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Many-Body Aspects of Dipolar Interaction in Crystal Lattices

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The moment expansion of the magnetic resonance line and the semi-invariant expansion of the free energy of a dipolar lattice are expressed in powers of the Hamiltonian. The expansions are looked at from the point of view of the number of particles in each term. Intercomparison is made of the terms in a density expansion and the moment expansions. The third and fourth semi-invariants of the simple cubic dipolar lattice are evaluated by a computing machine. The results suggest the general conclusion that the cycle diagrams predominate for dipolar interaction and a general formal expression for the contribution of the nth order diagram is derived. The calculation of the higher order moments and semi-invariants is, thus, simplified but still remains formidable. For the short-range exchange potential, on the other hand, the cycle diagrams do not predominate.

INTRODUCTION

THE physical properties of principal interest of a lattice of magnetic dipoles are the thermodynamic functions and the real and imaginary parts of the susceptibility. The thermodynamic functions and the real part of the susceptibility, χ' are derivable from the partition function

$$Z=\mathrm{Tr}[\exp(-\beta\mathcal{H}/kT)], \tag{1}$$

where $\mathcal{H}$ is the spin Hamiltonian. The absorption of energy from an oscillating field, on the other hand, is proportional to the imaginary part of the frequency-dependent susceptibility,

$$\chi''(\omega)=\frac{\omega V}{kT}\int_0^\infty \cos\omega t'\frac{\mathrm{Tr}[M_x(t')M_x]}{\mathrm{Tr}1}dt', \tag{2}$$

where ω is the frequency of the oscillating field and M_x is the x component of the total magnetic moment of the lattice whose volume is V. In the following we will use the abbreviation

$$\mathrm{Tr}(\theta)/\mathrm{Tr}1=\langle\theta\rangle,$$

where θ is any operator.

The evaluation of the traces in Eqs. (1) and (2) is of monumental difficulty and so far has been attacked only by the method of moments in which the various operators are expanded in powers of the Hamiltonian and the traces evaluated term by term. As one must for practical reasons truncate the series at an early stage, one is confined to high temperatures in the case of the partition function. As far as the absorption is concerned, one obtains theoretically only the first few moments which are difficult to measure precisely and not the half-width, which is easier to observe.

In recent years, there has been an extensive development of the statistical mechanics of many-body systems in particular of an electron gas, Bose and Fermi liquids, and systems with Ising interactions. The central theme of these new developments is the analysis of the various terms in the expansions according to the number of particles interacting. In the analysis each term is represented by a graph (a "diagram") and the aim is to find a subset of graphs which represents the most important terms of the entire series. For example, in nuclear matter which is relatively dilute the diagrams in which only two particles appear are of major importance, whereas in a dense electron gas, the cycle diagrams, those in which each particle appears only twice, predominate. The aim of the present paper is to investigate the dipolar lattice from this point of view.

I. MOMENTS OF MAGNETIC RESONANCE LINE SHAPES

The moments of a magnetic resonance absorption may be defined by the relation

$$\langle(\Delta\omega)^{2n}\rangle=\int g(\omega-\omega_0)(\omega-\omega_0)^{2n}d\omega, \tag{3}$$

where $g(\omega-\omega_0)$ is the line shape function with the line centered on ω_0. Van Vleck[1] has deduced the following general expression for the $(2n)$th moment:

$$\langle(\Delta\omega)^{2n}\rangle=\left(\frac{1}{\hbar}\right)^{2n}\frac{\mathrm{Tr}|[\mathcal{H},\cdots[\mathcal{H},S_x]\cdots]|^2}{\mathrm{Tr}|S_x|^2}. \tag{4}$$

The Hamiltonian describing the dipolar interaction in the lattice is given by

$$\mathcal{H}=\frac{1}{2}\sum_j{}'\sum_k\frac{g^2\beta^2}{r_{jk}^3}\left(\mathbf{S}_j\cdot\mathbf{S}_k-3\frac{(\mathbf{S}_j\cdot\mathbf{r}_{jk})(\mathbf{S}_k\cdot\mathbf{r}_{jk})}{r_{jk}^2}\right), \tag{5}$$

where g is the Landé g factor for the spins, β is the magneton (nuclear or electronic), and r_{jk} is the radius vector connecting spins i and j; but only the truncated

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[1] J. H. Van Vleck, Phys. Rev. 74, 1174 (1948).

Hamiltonian,

$$\mathcal{H}=\tfrac{1}{2}\sum_j{}'\sum_k\sum_{\alpha'}A_{jk}{}^{\alpha'}S_{j\alpha'}S_{k\alpha'},\tag{6}$$

which commutes with the Zeeman energy is used in (4).

The summation over α' runs over z, x, and y which correspond, respectively, to $\alpha'=0$, 1, and 2:

$$\begin{aligned}A_{jk}{}^{\alpha'}&=A_{jk},\quad \alpha'=1,2\\ A_{jk}{}^{\alpha'}&=C_{jk}=A_{jk}+B_{jk},\quad \alpha'=0,\end{aligned}\tag{7}$$

where

$$A_{jk}=-\tfrac{1}{3}B_{jk}=(g^2\beta^2/2r_{jk}{}^3)(3\cos^2\theta_{jk}{}^{-1})$$

for pure dipolar interaction. When there is an exchange interaction also present, $A_{jk}\neq-\tfrac{1}{3}B_{jk}$.

From an examination of the commutators in (4) and the commutation relations[2]

$$\begin{aligned}[S_\alpha,S_{\alpha+1}]&=iS_{\alpha-1},\\ [S_{\alpha-1},S_{\alpha+1}]&=-iS_\alpha,\end{aligned}\tag{8}$$

it can be shown that the $(2n)$th moment contains terms involving 2, 3, $\cdots$, $n+1$ particles. The classification of the various terms according to the number of simultaneously interacting particles is not only of mathematical interest. In a dilute lattice in which most of the dipoles are replaced by nonmagnetic atoms or nuclei, it is desirable to know the moments as a function of f, the fractional concentration of magnetic spins in the lattice. Each moment can be expanded in powers of f:

$$\langle(\Delta\omega)^{2n}\rangle=\sum_{k=1}^{n}C_k{}^{(2n)}f^k.\tag{9}$$

The aim of this section is to investigate the coefficients $C_k{}^{(2n)}$.

By a direct evaluation, using Eq. (4), one can deduce the second and fourth moments, as was first done by Van Vleck. The results are

$$\langle(\Delta\omega)^2\rangle=[S(S+1)/3\hbar^2]\sum_k{}'B_{jk}{}^2,\tag{10}$$

$$\langle(\Delta\omega)^4\rangle=\left\{3\Big(\sum_k B_{jk}{}^2\Big)^2-\frac{1}{3N}\sum\sum_{j\neq k\neq l}\sum B_{jk}{}^2(B_{jl}-B_{kl})^2\right.$$
$$\left.-\frac{1}{5}\sum_k B_{jk}{}^4\left[8+\frac{3}{2S(S+1)}\right]\right\}\left\{\frac{S(S+1)}{3\hbar^2}\right\}^2.\tag{11}$$

It is instructive to examine Eq. (11) in some detail. The various terms in Eqs. (10) and (11) may be represented by the diagrams in Fig. 1. In these diagrams each line represents a particle and each vertex an interaction between the two particles whose lines intersect. Several variations may be made of the diagrams involving 3 particles by changing the order of the vertices. Since each vertex represents the occurrence in the commutators in (4) of a specific term in the summation (5), the order of the vertices is of importance. The possible diagrams can also be written down by inspection remembering that

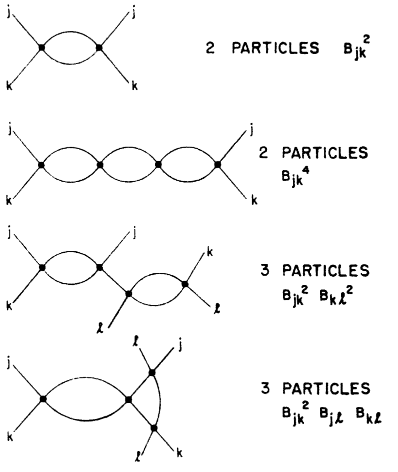


FIG. 1. Diagrammatic representation of the second and fourth moments of the magnetic resonance.

$$\mathrm{Tr}S_{xj}=\mathrm{Tr}S_{yj}=\mathrm{Tr}S_{zj}=0.$$

Therefore, in the expression for $(\Delta\omega)^{2n}$, no particle can take part in only one vertex in any diagram. This is why the term $B_{jk}{}^3B_{jl}$ represented by the diagram in Fig. 2 does not occur in the expression for the fourth moment. Keeping this rule in mind one can show that in the sixth moment, there will be basically one two-particle diagram, five three-particle diagrams and ten four-particle diagrams. A few of these diagrams are shown in Fig. 3.

There are no terms of the form $B_{jk}{}^5B_{kl}$ or $B_{jk}{}^3B_{kl}{}^2B_{lm}$. The contributions from terms involving $(n+1)$ particles in the $(2n)$th moment are easier to calculate than terms involving lesser number of particles for two reasons.

(a) The terms involving $(n+1)$ particles contain traces of products like $S_{zj}{}^2S_{xk}{}^2S_{yl}{}^2\cdots$ as contrasted to terms involving less than $(n+1)$ particles which involve traces of products like $S_{zj}{}^{2l}S_{xk}{}^{2m}\cdots$, where m and l are greater than unity.

(b) The $(n+1)$ particle term involves commutators of the form $U_{jklm\cdots}$ where

$$U_{jklm\cdots}=[\cdots[\mathcal{H}_{lm}[\mathcal{H}_{kl}[\mathcal{H}_{jk},S_{xj}]]]\cdots],\tag{12}$$

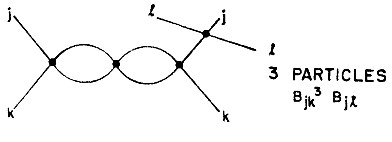
while the 2-particle term involves for example

$$U_{jk}=[\cdots[\mathcal{H}_{jk}[\mathcal{H}_{jk}[\mathcal{H}_{jk},S_{xj}]]]\cdots].\tag{13}$$

Evidently $U_{jklm\cdots}$ is much simpler to calculate than U_{jk}.

It is, therefore, very necessary to obtain information as to the relative contributions of diagrams involving

FIG. 2. Diagrammatic representation of a vanishing term in the three-particle fourth moment expression.



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[2] The subscripts α are understood to be congruent modulo 3 to 0, 1, 2.

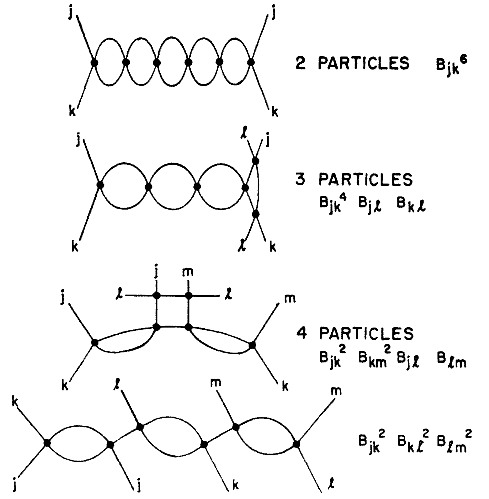

FIG. 3. Some two-, three-, and four-particle diagrams which contribute to the sixth moments.

2, 3, $\cdots (n+1)$ particles to the $(2n)$th moment. Before we do this, it will be useful to consider the case of a dilute lattice. An example of a dilute lattice is a paramagnetic species dissolved in a diamagnetic substance. At very low dilutions, only two-particle interactions will be significant, that is, one would have to consider only the term depending on f on the right-hand side of Eq. (9). With increasing concentration, one would have to consider three-particle interactions, i.e., the term involving f^2 in (9) and, subsequently, higher powers of f.

Kittel and Abrahams[3] have considered the f-dependent term in the moments of dilute spin-$\frac{1}{2}$ systems. They employed the following simple procedure. The truncated Hamiltonian for a two-spin system in a magnetic field in the z direction is given by

$$\mathcal{H} = -\gamma\hbar H(S_{1z}+S_{2z}) + A_{12}(S_{1x}S_{2x}+S_{1y}S_{2y}-2S_{1z}S_{2z}), \quad (14)$$

where γ is the magnetogyric ratio. For spin $\frac{1}{2}$, the energy levels are as shown in Fig. (4), where α_i and β_i correspond to the states of the ith spin with $m=\pm\frac{1}{2}$, respectively. Under the action of a radio-frequency field in the x direction, only the transitions shown, namely those between the energy levels of the triplet state differing by ±1 in the total magnetic quantum number are allowed. One would, thus, expect two lines of equal intensity at frequencies:

$$\omega = \gamma H \pm 3A_{12}/2\hbar = \gamma H \mp B_{12}/2\hbar.$$

The $2n$th moment is then given by

$$\langle(\Delta\omega)^{2n}\rangle = (1/2\hbar)^{2n}B_{12}^{2n}; \quad (15)$$

and, in general, for the f-dependent term in Eq. (9),

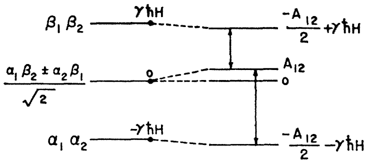

FIG. 4. Energy levels of two spin $\frac{1}{2}$ particles in a magnetic field interacting with each other via magnetic dipole-dipole interaction.

we have

$$C_1^{(2n)} = (1/2\hbar)^{2n} \textstyle\sum_k' B_{jk}^{2n}. \quad (16)$$

Andrew and Bersohn[4] have considered the energy levels of a three-spin system interacting through magnetic dipolar interaction only. The secular equation factors into two linear equations and two cubic equations, the latter further factoring into a quadratic and a linear equation each. From the energy levels and the intensities of the various allowed transitions, we have obtained the various moments by a procedure exactly similar to Kittel and Abrahams' procedure for two-spin systems. The expressions for the three-particle contributions to the fourth and sixth moments are given below.

$$C_2^{(4)} = (63/8) \textstyle\sum_{j,k,l\neq} [3A_{jk}^2A_{kl}^2 + (2/7)A_{jk}^2A_{kl}A_{jl}], \quad (17)$$

and

$$C_2^{(6)} = \frac{27}{128} \sum_{j,k,l\neq} \Big\{ 38A_{jk}^4A_{kl}^2 + 11A_{jk}^4A_{kl}A_{jl} - 21A_{jk}^3A_{kl}^3 + 5A_{jk}^3A_{jl}A_{kl} + \frac{63}{2}A_{jk}^2A_{kl}^2A_{lj}^2 \Big\}. \quad (18)$$

Equation (17) agrees exactly with the three-particle terms in (11) on substituting $A_{jk} = -\frac{1}{3}B_{jk}$. It is to be noted, however, that the contribution to the moments from three-particle diagrams cannot be obtained in an analytic form in the general case where we have some exchange interaction in addition to the dipolar interaction between the spins. In the general case,

$$A_{jk} \neq -\tfrac{1}{3}B_{jk} \quad (19)$$

and the factorization of the cubic equations in the secular equation referred to above, does not occur. Equations (16), (17), and (18) are not of much use in analyzing electron resonance line shapes in dilute crystals for in most cases we have appreciable exchange interaction and also hyperfine interaction with surrounding nuclei and the effects of these have to be incorporated. However, these equations enable us to obtain valuable information regarding the contributions of $(n+1)$-particle diagrams in the $(2n)$th moment relative to the contributions from diagrams involving

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[3] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

[4] E. R. Andrew and R. Bersohn, J. Chem. Phys. **18**, 159 (1950).

fewer particles. For the second moment, taking the case of a simple cubic lattice, with the magnetic field along one of the crystal axes [100], one gets for spin-$\frac{1}{2}$ nuclei, by carrying out the summation over k in Eq. (10),

$$\langle(\Delta\omega)^2\rangle=(\alpha/2\hbar)^2(59.837)=\mathcal{S}, \tag{20}$$

where $\alpha=g^2\beta^2/a^3$. Next, using Eqs. (16) and (17), one gets for the fourth moment,

$$\langle(\Delta\omega)^4\rangle=2.437\mathcal{S}^2 \tag{21}$$

which is the sum of the contributions $0.21\mathcal{S}^2$ from two-particle diagrams, and $2.227\mathcal{S}^2$ from three-particle diagrams. The two-particle contribution is, thus, 8.6% only of the total while the three-particle contribution is 91.4%.

For the sixth moment, the two- and three-particle contributions are given by Eqs. (16) and (18). We have obtained an expression for the contribution to the sixth moment from four-particle diagrams which is too cumbrous to present here. But we can use it to obtain the four-particle contribution to the sixth moment for any orientation of the field with respect to the crystal axes. However, Glebashev,[5] following the procedure of Van Vleck calculated the total sixth moment (sum of contributions from two, three, and four-particle diagrams) for a simple cubic lattice with magnetic field in the [100] direction. He obtains

$$\langle(\Delta\omega)^6\rangle=(\alpha/2\hbar)^6(131\,394.96)=0.6133\mathcal{S}^3. \tag{22}$$

Using Eqs. (16) and (18) we get

$(\alpha/2\hbar)^6(1002.4)=0.0047\mathcal{S}^3$ from two-particle diagrams,

$(\alpha/2\hbar)^6(2811.04)$
$=0.0132\mathcal{S}^3$ from three-particle diagrams,

and, therefore, from (22) one gets

$(\alpha/2\hbar)^6(127\,581.52)$
$=0.5955\mathcal{S}^3$ from four-particle diagrams.

Hence, the contribution from the two-particle diagrams is only 0.76%, from the three-particle diagrams it is 2.14%, and from four-particle diagrams 97.10%. It is, thus, reasonable to conclude that as the order of the moment ($2n$) increases, practically all of the contribution to the moment comes from $(n+1)$-particle diagrams. This result could have been anticipated since one expects the number of diagrams that one could obtain in the lattice with larger number of particles will be larger than the number of diagrams with lesser number of particles. But it would have been difficult to demonstrate this without actual calculation. The calculation of the moments higher than the sixth is still a laborious problem because in calculating $U_{jklm\cdots}$ at every place that $\mathcal{H}_{jk}$ occurs we can use $\alpha'=0$, 1, or 2 which lead to different results. However, the calculation is now relatively a lot simpler because we may omit the $2, 3, 4, \cdots, n$ particle contributions which are much more difficult to calculate.

Is there any practical—as opposed to conceptual—interest in the higher moments? In this connection we make use of an expansion discussed by Zernike[6] for an arbitrary even distribution $g(x)$ with second moment σ^2 in terms of the moments of Hermite polynomials:

$$g(x)=\frac{1}{(2\pi)^{1/2}\sigma}e^{-x^2/2\sigma^2}\left\{1+\sum_{n=4}^{\infty}\frac{C_n}{2^n n!}H_n\left(\frac{x}{\sqrt{2}\sigma}\right)\right\}, \tag{23}$$

where

$$C_n\equiv\int_{-\infty}^{\infty}g(x)H_n\left(\frac{x}{\sqrt{2}\sigma}\right)dx, \tag{24}$$

$$C_4=\langle x^4\rangle/\sigma^4-3, \tag{25}$$

$$C_6=\langle x^6\rangle/\sigma^6-15\langle x^4\rangle/\sigma^4+30. \tag{26}$$

All the C's are zero obviously if the distribution $g(x)$ is a Gaussian.

Let us consider the unknown distribution $g(x)$ for the classic case[7] of a simple cubic lattice of spin-$\frac{1}{2}$ nuclei with the field along the [100] axis. Not knowing the true line shape we can construct a theoretical line shape by assuming:

(a) A Gaussian function with the theoretical second moment, i.e., $C_n=0$, $n>2$;

(b) a function with the theoretical second and fourth moments as calculated by Van Vleck but with all higher moments the same as the Gaussian, i.e.,

$$C_4=-0.536,\quad C_n=0\quad\text{for}\quad n>4;$$

(c) a function with the theoretical second and fourth moments as calculated by Van Vleck and the theoretical sixth moment as calculated by Glebashev but with all higher moments the same as the Gaussian, i.e.,

$$C_4=-0.536,\quad C_6=-5.942,\quad C_n=0\quad\text{for}\quad n>6.$$

The results are plotted in Fig. 5 from which it is clear that an attempt to use correct higher moments results in a negligible change over the simple Gaussian approximation at least near the center of the line which is principally what is observed when a line shape is measured.

The cross-relaxation phenomenon, on the other hand, depends decisively on the overlap of the wings of two neighboring absorption curves. Bloembergen *et al.*[8] showed that the probability per unit time of mutual

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[5] I. Glebashev, Soviet Phys.—JETP **5**, 38 (1957).

[6] F. Zernike, in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1928), Vol. III, p. 448.

[7] G. E. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

[8] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

spin flips of two spins, j and k in two spin systems of resonance frequencies ν_α and ν_β is given by

$$w_{jk}=\frac{1}{\hbar^2}|\mathcal{H}_{jk}|^2\int\int g_\alpha(\nu')g_\beta(\nu'')\delta(\nu'-\nu'')d\nu'd\nu''$$

$$=\frac{1}{\hbar^2}|\mathcal{H}_{jk}|^2\frac{1}{2\pi^{1/2}\Delta\nu}e^{-(\nu_\alpha-\nu_\beta)^2/4(\Delta\nu)^2} \tag{27}$$

if

$$g_{\alpha,\beta}(\gamma)=e^{-(\nu-\nu_{\alpha,\beta})^2/2(\Delta\nu)^2}, \tag{28}$$

where $(\Delta\nu)$ is the root-mean-square second moment of the two lines which are assumed for simplicity to have the same shape. If we introduce the parameter $a=(\nu_\alpha-\nu_\beta)/\Delta\nu$, we have, from Eqs. (23) and (27), the following asymptotic form (for large a) for $\int g_\alpha(\nu)g_\beta(\nu)d\nu$, namely,

$$\frac{e^{-a^2/4}}{2\pi^{1/2}(\Delta\nu)}\left[1+2\sum_{p=2}\frac{C_{2p}a^{2p}}{2^p(2p)!}+\sum_{p=2}^{\infty}\sum_{q=2}^{\infty}\frac{C_{2p}C_{2q}a^{2(p+q)}}{2^{p+q}(2p)!(2q)!}+\cdots\right]. \tag{29}$$

What the numerical values show is that—judging on the basis of the C_4 and C_6 terms—the series in a hardly converges for $a\geqslant 3$. The value of the overlap deduced from the Gaussian function has no obvious validity.

The problem of the line shape is thus highlighted. What is really needed to determine the shape of the wings of the resonance curves are the high moments. A clue to the approximate calculation of these moments is the conjecture that in high order only the cycle diagram is of any importance. The unfinished tasks are to prove the conjecture and to act on it, that is to calculate the general $2n$th moment. The validity of the conjecture is related to the range of the potential. Wherever an interaction between a pair of particles j and k is repeated n times a factor r_{jk}^{-3n} occurs which considerably reduces the number of arrangements of lattice points with appreciable contributions. For the cycle diagram no inverse distance occurs to more than the third power; hence, the number of appreciable terms will be large. The importance of the cycle diagrams depends on the range of the potential, being maximum for Coulomb forces and least for exchange potentials limited to nearest neighbors.

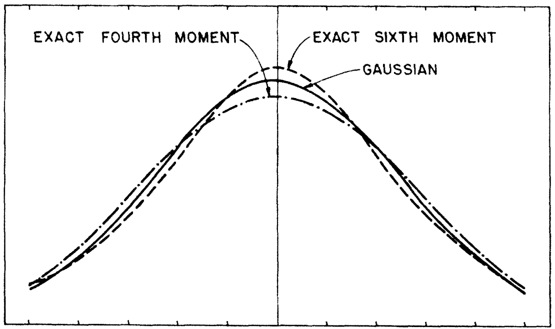

FIG. 5. Line shape for a simple cubic lattice of spin-$\frac{1}{2}$ dipoles with H_0 along the [100] axis. Abscissa is the field in units of the square root of the second moment which is the same for all curves.

II. PARTITION FUNCTION OF A LATTICE OF MAGNETIC DIPOLES

A. General Form of Semi-Invariants

The interaction of a lattice of magnetic dipoles was rigorously studied by Van Vleck[9] who expanded the partition function in powers of $\mathcal{H}/kT$. What is presented below is essentially a recalculation by a computer of Van Vleck's expansion and an interpretation of the various terms through the linked cluster expansion. It is not our intention to obtain quantitative results for comparison with experiment but merely to analyze the relative contributions from diagrams involving $1, 2, 3, \cdots, n$ particles. We shall, therefore, consider only the cases of pure exchange (Sec. III) and pure dipolar (Sec. II) interactions. In the general case when both interactions are present, there will be cross terms between the two interactions but these are omitted here.

The basic problem is to determine the partition function $\mathrm{Tr}e^{-\mathcal{H}/kT}$. The apparent impossibility of obtaining exact eigenvalues of this Hamiltonian forces one to approximate in some way. Here we investigate the high-temperature limit.

$$|\mathcal{H}|/kT\ll 1. \tag{30}$$

On expanding Z in powers of $1/T$ one finds

$$Z=\langle\mathcal{H}^0\rangle-\frac{\langle\mathcal{H}\rangle}{kT}+\frac{\langle\mathcal{H}^2\rangle}{2!(kT)^2}-\frac{\langle\mathcal{H}^3\rangle}{3!(kT)^3}+\cdots, \tag{31}$$

where the nth moment $\langle\mathcal{H}^n\rangle$ is defined by

$$\langle\mathcal{H}^n\rangle=\mathrm{Tr}(\mathcal{H}^n)/\mathrm{Tr}(\mathcal{H}^0)=M_n. \tag{32}$$

The matrix $(\mathcal{H}^n)$ would have $(2S+1)^N$ dimensions in our case where S is the spin of each particle and N is the total number of particles. In general, M_n will contain terms proportional to N, N^2, N^3, $\cdots$, etc. The terms not proportional to N are physically meaningless and would have to cancel out in any expression for an observable. Also it is rather laborious to compute $\ln Z$ from Eq. (4). Both these difficulties can be avoided by using the method of semi-invariants,[10] viz.,

$$\ln Z=\sum_{n=0}^{\infty}(\lambda_n/n!)(1/kT)^n, \tag{33}$$

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[9] J. H. Van Vleck, J. Chem. Phys. 5, 320 (1937).

[10] J. G. Kirkwood, J. Chem. Phys. 6, 70 (1938).

where the λ_n satisfy the equations

$$\sum_{m=1}^{n}\binom{n-1}{m-1}\lambda_m M_{n-m}=M_n. \tag{34}$$

Expressions for a few of the semi-invariants of lower order are given below:

$$\begin{aligned}
\lambda_1&=M_1,\\
\lambda_2&=M_2-M_1^2,\\
\lambda_3&=M_3-3M_1M_2+2M_1^3,\\
\lambda_4&=M_4-2M_1M_3-3M_2^2+12M_1^2M_2-6M_1^4,\\
\lambda_5&=M_5-5M_1M_4-10M_2M_3+12M_1^2M_3\\
&\quad+30M_1M_2^2-60M_1^2M_3+6M_1^5.
\end{aligned} \tag{35}$$

In the cases of pure exchange and pure dipolar interaction, $\mathcal{H}_{kj}$ is given, respectively, by

$$\mathcal{H}_{kj}=-J\mathbf{S}_k\cdot\mathbf{S}_j \tag{36}$$

and Eq. (5), where J is the exchange coupling.

From Eqs. (32), (36), and (5),

$$\lambda_1=M_1=\textstyle\sum_{j<k}\langle\mathcal{H}_{jk}\rangle=0, \tag{37}$$

which simplifies the semi-invariants as follows:

$$\begin{aligned}
\lambda_2&=M_2,\\
\lambda_3&=M_3,\\
\lambda_4&=M_4-3M_2^2,\\
\lambda_5&=M_5-10M_2M_3.
\end{aligned} \tag{38}$$

It can easily be seen from Eqs. (32) and (34) that λ_n involves contributions from 2, 3, 4, $\cdots$, n particles. One can assemble the contributions to λ_n from terms involving different numbers of particles as follows:

$$\lambda_2=\textstyle\sum_{j<k}\langle\mathcal{H}_{jk}^2\rangle, \tag{39a}$$

$$\lambda_3=\sum_{j<k}\langle\mathcal{H}_{jk}^3\rangle+\sum_{j\neq k\neq l}\sum\sum\langle\mathcal{H}_{jk}\rangle\langle\mathcal{H}_{kl}\rangle\langle\mathcal{H}_{lj}\rangle, \tag{39b}$$

$$\begin{aligned}
\lambda_4=\sum_{j<k}\left[\langle\mathcal{H}_{jk}^4\rangle-3\langle\mathcal{H}_{jk}^2\rangle^2\right]+\sum_{j\neq k\neq l}&\left[4\langle\mathcal{H}_{jk}^2\mathcal{H}_{kl}\mathcal{H}_{lj}\rangle+2\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{jk}\mathcal{H}_{lj}\rangle+2\langle\mathcal{H}_{jk}^2\mathcal{H}_{kl}^2\rangle+\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{jk}\mathcal{H}_{kl}\rangle\right.\\
&\left.-3\langle\mathcal{H}_{jk}^2\rangle\langle\mathcal{H}_{kl}^2\rangle\right]+\sum_{j\neq k\neq l\neq m}\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{lm}\mathcal{H}_{mj}\rangle+3\sum_{j,k\neq l,m}\left[\langle\mathcal{H}_{jk}^2\mathcal{H}_{lm}^2\rangle-\langle\mathcal{H}_{jk}^2\rangle\langle\mathcal{H}_{lm}^2\rangle\right].
\end{aligned} \tag{40}$$

It is useful to write this equation in a symbolic fashion representing each term or group of terms by a diagram with a line segment representing each pair interaction. Figure 6 shows symbolically the various contributions to the first three semi-invariants. Diagrams can be classified as connected, disconnected or reducible. A disconnected diagram contains separate diagrams with no vertices in common. A reducible diagram contains two diagrams with one vertex in common. All the diagrams in Fig. 6 are irreducible (except the next to the last).

One can see that disconnected diagrams contain independent summations over lattice points, and therefore, are proportional to higher powers of N, the number of particles in the system. They, therefore, do not represent any physically observable quantity and should not appear in the expression for the free energy. It has been shown quite rigorously by Bloch and de Dominicis[11] that unlinked diagrams cancel in all orders as they must. One has the paradox that Z contains unlinked clusters in its expansion according to powers of $1/T$ but that the free energy $-kT\ln Z$ contains no such terms. The explanation is that the contribution of the unlinked clusters can be factored from the contribution of the linked clusters and added together to give $-kT\ln 1$.

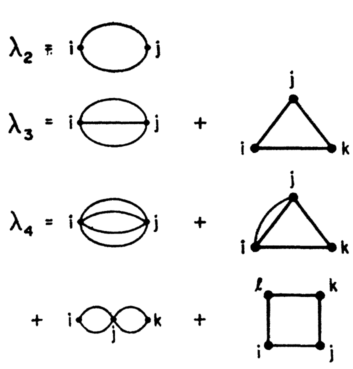

FIG. 6. Diagrammatic representation of the first three semi-invariants. The vertices of the diagrams represent particles and the lines the interaction $\mathcal{H}_{ij}$ between them.

The reducible diagrams do not cancel. It was shown by Brout[12] that in the Ising model the reducible diagrams cancel but this is because Hamiltonians $\mathcal{H}_{ij}$ and $\mathcal{H}_{jk}$ commute with each other. In quantum mechanics the noncommuting Hamiltonian operators give rise to nonvanishing contributions from reducible diagrams. These contributions should become smaller as the spin S of the individual dipole increases.

B. Evaluation of Semi-Invariants of Dipolar Lattices

1. *Calculation of* λ_2

The semi-invariants λ_2, λ_3, and λ_4 are again given by Eqs. (35) and $\mathcal{H}_{jk}$ by Eq. (5). For λ_2 we, then, have

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[11] C. Bloch and C. de Dominicis, Nucl. Phys. 7, 459 (1958).

[12] R. Brout, Phys. Rev. 115, 824 (1959).

$$\lambda_2=\textstyle\sum_{j<k}\langle\mathcal{H}_{jk}^2\rangle=g^4\beta^4\sum_{j<k}r_{jk}^{-6}[\langle(\mathbf{S}_k\cdot\mathbf{S}_j)^2\rangle-6\langle(\mathbf{S}_k\cdot\mathbf{S}_j)(\mathbf{S}_k\cdot\mathbf{r}_{jk})(\mathbf{S}_j\cdot\mathbf{r}_{jk})r_{jk}^{-2}\rangle+9\langle(\mathbf{S}_j\cdot\mathbf{r}_{jk})^2(\mathbf{S}_k\cdot\mathbf{r}_{jk})^2r_{jk}^{-4}\rangle]. \tag{41}$$

Taking the necessary traces, one has

$$\lambda_2=\tfrac{2}{3}g^4\beta^4S^2(S+1)^2\textstyle\sum_{j<k}r_{jk}^{-6}=g^4\beta^4S^2(S+1)^2(5.58)Na^{-6} \tag{42}$$

for a simple cubic lattice with interatomic spacing a.

2. *Calculation of* λ_3

λ_3 according to (39b) contains a two-particle as well as a three-particle term. The two-particle term is

$$\begin{aligned}\lambda_3^{(2)}&=\sum_{j<k}\langle\mathcal{H}_{jk}^3\rangle=g^6\beta^6\frac{S^2(S+1)^2}{3}\sum_{j<k}r_{jk}^{-9}\\&=g^6\beta^6S^2(S+1)^2N(2.210)a^{-9},\end{aligned} \tag{43}$$

for a simple cubic lattice. The three-particle term is

$$\lambda_3^{(3)}=g^6\beta^8\frac{S^3(S+1)^3}{9}\sum_{j<k<l}\sum\sum[1-3+3(\cos^2\gamma_{jkl}+\cos^2\gamma_{klj}+\cos^2\gamma_{ljk})-9\cos\gamma_{jkl}\cos\gamma_{klj}\cos\gamma_{ljk}](r_{jk}r_{kl}r_{lj})^{-3}, \tag{44}$$

where γ_{jkl} is the angle between the vectors $\mathbf{r}_{kj}$ and $\mathbf{r}_{lk}$. Subsequently, we shall also use the notation of $\gamma_{jk,kl}$ for γ_{jkl}.

The value obtained by a computer summation for this series on a simple cubic lattice is

$$\lambda_3^{(3)}=g^6\beta^6S^3(S+1)^3N\times 23.69a^{-9}. \tag{45}$$

It is worth commenting about the technique of summation. Each particle index j, k travels over a cubic section of the lattice whose eight vertices are given by $\pm n$, $\pm n$, $\pm n$. For $n=1, 2, 3, 4$ the cumulative sums are, respectively, 7.980, 19.27, 22.48, 23.69. In contrast, Van Vleck estimated 3.68 from the contribution of all right triangles with a given vertex multiplied by a factor of 1.3 to take into account other contributions. The machine calculations show that the number of triangles with small contributions is so large that their total contribution predominates. It is obviously not clear how close the quoted result is to the true value but the length of the calculation even on the IBM 7090 forbids use of more terms.

Collecting terms we have

$$\lambda_3=\lambda_3^{(2)}+\lambda_3^{(3)}=\frac{Ng^6\beta^6S^2(S+1)^2}{a^9}\times[2.210+23.69S(S+1)], \tag{46}$$

from which result it is clear that the cycle diagram predominates.

3. *Calculation of* λ_4

As shown in Eq. (40), λ_4 contains terms involving two, three, and four particles, i.e., $\lambda_4=\lambda_4^{(2)}+\lambda_4^{(3)}+\lambda_4^{(4)}$. $\lambda_4^{(2)}$ is, according to Eq. (40c),

$$\begin{aligned}\textstyle\sum_{j<k}[\langle\mathcal{H}_{jk}^4\rangle-3\langle\mathcal{H}_{jk}^2\rangle\langle\mathcal{H}_{jk}^2\rangle]&=g^8\beta^8S^4(S+1)^4\sum_{j<k}r_{jk}^{-12}\left[\left(\frac{24}{25}-\frac{16}{25}\frac{11}{S(S+1)}+\frac{11}{25}\frac{1}{S^2(S+1)^2}\right)-\frac{4}{3}\right]\\&=Ng^8\beta^8S^4(S+1)^4a^{-12}\left(-\frac{28}{75}-\frac{16}{25}\frac{1}{S(S+1)}+\frac{11}{25}\frac{1}{S^2(S+1)^2}\right)(6.202),\end{aligned} \tag{47}$$

for a simple cubic lattice.

$\lambda_4^{(3)}$ is composed of two different types of terms (c.f., Fig. 6), the "triangle bubble" and the "double bubble". The triangle bubble consists of the terms

$$\textstyle\sum_{j\neq k\neq l}[4\langle\mathcal{H}_{jk}\mathcal{H}_{kl}^2\mathcal{H}_{lj}\rangle+2\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{lj}\mathcal{H}_{kl}\rangle]. \tag{48}$$

After a lengthy calculation one finds

$$\begin{aligned}\langle\mathcal{H}_{jk}\mathcal{H}_{kl}^2\mathcal{H}_{lj}\rangle=-\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{kj}\mathcal{H}_{kl}\rangle=S^3(S+1)^3g^8\beta^8r_{jk}^{-3}r_{kl}^{-6}r_{lj}^{-3}\Bigg[&\tfrac{1}{6}-\tfrac{1}{6}\cos^2\gamma_{kjl}-\frac{1}{6}\frac{(\mathbf{r}_{jl}\times\mathbf{r}_{kl})^2}{r_{jl}^2r_{kl}^2}-\frac{1}{6}\frac{(\mathbf{r}_{jk}\times\mathbf{r}_{kl})^2}{r_{jk}^2r_{kl}^2}\\&+\frac{1}{2}\frac{(\mathbf{r}_{jk}\cdot\mathbf{r}_{jl})(\mathbf{r}_{jk}\times\mathbf{r}_{kl})\cdot(\mathbf{r}_{jl}\times\mathbf{r}_{kl})}{r_{jk}^2r_{jl}^2r_{kl}^2}\Bigg].\end{aligned} \tag{49}$$

A machine calculation out to $n=4$ gives for the total contribution of the triangle bubble on a simple cubic lattice

$$NS^3(S+1)^3(g^8\beta^8/a^{12})(64.62). \tag{50}$$

The double bubble consists of the terms

$$\sum_{j\neq k\neq l}[2\langle\mathcal{H}_{jk}{}^2\mathcal{H}_{kl}{}^2\rangle+\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{jk}\mathcal{H}_{kl}\rangle-3\langle\mathcal{H}_{jk}{}^2\rangle\langle\mathcal{H}_{kl}{}^2\rangle]. \tag{51}$$

Lengthy calculations yield the results

$$\langle\mathcal{H}_{jk}{}^2\mathcal{H}_{kl}{}^2\rangle=\frac{S^3(S+1)^3g^2\beta^2}{r_{jk}{}^6r_{kl}{}^6}\left\{\left[\frac{2}{5}S(S+1)+\frac{1}{30}\right]+\left[\frac{2}{15}S(S+1)-\frac{1}{10}\right]\frac{(\mathbf{r}_{jk}\cdot\mathbf{r}_{kl})^2}{r_{jk}{}^2r_{kl}{}^2}\right\}, \tag{52}$$

$$\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{jk}\mathcal{H}_{kl}\rangle=\frac{S^3(S+1)^3g^2\beta^2}{r_{jk}{}^6r_{kl}{}^6}\left\{\left[\frac{2}{5}S(S+1)-\frac{7}{15}\right]+\left[\frac{2}{15}S(S+1)+\frac{1}{15}\right]\frac{(\mathbf{r}_{jk}\cdot\mathbf{r}_{kl})^2}{r_{jk}{}^2r_{kl}{}^2}\right\}, \tag{53}$$

$$\langle\mathcal{H}_{jk}{}^2\rangle\langle\mathcal{H}_{kl}{}^2\rangle=\frac{4}{9}S^4(S+1)^4g^8\beta^8\frac{1}{r_{jk}{}^6r_{kl}{}^6}. \tag{54}$$

The total of the double bubble is, then,

$$\sum_{j\neq k\neq l}\{S(S+1)\}^3\left[\left(\frac{6}{5}S(S+1)-\frac{2}{5}\right)+\left(\frac{2}{5}S(S+1)-\frac{2}{15}\right)\frac{(\mathbf{r}_{jk}\cdot\mathbf{r}_{kl})^2}{r_{jk}{}^2r_{kl}{}^2}-\frac{4}{9}S(S+1)\right]\frac{g^8\beta^8}{r_{jk}{}^6r_{kl}{}^6}. \tag{55}$$

On a cubic lattice,

$$\sum_{j\neq k\neq l}\frac{(\mathbf{r}_{jk}\cdot\mathbf{r}_{kl})^2}{r_{jk}{}^2r_{kl}{}^2}\frac{1}{r_{jk}{}^6r_{kl}{}^6}=\tfrac{1}{3}\sum_{j\neq k\neq l}\frac{1}{r_{jk}{}^6r_{kl}{}^6}, \tag{56}$$

so we have as a final sum

$$g^8\beta^8S^3(S+1)^3\left[\frac{28}{45}S(S+1)-\frac{4}{9}\right]\sum_{j\neq k\neq l}\frac{1}{r_{jk}{}^6r_{kl}{}^6}. \tag{57}$$

The cumulative sum has the value N/a^{12} times 45.53, 66.47, 69.28, 70.00 when n takes on the values 1, 2, 3, 4, respectively. The final contribution of the double bubble is

$$NS^3(S+1)^3\frac{g^8\beta^8}{a^{12}}\left[\frac{28}{45}S(S+1)-\frac{4}{9}\right](70.00). \tag{58}$$

$\lambda_4{}^{(3)}$, the sum of the triangle bubble and double bubble contributions is

$$NS^4(S+1)^4(g^8\beta^8/a^{12})[43.55-(33.51)/S(S+1)]. \tag{59}$$

The four-particle contribution to λ_4, the square diagram is given by

$$\sum\sum\sum_{j\neq k\neq l\neq m}\sum\langle\mathcal{H}_{jk}\mathcal{H}_{kl}\mathcal{H}_{lm}\mathcal{H}_{mj}\rangle=g^8\beta^8\frac{\{S(S+1)\}^4}{27}\sum\sum\sum_{j\neq k\neq l\neq m}\sum r_{jk}{}^{-3}r_{kl}{}^{-3}r_{lm}{}^{-3}r_{mj}{}^{-3}$$

$$\times[1-4+3(\cos^2\gamma_{jm,lm}+\cos^2\gamma_{jk,kl}+\cos^2\gamma_{jk,jm}+\cos^2\gamma_{jm,kl}+\cos^2\gamma_{lm,kl}+\cos^2\gamma_{jk,lm}) \tag{60}$$

$$-9(\cos\gamma_{mj,kl}\cos\gamma_{mj,lm}\cos\gamma_{kl,lm}+\cos\gamma_{lm,kl}\cos\gamma_{kl,jk}\cos\gamma_{lm,jk}+\cos\gamma_{kl,jk}\cos\gamma_{jk,mj}\cos\gamma_{kl,mj}$$

$$+\cos\gamma_{jk,mj}\cos\gamma_{lm,mj}\cos\gamma_{jk,lm})+27\cos\gamma_{mj,kl}\cos\gamma_{jk,mj}\cos\gamma_{jk,kl}\cos\gamma_{lm,mj}]$$

$$=[g^8\beta^3S^4(S+1)^4/a^{12}]\times\text{constant}. \tag{61}$$

The determination of the constant in the above equation is far more difficult than with the other summations. For with three particles indices to be summed over the number of terms necessary is $(2n+1)^9$ which for $n>2$ is too lengthy on the presently available IBM 7090. For $n=1, 2$ the constant is 14.33, 48.73, respectively. This is as far as we can go at present. If we write

$$\lambda_4{}^{(4)}>(g^8\beta^8/a^{12})NS^4(S+1)^4(48.73), \tag{62}$$

it is clear that

$$\lambda_4^{(4)}>\lambda_4^{(3)}\gg\lambda_4^{(2)}. \tag{63}$$

Although we have failed to obtain a numerical value for λ_4, Eqs. (46) and (63) clearly indicate that in calculating λ_n, $\lambda_n^{(n)}$ will be of real importance. Only the cycle diagrams in all probability need to be considered. In spite of the failure in the present paper, the suggested hypothesis could be tested with the use of more highly convergent series for the dipole sums.

C. General Expression for Cycle Diagram

Inspection of Eqs. (44) and (60) shows that it is possible to write down the general form of the cycle diagram with n particles because the trace of any particular product of n operators of the form $\mathcal{H}_{ij}\mathcal{H}_{jk}\mathcal{H}_{kl}\cdots$ can be evaluated. The general expression

$$\begin{aligned}\lambda_n^{(n)}=g^{2n}\beta^{2n}\frac{S^n(S+1)^n}{3^{n-1}}\sum_{i\neq j\neq k\neq\cdots}\Big[1-n+3\sum_{\alpha}\cos^2\gamma_\alpha-9\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\cos\gamma_\alpha\cos\gamma_\beta\cos\gamma_\gamma\\ +27\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}\cos\gamma_\alpha\cos\gamma_\beta\cos\gamma_\gamma\cos\gamma_\delta\\ +\cdots+\sum_{\alpha\beta\gamma\cdots n}\cdots\sum\cos\gamma_\alpha\cos\gamma_\beta\cdots\cos\gamma_n(-)^n3^{n-1}\Big]r_{12}^{-3}r_{23}^{-3}\cdots r_{n,1}^{3},\end{aligned} \tag{64}$$

is where γ_α, γ_β, $\cdots$ refer to angles between pairs of sides of the n-particle cycle diagram.

If $\lambda_n\cong\lambda_n^{(n)}$ then, formally, Eq. (64) constitutes the solution to the dipole-dipole interaction problem. This equation clearly needs to be investigated further but one definite result can be extracted without evaluating the n-particle sums. If the dipolar lattice possesses a Curie temperature, it will be proportional to the limiting ratio λ_n/λ_{n-1},[13] hence to $S(S+1)$. The results obtained above will be relevant to future measurements on nuclear magnetic dipole systems at extremely low temperatures.

D. Classical Dipolar Lattice

Rosenberg and Lax[14] have reorganized the terms of Van Vleck's treatment of a lattice of classical dipoles in a fashion exactly analogous to our reorganization of Van Vleck's treatment of a lattice of quantized magnetic dipoles. Their treatment included four basic diagrams shown in Fig. 7. Term C corresponds to the ordinary dipole sum whose value depends on the shape of the sample. R, T, and S are the shape-independent higher order terms which we have described as the second-order bubble, the triangle, and the third-order bubble. In Lax's words C represents the direct action of dipoles j and k, whereas the higher diagrams represent the reactions of dipole j on itself via one or more intermediate dipoles. The effective molecular polarizability α_s can be written as a series in $N\alpha$, where α is the isolated molecular polarizability.

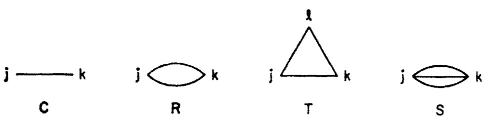

FIG. 7. Two- and three-particle diagrams representing interactions on the dipolar lattice.

$$\alpha_s=\alpha\{1-R(N\alpha)^2+[T+(4/25)S](N\alpha)^3+\cdots\}. \tag{65}$$

For a simple cubic lattice $(4/25)S$ is 2.12 and T is 38.7, leading to the now familiar conclusion concerning the cycle diagrams.

Lax makes another point: The spherical model of Kac and Berlin[15] corresponds to the omission of diagram S. The spherical model originally introduced for the Ising system and generalized by Lax[16] to the classical dipole moment only requires that

$$\textstyle\sum_{n=1}^{N}\mu_i^2=N, \tag{66}$$

where μ_i is an erstwhile unit vector with the orientation of the ith dipole. A more stringent requirement is $\mu_i^2=1$.

The restriction of a partition function to cycle diagrams implies that the individual dipoles are as independent as possible and that the density is very high. Brout[17] has shown, for the Ising model, the restriction to cycle diagrams corresponds to a Gaussian distribution for the μ_i^2. The spherical approximation is only slightly more restrictive and it is plausible, but not proved, that the spherical model gives results close to the approximation of using only cycle diagrams.

E. Dilute Lattices

In one special case the partition function can be calculated accurately. This is the case of particles with spin $\frac{1}{2}$ in a dilute lattice, as for example, paramagnetic ions dissolved in a diamagnetic material. Brout has calculated the partition function of a dilute lattice where only the exchange interaction is considered.

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[13] G. S. Rushbrooke and P. J. Wood, Proc. Phys. Soc. (London) **A68**, 1161 (1955).

[14] R. Rosenberg and M. Lax, J. Chem. Phys. **21**, 424 (1953).

[15] T. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).

[16] M. Lax, J. Chem. Phys. **20**, 1351 (1952).

[17] R. Brout, Phys. Rev. **118**, 1009 (1960).

The partition function Z is given by

$$\langle\exp(-\sum_{j<k}\beta\mathcal{H}_{jk})\rangle=\langle\prod_{j<k}[1+\exp(-\beta\mathcal{H}_{jk})-1]\rangle$$
$$=1+\sum_{j<k}\langle\exp(-\beta\mathcal{H}_{jk})-1\rangle$$
$$+(3,4,\cdots,N\text{-particle terms}),\quad (67)$$

where $\beta=1/kT$, not to be confused with the magneton or spin function.

Suppose that the N lattice points are not all occupied by spins but only have an average fractional occupancy f. The partition function is to be averaged over an ensemble of different crystals with the Nf paramagnetic spins on random sites. Then

$$\langle Z\rangle=1+\sum_{n=2}^{Nf}Z_nf^n.\quad (68)$$

The two-particle term is

$$Z_2=\sum_{j<k}\langle\exp(-\beta\mathcal{H}_{jk})-1\rangle.\quad (69)$$

The average in brackets needs to be taken only over the known energy levels of the two-spin system, i.e.,

$$Z_2=\sum_{j<k}\sum_\alpha[\exp(-\beta E_\alpha{}^{jk})-1],\quad (70)$$

where $E_\alpha{}^{jk}$ is the energy eigenvalue of the two-spin system (jk) for the state α. (There are four such states corresponding to the three triplet and one singlet state.) The energy eigenvalues are obtained from the Hamiltonian given by the sum of the terms (5) and (36). The eigenvalues and corresponding eigenfunctions are

$$\begin{aligned}E_1{}^{jk}&=-\tfrac{1}{2}g^2\beta^2r_{jk}{}^{-3}-\tfrac{1}{4}J_{jk}, && \alpha_j\alpha_k\\ E_2{}^{jk}&=-\tfrac{1}{2}g^2\beta^2r_{jk}{}^{-3}-\tfrac{1}{4}J_{jk}, && \beta_j\beta_k\\ E_3{}^{jk}&=\quad g^2\beta^2r_{jk}{}^{-3}-\tfrac{1}{4}J_{jk}, && (1/\surd 2)(\alpha_j\beta_k+\beta_j\alpha_k)\\ E_4{}^{jk}&=-\tfrac{3}{4}g^2\beta^2r_{jk}{}^{-3}+\tfrac{3}{4}J_{jk}, && (1/\surd 2)(\alpha_j\beta_k-\beta_j\alpha_k).\end{aligned}\quad (71)$$

Putting $g^2\beta^2r_{jk}{}^{-3}=K_{jk}$ we have

$$Z_2=\sum_{j<k}[\tfrac{1}{4}(2e^{\beta(K_{jk}/2+J_{jk}/4)}+e^{-\beta(K_{jk}-J_{jk}/4)}$$
$$+e^{\frac{3}{4}\beta(K_{jk}-J_{jk})})-1].\quad (72)$$

If we put $K_{jk}=0$, then Eq. (72) reduces to Brout's equation. One can use Eq. (72) for Z to obtain the magnetic specific heat of dilute solid solutions when only the f-dependent term is important, viz:

$$\frac{C_V}{k}=\frac{\partial}{\partial\beta}\Bigg[\beta^2\frac{\partial}{\partial\beta}\ln(1+f\sum_{j<k}[\tfrac{1}{4}(2e^{\beta(K_{kj}+J_{kj}/4)}$$
$$+e^{-\beta(K_{jk}-J_{jk}/4)}+e^{\frac{3}{4}\beta(K_{jk}-J_{jk})})-1])\Bigg].\quad (73)$$

III. EXCHANGE COUPLED LATTICES

The high-temperature expansion of the partition function of a lattice whose dipoles interact via a nearest neighbor exchange interaction has been carried out extensively by Rushbrooke and Wood.[18,19]

The formalism of Sec. II can be applied to the calculation of the semi-invariants for this system. For example,

$$\lambda_2=\sum_{j<k}\langle\mathcal{H}_{jk}{}^2\rangle=J^2\sum_{j<k}\sum_\alpha\langle S_{j\alpha}{}^2\rangle\langle S_{k\alpha}{}^2\rangle,\quad (74)$$

where the summation over α extends over the three components x, y, and z. As $\mathrm{Tr}S_\alpha{}^2=S(S+1)/3$, one has

$$\lambda_2=[J^2S^2(S+1)^2/3]\sum_{j<k}\text{“lines”}.\quad (75)$$

Corresponding for λ_3, one gets

$$\lambda_3=\frac{-J^3S^2(S+1)^2}{6}\sum_{j<k}\text{“lines”}$$
$$+\tfrac{2}{3}J^3S^3(S+1)^3\sum_{j<k<l}\text{“closed triangles,”}\quad (76)$$

and for λ_4

$$\lambda_4=\frac{J^4S^2(S+1)^2}{5}\left[S^2(S+1)^2-\frac{7}{3}S(S+1)+\tfrac{2}{3}\right]\sum_{j<k}\text{“lines”}$$
$$-\tfrac{2}{3}J^4S^3(S+1)^3\sum_{j<k<l}(\text{“closed triangles”}$$
$$+\text{“open triangles”})+\frac{8}{9}J^4S^4(S+1)^4$$
$$\times\sum_{j<k<l<m}\text{“quadrilaterals”}.\quad (77)$$

The summands of the above equations are lines, closed triangles, open triangles, and quadrilaterals connecting lattice points. In all these polygons, each side has to be one joining nearest neighbors because the exchange interaction vanishes between non-nearest neighbors. One can evaluate these summations by counting the number of two point line diagrams, triangles, etc., around any lattice point as origin. Thus,

$$\sum_{j<k}\text{“lines”}=Nz/2,\quad (78a)$$

$$\sum_{j<k<l}\text{“closed triangles”}=Nq_3z/6,\quad (78b)$$

$$\sum_{j<k<l}\text{“open triangles”}=Nz(z-1)/6,\quad (78c)$$

$$\sum_{j<k<l<m}\text{“quadrilaterals”}=Nq_4z/8,\quad (78d)$$

and, in general,

$$\sum_{j<k<l<\cdots}n\text{-sided cycle diagram}=Nq_nz/2n.\quad (78e)$$

In Eqs. (78), z is the number of nearest neighbors around any lattice point, q_3 is the number of triangles with sides equal to nearest neighbor distances around a lattice point as vertex, $\cdots$, and q_n is the number of n-sided figures with sides equal to nearest neighbor distances around a lattice point as vertex.

If Eqs. (78) are substituted into Eqs. (77) and (76),

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[18] P. J. Wood and G. S. Rushbrooke, Proc. Phys. Soc. (London) **A70**, 765 (1957).

[19] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).

one obtains

$$\lambda_3=\frac{J^3S^2(S+1)^2Nz}{12}[-1+8S(S+1)q_3]$$
$$=\lambda_3{}^{(2)}+\lambda_3{}^{(3)}, \quad (79)$$
$$\lambda_4=\frac{J^4S^2(S+1)^2Nz}{15}\biggl\{[1-\tfrac{7}{2}S(S+1)+\tfrac{3}{2}S^2(S+1)^2]$$
$$-\frac{5}{3}[q_3+S(S+1)(z-1)]+\frac{5}{3}q_4S^2(S+1)^2\biggr\}$$
$$=\lambda_4{}^{(2)}+\lambda_4{}^{(3)}+\lambda_4{}^{(4)}. \quad (80)$$

The individual terms inside the curly brackets correspond to increasing numbers of particles. For the simple cubic lattice $z=6$, $q_3=0$, $q_4=12$, for the face-centered cubic lattice $z=12$, $q_3=0$, and $q_4=6$. Inspection of Eqs. (80) and (79) shows that there is no particular predominance of any one sort of diagram over another as was observed in the longer range dipole-dipole potential problem.

The Curie point has been inferred by Rushbrooke and Wood[17] to be proportional to $S(S+1)$. A sufficient condition for this is that the ring diagrams predominate in their contributions, for the ring diagram with n vertices has a factor $[S(S+1)]^n$. The results on λ_3 and λ_4, however, confirm one's intuitive feeling that for a very short range potential the cycle diagrams do not predominate. In contrast to the situation with the dipolar lattice, it is, therefore, not possible to obtain a natural explanation for the $S(S+1)$ dependence of the Curie temperature for an exchange-coupled lattice.

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Use of Green Functions in the Theory of Ferromagnetism. III. *s-d* Interactions

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We use the method of Part I of this series of papers to study the influence of *s-d* interactions, thus extending the work by Potapkov and Tyablikov to higher spin values and that of Vonsovskii and Izyumov to higher temperatures. Expressions are given for the energy shift and damping caused by the *s-d* interaction, using the first nontrivial approximation to the Green-functions equations of motion.

1. INTRODUCTION

IN the first two papers of this series[1] (we use throughout the same notations as in I and II and refer to these papers for the definition of the various symbols) we discussed an ideal ferromagnet with a Heisenberg Hamiltonian, that is, the interaction between the spins was assumed to be an isotropic exchange interaction. It is, however, well known[2–6] that, on the one hand, in crystals of metals and alloys of the iron group as well as direct-exchange interaction there is also an indirect interaction produced through *s-d* exchange while, on the other hand, this *s-d* exchange mechanism may well be the dominant one in crystals of rare-earth elements and for the case of solutions of paramagnetic ions in diamagnetic crystals where the direct exchange is small. Potapkov and Tyablikov[7] have used a Green-function method to discuss this problem for the case where $S=\frac{1}{2}$,

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[1] R. A. Tahir-Kheli and D. ter Haar, Phys. Rev. **127**, 88 and 95 (1962). These papers are referred to as I and II and their equations are quoted as (I3, 5), (II2.11), and so on. We should like to use this opportunity to rectify an incorrect statement in Appendix B of I and to apologize to Dr. Kawasaki and Dr. Mori for incorrectly criticizing their work. We have now found that their theory gives, indeed, the correct high-temperature expansion, at least up to terms of order $1/\tau^2$; our misinterpretation was caused by a misprint in their paper.

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