda)&=2p_{-+}{}^{(2)}(13,\lambda)\\ p_{-+-}{}^{(3)}(123,\lambda)+p_{---}{}^{(3)}(123,\lambda)&=2p_{--}{}^{(2)}(13,\lambda); \end{aligned} \quad (14)$$

$$\begin{aligned} p_{+++}{}^{(3)}(123,\lambda)+p_{++-}{}^{(3)}(123,\lambda)&=2p_{++}{}^{(2)}(12,\lambda)\\ p_{+-+}{}^{(3)}(123,\lambda)+p_{+--}{}^{(3)}(123,\lambda)&=2p_{+-}{}^{(2)}(12,\lambda)\\ p_{-++}{}^{(3)}(123,\lambda)+p_{-+-}{}^{(3)}(123,\lambda)&=2p_{-+}{}^{(2)}(12,\lambda)\\ p_{--+}{}^{(3)}(123,\lambda)+p_{---}{}^{(3)}(123,\lambda)&=2p_{--}{}^{(2)}(12,\lambda). \end{aligned} \quad (15)$$

For the sake of clarity, we have introduced a vertical slash in each $p_{\alpha\beta}^{(2)}(23|\lambda)$ to stress that this function is only indirectly dependent on λ, since neither μ_2 nor μ_3 are themselves partially coupled. This latter set of spin-pair correlation functions depends on both $\mathbf{r}_2$ and $\mathbf{r}_3$ (and not just the relative position $\mathbf{r}_{23}$) since the position of the partially coupled spin μ_1 can vary relative to both.

The twelve relations (13)–(15) obviously are not all independent; in particular, it has already been noted two such equations differing only by complete sign reversal of all subscripts are actually identical. Nevertheless, this set does include enough information to allow all $p^{(3)}$'s to be formally replaced by $p^{(2)}$'s. Thus, for example, if the third of Eq. (14) is used to eliminate $p_{-++}^{(3)}$ from the first of Eqs. (13), and then the last of Eqs. (15) utilized in elimination of $p_{--+}^{(3)}$ from the result, one finds:

$$p_{+++}^{(3)}(123,\lambda)=2p_{++}^{(2)}(23|\lambda)-2p_{-+}^{(2)}(13,\lambda)+2p_{--}^{(2)}(12,\lambda)-p_{---}^{(3)}(123,\lambda). \quad (16)$$

By virtue of subscript sign change invariance, the remaining triplet-correlation functions are identical. Making as well the substitutions

$$p_{--}^{(2)}(12,\lambda)=p_{++}^{(2)}(12,\lambda),$$
$$p_{-+}^{(2)}(13,\lambda)=2-p_{++}^{(2)}(13,\lambda),$$

one obtains

$$p_{+++}^{(3)}(123,\lambda)=p_{++}^{(2)}(12,\lambda)+p_{++}^{(2)}(13,\lambda)+p_{++}^{(2)}(23|\lambda)-2. \quad (17)$$

The relations (13)–(15) may now be used in turn to find similar expressions for the remaining $p^{(3)}$'s. For any $\alpha,\beta,\gamma=+,-$, the general result may simply be written

$$p_{\alpha\beta\gamma}^{(3)}(123,\lambda)=p_{\alpha\beta}^{(2)}(12,\lambda)+p_{\alpha\gamma}^{(2)}(13,\lambda)+p_{\beta\gamma}^{(2)}(23|\lambda)-2. \quad (18)$$

It should be emphasized that this reduction Eq. (18) depends in no way on the fact that site 1 is partially coupled, for a similar expression involving exclusively $p_{\alpha\beta}^{(2)}(ij|\lambda)$ functions would apply to three sites not including 1. It is also noteworthy that Eq. (18) is rigorously true for lattices of arbitrary dimensionality; it is also valid for any interaction $v(\mathbf{r})$, and thus is not restricted to Ising models. The fact that triplet-correlation functions may be eliminated in favor of pair functions is a result of symmetry inherent in the zero-field model under consideration. In the case of a non-vanishing external field, however, reduction (18) is no longer valid, and apparently has no obvious generalization.

Equation (18) may now be used to simplify Eq. (11):

$$\frac{\partial\psi(12,\lambda)}{\partial\lambda}=-w(12)+F(\lambda)\psi(12,\lambda)-\sum_{j=3}^{N}w(1j)\psi(j2|\lambda), \quad (19)$$

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

On account of the relation (9) of ψ to the density of spin pairs in the lattice, the auxiliary function $F(\lambda)$ may easily be identified as proportional to the mean energy of interaction at temperature T of a partially coupled spin to its surroundings. Equation (19) is consistent with the intuitively clear facts that $\psi(12,\lambda)$ must be an odd function of λ, and each $\psi(j2|\lambda)$ must be even.

On account of distinction between the functions $\psi(\mathbf{r}_{1j},\lambda)$ and $\psi(\mathbf{r}_i,\mathbf{r}_j|\lambda)$, Eq. (19) is certainly not sufficient to predict the distribution of spin pairs in the lattice. If both members of the pair ij are sufficiently far removed from the partially coupled site, though, they will be completely unaffected by the existence of this "weakened" site, and as a consequence, one has the identity

$$\psi(\mathbf{r}_i,\mathbf{r}_j|\lambda)=\psi(\mathbf{r}_{ij},\lambda=1), \quad (r_{1i}\text{ and }r_{1j}\text{ large}), \quad (20)$$

for all values of λ in the left member. As a crude theory of pair correlation, one could assume Eq. (20) were valid for *all* pairs ij not including site 1, and solve the corresponding approximate version of Eq. (19); we shall not however attempt such a program. The following section is devoted especially to examination of the λ dependence of $\psi(ij|\lambda)$, and we shall presume that even partial success in establishing this dependence will be useful in more fully understanding the statistical mechanics of lattices beyond what is possible with the crude approach.

We close this section by noting that functional Eq. (19) has a very simple solution for the one-dimensional Ising model. Here, it may be supposed that the linear array of sites are unit distance apart, and

$$w(x)=\begin{cases}-J/kT, & x=1;\\ 0, & x>1.\end{cases} \quad (21)$$

Equation (19) may adopt either of two forms, depending on whether or not sites 1 and 2 are nearest neighbors; if they are nearest neighbors, the sum on the right side of Eq. (19) has only one nonvanishing term, otherwise there are two. It may readily be shown by substitution that the ψ function for any two sites may be found just by multiplying together factors for each nearest-neighbor interval between the chosen pair of sites. One utilizes a factor $\tanh(J/kT)$ for each interval between two fully coupled sites, and a factor $\tanh(\lambda J/kT)$ for intervals one end point of which is a partially coupled site. Hence, for two sites an integer distance x apart, where one of these sites is the partially coupled one:

$$\psi(x,\lambda)=\tanh(\lambda J/kT)[\tanh(J/kT)]^{x-1}. \quad (22)$$

On the other hand, if the chosen sites for which spin-pair correlation is sought are fully coupled,

$$\psi(x|\lambda)=[\tanh(J/kT)]^{x}, \quad (23)$$

if the partially coupled site lies outside the segment

joining the pair, or

$$\psi(x|\lambda)=[\tanh(\lambda J/kT]^2[\tanh(J/kT]^{x-2}, \quad (24)$$

if it lies between the pair.

IV.

Attention now may be turned to the indirect effect of a nearby partially coupled site on the correlation between spins on a chosen pair of sites, both fully coupled. The neighboring partially coupled site will still be identified as that numbered 1, and the chosen sites in its vicinity for which we seek the pair correlation may for convenience be identified as 2 and 3. We have

$$p_{\beta\gamma}{}^{(2)}(23|\lambda)=4[Z(T,\lambda)]^{-1}\sum_{\mu_1,\mu_4\cdots\mu_N=\pm1}\times\exp[-V(\mu_1\cdots\mu_N,\lambda)/kT]. \quad (25)$$

One proceeds to compute the λ derivative of $\psi(23|\lambda)$ from Eq. (25) with $\beta,\gamma=+$ which, after some simplifications analogous to those yielding Eq. (19), may be put into the form:

$$\frac{\partial\psi(23|\lambda)}{\partial\lambda}=-[w(12)+w(13)]\times[\psi(12,\lambda)+\psi(13,\lambda)]+F(\lambda)[1+\psi(23|\lambda)]-\frac{1}{4}\sum_{j=4}^{N}\sum_{\mu_1,\mu_j=\pm1}\mu_1\mu_j w(1j)p_{1++j}{}^{(4)}(123j,\lambda). \quad (26)$$

The point of major significance insofar as the result Eq. (26) is concerned, is occurrence of spin-quadruplet correlation functions, unlike the maximum of triplet functions in Eq. (11).[10] One therefore again faces the necessity of formally replacing these higher-order correlation functions by suitable combinations of purely spin-pair quantities before rigorous solution for the statistical thermodynamics of the lattice may be accomplished.

The immediate temptation is to try elimination of $p^{(4)}$'s from the set of normalization conditions obtained from Eq. (8) with $n=4$, in view of success in the $n=3$ case. All such attempts fail, however, for unlike the possibility of obtaining an expression analogous to Eq. (16) with $p_{++++}{}^{(4)}$ in one member and $p_{----}{}^{(4)}$ (the same function, by subscript sign change symmetry) in the other member with opposite sign, it invariably happens that both have the *same* sign, and therefore cancel. The success for $n=3$ and failure for $n=4$ is a direct result of the former integer's oddness, and the latter's evenness. In fact, it is always possible in principle to express rigorously the field-free lattice $p^{(n)}$'s of any odd order in terms of lower-order functions, but no analogous simplification presents itself in any even order.

[10] Certain $p^{(3)}$'s appearing at intermediate steps in deduction of Eq. (26) were eliminated by means of Eqs. (18) and (9).

Nevertheless, the simple reduction Eq. (18) for $p^{(3)}$'s is rather suggestive of the qualitative form of $p^{(4)}$'s. Since Eq. (18) consists of a sum of the three possible pair correlation functions minus a constant, one naturally examines the four-spin analog (qualitatively correct in the absence of long-range order):

$$p_{\alpha\beta\gamma\delta}{}^{(4)}(1234,\lambda)=p_{\alpha\beta}{}^{(2)}(12,\lambda)+p_{\alpha\gamma}{}^{(2)}(13,\lambda)+p_{\alpha\delta}{}^{(2)}(14,\lambda)+p_{\beta\gamma}{}^{(2)}(23|\lambda)+p_{\beta\delta}{}^{(2)}(24|\lambda)+p_{\gamma\delta}{}^{(2)}(34|\lambda)-5, \quad (27)$$

where now six $p^{(2)}$'s must be included. Above T_c (below which long-range order sets in) each $p^{(n)}$ must approach unity as the positions of its arguments recede from one another to infinity; the subtractive constant 5 was selected in Eq. (27) in order that this equation be consistent with that fact. It may easily be checked that expression (27) exactly satisfies the normalization conditions (8).

In the next section, we consider (in detail for ferromagnetism) the $T<T_c$ situation, where it will be seen that Eq. (27) is no longer appropriate. It will therefore be understood for the remainder of this section that $T>T_c$, and we shall accordingly examine the effect of approximation (27) on fundamental Eq. (26). If the appropriate substitutions are made, Eq. (26) adopts the approximate form:

$$\partial\psi(23|\lambda)/\partial\lambda=-w(12)\psi(13,\lambda)-w(13)\psi(12,\lambda)+F(\lambda)\psi(23|\lambda). \quad (28)$$

This expression, together with Eq. (19), constitute a coupled pair of differential equations which are subject to boundary conditions (12) and (20). Their solution should provide an approximate account of spin-pair correlations above T_c.

It is convenient to define a new function:

$$\eta(12|\lambda)=\sum_{j=3}^{N}w(1j)\psi(2j|\lambda). \quad (29)$$

Then Eqs. (19) and (28) may be rewritten [when in the latter 3 is replaced by j, and j is summed as in Eq. (29)]:

$$\begin{aligned}\partial\psi(12,\lambda)/\partial\lambda&=-w(12)+F(\lambda)\psi(12,\lambda)-\eta(12|\lambda),\\ \partial\eta(12|\lambda)/\partial\lambda&=-F(\lambda)w(12)-\theta^2(12)\psi(12,\lambda)+F(\lambda)\eta(12|\lambda),\end{aligned} \quad (30)$$

where

$$\theta^2(12)=-2w^2(12)+\sum_{j=2}^{N}w^2(1j). \quad (31)$$

In Appendix A it is shown that the solution to Eqs. (30)

for $\psi(12,\lambda)$, subject to condition (12), is $(\theta(12)\geq 0)$.

$$\psi(12,\lambda)=2w(12)\exp\left[\int_0^\lambda F(\lambda')d\lambda'\right]\left\{\frac{\sinh[\theta(12)\lambda]}{\theta(12)}\right.$$
$$\left.-\int_0^\lambda d\lambda'\cosh[\theta(12)(\lambda-\lambda')]\exp\left[-\int_0^{\lambda'}F(\lambda'')d\lambda''\right]\right\}$$
$$+\sinh[\theta(12)\lambda]\exp\left[\int_0^\lambda F(\lambda')d\lambda'\right]f(12), \quad (32)$$

where $f(12)$ is a function only of the relative positions of spins 1 and 2, and not of λ. If the reduced interaction w has only a short range, then the function f alone holds the key to the way in which spin-pair correlations decay as the pair distance increases. f is determined by the requirement when $\lambda=1$ that solution (32) satisfy Eq. (20) for all $\mathbf{r}_i$ and $\mathbf{r}_j$ when this latter condition is transformed to one involving η by means of the operation (29); setting the resulting η expression equal to that obtained upon substituting Eq. (32) directly into the first of Eqs. (30) leads to a difference equation for $f(12)$:

$$-\theta(12)\cosh[\theta(12)]f(12)=h(12)$$
$$+\sinh[\theta(12)]\sum_{j=3}^{N}w(1j)f(j2), \quad (33)$$

where the "inhomogeneous" function h is defined

$$h(12)=-2w(12)\left\{\cosh[\theta(12)]-\theta(12)\right.$$
$$\times\int_0^1\sinh[\theta(12)(1-\lambda)]\exp\left[\int_0^\lambda F(\lambda')d\lambda'\right]d\lambda\Big\}$$
$$+2\sum_{j=3}^{N}w(1j)w(j2)\left\{-\frac{\sinh[\theta(12)]}{\theta(12)}\right.$$
$$\left.+\int_0^1\cosh[\theta(12)(1-\lambda)]\exp\left[\int_0^\lambda F(\lambda')d\lambda'\right]d\lambda\right\}. \quad (34)$$

For the Ising model, $h(12)$ vanishes identically for distances beyond the second nearest-neighbor separation.

By virtue of the dependence of the auxiliary function $F(\lambda)$ on the desired result for ψ, the detailed solution of Eq. (33), whose inhomogeneous part requires knowledge of F, involves a problem of self-consistency. Nevertheless, Eqs. (33) and (34), which represent the approximate theory of spin-pair correlations, are amenable to standard numerical techniques, and may thus form a convenient basis for investigation of certain complicated lattice systems.

Since we are interested for the moment in temperatures above T_c, so that $f(12)$ decays to zero with increasing r_{12}, h serves only as a "source" term in Eq. (33) which determines the *magnitude* of large-r_{12} correlations, but not their distance rate of decay. For this reason, one can circumvent the complication in determination of h, while obtaining an explicit expression giving the dependence of T_c for ferromagnetic systems upon the nature of the interaction v.

When examined just above T_c, lattices which exhibit low-temperature ferromagnetic order exhibit very large susceptibility, as well as critical opalescence to incident radiation. This indicates that the rate of decay of spin-pair correlations with increasing distance is very slow. At T_c one may therefore choose r_{12} in Eq. (33) sufficiently large that not only is $h(12)$ zero, but also that $f(j2)$ is sensibly constant over the short range of $w(1j)$. Thus, replacing the f's in Eq. (33) by a constant leads to the critical point condition:

$$-\theta(12)\cosh[\theta(12)]=\sinh[\theta(12)]\sum_{j=3}^{N}w(1j),$$

or, utilizing the definition of θ in Eq. (31), and realizing that r_{12} is sufficiently large that $w(12)$ is a vanishing quantity:

$$\left\{\sum_{j=2}^{N}w(1j)\Big/\left[\sum_{j=2}^{N}w^2(1j)\right]^{\frac{1}{2}}\right\}$$
$$\times\tanh\left[\sum_{j=2}^{N}w^2(1j)\right]^{\frac{1}{2}}=-1. \quad (35)$$

The sums of the reduced interaction and its square have been extended to include all relative positions in the lattice.

For reference, it may be recognized that Eq. (35) is especially simple for the Ising model, where w is $-J/kT$ for the z nearest neighbors of a given site, but 0 otherwise. One finds

$$z^{\frac{1}{2}}\tanh[z^{\frac{1}{2}}J/kT_c]=1,$$

or

$$kT_c/zJ=[z^{\frac{1}{2}}\operatorname{arctanh}(1/z^{\frac{1}{2}})]^{-1}. \quad (36)$$

As demonstrated by Table I, this critical temperature relation is not remarkable for its accuracy. It is more reliable than the Bragg-Williams (mean-field) estimate, but not as good as Guggenheim's quasi-chemical approach. In common with all approximate theories of the Ising model, it becomes more and more accurate as z increases.

The value of approximate result Eq. (35) lies not in its absolute accuracy, but rather in its ability to estimate relative changes in T_c brought about by variations in the range of the pair interaction. Thus, for example, if the original Ising potential is expanded to

TABLE I. Values of the reduced critical temperature kT_c/zJ in various lattices for the Ising model, computed on the basis of Eq. (36), and compared with the results of other methods [BW = Bragg-Williams (mean field approximation),[a] QC = quasi-chemical,[a] E = "exact").[b]

	BW	Eq. (36)	QC	E
linear ($z=2$)	1	0.802	0	0
square ($z=4$)	1	0.910	0.721	0.567
simple cubic ($z=6$)	1	0.942	0.822	0.75
body-centered cubic ($z=8$)	1	0.957	0.869	0.79
face-centered cubic ($z=12$)	1	0.972	0.914	0.81

[a] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), Chap. 12.
[b] See reference 14.

include a larger number z^* of neighbors than the original set of z, but where each of the z^* interacts with the central site with a strength J^* satisfying

$$zJ=z^*J^*,$$

so as to preserve "total interaction strength," Eq. (35) suffices to demonstrate that T_c always increases. More generally, if one considers a set of interaction functions $v(ij)$ all of which have identical values of the total strength

$$\sum_{j=2}^{N} v(1j), \tag{37}$$

then the higher the value of

$$\sum_{j=2}^{N} v^2(1j), \tag{38}$$

the lower the corresponding T_c. One concludes therefore that an interaction potential which is long ranged and slowly varying in space (not only in the radial direction, but for angular variations as well) is more effective in cooperatively producing long-range order than a locally stronger, but abruptly decaying potential of the same total interaction strength Eq. (37).

Appendix B points out conditions on $v(ij)$ under which the approximate formulation of this section leads one to conclude spin-pair correlations at large distances become isotropic as T_c is approached. For this class of v's, the principle directions of the lattice have no tendency to orient the large wavelength spin-density fluctuations which cause critical opalescence. Also, Appendix B indicates the manner in which T_c may be located for lattice systems whose low-temperature behavior is not ferromagnetic, as well as partially to establish what is the alternative type of long-range order in these lattices.

V.

The considerations of the preceding section were directed toward computation of pair distribution above T_c. We now turn attention to the case $T<T_c$, specifically for ferromagnetic ordering. Figure 1 shows schematically the phase diagram of a system which undergoes the requisite ferromagnetic transition. The abscissa represents the fraction of + spins in the lattice, which may be varied by application of a homogeneous external field.[11] The vertical dotted line bisecting the diagram, and passing through the critical point, is the locus of field-free points, on which we have assumed from the outset our lattice of spins lies. The phase diagram must of course be symmetric about this line.

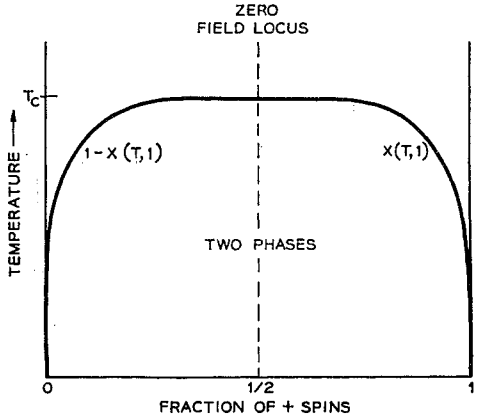

FIG. 1. Phase diagram for a ferromagnetic lattice; it is completely symmetrical about the composition corresponding to zero external field. The two branches of the boundary to the two-phase region are denoted by $x(T,1)$ and $1-x(T,1)$.

Below T_c, the lattice of spins will break up into domains predominately of one type of spin or the other. Since we shall continue to consider only the field-free situation, it is necessary to acknowledge that any given site in the lattice chosen at random may be found with equal probability in either of the two types of domains. On the other hand, if this site is examined only when it possesses a + spin, the chances are greater that the site is immersed at that moment in a predominately + domain. We shall denote by $x(T,\lambda)$ the probability that a + spin, coupled to extent λ, is found in a predominately + domain; likewise then, $x(T,\lambda)$ also equals the fraction of time a given partially coupled − spin spends in predominately − domains. One has

$$x(T,\lambda)\geq\tfrac{1}{2}, \tag{39}$$

where equality is attained for $\lambda=0$, or when $T=T_c$.

It should be realized that below T_c the domains are of macroscopic extent, comparable in dimension to the system itself. In fact, if as expected the interfacial free energy between opposite domains is positive, and if v is sufficiently short ranged, then in the overwhelming majority of cases the system will instantaneously consist of single domains occupying the whole lattice. If the size of the lattice system is allowed to become

[11] The total configurational energy, analogous to Eq. (3), then would be of the form (I represents the field):

$$V(\mu_1\cdots\mu_N,\lambda)=\lambda\mu_1\left[I+\sum_{j=2}^{N}v(1j)\mu_j\right]+I\sum_{j=2}^{N}\mu_j+\sum_{i<j=2}^{N}v(ij)\mu_i\mu_j.$$

infinite, the mean domain size becomes infinite as well, so that if one site of a given pair separated by a fixed distance is located, say, in a + rich domain, the other will be found in the same domain, except for a small probability which vanishes as system size becomes infinite.

We may now examine in the light of these observations the nature of (ferromagnetic) spin-distribution functions below T_c. It will be assumed that the infinite-system size limit has already been taken, so that the chance of a given set of positions spanning a domain boundary is negligible. Let the set of sites be as before denoted by $1\cdots n$. The *a priori* probability that these sites are instantaneously in + rich, or a − rich, domain is just $\frac{1}{2}$. By virtue of the differing compositions in the two types of domains, the nth order spin probability functions $P^{(n)}$ for regions characterized by these domain compositions will not be the same, and might, respectively, be denoted by[12]

$$P_{\alpha\beta\cdots\nu}{}^{(n,+)}(12\cdots n,\lambda) \quad \text{and} \quad P_{\alpha\beta\cdots\nu}{}^{(n,-)}(12\cdots n.\lambda);$$

once again the possibility of a partially coupled spin is indicated by appearance of λ as a variable. These functions will be the two distinct limits obtained for $P^{(n)}$ if one passes, at a fixed $T<T_c$, to zero external field from either positive or negative field values. The $P^{(n)}$ at zero field is just $P^{(n,+)}$ times the probability that sites $1\cdots n$ are in a predominately + domain, added to the analogous quantity for the predominately − domain:

$$P_{\alpha\beta\cdots\nu}{}^{(n)}(12\cdots n,\lambda)=\tfrac{1}{2}P_{\alpha\beta\cdots\nu}{}^{(n,+)}(12\cdots n,\lambda) +\tfrac{1}{2}P_{\alpha\beta\cdots\nu}{}^{(n,-)}(12\cdots n,\lambda). \quad (40)$$

When positions $1\cdots n$ are each significantly farther from one another than the interaction range (though still within the same domain, by our order of limit taking), $P_{\alpha\beta\cdots\nu}{}^{(n,+)}$ and $P_{\alpha\beta\cdots\nu}{}^{(n,-)}$ each reduce to a product of factors $x(T,\lambda)$ or $1-x(T,\lambda)$ depending on the subscripts $\alpha\beta\cdots\nu$, as a consequence of spins on the sites being uncorrelated beyond the effect of long-range order inherent in the domain. Thus, for example,

$$P_{+--+-}{}^{(5,+)}(12345,\lambda)\rightarrow x(T,\lambda)[1-x(T,1)] \times[1-x(T,1)]x(T,1)[1-x(T,1)],$$

and

$$P_{+--+-}{}^{(5,-)}(12345,\lambda)\rightarrow [1-x(T,\lambda)]x(T,1)x(T,1) \times[1-x(T,1)]x(T,1).$$

In particular, above T_c, the spin-pair correlation quantity $\psi(12,\lambda)$ was found to drop to zero as the distance r_{12} increased. Below T_c, on the other hand, Eq. (40) leads to the asymptote

$$\lim_{r_{12}\rightarrow\infty}\psi(12,\lambda)=[2x(T,\lambda)-1][2x(T,1)-1]. \quad (41)$$

Because of this result, we see that if one can compute the correlation between spin pairs in the absence of external fields at all temperatures, it will be possible to map out in detail the boundary of the two-phase region which, as Fig. 1 shows, lies off the zero-field locus.

The rigorous reduction Eq. (18) of triplet correlation functions must of course be consistent with these asymptotes. One may readily check that the asymptotic result for each $p^{(3)}$ obtained from Eq. (40) with $n=3$, and replacement of $P^{(n,+)}$ and $P^{(n,-)}$ with the appropriate product of x's and $(1-x)$'s, equals the expression obtained by use of Eq. (41) in the right member of Eq. (18).

In the case of spin quadruplets, though, the situation is not entirely trivial. Although above T_c the approximation Eq. (27) for $p^{(4)}$ is qualitatively correct, with a subtractive constant chosen equal to 5, this is no longer valid below T_c, since the right member of Eq. (27) fails to exhibit the correct asymptote. It is however true that Eq. (27) may be made formally exact for all $\alpha\beta\gamma\delta$ and all positions 1234, by adding to (or subtracting from) its right side a *single* function y:

$$p_{\alpha\beta\gamma\delta}{}^{(4)}(1234,\lambda)=p_{\alpha\beta}{}^{(2)}(12,\lambda)+p_{\alpha\gamma}{}^{(2)}(13,\lambda) +p_{\alpha\delta}{}^{(2)}(14,\lambda)+p_{\beta\gamma}{}^{(2)}(23|\lambda) +p_{\beta\delta}{}^{(2)}(24|\lambda)+p_{\gamma\delta}{}^{(2)}(34|\lambda) -5\pm y(1234,\lambda); \quad (42)$$

the sign of y is positive or negative depending on whether there are an even or an odd number of +'s in the set $\alpha\beta\gamma\delta$.[13] Above T_c, y vanishes as the positions 1234 are far removed from one another, but below T_c one finds in this limit:

$$y(1234,\lambda)\rightarrow 1+4x(\lambda)-12x(1) +24[x(1)]^2-24x(\lambda)[x(1)]^2 -8[x(1)]^3+16x(\lambda)[x(1)]^3, \quad (43)$$

(for simplicity the temperature argument of x has been suppressed).

If the complete expression (42), rather than Eq. (27), it utilized for $p^{(4)}$'s in fundamental Eq. (26), the formally exact version of approximate Eq. (28) is

$$\frac{\partial\psi(23|\lambda)}{\partial\lambda}=-w(12)\psi(13,\lambda)-w(13)\psi(12,\lambda) +F(\lambda)\psi(23|\lambda)-\sum_{j=4}^{N}w(1j)y(123j,\lambda). \quad (44)$$

[12] Originally, as in Eq. (4), the $P^{(n)}$'s were written with the relevant μ's as arguments. Now, however, for the sake of notational clarity and conceptual completeness, we utilize the $p_{\alpha\cdots\nu}{}^{(n)}(\mathbf{r}_1\cdots\mathbf{r}_n,\lambda)$ scheme, Eq. (5), indicating by subscript the spin signs, and using site positions as arguments. No confusion should be created.

[13] The fact that only a single defect function y serves to remove the error of the simple closure relation (27) stems from the necessity of satisfying all $p^{(4)}$ normalization conditions (8); in these conditions the defects must always cancel exactly between pairs of $p^{(4)}$'s (one having an even and the other an odd number of + subscripts) to leave just a $p^{(3)}$ of form (18).

The approximate spin-pair correlation theory outlined in the previous section for $T>T_c$ amounts to replacement of $y(1234,\lambda)$ for all positions 1234 by its vanishing asymptote. If, analogously, expression (43) is used everywhere in place of y in Eq. (44), it is possible to predict an approximate boundary for the two-phase region. Once again, T_c (the temperature at the "top" of this region) will be implicitly given by solution to Eq. (35). Unfortunately, it does not seem possible to obtain $x(T,\lambda)$ without solving for the entire position dependence of $\psi(12,\lambda)$ [in spite of result Eq. (41), which would lead one to try to determine only the large-distance asymptote] since the occurrence of $F(\lambda)$ in both Eq. (19) and (44) necessitates finding values of ψ for small separations. Nevertheless, we have been able to display the pair of functional Eqs. (19) and (44) [the latter using approximation (43)] which are capable of reproducing at all temperatures the qualitative character of spin-pair correlations, as well as an approximation to the complete statistical thermodynamics of zero-field classical lattice theories with arbitrary ferromagnetic pair interaction.

VI.

In the notation of Sec. V, the fact which prevents exact deduction of pair correlation functions is lack of complete knowledge about $y(1234,\lambda)$. We now present an interpolation scheme for y from which an approximation to this function may be deduced above T_c. If this approximation is used in Eq. (44), it should permit more accurate calculation of ψ than is possible by the less exacting approach of Sec. IV.

Consider the quotient (for $T>T_c$):

$$Q(1234,\lambda)=\frac{p_{++++}{}^{(4)}(1234,\lambda)p_{++--}{}^{(4)}(1234,\lambda)p_{+-+-}{}^{(4)}(1234,\lambda)p_{+--+}{}^{(4)}(1234,\lambda)}{p_{-+++}{}^{(4)}(1234,\lambda)p_{+-++}{}^{(4)}(1234,\lambda)p_{++-+}{}^{(4)}(1234,\lambda)p_{+++-}{}^{(4)}(1234,\lambda)}. \tag{45}$$

The numerator contains $p^{(4)}$'s each with an even number of + subscripts; the denominator contains only those with an odd number.

Note that Q reduces to unity:

(a) if $\lambda=0$, for in this limit, Eq. (7) shows

$$p_{\alpha,\beta\cdots\nu}{}^{(n)}(12\cdots n,\lambda=0)=p_{-\alpha,\beta\cdots\nu}{}^{(n)}(12\cdots n,\lambda=0)$$
$$=p_{\alpha,-\beta\cdots-\nu}{}^{(n)}(12\cdots n,\lambda=0),$$

and complete cancellation occurs between the factors in numerator and denominator of Eq. (45);

(b) if any one of the sites 1234 is very much farther from the other three than the range of $v(\mathbf{r})$, because a reduction of numerator and denominator to a product of $p^{(3)}$'s occurs, and complete cancellation takes place again; and also for an analogous reason if 1234 constitute two widely separated pairs;

(c) at high temperature, where each $p_{\alpha\beta\gamma\delta}{}^{(4)}$ reduces to a product of Boltzmann factors

$$\exp[-v(ij)\mu_i\mu_j/kT],$$

or

$$\exp[-v(1j)\lambda\mu_1\mu_j/kT],$$

for each of the six pairs in the set 1234;

(d) if the system is a linear array with only nearest-neighbor interactions (the one-dimensional Ising model), because then the $p^{(4)}$'s are precisely equal to the product of three $p^{(2)}$'s corresponding to the sequence of pairs along the line, and once again identical factors cancel.

Below T_c, the quantity Q definitely deviates significantly from unity. In fact, the $p^{(4)}$ asymptotes that follow from Eqs. (41)–(43) show that at these lower temperatures, even if all four sites are far removed from one another, Q is a rather complicated combination of x's. For this expanded configuration, however, Q smoothly reduces to unity as T approaches T_c from below, consistent with (b).

In view of exact conditions (a)–(d) on Q, it appears convenient to set Q equal to unity for all configurations of 1234, all λ, and all temperatures greater than T_c, and to regard the resulting expression as an interpolation formula which implicitly determines the unknown quantity $y(1234,\lambda)$. It also appears that the resulting procedure, which may prove to be a valuable closure relation in detailed numerical solution of the spin-pair correlation equations, is the simplest one that may be formulated to draw simultaneously on all four exact relations (a)–(d).

It must of course be acknowledged that Eq. (45), with Q set equal to 1, may not have a unique solution; it leads generally to a cubic equation in y whose coefficients involve sums of products of ψ's. But in connection with (b), for example, one knows that the proper root becomes zero as any one of the four sites recedes from the other three. Inversely, it might be supposed that the appropriate root for a given close grouping of four sites is the one which steadily increases from zero as one of these sites is brought up from infinity to the required position.

It may readily be established that the $Q=1$ relation implies that the rate of decay of y to zero as one of 1, 2, 3, or 4 recedes to infinity is of the same order as the rate of decay of ψ evaluated for any of the increasing pair distances. For this reason, inclusion of such a function y in the ψ equations causes a shift in the predicted temperature T_c at which the exponential rate of decay of ψ to zero with increasing distance vanishes. For the cases in which exact temperatures T_c are available from other analyses (specifically the one- and two-dimensional Ising models), approximate relation (35) does not yield the correct T_c. By implication, then,

the exact y must have the same sort of asymptotic decay rate property as implied by Eq. (45) with $Q=1$.

Another indication of the comparable decay rates of y and ψ is mentioned in Appendix B, based upon the predicted critical spin-pair correlations. In addition, the "reduced" value of T_c, at least for Ising models, depends only on z according to Eq. (36), in spite of the fact that pairs of lattices with the same z (two-dimensional triangular and the simple cubic with $z=6$, or the hexagonal close-packed and the face-centered cubic with $z=12$) exhibit different T_c's.[14] The $Q=1$ closure relation will begin to distinguish between members of these pairs.

Observation (d) above indicates that this more elaborate closure relation yields an exact one-dimensional Ising theory, so T_c predicted by Eq. (36) is lowered from the finite value exhibited in Table I to its proper value 0. The information available from other analyses for T_c in higher-dimensional lattices, at least with nearest-neighbor interactions, demonstrates that the estimated T_c found from Eq. (36) is always high. The interpretation that may be assigned to the apparent existence of long-range order at temperatures that are too high, is that approximation (27) for $p^{(4)}$'s tends to correlate spin quadruplets too strongly. The effect of y, if properly taken into account, is therefore to reduce such correlation. In view of exactness in reducing such correlation for the one-dimensional Ising model, it would seem not unreasonable to guess that the corrected T_c's computed on the basis of Eq. (45) are always nearer to their true values than when the rougher closure relation (27) is used.

Application of the $Q=1$ closure relation does not appear exceptionally easy in practice. Specifically, we have not yet been able to deduce an explicit relation for the resulting T_c in terms of the interaction potential v, analogous to the simple expression (35).

It seems desirable, then, as a future investigation, either to seek partial justification of the $Q=1$ assumption by a Monte Carlo calculation, or to replace it by a suitable alternative. In the former case, it would probably be wise to examine the two-dimensional Ising model, with $\lambda=1$, for a configuration having sites 1, 2, 3, and 4 all close to one another, since just above T_c this should provide the most severe test of the proposed closure relation.

APPENDIX A

Simultaneous Eqs. (30) may immediately be simplified by introduction of a suitable integrating factor; let

$$(\bar{\psi},\bar{\eta})=(\psi,\eta)\exp\left[-\int_0^\lambda F(\lambda')d\lambda'\right]. \quad \text{(A1)}$$

The pair Eq. (30) is equivalent to

$$\frac{\partial\bar{\psi}(12,\lambda)}{\partial\lambda}=-w(12)\exp\left[-\int_0^\lambda F(\lambda')d\lambda'\right]-\bar{\eta}(12|\lambda), \quad \text{(A2)}$$

$$\frac{\partial\bar{\eta}(12|\lambda)}{\partial\lambda}=-w(12)F(\lambda)\exp\left[-\int_0^\lambda F(\lambda')d\lambda'\right]-\theta^2(12)\bar{\psi}(12,\lambda). \quad \text{(A3)}$$

Differentiate Eq. (A2) once with respect to λ, then insert Eq. (A3) to obtain:

$$\partial^2\bar{\psi}(12,\lambda)/\partial\lambda^2-\theta^2(12)\bar{\psi}(12,\lambda)=W(12,\lambda), \quad \text{(A4)}$$

where

$$W(12,\lambda)=2w(12)F(\lambda)\exp\left[-\int_0^\lambda F(\lambda')d\lambda'\right].$$

The independent solutions to the homogeneous equation corresponding to Eq. (A4) may be taken as ($\theta(12)\geq 0$):

$$\sinh[\theta(12)\lambda], \quad \cosh[\theta(12)\lambda]. \quad \text{(A5)}$$

By means of these functions, it is possible to construct the general solution to inhomogeneous Eq. (A4) by standard techniques[15]:

$$\bar{\psi}(12,\lambda)=\sinh[\theta(12)\lambda]\left\{f(12)+\frac{1}{\theta(12)}\times\int_0^\lambda d\lambda'\cosh[\theta(12)\lambda']W(12,\lambda')\right\}+\cosh[\theta(12)\lambda]\left\{g(12)-\frac{1}{\theta(12)}\times\int_0^\lambda d\lambda'\sinh[\theta(12,\lambda')]W(12,\lambda')\right\}, \quad \text{(A6)}$$

f and g are arbitrary functions of relative configuration $\mathbf{r}_{12}$, but are independent of λ.

Since ψ, and hence $\bar{\psi}$, must vanish when $\lambda=0$, we may immediately set $g=0$ for all $\mathbf{r}_{12}$. If the full expression for W is inserted into the correspondingly shortened $\bar{\psi}$ expression the final form for ψ is easily verified to be

$$\psi(12,\lambda)=\exp\left[\int_0^\lambda F(\lambda')d\lambda'\right]\left\{\sinh[\theta(12)\lambda]f(12)+\frac{2w(12)}{\theta(12)}\int_0^\lambda d\lambda'\sinh[\theta(12)(\lambda-\lambda')]F(\lambda')\times\exp\left[-\int_0^{\lambda'}F(\lambda'')d\lambda''\right]\right\}. \quad \text{(A7)}$$

The function f, as yet arbitrary, is determined by Eq. (33). Equation (32) differs from Eq. (A7) only by a partial integration.

[14] Reference 6, p. 287.

[15] Reference 4, p. 346.

APPENDIX B

For relative pair distances r_{12} greater than the range of interaction $v(\mathbf{r})$, $\theta(12)$ is constant (we denote this limit simply by θ), and result Eq. (32) for $\psi(12,\lambda)$ shows that at these separations, it is essentially the behavior of $f(12)$ that determines the rate of decay, or the persistence, of spin-pair correlations in the lattice. Equation (33), which determines f, may be slightly modified to read

$$\mathbf{O}\cdot f(\mathbf{r}_{12})=l(\mathbf{r}_{12}), \tag{B1}$$

where the linear difference operator $\mathbf{O}$ is defined

$$\mathbf{O}\cdot f(\mathbf{r}_{12})=-\frac{\sinh\theta}{kT}\sum_{r_{13}>0} v(\mathbf{r}_{13})f(\mathbf{r}_{32})-\theta\cosh\theta f(\mathbf{r}_{12}), \tag{B2}$$

and the inhomogeneous "source" function l differs from h in Eq. (33) only to the extent that the $\mathbf{r}_{12}$-independent limit θ appears in Eq. (B2), as well as a sum over *all* lattice sites exclusive of the origin, $\mathbf{r}_{13}=0$, whereas in Eq. (33), two sites were exempted from summation. Both l and h vanish identically beyond twice the range of v.

The desired solution f may formally be written

$$f(\mathbf{r}_{12})=\sum_{r_3} l(\mathbf{r}_{13})G(\mathbf{r}_{23}), \tag{B3}$$

where G is the Green's function for the operation $\mathbf{O}$. G satisfies the relations

$$\begin{aligned}&\mathbf{O}\cdot G(\mathbf{r})=\delta(\mathbf{r}),\\ &\lim_{|\mathbf{r}|\to\infty} G(\mathbf{r})=0 \quad (T>T_c);\end{aligned} \tag{B4}$$

$\delta(\mathbf{r})$ is the Kronecker delta function for the lattice, vanishing everywhere but at the origin, where its value is unity.

If the lattice consists of a total of N sites subject to periodic boundary conditions, the normalized eigenfunctions of $\mathbf{O}$ are just plane waves:

$$\begin{aligned}&\mathbf{O}\cdot\varphi_\lambda(\mathbf{r})=\lambda\varphi_\lambda(\mathbf{r}),\\ &\varphi_\lambda(\mathbf{r})=N^{-\frac{1}{2}}\exp(i\mathbf{k}\cdot\mathbf{r}),\\ &\lambda=\lambda(\mathbf{k}),\end{aligned} \tag{B5}$$

in which the vectors $\mathbf{k}$ are chosen to satisfy the requisite boundary periodicity.

It is well known[16] that G may be formally expressed as a bilinear sum involving the entire set of φ_λ's:

$$G(\mathbf{r}_2-\mathbf{r}_1)=\sum_{\mathbf{k}} \varphi_\lambda^*(\mathbf{r}_2)\varphi_\lambda(\mathbf{r}_1)/\lambda(\mathbf{k}). \tag{B6}$$

If the plane wave expression (B5) for φ_λ is operated on by the specific operator form Eq. (B2), $\lambda(\mathbf{k})$ is found explicitly to be

$$\lambda(\mathbf{k})=-\frac{\sinh\theta}{kT}\sum_{\mathbf{r}'>0} v(\mathbf{r}')\cos(\mathbf{k}\cdot\mathbf{r}')-\theta\cosh\theta. \tag{B7}$$

In this result, we have used reflection symmetry of $v(\mathbf{r}')$ to convert complex exponentials to cosines.

For a lattice of macroscopic extent, the $\mathbf{k}$ vectors form a very dense set confined to the first Brillouin zone τ.[17] For this reason it is permissible to convert the $\mathbf{k}$ summation in Eq. (B6) to an integral. Inserting Eq. (B7), one finds:

$$G(\mathbf{r})=\frac{1}{\tau}\int_\tau d\mathbf{k}\Bigg[\exp(i\mathbf{k}\cdot\mathbf{r})\Big/\left(-\frac{\sinh\theta}{kT}\sum_{\mathbf{r}'>0} v(\mathbf{r}')\cos(\mathbf{k}\cdot\mathbf{r}')-\theta\cosh\theta\right)\Bigg] \tag{B8}$$

When the temperature T is very high, the integrand's denominator in Eq. (B8) varies fractionally very little from the value θ over the entire zone τ. Under this condition, techniques exist[18] for demonstrating that $G(\mathbf{r})$ decays to zero with increasing $|\mathbf{r}|$ no less rapidly than exponentially. The corresponding large-$|\mathbf{r}_{12}|$ form of f, given by Eq. (B3), will generally exhibit non-negligible angular variation for different directions of $\mathbf{r}_{12}$ relative to the fundamental lattice directions.

As T is lowered, the first term in the denominator of Eq. (B8) provides variation over τ which becomes more and more pronounced. In the case of ordinary ferromagnetic coupling, the quantity

$$-\sum_{\mathbf{r}'>0} v(\mathbf{r}')\cos(\mathbf{k}\cdot\mathbf{r}') \tag{B9}$$

has a maximum value within τ which is greater than zero, and which occurs at the origin of $\mathbf{k}$ space. The ferromagnetic Curie point, T_c, is that temperature at which the denominator of Eq. (B8) first displays a zero (it of course occurs at $\mathbf{k}=0$), and therefore it is the temperature at which the integrand becomes singular. This T_c is precisely given by Eq. (35).

For nearest-neighbor interactions (Ising model) the Green's function $G(\mathbf{r})$ is well-known quantity.[19,20] Even for a more general ferromagnetic v, though, it is possible to examine the large-r decay property of $G(\mathbf{r})$ at T_c using slight generalization of a technique that has been used for the nearest neighbor case.[21] We quote only the result (valid at T_c and asymptotically for large $|\mathbf{r}|$, and assuming for concreteness that the lattice is three

[16] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 884.

[17] For the simple cubic lattice it will be recalled that τ is: $-\pi\leq k_x,k_y,k_z\leq+\pi$.

[18] E. W. Montroll and R. B. Potts, Phys. Rev. **102**, 72 (1956).

[19] E. W. Montroll, *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University of California Press, Berkeley, California, 1956), p. 237.

[20] E. W. Montroll, J. Soc. Indust. Appl. Math. 4, 241 (1956).

[21] Reference 19, Appendix III.

dimensional):

$$G(\mathbf{r})\sim\frac{4\pi^2kT_c}{\tau\sin\theta_c\left[\left(-\sum_{\mathbf{r}'>0}(x')^2v(\mathbf{r}')\right)\left(-\sum_{\mathbf{r}'>0}(y')^2v(\mathbf{r}')\right)\left(-\sum_{\mathbf{r}'>0}(z')^2v(\mathbf{r}')\right)\right]^{\frac{1}{2}}}|\mathbf{t}|^{-1}, \tag{B10}$$

in which $\theta_c=\theta(T_c)$, and $\mathbf{t}$ is related to $\mathbf{r}$ by a suitable scaling of each of the latter's components:

$$\mathbf{r}=x\mathbf{u}_x+y\mathbf{u}_y+z\mathbf{u}_z,$$

$$\mathbf{t}=\left[-\sum_{\mathbf{r}'>0}(x')^2v(\mathbf{r}')\right]^{-\frac{1}{2}}x\mathbf{u}_x+\left[-\sum_{\mathbf{r}'>0}(y')^2v(\mathbf{r}')\right]^{-\frac{1}{2}}y\mathbf{u}_y+\left[-\sum_{\mathbf{r}'>0}(z')^2v(\mathbf{r}')\right]^{-\frac{1}{2}}z\mathbf{u}_z; \tag{B11}$$

the $\mathbf{u}$'s are unit vectors along arbitrarily chosen Cartesian axes. If the interaction $v(\mathbf{r})$ is isotropic to the extent that each of its second moments appearing as scaling factors in $\mathbf{t}$ are identical, then $G(\mathbf{r})$ is asymptotically proportional just to inverse distance $|\mathbf{r}|^{-1}$, and so is isotropic itself in this limit. If $v(\mathbf{r})$ has finite range, so that the inhomogeneous function l in Eq. (B3) has also finite range, one may conclude from Eq. (B3) that the spin-pair correlations at T_c (but not at higher temperatures) are asymptotically isotropic. If the second moments are not identical, the asymptotic nature of G at T_c, and of the spin-pair correlations, will be given by Eq. (B10), and the angular dependence of $\mathbf{t}$, from Eq. (B11).

Although our conclusions about development of asymptotically isotropic correlations (for certain v's) as T decreases to T_c are probably true, in spite of the approximate analysis used to establish them, there are strong indications that the simple inverse distance asymptote is not quite correct, but that decay should follow a larger inverse power of $|\mathbf{r}|$.[22] To render the critical point theory correct requires a function $y(1234,\lambda)$ with the rate of decay (as one of the four sites recedes) comparable to the pair correlations themselves, as mentioned in Sec. VI. We are unable to answer as yet the delicate question of whether closure relation Eq. (45) can at T_c lead to a greater inverse power of distance for spin-pair correlations.

For the case of antiferromagnetic coupling, which tends to force nearest neighbors to be unlike pairs, the integrand of Eq. (B8) develops simultaneous singularities at the *vertices* of τ, rather than at its center. $G(\mathbf{r})$ and the spin-pair correlations are found to vary in sign from site to site, consistent with long-range antiferromagnetic ordering below the characteristic Néel temperature.

Finally, brief mention should be made of the possible appearance of singularities in the integrand of Eq. (B8), as T decreases, at points neither at the center nor boundary of τ. By virtue of the arbitrary nature of v, it seems easily possible to ensure such behavior, since it is necessary only to select a form of the discrete Fourier transform (B9) with maxima at these intermediate points, then invert the transform to yield the corresponding suitable v. The long-range order of the low-temperature phase produced by such an interaction, if the maxima of Eq. (B9) were fairly close to $\mathbf{k}=0$, would have predominantly similar spins on nearest-neighbor sites, but at large distances, opposite spin pairs would be most probable. The over-all appearance of such a phase would be that of a "crystal" of alternating regions of + and − spins, the period of which is not necessarily commensurate with that of the lattice sites.

[22] F. H. Stillinger and H. L. Frisch, Physica **27**, 751 (1961).