Statistical Mechanical Theory of a Random Ferromagnetic System

R. BROUT
Department of Physics, Cornell University, Ithaca, New York, and Bell Telephone Laboratories, Murray Hill, New Jersey
(Received March 11, 1959)

The behavior of solid solutions of paramagnetic impurities which are exchange coupled in a nonmagnetic substrate turns out to yield a considerable body of information with regard to the nature of the exchange coupling as well as detailed temperature dependence of the spin system. In the present paper, a rigorous expansion of the mean free energy averaged over random sites is presented. It is shown that a ferromagnetic phase transition does occur. The Curie point is given as a function of concentration for the case of weak dilution in an implicit power series form.

Many interesting qualitative features arise in the study of these systems. If the curve of magnetic moment *vs* temperature has inflections this indicates short-range exchange forces, whereas smooth curves indicate long-range forces. Similarly, long-range forces give rise to smooth behavior of the Curie point as a function of concentration for dilute samples. Alternatively, short-range forces give rather violent changes in Curie point near atomic fractions$\approx$(number of nearest neighbors)$^{-1}$. The method of series development used in this paper gives rise to this expected qualitative behavior and also enables one to make quantitative prediction if the exchange potential is known.

Consideration is also given to the antiferromagnetic analog together with a discussion of expected behavior of such systems in a resonance experiment.

I. INTRODUCTION

IN view of recent experimental investigation[1] on ferromagnetic systems in which the ions are dispersed at random in a nonmagnetic matrix, the theoretical analysis of such systems is in order. Somewhat surprisingly, these ferromagnetic systems are more amenable to statistical mechanical analysis than the usual regular ferromagnetic array. Owing to the random distribution it is possible to express the free energy as a power series in the density (or atomic fraction) of the paramagnetic constituent. In analogy to the cluster expansion in the theory of real gases,[2] the coefficients of various powers of the density involve interactions among clusters of a finite number of particles. Only the first few terms of the series can be explicitly evaluated so that the present theory has utility in the limit of weak dilution. This region, conveniently accessible to experimental investigation, presents interesting effects which would not be observed in the regular ferromagnet.

Section II is devoted to a qualitative discussion of the dilute random ferromagnet. It will become apparent that rather anomalous temperature dependence of the saturation magnetization may be expected under certain conditions. This behavior may turn out to be useful in determining the range of exchange forces. For example the very existence of a ferromagnetic transition of Gd dissolved in La[1] at atomic concentrations of a few percent and at temperatures of the order of 1°K is sufficient to conclude that the exchange interaction is long range in character.

Section III develops the necessary mathematical apparatus to handle the problem. The spin sums are carried out by the method of semi-invariants developed by Kirkwood[3] in the order-disorder problem. It turns out that partial summation of the semi-invariant series is possible. What this achieves is a rearrangement of a series in powers of V/kT to a power series in the density. Because of the analogy with the cluster series of Mayer,[2] we shall develop for spin-independent forces the familiar virial expansion by the semi-invariant technique. This exercise, interesting in itself as a rather expeditious way to get to the virial expansion, serves to familiarize the reader with the technique used in the present work. It is then shown that the cluster expansion is sometimes valid even when the forces are the spin-dependent exchange forces. This fact is nontrivial and is true in the Ising model and the quantum theory for particles of spin $\frac{1}{2}$. It does not seem to be true for spin$>\frac{1}{2}$, but this point is not yet established.

Up to this point what is achieved is the formal evaluation of the partition function with spin-dependent forces. This includes both spin sums and spatial integrations. We call this partition function $\langle Z\rangle_{s,c}$ where s designates spin average and c means spatial or configuration average. Correspondingly $\log\langle Z\rangle_{s,c}$ is the free energy of the system. (We use "log" to denote natural logarithm throughout.) This is *not* the measured free energy in the experiments envisioned in this paper. The argument above shows clearly that what has been calculated is the free energy of a gas of paramagnetic particles with exchange forces among them. We are, however, interested not in the free energy of such a system, but rather the free energy of a given system of ions frozen into their positions, i.e., in a specified nonequilibrium situation. Any correlation between spin and spatial configuration is absent in this model whereas in the gas this is obviously not the case. Since we are interested in a random sample, it is clear that it is desired first to calculate the spin sum in the partition function (since the spin system is assumed to be in thermal equilibrium) and then to average the logarithm of this quantity over all spatial configurations. In short, we must calculate $\langle\log\langle Z\rangle_s\rangle_c$, i.e., the mean free energy.

The above point is sufficiently delicate and important

[1] Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 92 (1958).
[2] J. Mayer and M. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 13.
[3] J. G. Kirkwood, J. Chem. Phys. **6**, 70 (1938).

to warrant further argument. Consider a very large sample divided up into a statistically large number of subunits each of which itself contains a statistically large number of atoms. Because of the latter condition, we neglect the surface interactions among the subunits, the usual device in deriving the canonical and grand canonical ensembles from the microcanonical ensemble. Now, in the gas case, all configurations are possible in each of the subunits and hence the free energy per particle of each is the same (the conventional condition of thermodynamic equilibrium). In the case of the random frozen sample, neglect of surface interactions implies that the total partition function factors into products over the subunits and hence

$$\log\langle Z\rangle_s = \sum_{\text{subunits}} \log\langle Z_i\rangle_s.$$

Dividing by the number of subunits, it is seen that the quantity to be calculated is the free energy averaged over random spatial distributions. It will become evident from our calculations that the difference between $\langle\log\langle Z\rangle_s\rangle_c$ and $\log\langle Z\rangle_{s,c}$ is an essential one. Fluctuations are important and lead to qualitative differences between the two systems.

Having established this point, we then show that the whole analysis leading to $\log\langle Z\rangle_{s,c}$ can be taken over for $\langle\log\langle Z\rangle_s\rangle_c$ but with different cluster integrals. We then show how to calculate magnetization curves and the Curie temperature in the limit of extreme dilution.

In Sec. VI we briefly indicate the results for the random antiferromagnet and discuss the possible results of a resonance experiment on such a system.

II. QUALITATIVE DISCUSSION

We take a system of ferromagnetically exchange-coupled ions distributed at random in a nonmagnetic host lattice. Consider first an exchange interaction which is of extremely short range so that only nearest neighbor interaction is important—all interactions with other than nearest neighbors will for the moment be set equal to zero. Let Z_1 be the number of nearest neighbors and x the atomic fraction of paramagnetic ions. It is clear that for $x \lesssim 1/Z_1$, the state of ferromagnetic long-range order is impossible. This is so because it is impossible to link all neighbors into macroscopically long chains in the random situation. For x slightly greater than $1/Z_1$ there is a finite probability of forming such sequences thereby making ferromagnetism possible. It is evident, however, that not all the ions can be linked together. Hence, the saturation magnetization near $T=0$ for this ferromagnet is necessarily less than the full spin moment. In fact, it can be shown that the ratio of magnetic moment at $T=0$ to its maximum value (this ratio we call R_0) for $x=(1/Z_1)+\epsilon$ is such that $R_0 \sim \sqrt{\epsilon}$ when $\epsilon \ll 1$. This situation is schematically given by the dotted line graph (Fig. 1) of magnetic moment *vs* temperature. The magnetic moment is always expressed in units of the full saturated moment. This is also called the long-range order and we designate it with the symbol R, $0 \leq R \leq 1$.

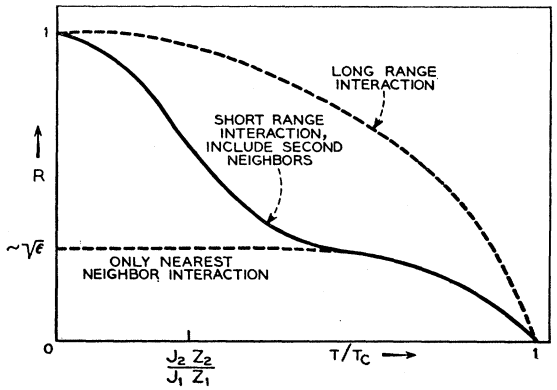

FIG. 1. Expected behavior of long-range order R *vs* T for $x=(1+\epsilon)/Z_1$.

We now consider the effect of second and higher order neighbor interactions. Strictly speaking, an interaction potential never has an absolute cutoff so that at the exact absolute zero of temperature all ions will be effectively coupled to give $R_0=1$. Thus there must be some temperature where the levelled off "nearest neighbor" curve of Fig. 1 bends up to the point $R_0=1$. This will be the temperature where second neighbor interactions are important. To estimate this temperature, let J_1 and J_2 be the first and second neighbor interaction strengths and let Z_2 be the effective number of second neighbors (we schematize here and group a number of coordination shells in what we classify as "second neighbors" calling J_2 a mean interaction energy for the group). Then the temperature at which bending up starts to take place may be estimated as $T \sim (J_2Z_2/J_1Z_1)T_c$. This is sketched schematically in Fig. 1.

The above paragraph was predicated on the assumption of short-range exchange forces which is the type currently supposed to be present in transition metals. On the other hand, if the interaction is of long range, the expected behavior would be the customary M *vs* T curve without inflection points. This is the dashed line graph in Fig. 1.

From the above discussion, it is seen that experimental knowledge of M *vs* T in dilute random ferromagnets yields interesting information about the range of exchange interactions. A curve without inflection indicates long-range forces; a curve with inflection indicates short-range forces where the inflection temperature gives the relative strengths of near and distant neighbors.

Further, a smooth curve of T_c *vs* x down to very small x indicates long-range forces, whereas for short-range forces one expects irregular behavior since for $x<1/Z_1$ it is the weak distant-neighbor interaction

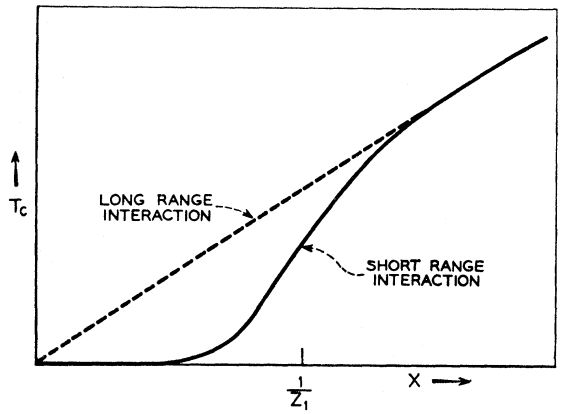

FIG. 2. Expected plot of Curie point T_c *vs* atomic fraction x.

that causes ferromagnetism. This is sketched schematically in Fig. 2. Of course at sufficiently small concentration, ferromagnetism will cease even for long-range forces. If Z_{eff} is the number of sites falling within the range of the potential, then for $x<1/Z_{\text{eff}}$ ferromagnetism will cease.

For this reason the experimental findings of Matthias *et al.*[1] on smooth behavior of T_c *vs* x_{Gd} for Gd in La down to $x_{\text{Gd}}\sim 1\%$ indicates a long-range exchange interaction among the Gd ions. Such an interaction favors the idea of superexchange via the conduction electrons since this potential drops off comparatively slowly[4] (like $1/R^3$). This is consistent with Herring's idea on ion-conduction electron exchange being the fundamental spin mechanism in these systems. At this point, we shall not go further into the interesting question of ferromagnetism in the rare earths, but reserve it for later investigation. It was brought up here as an interesting system that has been studied experimentally to show how the dilute ferromagnet does yield information on exchange mechanisms.

III. DERIVATION OF THE CLUSTER EXPANSION

As announced in the introduction, we first introduce for pedagogical reasons a new proof of the familiar Ursell-Mayer cluster expansion for spin-independent forces. The problem at hand is the evaluation of

$$\log Z=\left[\log\frac{1}{\Omega^N}\int dr_1\cdots dr_N \exp\Big[-\beta\sum_{1\le i<j\le N} v_{ij}\Big]\right] \equiv\log\langle e^{-\beta V}\rangle, \quad (1)$$

where v_{ij} is assumed to be a short-ranged potential and for the moment $\int v_{ij}dr_{ij}$ is assumed to exist (this will be subsequently relaxed).

In the methods of probability theory, the use of the semi-invariant expansion is often convenient. The nth

[4] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

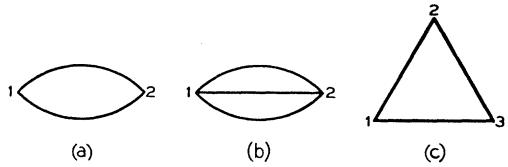

FIG. 3. Diagrams of terms contributing to the semi-invariant expansion of log$Z$.

semi-invariant M_n is defined by the relation

$$\log\langle e^{\beta x}\rangle=\sum_{m=1}^{\infty}\frac{M_n\beta^n}{n!}, \quad (2)$$

where x is a random variable and the bracket $\langle\ \rangle$ indicates the average over x according to a known distribution function.

The following important fact is immediately evident. Let x, y be independent random variables corresponding to which exist the semi-invariants $M_n{}^x$, $M_n{}^y$, respectively. Then by the definition (2) and the assumed independence

$$M_n{}^{x+y}=M_n{}^x+M_n{}^y, \quad x, y \text{ independent} \quad (3)$$

since $\langle e^{\beta(x+y)}\rangle=\langle e^{\beta x}\rangle\langle e^{\beta y}\rangle$. Equation (3) is obviously generalizable to n independent variables. This equation will be extremely useful in what is to follow. It says that when dealing with independent random variables no cross terms may exist in the semi-invariant $M_n{}^{x+y}$.

It is apparent that the tool of the semi-invariant may serve a useful purpose in the evaluation of Eq. (1) with $V=\sum v_{ij}$ being a random variable. The distribution law is that the random variables $r_1, \cdots, r_N$ are each dispersed with equal probability $(1/\Omega)$ through configuration space. For orientation, we first evaluate the most simple semi-invariants M_1 and M_2.

$$M_1=\langle V\rangle=\sum\langle v_{ij}\rangle=\binom{N}{2}\langle v\rangle, \quad (4)$$

$$M_2=\langle V^2\rangle-\langle V\rangle^2 \quad (5)$$

$$=\sum\langle v_{ij}v_{kl}\rangle-\langle v_{ij}\rangle\langle v_{kl}\rangle. \quad (6)$$

In Eq. (6) three types of terms occur: *viz.*, no indices in common, one index in common and two indices in common. We treat the three separately

$$\langle v_{12}v_{34}\rangle=\langle v_{12}\rangle\langle v_{34}\rangle, \quad (6a)$$

$$\langle v_{12}v_{23}\rangle=\langle v_{12}\rangle\langle v_{23}\rangle, \quad (6b)$$

$$\langle v_{12}v_{12}\rangle=\langle v_{12}{}^2\rangle. \quad (6c)$$

(6a) is obviously true. (6b) is true because in integrating over $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ one may pass to independent variables $\mathbf{r}_{12}$, $\mathbf{r}_{23}$, $\mathbf{r}_3$. Integration over $\mathbf{r}_3$ gives a factor of Ω whereas integration of $\mathbf{r}_{12}$, $\mathbf{r}_{23}$ is a product of integrals since $\mathbf{r}_{12}$ and $\mathbf{r}_{23}$ are independent. It is thus seen that only terms with two indices in common survive in Eq. (6),

leading to

$$M_2=\binom{N}{2}[\langle v^2\rangle-\langle v\rangle^2]=\tfrac{1}{2}N^2\langle v^2\rangle+O(1). \quad (7)$$

The last step in Eq. (7) is true because $\langle v\rangle^2$ involves one extra factor of $[(1/\Omega)\times(\text{range of force})^3]$.

The important result in our evaluation of M_2 is that the unlinked parts drop out (no indices in common) as well as the reducible parts (one index in common). We should like to rephrase the analysis in slightly different language in order to make evident the generalization in higher order. Whenever unlinked or reducible parts arise in a semi-invariant, a factorization takes place analogous to Eqs. (6a) and (6b). Thus the variables that appear in the separate parts are statistically independent. Then, that contribution to the complete semi-invariant M_n that arises from unlinked or reducible parts must satisfy Eq. (3), i.e., all cross products of unlinked or reducible parts necessarily vanish in M_n. One is left only with the sum of the irreducible parts in M_n. For example in M_3 there are two irreducible combinations which we diagram in Fig. 3(b) and 3(c). In Fig. 3(a) we diagram the single irreducible part that arises in M_2. [The diagram convention is rather evident—vertices label the particles and a single bond is drawn for every v interaction among the particle in the diagram.] Figure 3(b) corresponds to the terms

$$\binom{N}{2}[\langle v_{12}^3\rangle-3\langle v_{12}^2\rangle\langle v_{12}\rangle+2\langle v_{12}\rangle^3]=\frac{N^2}{2!}\langle v_{12}^3\rangle+O(1), \quad (8)$$

and Fig. 3(c) corresponds to the terms

$$\binom{N}{3}[\langle v_{12}v_{23}v_{31}\rangle-3\langle v_{12}v_{23}\rangle\langle v_{31}\rangle+2\langle v_{12}\rangle\langle v_{23}\rangle\langle v_{31}\rangle]=\frac{N^3}{3!}\langle v_{12}v_{23}v_{31}\rangle+O(1). \quad (9)$$

The rule for writing down all the diagrams contributing to M_n is now evident. They consist of all the irreducibly linked diagrams containing n bonds among ν vertices where $2\leq\nu\leq n$. The combinatorial factor for a diagram containing ν vertices is $\binom{N}{\nu}=N^\nu/\nu!$ for fixed ν in the limit as $N\to\infty$ such that N/Ω is fixed. (This is, of course, multiplied by the number of topologically distinct ways of ordering the vertices $1,\cdots,\nu$ for a given diagram; e.g., $v_{12}v_{23}v_{34}v_{41}$ has three topologically distinct diagrams, the other two being $v_{12}v_{24}v_{43}v_{31}$ and $v_{13}v_{34}v_{42}v_{21}$). In this limit it is only the first or fully correlated part of the semi-invariant that contributes [see Eqs. (7), (8), (9)].

Up to this point we have proven the analog of the linked cluster expansion in quantum mechanics.[5] We have shown in a perturbation expansion in βV how clusters containing higher powers of N drop out. To arrive at the Ursell-Mayer density expansion we must now partially sum the series. We first sum the simplest set of diagrams, those with two vertices containing the series in Fig. 3(a)+Fig. 3(b)+etc. The contribution to $\log Z$ from this set is

$$\tfrac{1}{2}N^2\sum_{n=1}^{\infty}\frac{(-\beta)^n\langle v^n\rangle}{n!}=\tfrac{1}{2}N^2\langle e^{-\beta v}-1\rangle=N\left[\frac{1}{2!}\frac{N}{\Omega}\int(e^{-\beta v}-1)d^3r\right], \quad (10)$$

which is the familiar second virial coefficient.

Proceeding now to the set of all diagrams containing three vertices each connected to the other by at least one bond, let us label the three vertices by 1, 2, and 3 and the bonds by (12), (23), and (31). We must first inquire into how many diagrams contribute to M_n such that there are l_{12} bonds of type (12), l_{23} of type (23) and l_{31} of type (31). This is simply the number of arrangements of n things into three classes (12), (23), and (31) such that $l_{12}+l_{23}+l_{31}=n$, i.e., the multinomial coefficient $n!/l_{12}!l_{23}!l_{31}$. We then have for the sum of all graphs with three vertices

$$\sum_{n=1}^{\infty}\frac{M_n(\text{part from three irreducibly linked vertices})}{n!}(-\beta)^n$$

$$=\frac{N^3}{3!}\sum_{n=3}^{\infty}\sum_{\substack{l_{12},l_{23},l_{31}=1\\ l_{12}+l_{23}+l_{31}=n}}^{\infty}(-\beta)^n\frac{1}{n!}\frac{n!}{l_{12}!l_{23}!l_{31}!}\langle v_{12}^{l_{12}}v_{23}^{l_{23}}v_{31}^{l_{31}}\rangle$$

$$=\left\langle\left(\sum_{l_{12}=1}^{\infty}\frac{(-\beta v_{12})^{l_{12}}}{l_{12}!}\sum_{l_{23}=1}^{\infty}\frac{(-\beta v_{23})^{l_{23}}}{l_{23}!}\sum_{l_{31}=1}^{\infty}\frac{(-\beta v_{31})^{l_{31}}}{l_{31}!}\right)\right\rangle$$

$$=N\frac{1}{3!}\left(\frac{N}{\Omega}\right)^2\int(e^{-\beta v_{12}}-1)(e^{-\beta v_{23}}-1)(e^{-\beta v_{31}}-1)d^3r_1d^3r_2. \quad (11)$$

[5] J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957). It is worth while to mention here that Goldstone's derivation is easily obtained by the semi-invariant method as well. We define $\psi(t)=P\int_{-\infty}^{t}\exp[iH'(t')dt']\Phi_0$, where $H'(t)$ is the interaction Hamiltonian in interaction representation, including the usual damping factor, Φ_0 the unperturbed wave function, and P the time-ordering operator. Then defining $F(t)=\langle\psi(t)|\Phi_0\rangle$, the well-known adiabatic-switching-on theorem gives $\Delta E=\partial\log F/\partial(it)|_{t=0}$. $\log F$ may then be developed in a semi-invariant expansion in powers of (it). By the theorem of factorization of unlinked parts, only linked parts survive and the linked cluster theorem follows.

Equation (11) is the familiar expression for the third virial coefficient.

Continuing in this manner, we see that the coefficient of $(N^\nu/\nu!)$ [or alternatively of $(1/\nu!)(N/\Omega)^{\nu-1}$] in the expression for $(1/N)\log Z$ is the sum of all irreducible diagrams involving ν vertices. Each such set of diagrams is further broken up into a set of subdiagrams in which only a given set of types of bonds is admitted. By bond type we mean its double index labelling the two vertices it connects. Thus the coefficient of $(N/\Omega)^3$ contains four vertex diagrams and a possible subset of diagrams is that which has bonds of type (12)(23)(34)(41)(24) and none other. If (ij) labels a bond type, then the factor that contributes to M_n from a diagram with ν vertices and l_{ij} bonds of type (ij) is

$$\frac{N^\nu}{\nu!}\frac{n!}{\Pi l_{ij}!}\Pi(v_{ij})^{l_{ij}} \tag{12}$$

where

$$\sum_{1\le i<j\le \nu} l_{ij}=n \quad \text{and} \quad \nu\le n. \tag{13}$$

Summation over-all diagrams of this subset leads to

$$N\frac{1}{\nu!}\left(\frac{N}{\Omega}\right)^{\nu-1}\int \prod_{\substack{\text{bonds in the}\\ \text{given subset}}}[e^{-\beta v_{ij}}-1]d^3r_1\cdots d^3r_{\nu-1}, \tag{14}$$

where the same steps are used as those that led to Eq. (11). Summation over all terms with fixed ν leads to

$$N\frac{1}{\nu!}\left(\frac{N}{\Omega}\right)^{\nu-1}\sum_{\substack{\text{all irreducible}\\ \text{linked diagrams}\\ \text{among } \nu \text{ vertices}}}\int\cdots$$

$$\times\int\prod(e^{-\beta v_{ij}}-1)d^3r_1\cdots d^3r_{\nu-1} \tag{15}$$

$$\equiv N(N/\Omega)^{\nu-1}\beta_{\nu-1}, \tag{16}$$

where the notation in Eq. (16) is the same as Mayer's.[2]

Finally we have

$$\lim_{\substack{N\to\infty\\ N/\Omega=1/v}}\left(\frac{1}{N}\log Z\right)=\sum_{\nu=1}^{\infty}\beta_\nu v^{-\nu}, \tag{17}$$

which is the well-known cluster expansion.

It is not immediately apparent that the above reasoning is valid for spin-dependent forces. In the model of the Ising lattice $V=\sum v_{ij}(r_{ij})\mu_i\mu_j$ where $\mu_i=\pm 1$ according to the spin direction. Z is defined by

$$Z=\frac{1}{\Omega^N}\sum_{\{\mu_i\}}\int dr_1\cdots dr_N e^{-\beta V}. \tag{18}$$

Now one of the essential steps that led to Eq. (17) was the factorization property obeyed by unlinked and reducible linked parts of a diagram. It is not obvious that for spin-dependent forces that factorization of the reducible parts [e.g., Eq. (6b)] takes place since $\mu_1\mu_2$ is not independent of $\mu_2\mu_3$. The next part of the paper is devoted to this point.

Since we are interested in the problem of spontaneous magnetization, we shall use a technique due to Kirkwood[3] of summing only over spin configurations with a given long-range order R, where R is defined by

$$R=(1/N)\sum\mu_i. \tag{19}$$

This will give us the free energy as a function of R. R is determined by minimization. The statistical mechanical justification of this procedure is only found by consideration of a small magnetic field H which is independent of N, the number of particles. This multiplies the field free terms in the partition function by $(e^{\beta\mu_0 HR})^N$ where μ_0 is the magnetic moment per spin. Thus the partition function is

$$Z=\sum_{R=0}^{1} Z_{\text{field-free}}(R)(e^{\beta\mu_0 HR})^N, \tag{20}$$

The sum on R is well approximated by an integral which may be done by steepest descents (alternatively the maximum term in Eq. (20) dominates everything else, i.e., one minimizes the free energy with respect to R). The evaluation of $\log Z$ is done, of course, in the asymptotic limit of large N holding H fixed. Finally one lets $H\to 0$ to give the spontaneous magnetization moment *vs* T. A logical error arises if the limits are not done in this order, since the leading terms contributing to Eq. (20) for $H=0$ are those for which $R=O(1/\sqrt{N})$. We make this point clear at the outset in order to justify the consideration of $Z_{\text{field-free}}(R)$ for finite R, independent of N. From now on $Z_{\text{field-free}}(R)$ will be simply noted as $Z(R)$. We evaluate $[(1/N)\log Z(R)]$ for fixed R in the limit $N\to\infty$. Let $W(R)$ be the number of configurations of spin for fixed R. Clearly

$$W(R)=\frac{N!}{[\frac{1}{2}N(1+R)]![\frac{1}{2}N(1-R)]!}. \tag{21}$$

Following Kirkwood, we write

$$\log Z(R)=\log W(R)+\log\langle\exp(-\beta\sum v_{ij}\mu_i\mu_j)\rangle_{R,C}, \tag{22}$$

where

$$\langle\exp(-\beta\sum v_{ij}\mu_i\mu_j)\rangle_R\equiv\frac{1}{W(R)}\sum_{\substack{\{\mu_i\}\\ \sum\mu_i=NR}}\frac{1}{\Omega^N}$$

$$\times\int\exp(-\beta\sum v_{ij}\mu_i\mu_j)d^3r_1\cdots d^3r_N. \tag{23}$$

We now develop Eq. (22) in a semi-invariant expansion remembering that both r_i and μ_i are random variables. (Averages over r_i will be designated $\langle\ \rangle_C$

and over μ_i will be designated $\langle\ \rangle_R$.) We have

$$\log\langle\exp(-\beta\sum v_{ij}\mu_i\mu_j)\rangle_{R,C}=\sum\frac{(-\beta)^n}{n!}M_n, \quad (24)$$

$$M^{(1)}=\langle\sum v_{ij}\mu_i\mu_j\rangle_{R,C}=\langle v\rangle\langle\tfrac{1}{2}\sum_{i\neq j}\mu_i\mu_j\rangle_R \quad (25a)$$

$$=\tfrac{1}{2}\langle v\rangle[\langle\sum\mu_i\sum\mu_j\rangle-\langle\sum\mu_i^2\rangle] \quad (25b)$$

$$=\tfrac{1}{2}\langle v\rangle[N^2R^2-N], \quad (25c)$$

since $\mu_i^2=1$, and the distribution over μ_i is such that $\sum\mu_i$ is fixed$=NR$. In Eq. (25c), note that in a perfectly random distribution $\langle R^2\rangle\equiv(1/2^N)\sum R^2W_R=1/N$ and $M^{(1)}=0$ which is as it should be. This situation is avoided when, as discussed above, a magnetic field is present. Only in this circumstance may Eq. (25c) be calculated for fixed R with retention of the highest power of N.[6] Thus Eq. (25c) for fixed R is

$$M_1=\tfrac{1}{2}\langle v\rangle N^2R^2+O(1), \quad (25d)$$

where the retained term is taken to be of $O(N)$. This procedure will be followed consistently in the calculation of the higher semi-invariants.

M_2 is given by

$$M_2=\sum_{ij}\sum_{kl}[\langle v_{ij}v_{kl}\mu_i\mu_j\mu_k\mu_l\rangle_{R,C}-\langle v_{ij}\mu_i\mu_j\rangle_{R,C}\langle v_{kl}\mu_k\mu_l\rangle_{R,C}]. \quad (26)$$

In Eq. (6) there are the three various combinations of unlinked, reducible and irreducible diagrams corresponding to the spin-independent case (6a), (6b), and (6c). Further, we again have $\langle v_{12}v_{23}\rangle=\langle v_{12}\rangle\langle v_{23}\rangle$ so that

$$M_2=\langle v\rangle_C^2\sum_{(ij)\neq(kl)}[\langle\mu_i\mu_j\mu_k\mu_l\rangle_R-\langle\mu_i\mu_j\rangle_R\langle\mu_k\mu_l\rangle_R]+\sum_{ij}[\langle v^2\rangle_C\langle\mu_i^2\mu_j^2\rangle_R-\langle v\rangle_C^2\langle\mu_i\mu_j\rangle_R^2]. \quad (27)$$

In the first summation of Eq. (27) we add and subtract the term $(ij)=(kl)$ as well as $i=j$ and $k=l$, to give

$$M_2=\langle v\rangle_C^2\sum_{\substack{ijkl\\ \text{unrestricted}}}\langle\mu_i\mu_j\mu_k\mu_l\rangle_R-\langle\mu_i\mu_j\rangle_R\langle\mu_k\mu_l\rangle_R-2\langle v\rangle_C^2\sum_{i,kl}[\langle\mu_i^2\mu_k\mu_l\rangle_R-\langle\mu_i^2\rangle_R\langle\mu_k\mu_l\rangle_R]-\langle v\rangle_C^2\sum_{i,j}[\langle\mu_i^2\mu_j^2\rangle_R-\langle\mu_i\mu_j\rangle_R^2]+\sum_{i,j}[\langle v^2\rangle_C\langle\mu_i^2\mu_j^2\rangle_R-\langle v\rangle_C^2\langle\mu_i\mu_j\rangle_R^2]. \quad (27a)$$

The first term is zero in (27a) since $\sum\mu_i=NR$ is fixed and all semi-invariants involving constants necessarily vanish for $n>1$. [This follows from the definition (2).] The second term in (27a) obviously vanishes since $\mu_i^2=1$. Further, since $\langle v^2\rangle/\langle v\rangle^2=O(1/N)$, one may neglect terms involving $\langle v\rangle^2$ compared to those containing $\langle v^2\rangle$. Thus Eq. (27a) becomes

$$M_2=\tfrac{1}{2}N^2\langle(v\mu_1\mu_2)^2\rangle_{R,C}+O(1), \quad (27b)$$

which is the same as the spin-free case except that spin averages are now included.

The argument in general order follows the same pattern as the above. One decomposes all the terms in a semi-invariant into summations over products of unlinked and reducible parts plus the summation over all irreducibly linked diagrams. The summation over unlinked and reducible parts contains restrictions on indices (the restriction to unlinked and reducible parts) which are handled by adding and subtracting off the restrictions. The main term now has a free summation over all indices. Thus a term involving a sum of products of spin variables μ_i becomes a product of sums. But every sum of the type $\sum\mu_i^n$ is fixed in the Ising problem since $\mu_i^n=\mu_i$ or 1 according to n odd or even and we are taking terms only where $\sum\mu_i=NR$. Thus every term in the semi-invariant coming from unlinked clusters is evaluated by replacing each power of a spin variable μ_i by 1 or R according to whether the power is even or odd. However this implies that this contribution to the semi-invariant is zero since the nth semi-invariant of a "random variable" which is a constant or sum of constants is zero by the definition (2).

Let us now look at the subtracted corrections. Either the correction is a sum of unlinked or reducible terms or irreducibly linked terms. In the first cases, repeat the same process as above. Continuing until one is left only with irreducibly linked terms, we now notice that all the subtracted correction terms resulting from adding and subtracting annoying restrictive terms on indices are at least of $O(1/N)$ smaller than the original irreducibly linked diagrams in the semi-invariant. This is because a product of two unlinked or reducible parts carries an extra factor of $(1/\Omega)$ when compared to a corresponding linked irreducible part in the same order. The correction terms discussed above resulted from contraction of two indices in the sum over unlinked clusters so that a term which contributed $O(N^2/\Omega)$ compared to the linked irreducible part will contribute only something of $O(1/\Omega)$ in the correction term in question. The argument is made more clear by example, but rather than carry this out here we reserve a detailed example for the more interesting calculation of $\langle\log\langle Z\rangle_R\rangle_C$. Without further comment, we state that in the above case the nth semi-invariant is the same as obtained in the spin-independent case and hence Eq. (17) is correct in the present spin-dependent case. The β_ν are defined now according to Eq. (16) but with spin

[6] I am indebted to Professor Mark Kac for clarifying this point.

averages as well as space integrations included, i.e.,

$$\beta_{\nu-1}=N\frac{1}{\nu!}\left(\frac{N}{\Omega}\right)^{\nu-1}\sum_{\substack{\text{all reducible}\\ \text{linked diagrams}\\ \text{among } \nu \text{ vertices}}}\int\cdots \times\int\langle\prod(e^{-\beta v_{ij}(r_{ij})\mu_i\mu_j}-1)d^3r_1\cdots d^3r_{\nu-1}\rangle_R. \quad (28)$$

For emphasis, we repeat that the crucial point in the analysis has been that $\mu_i{}^n=\mu_i$ or 1 according to n odd or even. Hence $\sum\mu_i{}^n$ is fixed in the spin-averaging process.

As discussed in the introduction, the physical system of interest dictates that one must calculate $\langle\log\langle Z\rangle_R\rangle_C$ rather than $\log\langle Z\rangle_{R,C}$. Thus a semi-invariant expansion is made on the spin variables and then each semi-invariant is averaged in configuration space, i.e.,

$$\langle\log\langle Z\rangle_R\rangle_C=\sum_{n=1}\frac{\langle M_n\rangle_C}{n!}(-\beta)^n. \quad (29)$$

Clearly $\langle M_1\rangle_C$ is still given by Eq. (25d). However, $\langle M_2\rangle_C$ differs from (26). Explicitly

$$M_2=\sum_{ij}\sum_{kl}\langle v_{ij}v_{kl}\rangle_C[\langle\mu_i\mu_j\mu_k\mu_l\rangle-\langle\mu_i\mu_j\rangle\langle\mu_k\mu_l\rangle]. \quad (30)$$

The reduction of Eq. (30) to a sum over linked irreducible parts alone is the same as followed through in Eq. (27) with the exception that the linked irreducible terms now include the subtracted term $\langle\mu_i\mu_j\rangle\langle\mu_i\mu_j\rangle$ whereas in Eq. (27) such terms were multiplied by $\langle v\rangle^2=O(1/N)\langle v^2\rangle$. This is the major difference in the two calculations, but aside from this point everything goes through as before. Thus

$$M_2=\tfrac{1}{2}N^2\langle v^2\rangle[\langle(\mu_1\mu_2)^2\rangle-\langle\mu_1\mu_2\rangle^2]\equiv\tfrac{1}{2}N^2\langle v^2\rangle M_2{}^{(\mu_1\mu_2)}. \quad (31)$$

Rather than immediately presenting the general argument, clarity is gained by first considering another simple example, *viz.*, the calculation of M_3

$$\begin{aligned}M_3=&\sum_{(ij)(kl)(mn)}\langle v_{ij}v_{kl}v_{mn}\rangle_C[\langle\mu_i\mu_j\mu_k\mu_l\mu_m\mu_n\rangle_R\\&-\langle\mu_i\mu_j\rangle_R\langle\mu_k\mu_l\mu_m\mu_n\rangle_R-\langle\mu_k\mu_l\rangle_R\langle\mu_i\mu_j\mu_m\mu_n\rangle_R\\&-\langle\mu_m\mu_n\rangle_R\langle\mu_i\mu_j\mu_k\mu_l\rangle_R+2\langle\mu_i\mu_j\rangle_R\langle\mu_k\mu_l\rangle_R\langle\mu_m\mu_n\rangle_R]\\\equiv&\sum M^{(3)}(ij;kl;mn). \quad (32)\end{aligned}$$

In Eq. (32), it is of course specified that $i\neq j$; $k\neq l$; $m\neq n$. However, it is easily shown that these terms contribute zero or $O(1)$ to the spin averages after first carrying out the space averages. This is true in general so that from this point on we will ignore this type of restriction on indices. Now, the expression (29) is decomposable according to no pairs, one pair, two pairs and three pairs in common together with the triangle configuration. Thus

$$\begin{aligned}M_3=&\sum_{\substack{ij\neq kl\neq mn\\ \text{no triangle}\\ \text{configurations}}}M^{(3)}(ij;kl;mn)\\&+3\sum_{ij\neq kl}M^{(3)}(ij;ij;kl)+\sum_{ij}M^{(3)}(ij;ij;ij)\\&+\sum_{\substack{i,j,k\\ \text{distinct triples}}}M^{(3)}(ij;jk;ki). \quad (32a)\end{aligned}$$

The first summation in Eq. (32a) is written

$$\begin{aligned}\langle v\rangle^3\sum_{\substack{ij\neq kl\neq mn\\ \text{no triangle}\\ \text{configurations}}}&[\langle\mu_i\mu_j\mu_k\mu_l\mu_m\mu_n\rangle-3\langle\mu_i\mu_j\rangle\langle\mu_k\mu_l\mu_m\mu_n\rangle\\&+2\langle\mu_i\mu_j\rangle\langle\mu_k\mu_l\rangle\langle\mu_m\mu_n\rangle]. \quad (32b)\end{aligned}$$

If there were no restrictions on indices in the above, the result would be zero since $\sum\mu_i=NR$ is fixed. This result is general since the semi-invariant M_n vanishes when it is generated by a "random" variable which is in fact a fixed number (except of course for $n=1$). To avail ourselves of this simplification, we add and subtract all contractions of indices and consider the remainder. Taking these new subtracted terms into account, the second summation in Eq. (32) is

$$\begin{aligned}3[\langle v^2\rangle\langle v\rangle-\langle v\rangle^3]\sum_{ij\neq kl}&[\langle\mu_i{}^2\mu_j{}^2\mu_k\mu_l\rangle-2\langle\mu_i\mu_j\rangle\langle\mu_i\mu_j\mu_k\mu_l\rangle\\&-\langle\mu_i{}^2\mu_j{}^2\rangle\langle\mu_k\mu_l\rangle+2\langle\mu_i\mu_j\rangle\langle\mu_i\mu_j\rangle\langle\mu_k\mu_l\rangle]. \quad (32c)\end{aligned}$$

We first remark that $\langle v\rangle^3/\langle v^2\rangle\langle v\rangle=O(1/N)$ so that the correction term due to contraction of indices in the first summation of Eq. (32) need not be considered. This result is again general. Whenever indices are contracted in a summation over unlinked parts in order to add and subtract inconvenient restrictions, the subtracted correction may be neglected since, as already discussed after Eq. (27), it is $O(1/N)$ less than an identical spin term already present in the semi-invariant.

We now consider the spin average in (32c). The most obvious step is to put $\mu_i{}^2=\mu_j{}^2=1$, but we proceed in a more systematic fashion in order to state the generalization. Again the restriction in the summation is annoying so we add and subtract it, neglecting the subtracted part by the above argument. Then we may freely sum on all four indices. Summation on the indices, k, l then leads immediately to zero since $\sum\mu_k$ is fixed. This is again because (kl) is unlinked from (ij) and we have a situation which would arise from a semi-invariant expansion on the random variable $c+x$ where c is a constant (in the present context $c=\sum_k\mu_k\sum_l\mu_l$) and x is a random variable (in the present context $x=\mu_i\mu_j$). Since there may not exist cross products of c with semi-invariants generated by x, these terms are zero. Generally, when there exists two unlinked terms, after the restrictions on summations

are removed, summation on one member of the product always leads to zero since $\sum \mu_i{}^n$ is fixed for any n.

Finally Eq. (32) is reduced to

$$M_3=\frac{N^2}{2!}\langle v^3\rangle[\langle\mu_1{}^3\mu_2{}^3\rangle-3\langle\mu_1{}^2\mu_2{}^2\rangle\langle\mu_1\mu_2\rangle+2\langle\mu_1\mu_2\rangle^3]$$
$$+\frac{N^3}{3!}\langle v_{12}v_{23}v_{31}\rangle[\langle\mu_1\mu_2\mu_2\mu_3\mu_3\mu_1\rangle$$
$$-3\langle\mu_1\mu_2\rangle\langle\mu_2\mu_3\mu_3\mu_1\rangle+2\langle\mu_1\mu_2\rangle^3]$$
$$\equiv\frac{N^2}{2!}\langle v^3\rangle M_3{}^{(\mu_1\mu_2)}+\frac{N^3}{3!}\langle v_{12}v_{23}v_{31}\rangle M_3{}^{(\mu_1\mu_2\mu_3)}. \quad (33)$$

In the above example all the nontrivial features that arise in the calculation of any M_n are clearly exhibited. In particular it is seen, in general, how the condition that $\sum \mu_i{}^n$ is fixed in the averaging procedure, necessarily implies that the unlinked and reducible parts cancel. One may state the general line of reasoning as follows: When unlinked parts exist in a semi-invariant, it is possible to rid oneself of all index restriction in calculating spin averages. Further, for every term involving a mean of a product of spin variables of two or more unlinked parts, there will be another term involving the product of the means with opposite sign. [That the structure of all the semi-invariants is necessarily of this form follows in order to insure that Relation (3) is true for independent random variables.] Finally, free summation then guarantees that the above difference is zero since $\sum_{i=1}^{N}\mu_i{}^n$ is fixed. This is because summing on all the indices of one of the unlinked parts merely replaces all spin variables of this unlinked part by constants.

Having shown that one need only consider irreducibly linked graphs, we now proceed with partial summation to get the "virial expansion." Thus the coefficient of N/Ω in $(1/N)\log Z/N$ is given by

$$\frac{N}{2!}\sum_{n=1}^{\infty}\frac{(-\beta)^n}{n!}\langle v^n\rangle_c M_n{}^{(\mu_1\mu_2)}=\frac{N}{2!}\left\langle\sum_{n=1}^{\infty}\frac{(-\beta v)^n}{n!}M_n{}^{(\mu_1\mu_2)}\right\rangle_C$$
$$=N^2\frac{1}{2!}\langle\log\langle e^{-\beta v\mu_1\mu_2}\rangle_R\rangle_C, \quad (34)$$

where the definition (2) has been used. The spin average in (34) is trivially obtained by expansion of the exponential, averaging, and resumming, whereupon we have [replacing $\langle\ \rangle_c$ by $(1/\Omega)\int$]

$$N\left[\frac{1}{2!}\left(\frac{N}{\Omega}\right)\int d^3r\log[\cosh\beta v(r)-R^2\sinh\beta v(r)]\right]. \quad (35)$$

Alternatively, if the particles go on lattice points, $\langle\ \rangle_c\to(1/N_0)\sum$, where N_0 is the total number of lattice sites labeled by i, then (34) becomes

$$N\left[\frac{1}{2!}\left(\frac{N}{N_0}\right)\sum_i\log[\cosh\beta v(r_i)-R^2\sinh\beta v(r_i)]\right]; \quad (36)$$

i is taken with respect to some arbitrary origin.

The coefficient of $(N/\Omega)^2$ or $(N/N_0)^2$ is given by the summation over all triangle diagrams, i.e.,

$$\frac{N^3}{3!}\left\langle\sum_{n=3}^{\infty}\frac{M_n{}^{(\mu_1\mu_2\mu_3)}}{n!}(-\beta)^n\right\rangle, \quad (37)$$

where $M_n{}^{\mu_1\mu_2\mu_3}$ means that contribution to M_n that arises from all diagrams connecting all three vertices 1, 2, 3 by one or more bonds. Now the semi-invariants generated by the random variable $[v_{12}\mu_1\mu_2+v_{23}\mu_2\mu_3+v_{31}\mu_3\mu_1]$ contains all the graphs containing linkages between (12) alone and (12)(23) together. These latter of course are not contained in $M_n{}^{\mu_1\mu_2\mu_3}$. Such terms must be subtracted. However, when the semi-invariant corresponding to $v_{12}\mu_1\mu_2+v_{23}\mu_2\mu_3$ is subtracted one has also subtracted the single links corresponding to $v_{12}\mu_1\mu_2$ and $v_{23}\mu_2\mu_3$ separately. Thus we have

$$M_n{}^{(\mu_1\mu_2\mu_3)}=M_n{}^{(\mu_1\mu_2v_{12}+\mu_1\mu_3v_{13}+\mu_2\mu_3v_{23})}$$
$$-3M_n{}^{(\mu_1\mu_2v_{12}+\mu_2\mu_3v_{23})}+3M_n{}^{(\mu_1\mu_2v_{12})}. \quad (38)$$

Substituting into Eq. (37), we may now extend the sum down to $n=1$ since (38) vanishes for $n=1, 2$. Thus (37) becomes, using the definition (2),

$$\frac{N^3}{3!}[\langle\log\langle\exp-\beta[\mu_1\mu_2v_{12}+\mu_2\mu_3v_{23}+\mu_3\mu_1v_{31}]\rangle_R\rangle_C$$
$$-3\langle\log\langle\exp-\beta[\mu_1\mu_2v_{12}+\mu_2\mu_3v_{23}]\rangle_R\rangle_C$$
$$+3\langle\log\langle\exp-\beta[\mu_1\mu_2v_{12}]\rangle_R\rangle_C]. \quad (39)$$

The general procedure is now obvious. Corresponding to a given term in β_ν defined by Eq. (16), there is a product of the type $\prod(e^{-\beta v_{ij}}-1)$. Terms will arise which carry subsums $\sum v_{ij}$ in an exponential. For every such term in β_ν, there will be a term in β_ν' where the expression $\int\cdots\int\exp[-\beta\sum_{\text{subset}}v_{ij}]dr_1\cdots dr_\nu$ is to be replaced by $\langle\log\langle\exp\beta\sum_{\text{subset}}v_{ij}\rangle_R\rangle_C$. And we then have

$$\langle(1/N)\log Z_R\rangle_c=\log W(R)+\sum N^\nu\beta_\nu'(R)+\beta\mu_0HR, \quad (40)$$

with β_ν' calculated according to the above rules. We have included the magnetic field H for completeness. R is given by $\partial\langle\log Z_R\rangle/\partial R=0$, which gives

$$0=\tfrac{1}{2}\log\left(\frac{1-R}{1+R}\right)+\sum N^\nu\frac{\partial\beta_\nu'(R)}{\partial R}+\beta\mu_0H. \quad (41)$$

Up to this point we have discussed a perfectly random distribution of paramagnetic impurity ions. For the systems we have in mind this is an adequate

description (the alloys are fabricated at high temperatures and rapidly quenched), but we must include the proviso that there is no multiple occupancy of a lattice point. This introduces a kind of correlation that is formally not included in the theory up to this point. The additional complication is handled by adopting all preceding formulas but interpreting the symbol $\langle\ \rangle_c$ as the average over configuration space taken with a certain given probability distribution function. Thus the integral in Eq. (35) has a pair probability function $g^{(2)}(r)$ in the integrand and Eq. (36) is understood to be taken as a sum such that the index i does not coincide with the origin which has been chosen at some one impurity ion.

Now, however, it is no longer true that the reducible linked clusters drop out, since $\langle v_{12}v_{23}\rangle \neq \langle v_{12}\rangle\langle v_{23}\rangle$. (Of course unlinked clusters drop out as their factorization property is unaffected.*) In particular, we have for a lattice

$$\langle v_{12}v_{23}\rangle = \frac{1}{N^2}\sum_{j,k} g_{ijk}v_{ij}v_{jk}. \tag{42}$$

Since the only correlation under consideration is one in which no two particles can overlap, we have $g_{123} = g_{12}g_{23}g_{31}$ where $g_{ij}=1$ for $i\neq j$ and $g_{ij}=0$ for $i=j$. We therefore write Eq. (42) in the form

$$\langle v_{12}v_{23}\rangle = \langle v_{12}\rangle\langle v_{23}\rangle + \frac{1}{N^2}\sum_{jk} g_{ij}g_{jk}(g_{kl}-1)v_{ij}v_{jk}, \tag{43}$$

where

$$\langle v_{12}\rangle\langle v_{23}\rangle = \left[\frac{1}{N}\sum_j g_{ij}v_{ij}\right]^2. \tag{44}$$

The first term of Eq. (43) is now treated just as the reducible clusters in the case where correlations were not considered. The second term may be considered an irreducible cluster if a new kind of bond is introduced, *viz.*, $(g_{ij}-1)$. The magnetic interaction has a bond $(g_{ij}v_{ij})$.

This procedure is easily generalized with the result that β_ν' must now include all irreducible graphs containing ν vertices with the proviso that all bonds associated with the magnetic interaction be at least reducibly linked. We shall not pursue this point further. However, in an Appendix we shall use our prescription to calculate M_2 and M_3 for the case $x=1$ and show that our prescription yields the exact well-known results for this case. Since for the case $x=1$ our prescription of keeping ions out of each others way means that each ion goes on to a regular site, this agreement must hold. Our method simplifies the standard method of calculation considerably.

* *Note added in proof.*—The reason for dropping unlinked clusters given above is incorrect. The factorization property is effected. The correct reason is that spins arranged in unlinked combinations give rise to semi-invariants of $0(1/N)$.

IV. FORMULAS FOR THE DILUTE CASE

In the remaining part of the paper we shall be interested in developing semiquantitative expressions for small x by taking the leading term in our expansion for $\log Z$. It is not to be construed that this procedure yields an exact limiting expression. However, physical considerations lead one to believe that for small x, the retention of chains alone should be sufficient to give a semiquantitative theory. Indeed, the conclusions drawn from the expressions derived in this approximation are identical with the qualitative sketch given in Sec. II. As far as an estimate of convergence and the errors involved, this will not be undertaken in this paper, but relegated to another publication where a specific choice of exchange interaction will be made. The error estimates depend quite sensitively on the range of the potential. The leading term in Eq. (41) is obtained from Eq. (35) or (36) [we take (36) for definiteness] to give

$$0 = \tfrac{1}{2}\log\left(\frac{1-R}{1+R}\right) - Rx\sum_{\substack{i\\ i\neq 0}} \frac{\tanh\beta v(r_i)}{1-R^2\tanh\beta v(r_i)} + \beta\mu_0 H + O(x^2). \tag{45}$$

It is easily verified that for short-range forces Eq. (45) duplicates the qualitative behavior sketched in Sec. 2. For long-range forces, βv is small in the range of interest; $\beta v \approx (1/xZ_{\text{eff}})$ near the Curie point so that the hyperbolic tangent may be expanded and dropped in the denominator. This gives the molecular field theory as expected. This is only true for $x \gg 1/Z_{\text{eff}}$.

In Eq. (45) one may now go the limit $H \to 0$ without further hesitation, as previously discussed. The Curie point, is where two roots of Eq. (45) for $H=0$, coalesce, i.e., where $\partial^2\langle \log Z\rangle/\partial R^2|_{R=0}=0$, to give

$$1 + x\sum_{\substack{i\\ i\neq 0}} \tanh\frac{v(r_i)}{kT_c} + O(x^2) = 0. \tag{46}$$

For a ferromagnetic exchange coupling, one has $v<0$, say $v(r_{ij}) = -J(r_{ij})$, so that Eq. (46) for ferromagnetic interactions reads

$$\sum_{\substack{i\\ i\neq 0}} \tanh\left(\frac{J(r_i)}{kT_c}\right) = \frac{1}{x}, \quad x \ll 1. \tag{47}$$

Equation (47) approximates the Curie point as a function of x for small x. It should also be stated that above the Curie point one may use Eq. (41) to calculate the susceptibility, i.e., $\lim_{H\to 0}(\mu_0 R/H)$. As an application let there be only nearest neighbor interactions, each of strength J, Eq. (47) reads

$$Z\tanh(J/kT_c) = 1/x. \tag{48}$$

From Eq. (48) we see that for $x<1/Z$ there is no solution as expected from our considerations in Sec. II.

Of course this result has been obtained only through the retention of the second virial coefficient. Other terms will give a value of xZ different from 1 for the suppression of ferromagnetism, but preliminary calculations indicate a small effect. It should be noted at this point that had we calculated $\log\langle Z\rangle_{R,C}$ using the cluster integrals (28), we would have found in the same approximation

$$\left(\frac{N}{\Omega}\right)\int \sinh\left(\frac{v(r)}{kT_c}\right)d^3r=1, \tag{49}$$

so that no matter how small the density, a Curie point would always be present. This example points up the necessity of keeping averaging procedures straight.

V. QUANTUM MECHANICAL CONSIDERATIONS

Equation (40) formally solves the problem of the random Ising model with the practical outcome being relations (45) and (47) for the extreme dilute case. We now briefly turn attention to the quantum mechanical case for spin $\frac{1}{2}$. We follow, in principle, the procedure of Heisenberg as outlined in Van Vleck's book.[7] In brief, Heisenberg has shown that when a magnetic field is present (again it may be very small) that, of the states with fixed spin S', the states where the Z component M_Z' is nearly equal to S' overwhelmingly dominate the partition function. The reasoning is analogous to the discussion around Eq. (20). Thus with very good approximation it suffices to look at the partition function for given S'. The degeneracy factor for spin $\frac{1}{2}$ to a good approximation is given by Eq. (21) where $M_Z'=NR/2$. Thus the problem is quite analogous to the Ising lattice, but one now must sum over-all states consistent with S', where the interaction is $\sum v_{ij}S_i\cdot S_j$. Again the semi-invariant method is used.

The crucial point is this. The spin operators may be represented by Pauli matrices. Further, since any power of a Pauli matrix is a linear combination of Pauli matrices, we have again the same situation as in the Ising model. Use of this fact is specifically made in calculating terms like

$$\sum_{i,j}(S_i\cdot S_j)^n=A_n\sum_{i,j}1+B_n\sum S_iS_j$$
$$=A_nN^2+B_n(S')^2.$$

This assures that $\sum_{ij}(S_i\cdot S_j)^n=$ constant in the spin averaging process. This is sufficient to prove that all unlinked and reducible clusters drop out just as they did for the Ising lattice example.† We conclude that Eq. (40) is still correct for the quantum mechanical spin $\frac{1}{2}$ case, where spin averages are now quantum spin averages. We work out in detail β_1'

$$(\beta_1')_{\text{spin }\frac{1}{2}}=\langle\log\langle e^{\beta S_1\cdot S_2v(r_{12})}\rangle_s\rangle_c. \tag{50}$$

The spin average is taken such that the total quantum number is S'. Since all powers of $(S_1\cdot S_2)$ are linear combinations of the type $a+bS_1\cdot S_2$, we must have

$$e^{\beta S_1\cdot S_2v(r_{12})}=A(\beta v)+B(\beta v)(S_1\cdot S_2). \tag{51}$$

A and B are determined by considering the eigenvalues of $S_1\cdot S_2$. In the triplet (singlet) we have $S_1\cdot S_2=\frac{1}{4}$ $(-\frac{3}{4})$ to give the simultaneous equations

$$\begin{aligned} e^{\beta v/4}&=A+\tfrac{1}{4}B, \quad A=\tfrac{3}{4}e^{\beta v/4}+\tfrac{1}{4}e^{-3\beta v/4},\\ e^{-3\beta v/4}&=A-\tfrac{3}{4}B, \quad B=e^{\beta v/4}-e^{-3\beta v/4}. \end{aligned} \tag{52}$$

Finally since $\langle S_1\cdot S_2\rangle=S'^2$ in the present context, we have

$$(\beta_1')_{\text{spin }\frac{1}{2}}=\langle\log\{[\tfrac{3}{4}e^{\beta v/4}+\tfrac{1}{4}e^{-3\beta v/4}] +S'^2[e^{\beta v/4}-e^{-3\beta v/4}]\}\rangle_C. \tag{53}$$

This relation is evidently very similar to (35) and the subsequent reasoning is the same.

For spin$>\frac{1}{2}$ the situation is more complicated since some powers of the spin operators will not be constant in the averaging process. It is easy to show that this will result in certain nonvanishing contributions from reducible linked diagrams. The unlinked diagrams still vanish. For example, in the semi-invariant M_4 appears the combination

$$\sum_{i,j,k,l}[\langle(S_i\cdot S_j)^2(S_k\cdot S_l)^2\rangle-\langle(S_i\cdot S_j)^2\rangle\langle(S_k\cdot S_l)^2\rangle].$$

Here all index restrictions are taken to be removed in previous steps. For spin $\frac{1}{2}$, this combination is obviously zero since $\sum(S_i\cdot S_j)^2=\sum_{i,j}[\frac{3}{16}-\frac{1}{2}(S_i\cdot S_j)]$ which is fixed in the averaging process. For spin$>\frac{1}{2}$, the dropping of the unlinked clusters is more subtle. We shall not go into detail on this point but merely point out that there is a strong analogy with the classical statistical mechanical problem of the derivation of the canonical distribution from the microcanonical. Here one finds that if $\sum\epsilon_i=E$ is fixed, then the probability of finding energy $\epsilon+\epsilon'$ in two *small* components n and n' is given by $P_{n+n'}(\epsilon+\epsilon')=P_n(\epsilon)P_{n'}(\epsilon')$ for n, n' fixed in the limit $N\to\infty$, such that E/N is fixed. For the spin problem the total spin[8] is fixed rather than the total energy, but the reasoning is the same. For *small* components, joint spin probability functions factorize. Thus when one has unlinked clusters, the semi-invariant will be zero since the spin distribution functions of the unlinked parts are independent. However, reducible linked combinations will contribute. It is also apparent that these new terms cannot effect the simple sequence

[7] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), pp. 316–342.

† *Note added in proof.*—In the quantum case the problem of commutativity arises. Thus each diagram in the Ising model is many diagrams in the quantum model corresponding to the various permutations of the spins. This does not effect the value of β_1'.

[8] It suffices to consider the Z component M_Z' alone since in the present context $M_Z'\cong S'$.

of diagrams contributing to β_1'. Thus the second virial coefficient is the same for all spins.

VI. ANTIFERROMAGNETISM

For completeness and interest we discuss random antiferromagnets. Here we suppose there exists a set of A sites and B sites which are antiferromagnetically coupled against one another through an intermediate superexchanger. All A sites (and B sites) are ferromagnetically exchange-coupled if at all. The above language about how sites are coupled of course refers to the situation where there is occupation by a paramagnetic impurity ion. For simplicity we develop the theory for the Ising model. Given this model, we proceed as follows. Define

$$R_A=\frac{1}{N_A}\sum_{i_A=1}^{N_A}\mu_{iA},\quad R_B=\frac{1}{N_B}\sum_{i_B=1}^{N_B}\mu_{iB}, \tag{54}$$

corresponding to which there is the combinatorial factor $W(R_A)\cdot W(R_B)$ where $W(R)$ is given by Eq. (21). The semi-invariant expansion goes through as before. The second virial coefficient, analogous to (36) (we take $N_A=N_B=\frac{1}{2}N$), is

$$\begin{aligned}B_1'=\tfrac{1}{2}N\langle\tfrac{1}{2}\log[\cosh\beta v_{AA}-R_A^2\sinh\beta v_{AA}]\\+\tfrac{1}{2}\log[\cosh\beta v_{BB}-R_B^2\sinh\beta v_{BB}]\\+\log[\cosh\beta v_{AB}-R_AR_B\sinh\beta v_{AB}]\rangle.\end{aligned} \tag{55}$$

Minimizing $\log Z$ with respect to R_A, R_B gives

$$\begin{aligned}\tfrac{1}{4}\log\left(\frac{1-R_A}{1+R_A}\right)=\tfrac{1}{2}N\Bigg\{R_A\left\langle\frac{\tanh\beta v_{AA}}{1+R_A^2\tanh\beta v_{AA}}\right\rangle\\+R_B\left\langle\frac{\tanh\beta v_{AB}}{1+R_B^2\tanh\beta v_{AB}}\right\rangle\Bigg\},\end{aligned} \tag{56}$$

and similarly for R_B. From these equations one can get the Neél point by taking first order in R and setting the determinant of the coefficients to 0, i.e.,

$$\begin{vmatrix}1+\frac{1}{4}N\langle\tanh(v_{AA}/kT_N)\rangle & +\frac{1}{4}N\langle\tanh(v_{AB}/kT_N)\rangle\\ +\frac{1}{4}N\langle\tanh(v_{AB}/kT_N)\rangle & 1+\frac{1}{4}N\langle\tanh(v_{BB}/kT_N)\rangle\end{vmatrix}=0, \tag{57}$$

where T_N is the Neél temperature. If v_{AB}/kT_N and v_{AA}/kT_N are small (i.e., long-range potential), the hyperbolic tangent may be replaced by its linear term and Eq. (57) is the usual Neél equation.

It would not be amiss to discuss here the possible outcome of a resonance experiment on random dilute antiferromagnetic samples.[9] We assume short-range forces and for simplicity spin $\frac{1}{2}$. Here most spins would remain uncoupled giving rise to the main line. The spins which occur in pairs are either singlets or triplets which are populated in the ratio 3:1 at high temperatures. As the temperature is lowered, singlet formation is favored and one should see the intensity in the main line diminish (the factor of three is a nice enhancement factor for the effect). If there is an anisotropy field, there is a possibility of seeing the singlet resonance in analogy to antiferromagnetic resonance. If this is so, one would see the singlet resonance grow as a function of temperature till it reaches four times its high-temperature value. One might also study the effects at higher concentrations to see when spin antialignment appears in clusters of spins. In general, such an experiment has the possibility of offering considerable insight into the onset of short-range order, perhaps including some kinetic information as well.

[9] The idea of a resonance experiment on dilute random systems was proposed to the authors by Dr. A. M. Clogston. Dr. R. H. Silsbee clarified my thinking to a considerable extent on this question.

ACKNOWLEDGMENT

In addition to those mentioned in the text, I should like to thank Dr. John Hopfield for many interesting conversations on almost all topics covered in this paper.

APPENDIX

We first calculate M_2 for $x=1$ taking into account the irreducibly linked combinations given in the text. These correspond to the two diagrams given in Figs. 4(a) and (b). Dashed line bonds are the factors (Fig. 1).

$$\begin{aligned}M_2=\sum_{i,j}\langle g_{ij}v_{ij}^2\rangle[\langle\mu_i^2\mu_j^2\rangle-\langle\mu_i\mu_j\rangle^2]\\+\sum_{ijk}\langle g_{ij}v_{ij}g_{jk}v_{jk}(g_{ik}-1)\rangle[\langle\mu_i\mu_j\mu_j\mu_k\rangle-\langle\mu_i\mu_j\rangle^2].\end{aligned} \tag{A1}$$

We evaluate this expression for nearest neighbor interactions of strength J on a square or cubic net to compare with other calculations.[10] Z is the number of

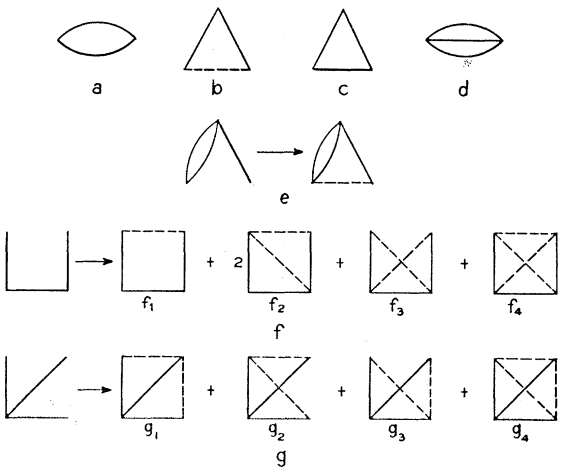

FIG. 4. Diagram of terms contributing to M_2 and M_3.

[10] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), pp. 273–280.

first neighbors. The first summation gives

$$\tfrac{1}{2}NZJ^2(1-R^4). \tag{A2}$$

To do the second summation, note there $N^3/3!$ triples, three orientations of the diagram and 2! ways to distribute the two solid bonds over the diagram. Thus there are N^3 terms. Finally since $(g_{ik}-1)=-\delta_{ik}$ we have

$$NZJ^2[\langle\mu_1\mu_2\mu_2\mu_3\rangle-\langle\mu_1\mu_2\rangle^2]=NZJ^2[R^2-R^4]. \tag{A3}$$

Adding (A2)+(A3) gives

$$M_2=\tfrac{1}{2}NZ(1-R^2)^2, \tag{A4}$$

which is the value given by ter Haar.[10]

We now proceed to the more complicated exercise of finding M_3. There are five sets of diagrams involving bonds containing magnetic interaction in reducible or irreducible linkages. These are given by Figs. 4(c) to (g). From each of these diagrams, one generates a set of irreducible diagrams by filling in with all possible combinations of dotted line diagrams. These "daughter" diagrams are indicated in the figure. We now evaluate these diagrams. This involves four factors: (1) the number of ways to choose the vertices out of N particles, i.e., $\binom{N}{\nu}$, (2) the number of ways to arrange the magnetic bonds on each figure among the ν vertices, (3) the number of distinct ways to place the n bonds on the given pattern, (4) the semi-invariant of the combination of μ's corresponding to the given diagram. These are all easy problems involving much less labor than the conventional method given in ter Haar. We proceed with a square or cubic net with nearest neighbor interactions only. Factors are given in the order set

FIG. 5. Diagrams leading to combinatorial factor in M_3.

above. In deriving the results below, we use $(g_{ij}-1)=-\delta_{ij}$.

Fig. 4(c) $=0$,

$$\text{Fig. 4(d)}=\tfrac{1}{2}N^2\langle g_{12}v_{12}{}^3\rangle[2R^6-2R^2]=-NZJ^3R^2(1-R^4),$$

$$\text{Fig. 4(e)}=\frac{N^3}{3!}\times 6\times\frac{3!}{2!1!}\langle g_{12}v_{12}{}^2g_{23}v_{23}(g_{31}-1)\rangle[2R^6-2R^4]$$
$$=6NZJ^3R^4(1-R^2),$$

$$\text{Fig. 4}(f_1)=\text{Fig. 4}(f_2)=\text{Fig. 4}(f_4)=0,$$

$$\text{Fig. 4}(f_3)=\frac{N^4}{4!}\times 12\times 3!\langle g_{12}v_{12}g_{23}v_{23}g_{34}v_{34}(g_{13}-1)(g_{23}-1)\rangle$$
$$\times[R^2-2R^4+R^6]=3NZJ^3R^2(1-R^2)^2,$$

$$\text{Fig. 4}(g_1)=\text{Fig. 4}(g_2)=\text{Fig. 4}(g_3)=-\text{Fig. 4}(g_4)$$
$$=\frac{N^4}{4!}\times 4\times 3!\times\langle g_{12}v_{12}g_{13}v_{13}g_{14}v_{14}(g_{34}-1)(g_{23}-1)\rangle$$
$$\times[2R^6-2R^4]=-2NZJ^3R^4(1-R^2).$$

The total of all diagrams is obtained by adding all the above results. It is $2NZR^2(1-R^2)^2$ which agrees with ter Haar's result.

The only difficult combinatory number in the above results is the factor of 12 appearing in Fig. 4(f_3). In Fig. 5 we give the three basic reducible diagrams of the type desired. Each has four orientations obtained by rotation or reflection, giving a factor of 12.

We close this Appendix by pointing out the obvious advantages of the present technique over the usual one. For one thing unlinked graphs do not appear at the outset. Thus for given R, one need compute semi-invariants on the μ variables only to $O(1)$. The usual method requires computation to $O(1/N;\ 1/N^2$, etc.). Further, the bookkeeping is made considerably easier. It is a matter of counting graphs and not of lattice counting.