succession, we have the less restrictive conditions:

$$|X_B| \geqslant 1; \quad |X_B+X_AT^{-1}| \geqslant 2; \quad |X_A+X_BT| \geqslant 2; \quad |X_A(X_B+X_AT^{-1})| \geqslant 2, \tag{43}$$

which imply that the energy is in a region forbidden to pure B, with the symmetric conditions if no more than two B atoms occur in succession.

If we further assume that no more than one A atom may occur between neighboring B atoms, we have the still less restrictive conditions

$$|X_B| \geqslant 1; \quad |X_B+X_AT^{-1}| \geqslant 2; \quad |X_A+X_BT| \geqslant 2, \tag{44}$$

with the symmetric conditions if no more than a single B atom lies between two neighboring A atoms.

If we require an A atom to follow a B atom we have the still less restrictive conditions:

$$|X_A+X_BT| \geqslant 2; \quad |X_B+X_AT^{-1}| \geqslant 2, \tag{45}$$

so that an energy gap may be in a region allowed to both pure A and pure B. For the Kronig-Penney alloy, however, an examination of conditions (44) shows that they cannot be satisfied; we are thus unable to prove the existence of an energy gap for values of the energy which are allowed to both pure A and pure B for the Kronig-Penney alloy.

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Low-Temperature Behavior of the Heisenberg Ferromagnet*

MICHAEL WORTIS
Faculté des Sciences, Université de Paris, Orsay, France
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The mechanics of spin deviations is formulated in a simple manner, which maintains the true spin kinematics and does not involve the introduction of any artificial interactions. A virial expansion for the thermodynamics, based on this mechanics, clearly distinguishes kinematical and dynamical effects. At low temperatures, low-density kinematical effects are easily proved exponentially small. The second virial coefficient is computed unambiguously. Dyson's low-temperature free energy is straightforwardly rederived, and an upper bound is estimated on the validity of the associated low-density boson picture.

1. INTRODUCTION

THE mechanics of the Heisenberg model is dominated by two properties: (a) It always obeys *spin* kinematics and (b) the low-lying states have a propagational, *particle*-like, "spin-wave" behavior. These opposing properties must be reconciled in any formalism. The problem of calculating the Heisenberg thermodynamics has been attacked by three major strategies, each with its insights and corresponding drawbacks. Cluster expansions,[1] taking the molecular field theory as their starting point, treat a local group of spins exactly in the presence of a self-consistent environment. Justice is done to (a), but (b) is difficult to exhibit. Second, "spin-deviation" methods[2–4] start from the mechanics of a small number of units of reversed spin in an otherwise aligned background. They are ideal for expressing (b) but tend to rely on particle analogs in a way that obscures (a). Finally, methods based on approximate solution of the equations of motion for the thermodynamical Green's functions[5] (canonically averaged products of time-dependent spin operators) have a great formal flexibility, being adaptable in a general way to both spin and particle pictures; however, they deal always with averaged quantities and are not, therefore, appropriate for a careful dissection of either kinematics or dynamics.

The present contribution[6] follows the spin-deviation strategy without, however, sacrificing the spin kinematics. The purpose is to provide a detailed understanding, both physical and formal, of the essential

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[1] Examples are P. J. Weiss, Phys. Rev. **74**, 1493 (1948); P. W. Kasteleijn and J. Van Kranendonk, Physica **22**, 317 (1956); B. Strieb, H. B. Callen, and G. Horwitz, Phys. Rev. **130**, 1798 (1963). For completeness we also include here (somewhat inappropriately) high-temperature expansions in powers of β, for example, the work of G. S. Rushbrooke and R. J. Wood, Proc. Phys. Soc. (London) **68A**, 1161 (1955).

[2] F. J. Dyson, Phys. Rev. **102**, 1217 and 1230 (1956). Hereafter these two papers will be referred to as Dyson I and Dyson II, respectively.

[3] J. Van Kranendonk, Physica **21**, 749 and 925 (1955); T. Morita, Progr. Theoret. Phys. (Kyoto) **20**, 614 and 728 (1958), for example.

[4] Another important line follows the work of T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

[5] Reviews of this literature are given in V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green Function Method in Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962), and C. W. Haas and H. S. Jarrett, Phys. Rev. **135**, A1089 (1964).

[6] Based in part on M. Wortis, Ph.D. thesis, Harvard University, 1963 (unpublished).

features of the spin mechanics and the way in which these features manifest themselves in the thermodynamics. The insights thus won establish a foundation for a low-temperature thermodynamical calculation. It is hoped that they will prove useful elsewhere as well.

Several authors have tried to enforce the spin kinematics (the limitation of the maximum number of spin deviations per site to $2S$) within a boson formalism by using an artificially introduced hard core[3] or by otherwise modifying the boson Hamiltonian in such a way that effects from boson states without spin analogs are suppressed at least at low temperatures.[2] Such devices, while certainly correct in principle, tend to raise more questions than they resolve.[7] The burden of proof is on the authors involved to show that the rather singular interactions introduced do not have unwanted side effects. Even such a careful treatment as Dyson's[2] suffers from an internal inconsistency (see Appendix A). Our viewpoint is that the spins themselves do not feel any singular interactions, and any valid simplifications which the introduction of such can produce must already be properties of the unembellished spin system.

Sections 2–4 discuss the mechanics of spin deviations. Section 2 formulates this mechanics in a straightforward way, involving no artificial interactions. The normalization of the spin-operator matrix elements dictates the appearance of certain kinematical projection operators. In Sec. 3 it is shown that the Schrödinger operator for the spin problem belongs also to a boson Hamiltonian H_B.[8] The spin-system energies constitute a subset of the eigenvalues of H_B. The remaining "improper" eigenvalues are kinematically projected out of the *exact* spin problem. For a number of bosons greater than or equal to a critical number n_c improper energies lower than the ground-state energy E_0 of the Heisenberg model may appear. Section 4 is devoted to a connected-kernel formulation of the spin mechanics which specifically eliminates improper energies.

Sections 5 and 6 develop and discuss a virial expansion for the Heisenberg free energy W. An exact formula is derived for the nth virial coefficient b_n in terms of the connected part of the mechanics. W has the form of the free energy of an assembly of bosons with H_B minus a set of terms involving the kinematical projections, which serve to exclude improper energies. This form, though somewhat cumbersome in calculation, allows a transparent distinction between kinematical and dynamical effects. At low temperatures the kinematical subtractions for b_n, $n<n_c$, are rigorously exponentially small. This fact serves in Sec. 7 as the basis for an unambiguous asymptotic low-temperature evaluation of b_2, a necessary condition on the correct low-temperature free energy.[9]

Section 8 examines the full low-temperature Heisenberg free energy. The evidently paradoxical upshot is that W can be calculated by summing low-density contributions to the free energy of an assembly of bosons with H_B, thus apparently disregarding property (a). The numerical result to order T^4 in temperature is obtained by directly summing boson "ladder diagrams." This "answer" is easy to come by[10,11]; the question is the logic by which seemingly large kinematical contributions[12] are eliminated. There are many ways of sweeping these terms under the rug (e.g., by using bosons with a hard core). The problem is to show why and up to what power of T they fail to appear (where, for example, does the presence of the hard core start to make itself felt?). In Sec. 8 improper (kinematical) subtractions corresponding to low-density terms are proved exponentially small. This proof—the key to our treatment of the thermodynamics—rests in a very natural way on the spin kinematics and the values of improper energies for $n<n_c$ (i.e., that they are all finitely above E_0). Remaining subtractions, while *not* small, cancel against improper energies in boson-like terms whose proper contributions are small.[13] In Sec. 9 the limit of validity of the low-density boson picture for calculating the low-temperature Heisenberg free energy is estimated.

Our development parallels Dyson's[2] quite closely in many respects. The relation between them is discussed in detail in Appendix A. Numerical results are the same but the logic is quite different, illuminatingly so, we hope.

2. THE SPIN HAMILTONIAN AND ITS GREEN'S FUNCTIONS

The Heisenberg model has been defined in detail elsewhere.[14] The present paper recapitulates the notation there introduced only insofar as will be useful for direct reference herein. The Heisenberg Hamiltonian is composed of the sum of a magnetic and an exchange term:

$$H=\mu\sum_1 S^z(1)-\tfrac{1}{2}\sum_{1,2} J(12)\mathbf{S}(1)\cdot\mathbf{S}(2). \qquad (1)$$

[7] For $S=\frac{1}{2}$, for example, there exist no states in which two or more spin deviations occupy a single site. Correct introduction of a hard core must have *no* effect on physical spin states.

[8] The Hermitian conjugate of the boson Hamiltonian of Dyson I. See Appendix A(i).

[9] Dyson's free energy (Ref. 2) passes this test.

[10] T. Morita (Ref. 3); T. Oguchi, Phys. Rev. **117**, 117 (1960); F. Keffer and R. Loudon, J. Appl. Phys. **32** Suppl. 2S (1961); R. A. Tahir-Kheli and D. ter Haar, Phys. Rev. **127**, 95 (1962); J. Szaniecki, *ibid.* **129**, 1018 (1963). All obtain Dyson's result or close approximations thereto. See also Ref. 11.

[11] N. I. Greenberg, J. Math. Phys. 4, 405 (1963), formulates the $S=\frac{1}{2}$ problem in terms of a binary kernel which contains both dynamics and kinematics. In principle valid, this method, like the hard core, obscures the simple physics behind the correctness of the low-density boson picture.

[12] An appealing (but wrong) argument: $(2S+1)$ particles cannot simultaneously occupy a given site. The effect of this exclusion should go as the $(2S+1)$th power of the spin-deviation density, i.e., as $T^{3(2S+1)/2}$ (T^3 for $S=\frac{1}{2}$).

[13] The weak point of the present work (and it is a weakness of all previous authors, as well) is an inability to estimate these high-density (intrinsically many-particle) proper contributions outside of (a highly suspect) perturbation theory. In our development it is at least clear that difficulties, if they occur, are associated with the real complexity of the Heisenberg mechanics.

[14] M. Wortis, Phys. Rev. **132**, 85 (1963).

The parameter μ, which characterizes the strength of the external magnetic field and the spin magnetic moment, may be taken non-negative without loss of generality because of the freedom of choice of coordinates. The exchange interaction is given by

$$J(12)=J(21)=J, \quad \begin{matrix}1 \text{ and } 2 \text{ nearest neighbors}\\ =0, \quad \text{otherwise.}\end{matrix} \tag{2}$$

We shall assume $J>0$, so the spins tend to align ferromagnetically at low temperatures.[15] The N individual spins which comprise the kinematics of the model are imagined to be arrayed on a simple cubic[16] lattice of unit spacing, dimensionality d, side L ($L^d=N$), and periodic connectivity. The spins obey the usual commutation relations and subsidiary conditions:

$$\begin{aligned}[S^{\pm}(1),S^z(2)]&=\mp\delta(12)S^{\pm}(2),\\ [S^-(1),S^+(2)]&=-2\delta(12)S^z(2),\end{aligned} \tag{3}$$

and

$$\mathbf{S}(1)\cdot\mathbf{S}(1)=S(S+1), \quad (S^+(1))^{2S+1}=(S^-(1))^{2S+1}=0. \tag{4}$$

The spin-deviation number operator,

$$n=NS+\textstyle\sum_1 S^z(1), \tag{5}$$

is a constant of the motion. The spin-deviation vacuum $|0\rangle$ is for $\mu\neq 0$ the unique ground state of H, satisfies

$$S^z(1)|0\rangle=-S|0\rangle, \quad S^-(1)|0\rangle=0, \tag{6}$$

and has energy $E_0=-\mu NS-dNJS^2$.

The spin-deviation mechanics is conveniently described by a set of vacuum Green's functions:

$$G_n(1\cdots n;1'\cdots n';t)=(-i)^n \times\langle 0|\prod_{i=1}^{n} S^-(i;t)\prod_{j=1}^{n} S^+(j';0)|0\rangle\eta(t), \tag{7}$$

where $\eta(t)$ is the step function,

$$\eta(t)=1, \quad t>0; \qquad =0, \quad t<0,$$

and the Heisenberg time dependence of the spin operators has been made explicit. The presence of the same number of S^- and S^+ operators in (7) reflects the conservation of spin deviations. The commutativity of the S^-'s and S^+'s among themselves makes G_n symmetrical separately in its primed and unprimed indices. The structure of G_n may be exhibited by introducing a complete orthonormal set of n-spin-deviation energy eigenstates $|\gamma\rangle$:

$$\begin{aligned}G_n(1\cdots n;1'\cdots n';\omega)&\equiv(-i)\int_{-\infty}^{\infty}dte^{i\omega t}G_n(1\cdots n;1'\cdots n';t)\\ &=(-i)^n\sum_{\gamma}\frac{\langle 0|\prod_{i=1}^{n}S^-(i)|\gamma\rangle\langle\gamma|\prod_{j=1}^{n}S^+(j')|0\rangle}{(\omega-(E_\gamma-E_0)+i\epsilon)}.\end{aligned} \tag{8}$$

The spin operators in (8) refer to $t=0$ and the $i\epsilon$ notation is shorthand for $\lim_{0<\epsilon\to 0}$, which recognizes the η function in (7).

It will facilitate further development to pause briefly here to introduce some convenient notation. We denote by 1_n the symmetrical n-dimensional unit matrix. Its matrix elements, $\langle 1\cdots n|1_n|1'\cdots n'\rangle$, consist in a sum of $n!$ terms, each of which is a product of n δ functions connecting the unprimed indices with one of the $n!$ orderings of the primed indices. For example,

$$\begin{aligned}\langle 1|1_1|1'\rangle&=\delta(11');\\ \langle 12|1_2|1'2'\rangle&=\delta(11')\delta(22')+\delta(12')\delta(21').\end{aligned}$$

A set of functions intimately related to the spin kinematics may now be defined by

$$\langle 0|\prod_{i=1}^{n}S^-(i)\prod_{j=1}^{n}S^+(j')|0\rangle =(2S)^n\langle 1\cdots n|1_n|1'\cdots n'\rangle h_n^{(S)}(1'\cdots n'). \tag{9}$$

The function $h_n^{(S)}$ is taken to be entirely symmetrical in its n arguments. Examples are

$$h_1^{(S)}(1)=1; \quad h_2^{(S)}(12)=1-\frac{\delta(12)}{2S};$$

$$h_3^{(S)}(123)=\left[1-\frac{\delta(12)+\delta(13)+\delta(23)}{2S}+\frac{2\delta(123)}{(2S)^2}\right],$$

where $\delta(123)$ has the value unity when the sites 1, 2, and 3 are identical and is zero otherwise. The significance of the $h_n^{(S)}$ is perhaps made clearest by the construction

$$\langle 0|\prod_{i=1}^{n}S^-(i)=[(2S)^n h_n^{(S)}(1\cdots n) \times\langle 1\cdots n|1_n|1\cdots n\rangle]^{1/2}P_n^{(S)}(1\cdots n)\langle 1\cdots n|, \tag{10}$$

where $\langle 1\cdots n|$ denotes the normalized bra representing the state with units of spin flipped away from the $\langle 0|$ alignment on each of the sites $1,\cdots,n$. $P_n^{(S)}$, the projection operator onto the "proper" space of n indices for spin S, is unity when no single site appears among its arguments more than $2S$ times and zero otherwise. Its presence in (10) is explicit recognition of the subsidiary

[15] Almost all of Secs. 2–5 is formally valid regardless of the sign of J. $J>0$ is crucial for our discussion of the low-temperature thermodynamics.

[16] This assumption has no bearing on the structure of the formulation, only on the details of the terminal numerics.

condition (4). Note the factored form,

$$P_n^{(S)}(1\cdots n)=\prod_{\{2S+1\}}(1-\delta(\{2S+1\}))$$
$$=\prod_{\{2S+1\}}P_{2S+1}^{(S)}(\{2S+1\}),\quad(11)$$

where $\{2S+1\}$ is intended to indicate a particular set of $(2S+1)$ indices chosen from among $1,\cdots,n$; $\delta(\{2S+1\})$ is unity when all $(2S+1)$ indices are alike and zero otherwise; and the product is over all possible sets. The projection $I_n^{(S)}$ onto the "improper" space of n indices is introduced by

$$P_n^{(S)}+I_n^{(S)}=1,$$
$$I_{2S+1}^{(S)}(1\cdots(2S+1))=\delta(1\cdots(2S+1)).\quad(12)$$

Note that $P_n^{(S)}=1$ and $I_n^{(S)}=0$ for $1\leqq n\leqq 2S$. The superscript indicating the S-dependence of h_n, P_n, and I_n will be omitted henceforth. Clearly

$$P_nI_n=h_nI_n=0.\quad(13)$$

The matrix elements in (8) may now be re-expressed in terms of the coordinate space wave functions of the n-spin-deviation states $|\gamma\rangle$

$$\langle 0|\prod_{i=1}^{n}S^-(i)|\gamma\rangle=[(2S)^nh_n(1\cdots n)]^{1/2}\psi_\gamma(1\cdots n),\quad(14)$$

where the ψ_γ are complete and orthonormal according to

$$\sum_\gamma\psi_\gamma^\dagger(1'\cdots n')\psi_\gamma(1\cdots n)=\langle 1\cdots n|1_n|1'\cdots n'\rangle\quad(15)$$

and

$$\sum_{1\cdots n}\psi_\gamma^\dagger(1\cdots n)\psi_{\gamma'}(1\cdots n)P_n(1\cdots n)=n!\delta(\gamma\gamma').\quad(16)$$

Equation (15) holds only when both $(1\cdots n)$ and $(1'\cdots n')$ are proper. We have now established the representation,

$$G_n(1\cdots n;1'\cdots n';\omega)$$
$$=(-i)^n(2S)^n[h_n(1\cdots n)h_n(1'\cdots n')]^{1/2}$$
$$\times\sum_\gamma\frac{\psi_\gamma(1\cdots n)\psi_\gamma^\dagger(1'\cdots n')}{\omega-(E_\gamma-E_0)+i\epsilon}.\quad(17)$$

The fundamental mathematical expression of the finiteness of the individual spin magnitudes follows from (13) and (17):

$$\text{(a)}\quad I_nG_n=0;\quad\text{(b)}\quad G_nI_n=0.\quad(18)$$

Picturesquely stated, no more than $2S$ spin deviations may occupy a given lattice site at any one time.

It is useful to point out the close parallel which can be drawn between our treatment of the spin system and that of a particle-conserving boson system. A set of boson Green's functions analogous to the G_n's may be defined by substituting into (7) the correspondences $S^-\leftrightarrow\psi$, $S^+\leftrightarrow\psi^\dagger$. The subsequent relations (8)–(10) and (14)–(17) remain valid provided that all factors of $(2S)$, h_n, and P_n are stricken out. Equations (18), however, have no boson analog.

Our program now is to formulate the calculation of the G_n from the dynamical equations of motion, supplemented by spatial periodicity and the temporal boundary condition provided by the η function in the definition (7). To obtain the equation of motion for G_n, commute the product $\prod_{i=1}^n S^-(i)$ with the Hamiltonian (1). The magnetic part of the Hamiltonian is trivial. Commutation with the exchange part yields a set of terms, each of which involves the product of n S^-'s and an S^z. The S^z factor can always be commuted to the left through the various intervening S^-'s by using (2). Once an S^z stands on the left, it projects in the formation of G_n onto $\langle 0|$ by (5). The result is

$$\left(i\frac{\partial}{\partial t}-\mathfrak{L}_n\right)G_n\equiv\left[i\frac{\partial}{\partial t}-n(\mu+2SdJ)\right]G_n(1\cdots n;)+S\sum_{i=1}^{n}\sum_{\bar{i}}J(i\bar{i})G_n(1\cdots\bar{i}\cdots n;)$$
$$+\sum_{\substack{\text{pairs}\\i,j}}^{n}J(ij)G_n(1\cdots n;)-\sum_{\substack{\text{pairs}\\i,j}}^{n}\delta(ij)\sum_{\bar{i}}J(i\bar{i})G_n(1\cdots\bar{i}\cdots n;)=(2S)^n(-i)^{n-1}\delta(t)\langle 1\cdots n|1_n|\rangle h_n.\quad(19)$$

All invariant indices have been omitted in (19). The right-hand side follows from (9) and the step-function discontinuity in (8). The first two terms on the left-hand side of (19) include the effect of the projected S^z's and may be regarded as representing the dynamics of n noninteracting spin deviations. The remaining two terms come from the $[S^-,S^z]$ commutators and have the form of interactions between pairs of spin deviations.[17] This kind of particle terminology is suggestive; however, it is crucial always to keep in mind that the same parameter J measures both the spin-deviation "mass" and the magnitude of the pair interactions, so that an explicit symmetry of the problem is obscured whenever the pair interactions are thought of as perturbations and treated on a different footing from the "kinetic energy."

The fundamental kinematical properties (18) must, of course, be contained in (19). To see them, observe in (19) that the time derivatives $i(\partial/\partial t)I_nG_n$ and

[17] The double commutator, $[S^-,[S^-,S^z]]=0$, guarantees that only pair interactions occur.

$i(\partial/\partial t)G_nI_n$ involve, respectively, only elements of I_nG_n and G_nI_n. The latter is obvious; the former comes about by means of a cancellation between the off-diagonal second and fourth terms on the left-hand side of (19). The relation (13) now shows that the equations of motion for I_nG_n and for G_nI_n are homogeneous, and the η-function condition guarantees (18).

The one-particle Green's function G_1 may be obtained directly from (19) for $n=1$. The solution dates essentially from Bloch[18] and has been rederived many times. In normalized form the result is

$$\Gamma_1(1;1';t)\equiv\frac{1}{(2S)}G_1(1;1';t)$$
$$=\frac{(-i)}{N}\sum_{\mathbf{k}\epsilon F}e^{i\mathbf{k}\cdot(1-1')}e^{-i\Omega(\mathbf{k})t}\eta(t) \quad (20)$$

with

$$\Omega(\mathbf{k})=\mu+2SJ\sum_{i=1}^{d}(1-\cos k_i), \quad (21)$$

where F denotes the first Brillouin zone. It is convenient now to define matrices,

$$\langle 1\cdots n|(\Gamma_1)^n|1'\cdots n'\rangle\equiv\sum_{i=1}^{n}\Gamma_1(i;i') \quad (22)$$

and

$$\Gamma_n=1_n(\Gamma_1)^n=(\Gamma_1)^n1_n, \quad (23)$$

where the matrix indices in (23) have been omitted, as will often be the practice henceforth. The function Γ_n solves an equation like (19) but with the interaction terms on the left and the factor $(2S)^nh_n$ on the right omitted. In a sense which will be clarified below, it may be thought of as the propagator of n noninteracting spin deviations. Note, however, that Γ_n explicitly violates the fundamental kinematical conditions (18). Equation (19) for $n>1$ may now be converted to an integral form incorporating the boundary conditions:

$$G_n=(2S)^n\Gamma_nh_n+\tfrac{1}{2}((i)^{n-1}/(n-2)!)\Gamma_nvG_n. \quad (24)$$

The interaction matrix,

$$\langle 12|v|1'2'\rangle=\tfrac{1}{2}[\delta(11')-\delta(12')]$$
$$\times[\delta(21')-\delta(22')]J(1'2'), \quad (25)$$

as it appears in (24) is to be regarded as a diagonal δ function in all variables beyond 1 and 2. Note that as a 2×2 matrix v is symmetric in primed and unprimed variables separately but not under interchange. The matrix product in (24) implicitly includes a time integration such that, if $G_n(t)$ is on the left, the interaction term reads $\int dt'\Gamma_n(t-t')vG_n(t')$. While (24) exhibits the kinematical property (18b) through (13) and the h_n factor, it effectively obscures (18a), which must now come about through a complicated cancellation of the free-particle propagation and the interaction term. This is another reflection of the fact that J is the only parameter in the spin problem.

[18] F. Bloch, Z. Physik **61**, 206 (1930); **74**, 295 (1932).

3. THE BOSON GREEN'S FUNCTIONS AND THEIR HAMILTONIAN

We are now in a position to discuss in a precise way those characteristics of the spin mechanics which have normal boson analogs and those which do not. If one disregards numerical factors, G_n is the formal inverse of the operator $(i(\partial/\partial t)-\mathfrak{L}_n)$, multiplied on the right by h_n. Let us motivate the discussion by an analysis of the role played by this inverse operator. Write the time transform of (19) in a notation in which the first row and column of each 2×2 matrix refer to proper indices and the second row and column refer to improper indices:

$$\begin{pmatrix}\omega-\Lambda_{11} & -\Lambda_{12}\\ -\Lambda_{21} & \omega-\Lambda_{22}\end{pmatrix}\begin{pmatrix}G_n(\omega) & 0\\ 0 & 0\end{pmatrix}$$
$$=(2S)^n(-i)^n\begin{pmatrix}1_nh_n & 0\\ 0 & 0\end{pmatrix}. \quad (26)$$

Equations (13) and (18) have been used, and the matrix $\mathfrak{L}_n$ is represented by $\begin{pmatrix}\Lambda_{11} & \Lambda_{12}\\ \Lambda_{21} & \Lambda_{22}\end{pmatrix}$. The boundary condition, $G_n(t)=0$ for $t<0$, precludes any homogeneous solutions, so $\Lambda_{21}=0$ can be directly inferred. [Note that this argument was used in reverse in the paragraph preceding Eq. (20).] Clearly, then, $G_n(\omega)$ depends only on the inverse of the matrix $P_n(i(\partial/\partial t)-\mathfrak{L}_n)P_n$. In particular the solutions, $\omega=E_{\gamma P}-E_0$, of the determinantal condition,

$$\det(\omega-\Lambda_{11})=0, \quad (27)$$

give the energy eigenvalues of the n-spin-deviation subspace of the Hamiltonian (1). The notation $E_{\gamma P}$ has been used instead of simply E_γ, as in (17), to emphasize that these eigenvalues belong exclusively to the 1, 1 component of (26). Other components of $\mathfrak{L}_n$ are irrelevant to the spin problem.

To make quite explicit the still unused structure of $(i(\partial/\partial t)-\mathfrak{L}_n)^{-1}$, let us define a new set of functions H_n by [c.f. (19)]

$$(i(\partial/\partial t)-\mathfrak{L}_n)H_n=(-i)^{n-1}\delta(t)1_n, \quad (28)$$

subject to the same boundary conditions as G_n. Once H_n is known,

$$G_n(1\cdots n;1'\cdots n')$$
$$=(2S)^nH_n(1\cdots n;1'\cdots n')h_n(1'\cdots n'), \quad (29)$$

where spatial indices have been exhibited to highlight the asymmetrical relation between H_n and G_n. Note that (29) can be inverted only when $(1'\cdots n')$ is proper. The function Γ_n may be employed to invert (28)

[c.f. (24)]:

$$H_n=\Gamma_n+\tfrac{1}{2}((i)^{n-1}/(n-2)!)\Gamma_n v H_n;\quad H_1=\Gamma_1. \tag{30}$$

The analog of (26) is

$$\begin{pmatrix}\omega-\Lambda_{11} & -\Lambda_{12}\\ 0 & \omega-\Lambda_{22}\end{pmatrix}\begin{pmatrix}P_nH_n(\omega)P_n & P_nH_n(\omega)I_n\\ I_nH_n(\omega)P_n & I_nH_n(\omega)I_n\end{pmatrix}$$
$$=(-i)^n\begin{pmatrix}P_n1_nP_n & 0\\ 0 & I_n1_nI_n\end{pmatrix}, \tag{31}$$

which implies

$$I_nH_nP_n=0. \tag{32}$$

as is also clear from (29) and (18a). In contradistinction to G_nI_n, the elements H_nI_n are generally nonvanishing. Of course, only $P_nH_nP_n$ is relevant to the spin problem. The solutions, $\omega=E_{\gamma I}-E_0$, of

$$\det(\omega-\Lambda_{22})=0$$

constitute the spectrum of $E_nH_nI_n$. $E_{\gamma P}$ and $E_{\gamma I}$ will be called, respectively, "proper" and "improper" energy eigenvalues.

So far the functions H_n are no more than symmetrical inverse of $(i(\partial/\partial t)-\mathcal{L}_n)$, useful auxiliaries [via (29)] in the formulation of the spin problem. However, we noted after Eq. (18) that the kinematics of bosons is related to that of spins by the simple omission of factors of $(2S)$, h_n, and P_n. Comparison of the inhomogeneous terms of (19) and (28) suggests the conjecture that the H_n are, in fact, vacuum Green's functions for a true boson system. This is indeed so, as Dyson I was the first to observe. If boson creation and annihilation operators are introduced and Green's functions H_n are defined in analogy to G_n with the correspondences $S^-\leftrightarrow\psi$, $S^+\leftrightarrow\psi^\dagger$, then the boson Hamiltonian,[8]

$$H_B=E_0+(\mu+2SdJ)\sum_1\psi^\dagger(1)\psi(1)-S\sum_{1,2}J(12)\psi^\dagger(1)\psi(2)$$
$$+\tfrac{1}{2}\sum_{\substack{1,2\\1',2'}}\psi^\dagger(1')\psi^\dagger(2')\langle 1'2'|v|12\rangle\psi(1)\psi(2), \tag{33}$$

leads straightforwardly to (28). The non-Hermiticity of H_B, which follows from the interchange asymmetry of (25), seems to be an essential feature of the relation between the spin and corresponding boson problems. Again, v is a function of J, so perturbation theory obscures important distinctions between proper and improper subspaces, e.g., (32).

The existence of a boson Hamiltonian corresponding to a given spin dynamics is not, of course, specific to the Heisenberg model. So long as the operator n of Eq. (5) commutes with the spin Hamiltonian,[19] our construction of $\mathcal{L}_n$ holds, although interactions between more than two particles will appear when the spin Hamiltonian has terms higher than bilinear. Given $\mathcal{L}_n$, one can easily write down a boson Hamiltonian with the proper one-particle, two-particle, etc., parts. The factorization (29) always relates the spin and boson Green's functions. Equations (18) and (28) hold.

The structure of eigenstates and wave functions of the non-Hermitian boson system is discussed briefly in Appendix B. The main point is already clear from the analysis of Eqs. (26)–(32): the spectrum of the n-particle states of H_B consists of all the energy eigenvalues $E_{\gamma P}$ of the n-spin-wave states *plus* a set of improper energies $E_{\gamma I}$ absent in the spin system. The relation between spin and boson wave functions is given by (B7). The wave functions belonging to $E_{\gamma I}$ are irrelevant to the spin system and do not appear in G_n. The proper projections of the wave functions belonging to $E_{\gamma P}$ are related by simple kinematical factors to the wave functions of the spin system. Special properties of the boson wave functions conspire to project the $E_{\gamma I}$ out of that part H_nP_n of the boson Green's function having to do with spins.

The above is quite general. Let us state the result in the context of the Heisenberg model. To any eigenstate of the Hamiltonian (1)—i.e., to any stationary configuration of interacting spin waves—there corresponds an eigenstate of H_B with the same energy eigenvalue and a closely related wave function. It is *not* permissible, however, to regard the bosons appearing in H_B as actual spin waves, since they possess configurations with no spin analogs. The spin system maps onto a *subspace* of the boson system.

It would be nice to think that the boson correspondence represents real progress towards a solution of the spin problem. Unfortunately this does not seem to be so. For small n computations with spins and bosons are essentially equivalent.[20] One might hope, on the other hand, to use the correspondence to apply known many-boson techniques to the calculation, for example, of the spin thermodynamics.[21] Sadly enough, the projection out of the improper eigenenergies is not easy to perform. This point will be expanded upon at some length. Let us use it here as a motivation to study a few of the properties of the improper boson dynamics.

What can be said about the improper spectrum of H_B? The answer is that not much can. The author knows of no resolution of even such a simple question as the reality of the $E_{\gamma I}$, though the reality of the matrix elements of H_B in the occupation number representation does show that complex energies, if they occur, come in conjugate pairs. Luckily H_B satisfies a simple selection rule,[22] which will lead us to some important observations. Label states according to an occupation

[19] Even if n is not conserved, a corresponding (now particle-nonconserving) boson Hamiltonian exists. Both the boson and spin mechanics are, then, complicated by the nonexistence of simple invariant subspaces.

[20] Compare, for example, the $n=2$ calculation of Dyson I with Ref. 14 or with N. Fukuda and M. Wortis, J. Phys. Chem. Solids **24**, 1675 (1963).

[21] This is what Dyson does (Ref. 2). See also Refs. 10 and 11.

[22] First noticed in Dyson II, Sec. 3.

number representation. Due to a cancellation of off-diagonal terms, H_B acting to the left cannot remove a particle from a site occupied $(2S+1)$ times. Let g represent a set of sites occupied by $(2S+1)$ or more particles; then

$$\langle g_1|H_B|g_2\rangle=\langle g_1|e^{-itH_B}|g_2\rangle=0 \quad \text{whenever} \quad g_1\not\subset g_2, \quad (34)$$

a more delicate form of the property involved in the proof of $I_nG_n=0$ in the paragraph preceding (20). Any $(2S+1)$-occupied site is a stationary feature of the left-handed dynamics of H_B. Other particles move in the presence of these sites in a manner roughly analogous to the motion of mobile charges in the field of a set of fixed ions.

If we introduce projection operators[23] P_g onto those labelings $(1\cdots n)$ in which each of the sites contained in g occurs $(2S+1)$ or more times, then

$$P_{g_1}H_nP_{g_2}=0 \quad \text{if} \quad g_1\not\subset g_2. \quad (35)$$

Equation (32) is a special case of (35), since $P_n=P_g$ for $g=0$ (the empty set) and $I_n=\sum_{g\neq 0}P_g$. The relation (35) will be useful in sorting out certain combinatorics in thermodynamical calculations.

The main importance of (34) is that it allows identification of a small but nonetheless important set of *exact* improper eigenstates of H_B. All left-handed states consisting *solely* of $(2S+1)$-occupied sites are automatically eigenstates. If q is the total number of such sites and p is the number of nearest-neighbor pairs of them, then the energy of the state is

$$E_{\gamma I}-E_0=\mu n+(2S+1)J[2Sdq-(2S+1)p]. \quad (36)$$

For example, if every site is $(2S+1)$-occupied,

$$E_{\gamma I}-E_0=N(2S+1)(\mu-Jd), \quad (37)$$

which for $Jd>\mu$ becomes negative and of order N. It is clear generally from (36) that lower energies are obtained by putting the $(2S+1)$-occupied sites closer together and, thus, increasing p relative to q. For $\mu=0$, which is of most interest thermodynamically, the simplest configuration for which (36) becomes zero is when a number $q=(2S+1)^d$ of $(2S+1)$-occupied sites are arrayed at the vertices of a d-dimensional cubic net, thus giving $p=2Sd(2S+1)^{d-1}$ nearest-neighbor pairs. The number of particles required is $(2S+1)^{d+1}$. There exist, therefore, bound states of H_B with $E_{\gamma I}\leqq E_0$. Let n_c be the smallest number of particles for which this can occur. Surely,[24]

$$(2S+2)<n_c\leqq(2S+1)^{d+1}. \quad (38)$$

Now, this is very serious. The $E_{\gamma I}$ project out of the *exact* G_n; however, any scheme of *approximate* solution which destroys (32) will mix the improper mechanics of H_B into the spin problem. Since the improper energies and wave functions have properties quite different from the proper ones, this mixing can lead to disastrous errors [e.g., Sec. 6(i)].

In the remaining sections of this paper we shall attempt to formulate first the mechanics and then the thermodynamics of the Heisenberg model in a manner which is manifestly free of the pitfalls surrounding the $E_{\gamma I}$. In this, though only partially successful, we shall be considerably more careful than previous authors. It is hoped that the insights gained thereby will justify the endeavor. Our main tool will be the knowledge of boson combinatorics and the selection rule expressed by (35).

4. THE CONNECTED PART OF THE GREEN'S FUNCTIONS

Let us return to the formulation of the evaluation of G_n or equivalently of H_nP_n. The integral equation (30) [or (24)] and the contraction,

$$\sum_{\bar{1}}\Gamma_1(1;\bar{1};t-\bar{t})\Gamma_1(\bar{1};1';\bar{t}-t')=\Gamma_1(1;1';t-t')\eta(t-\bar{t})\eta(\bar{t}-t'), \quad (39)$$

are the natural starting point for an iterative solution for G_n, formally perturbative in v. By utilizing the symmetry of H_n in its left-hand indices, we can rewrite (30) as

$$H_n=1_n(\Gamma_1)^n+(2(i)^{n-1}/n!)(\Gamma_1)^n[\sum_{\text{pairs}}(v1_{n-2})]H_n. \quad (40)$$

The notation $(v1_{n-2})$ in (40) symbolizes a matrix in which v connects a pair of left-hand variables with a pair of right-hand variables, the remaining $(n-2)$ variables of each type being connected symmetrically by the 1_{n-2}. The summation is over the v-coupling of all possible left and right pairs. The terms in the iterative expansion of (40) may be represented diagrammatically in the usual way, with a directed line standing for each unperturbed propagator, Γ_1, and some attractive polygon, for the four-point interaction, v. As an organization of the calculation, this schema is combinatorically complicated and severely limited by convergence difficulties associated with the formation of bound states.[25] These drawbacks are circumvented when methods of solution or approximation can be found which apply directly to the integral equation.[26] However, Weinberg[27] has shown that for $n>2$ the singularity of the kernel of (40), arising from its lack of connectivity,[28] makes usual approximation schemes inapplicable. A rearrangement of (40) involving a manifestly connected kernel is, therefore, indicated. This emphasis on connectivity will be further justified in Sec. 5, where it will be shown (in a slightly altered form) to be the key to the correct volume

[23] We suppress S and n dependence.

[24] We conjecture that n_c is, in fact, equal to this upper limit. It seems overwhelmingly probable that it is at least very close to it. The lower limit is provided by the fact that one can solve the *improper* $(2S+2)$-particle problem exactly (it is essentially a two-particle problem) and verify that $E_{\gamma I}>E_0$.

[25] See S. Weinberg, Phys. Rev. **131**, 440 (1963).

[26] For example, $n=2$ in Ref. 14.

[27] S. Weinberg, Phys. Rev. **133**, B232 (1964).

[28] We use "connected" in the sense of hanging together as a whole (when expressed, e.g., diagrammatically).

dependence of the extensive thermodynamic functions.

The form of the rearrangement which we shall use is due to Weinberg.[27] Proofs are available in Ref. 27; however, for the benefit of the uninitiated reader a very simple and direct alternative derivation is sketched in Appendix C. The Green's function H_n is divided into disconnected and connected parts, D_n and C_n, respectively,

$$H_n=D_n+C_n. \tag{41}$$

D_n can be thought of as the sum of all those parts of H_n which factor into two or more pieces depending separately on disjoint subsets of the position indices. C_n contains all of H_n which cannot be so factored. D_n and C_n may also be identified (disregarding convergence difficulties) with the totality of respectively disconnected and connected terms in the iterative expansion of (40). C_n is shown to be expressible as a matrix product,

$$C_n=K_nH_n, \tag{42}$$

where K_n is totally connected and appears as the kernel[29] of the resulting integral equation,

$$H_n=D_n+K_nH_n. \tag{43}$$

K_n contains a description of the intrinsically n-particle features of H_n. By convention $C_1=H_1=\Gamma_1$. The point now is that D_n and K_n can be written in terms of C_l, $l<n$. Appendix C and Ref. 27 derive the expressions,

$$D_n=\sum_P \prod_{l<n,\,\Sigma_l lm_l=n} C_l^{m_l}, \tag{44}$$

$$\tfrac{1}{2}n!(-i)^{n-1}K_n=\textstyle\sum_P C_lC_{n-l}v. \tag{45}$$

The v in (45) connects one right-hand index of C_l with one of C_{n-l}. In both (44) and (45) the sum is taken over all possible l's and m_l's and over all essentially different partitions P of the left- and right-hand indices among the various allowed C's and v. Note that v and the C's are totally symmetric in both left and right indices. The wording is intended to exclude terms differing only in the ordering of some set of symmetrically occurring indices. Thus, each term in the summations (44) and (45) is unique in that it cannot be obtained from any other term by a permutation either of factors or of the left or right indices belonging to a given factor. The numerical coefficients are all unity. For $n=2$, (43) is identical to (40). For $n=3$,

$$D_3(123;1'2'3')-\langle 123|(C_1)^3 1_3|1'2'3'\rangle=C_1(1;1')C_2(23;2'3')+C_1(1;2')C_2(23;1'3')+C_1(1;3')C_2(23;1'2')$$
$$+6 \text{ other terms from cyclic permutations of } (1,2,3), \tag{46}$$

$$(-3)K_3(123;1'2'3')=\sum_{a,b}[C_1(1;a)C_2(23;1'b)\langle ab|v|2'3'\rangle+C_1(1;a)C_2(23;2'b)\langle ab|v|1'3'\rangle$$
$$+C_1(1;a)C_2(23;3'b)\langle ab|v|1'2'\rangle+\text{cyclic permutations of } (1,2,3)]. \tag{47}$$

Higher D_n's and K_n's can be written down by inspection. A pictorial representation involving as elements v and the various C_n's is naturally suggested. The procedure is inductive in that the C_l's appearing in D_n and K_n must be obtained by solving of the l-particle problem for $l<n$.

While (43) has all the formal advantages of an integral equation with a connected kernel, it suffers, as a formulation of the spin problem, from one major drawback. The improper eigenenergies $E_{\gamma I}$ will be projected out of the exact H_nP_n; however, they still appear in K_n and will, therefore, tend to be mixed up with the proper energies $E_{\gamma P}$ in any *approximate* solution for H_nP_n. Luckily (28) provides a tool for totally extricating the superfluous $E_{\gamma I}$ from the spin mechanics. Multiply (43) on the right by P_n and use (32), obtaining

$$(H_nP_n)=(D_nP_n)+(K_nP_n)(H_nP_n). \tag{48}$$

We now have an integral equation for H_nP_n, the physical part of H_n. Note that the inhomogeneous term D_nP_n is no longer entirely disconnected. It remains to show that D_nP_n and the connected kernel K_nP_n can be written in terms of the physical functions H_lP_l for $l<n$. The idempotence of the projection operators and their product structure [cf. (11)] make it clear that D_nP_n and K_nP_n are unchanged if all the C's in the definitions (44) and (45) are replaced by the corresponding CP's. Finally, the relations (41) and (44) can be inverted to give C_n in terms of H_l for $l<n$, so C_nP_n can certainly be written as a sum of products of H_lP_l's, $l<n$, and various projection operators and, thus, depends in no way on the unphysical part of the boson problem.

This, then, is the endpoint of our analysis of the spin-deviation mechanics. To recapitulate: the schema described is inductive. One assumes given the solutions to the physical spin problem for l spin deviations, $l<n$. This means that H_lP_l and, therefore, C_lP_l are known. Equations (44) and (45) with C replaced always by CP are used to compute D_nP_n and K_nP_n. Equation (48) must then be solved for H_nP_n and C_nP_n, and so on. Contact with the Green's functions G_n can be made via (29) at any stage. In fact, it is clear that by proper insertion of factors of h_n and $2S$ the inductive format can be carried out and could have been derived in terms of the G_n's alone. The detour through the H_n's was com-

[29] Our K_n plays the role of Weinberg's (Ref. 27) $I_S(W)$.

putationally convenient but in principle extraneous.

A further observation concerning the C_n's is useful for future reference. The procedure for calculating higher C_n's from lower ones, though well defined, is, as we have seen, generally quite complicated. By contrast, the selection rule (35) provides in certain cases a very direct evaluation. Consider $S=\frac{1}{2}$ as an example. $H_2(11;1'2')=0$ unless $1=1'=2$ by (35). This implies immediately,

$$C_2(11;1'2')=-2C_1(1;1')C_1(1;2')$$

unless

$$1=1'=2'. \tag{49}$$

Such relations as (49) may, in turn, be employed to write a connected-part decomposition of, for example, $H_3(112;1'2'3')$ in which C_2's of the form (49) do not appear. It is always possible to write a connected part of the form $P_{g_1}C_nP_{g_2}$ with $g_1 \not\subset g_2$ in terms of connected parts not of this form C_l, $l<n$. Any H_n can thereby be expressed in terms of connected parts, no one of which possesses indices of the $P_{g_1}P_{g_2}$, $g_1 \not\subset g_2$ form. This apparently trivial remark will be of great importance in Sec. 8.

It must be stated that in one sense all the discussion since Eq. (40) has been rather metaphysical: the $n \geqq 3$ problems are as yet and as usual unamenable to exact solution in any form. There are two justifications for our development. First, it provides, the author feels, a sound basis for practical approximations to the spin-deviation mechanics, free of difficulties associated with the $E_{\gamma I}$. Second, in the logic of the introduction and subsequent elimination of the $E_{\gamma I}$, the development exhibits explicitly several very important structural features of the behavior of spin deviations.

Let us proceed now to apply these insights to the thermodynamics of the spin-wave system.

5. THERMODYNAMICS: THE VIRIAL EXPANSION

The parameter μ in the magnetic term of the spin Hamiltonian (1) plays a role closely analogous to that of the chemical potential in conventional many-particle theory. This observation motivates the expansion of the free energy W or, more precisely, of the sum $(W+\beta E_0)$ in a power series[30] in the "fugacity," $\mathfrak{z}=e^{-\beta\mu}$ $(\beta=1/kT)$:

$$W \equiv \ln \operatorname{tr} e^{-\beta H} = -\beta E_0 + \sum_{n=1}^{\infty} \frac{\mathfrak{z}^n b_n}{n!}. \tag{50}$$

The nth "virial coefficient" b_n contains, as we shall see, all the information of thermodynamical relevance concerning the n-spin-deviation mechanics. The other thermodynamic functions of the system may be determined from W in the usual way. In particular the magnetization

$$M=\langle \textstyle\sum_1 S^z(1)\rangle = -(\partial/\partial\beta\mu)W = -NS+\langle n\rangle, \tag{51}$$

where

$$\langle n\rangle = \mathfrak{z}\frac{\partial}{\partial\mathfrak{z}}(W+\beta E_0) = \sum_{n=1}^{\infty} \frac{\mathfrak{z}^n b_n}{(n-1)!}. \tag{52}$$

If

$$Z \equiv \operatorname{tr} e^{-\beta H} = e^{-\beta E_0} \sum_{n=0}^{\infty} (\mathfrak{z}^n Q_n/n!) \tag{53}$$

with

$$Q_n = n!\,\operatorname{tr}_n e^{-\beta(H_{\text{exch}}+dNJS^2)}, \quad Q_0=1, \tag{54}$$

where H_{exch} is (1) with the magnetic term omitted and tr_n signifies the trace over the n-spin-deviation subspace only, then the b_n's and the Q_n's are related inductively to one another just as in Ref. 30:

$$Q_n = n! \sum_P \prod_l \frac{(b_l)^{m_l}}{(m_l!)(l!)^{m_l}}, \qquad n=\textstyle\sum l m_l. \tag{55}$$

Each Q_n is expressed as a sum of products, $\prod_l (b_l)^{m_l}$. The sum is taken over all different partitions, P, of n into m_l groups of l. The associated coefficient is the number of different ways the partition P can be realized for a set of n distinguishable objects. Examples are

$$Q_1=b_1, \quad Q_2=b_1^2+b_2, \quad Q_3=b_1^3+3b_1b_2+b_3. \tag{56}$$

Direct summation shows that (55) and (53) produce (50).

For finite N all the Q_n are non-negative and finite (in fact, $Q_n=0$ for $n>2NS$). W is, therefore, analytic in $\mathfrak{z}$ for all finite $\mathfrak{z}$ for which Z does not vanish. There exists an open neighborhood of the positive real $\mathfrak{z}$ axis in which $Z\neq 0$. W is analytic in this region, and the virial expansion (50) has a finite radius of convergence. The analytic continuation of (50) then give W for all $\mathfrak{z}$. W is nonsingular for physical $\mathfrak{z}$ ($\mathfrak{z}$ real, $0 \leqq \mathfrak{z} \leqq 1$). Of course, in actual calculation we shall be interested in the $N\to\infty$ limit. The generally valid though seldom practical procedure is to calculate the quantity one wants (e.g., W/N or M/N) for finite N and *then* take $N\to\infty$. Lee and Yang[31] have shown in a somewhat different context that the $N\to\infty$ limit of the thermodynamic functions[32] may develop singularities for physical $\mathfrak{z}$, corresponding to actual phase transitions of the physical system. In one and two dimensions ($d=1, 2$) the Heisenberg model very probably does not exhibit a phase

[30] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959). Our H_n is their W_n. Note from (41) and (44) that our C_n is *not* their U_n.

[31] C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952).

[32] It is generally the free energy per unit *volume* which is well defined as $N,V\to\infty$ with N/V fixed. Here we have chosen unit spacing for the sites, so the appropriate limit is W/N with $N\to\infty$.

transition,[33] and the $N\to\infty$ thermodynamic functions are accordingly expected to be nonsingular for physical ϑ at all temperatures. For $d=3$ a singularity is anticipated as $\mu\to 0^+$, $\vartheta\to 1^-$, for $T<T_c$. Note that for $\mu=0$ the spherical symmetry of H guarantees that $M=0$. For finite N this value is always reached continuously as $\mu\to 0$. If one calculates M for $\mu\neq 0$, then takes $N\to\infty$, and finally $\mu\to 0$, one expects $M\to 0$ continuously for $d=1, 2$ and $d=3$ if $T>T_c$. However, for $d=3$, $T<T_c$, $N\to\infty$, the direction of the external magnetic field (even as its magnitude goes to zero) determines the direction of a magnetization whose magnitude does not approach zero with μ. Thus, as μ goes from 0^+ to 0^-, the macroscopic magnetization flips discontinuously. $M=0$ is not approached as $\mu\to 0$. This is the broken symmetry of the ferromagnetic phase transition. By the "zero-field magnetization" we shall mean first $M\to\infty$ for $\vartheta<1$ and then[34] $\vartheta\to 1^-$.

Unfortunately manipulations with finite N are seldom feasible, so it is necessary to take $N\to\infty$ at some intermediate point in the calculations. One possibility is to take the $N\to\infty$ limit of b_n/N *before* summing (50). It has been pointed out by various authors[31,35,36] that these operations are not necessarily commutative. In order to use the raw virial expansion (50) with the $N\to\infty$ form for b_n/N, one must assume that $(W+\beta E_0)/N$ with $N\to\infty$ does possess a valid power series expansion in ϑ in some neighborhood of $\vartheta=0$ for the temperature in question.[37] Note, however, that rearrangements of (50) (such as regroupings and partial summations) may be carried out for finite N. The $N\to\infty$ convergence properties of the new forms thus obtained may be quite different from those of the original expansion. The thermodynamic computation of Sec. 8 performs such a rearrangement and is implicitly based on the assumption that afterwards N may validly be taken to infinity before summation for sufficiently low temperatures and $\vartheta=1$.

The program now is to relate first the Q_n's and then the b_n's to the functions describing the spin-deviation mechanics. Equations (7), (10), and (29) show that

$$(i)^n H_n(1\cdots n;1\cdots n)\big|_{t\to -i\beta}=e^{\beta E_0}\vartheta^n\langle 1\cdots n|1_n|1\cdots n\rangle \times\langle 1\cdots n|e^{-\beta H_{\text{exch}}}|1\cdots n\rangle, \tag{57}$$

which holds only for proper indices $(1\cdots n)$ and where the analytic extension $t\to -i\beta$ is understood to be from the $t>0$ form of H_n. Converting the sum over states in (54) to a position representation, one finds that

$$Q_n=(i)^n\,\mathrm{tr}H_nP_n\big|_{\mu=0,\ t\to -i\beta}. \tag{58}$$

The trace notation for functions means an unrestricted sum over diagonal elements, i.e., each of the indices $(1\cdots n)$ is summed over all lattice sites. The qualifications $\mu=0$ and $t\to -i\beta$ will be left implicit henceforth. Equation (58) holds for an arbitrary *boson* system if the factor P_n is omitted.

In passing now from the Q_n's to the b_n's the property of connectivity will prove pivotal. Formula (58) refers only to diagonal elements of H_n, $H_n(1\cdots n;1\cdots n)$. Consider the expansion, (41) and (44), of the diagonal H_n in terms of C_l, $l\leqq n$. An individual term in this expansion consists of a product, $\prod_{l\leqq n}C_l^{m_l}$, where each argument $1\cdots n$ occurs once as a right-hand index and once as a left-hand index. Two C_l factors may now be "linked" by one or more indices, e.g., $C_\alpha(1\cdots;\cdots)\times C_\beta(\cdots;1\cdots)$. When all such linkages have been taken into account, a given term can be classified as "disconnected" or "connected" according as its factors do or do not fall into two or more unlinked groups. Denote the disconnected and connected parts of $H_n(1\cdots n;1\cdots n)$ as, respectively,

$$\mathfrak{D}(H_n)=\bar{D}_n;\quad \mathfrak{C}(H_n)=\bar{C}_n;\quad H_n=\bar{D}_n+\bar{C}_n. \tag{59}$$

The operations denoted by $\mathfrak{C}$ and $\mathfrak{D}$ may, of course, be applied to any set of terms involving products of C_l's, once the indices constituting the "links" have been specified. $\bar{D}_n$ and $\bar{C}_n$ are related but not equal to D_n and C_n of (41). For example,

$$\bar{D}_2(12)=\bar{C}_1(1)\bar{C}_1(2)=D_2(12;12)-C_1(1;2)C_1(2;1),$$
$$\bar{C}_2(12)=C_1(1;2)C_1(2;1)+C_2(12;12). \tag{60}$$

The general expression is

$$\bar{D}_n=\sum_P\prod_{l<n,\,\Sigma_l lm_l=n}\bar{C}_l^{m_l},\quad \bar{C}_1(1)=C_1(1;1), \tag{61}$$

where the sum is taken over all different partitions P of the indices $(1\cdots n)$ into two or more disjoint sets. Equation (61) should be compared with (44). For a system of ordinary bosons we would be finished at this point. Comparison of (61) and (58) (written for bosons, i.e., with P_n absent) with (53) identifies[38]

$$b_n{}^{\text{bosons}}=(i)^n\,\mathrm{tr}\bar{C}_n=(i)^n\,\mathrm{tr}\mathfrak{C}(H_n{}^{\text{bosons}}). \tag{62}$$

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[33] For $d=1$ this is a consequence of Landau's general argument, L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), p. 482. The lack of phase transition is generally believed for $d=2$ as well. In both cases it is suggested by the divergence of the free spin-wave approximation to the spin-deviation density [see Sec. 6(x)]. Certainly the low-density spin-wave picture holds for $\mu=0$ only if there exists a phase transition.

[34] For $\mu<0$ it is preferable to work away from $n=2NS$ rather than face the convergence questions associated with $\vartheta>1$. Note that $\mu\to -\mu$ changes the direction but not the magnitude of M; however, $\vartheta\to\vartheta^{-1}$ is not a symmetry of (50), since E_0 contains μ.

[35] S. Katsura and H. Fujita, J. Chem. Phys. **19**, 795 (1951); Progr. Theoret. Phys. (Kyoto) **6**, 489 (1951). G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, 1963), Chap. 3. See also S. Katsura, Progr. Theoret. Phys. (Kyoto) **13**, 571 (1955); **20**, 192 (1958); Advan. Phys. **12**, 391 (1963). The author is indebted to Dr. Katsura for bringing several of these valuable references to his attention.

[36] J. E. Mayer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 73.

[37] The radius of convergence of the series need bear no relation to the existence of a phase transition (Refs. 31, 35). Note that for $T=0$, $\mu>0$, (50) holds.

[38] Our Eq. (62) is Eq. (I.14) of Ref. 30.

This result—that the boson virial coefficient is related to the trace of the diagonally connected part of the boson Green's function—guarantees that the thermodynamical functions, in particular the free energy (50), are extensive.[39] It is natural to conjecture that this feature persists for the spin system despite the complicating appearance of the projection P_n in (58). This conjecture turns out to be correct.

The effect of the P_n projection on the spin problem is sorted out in detail in Appendix D. The outcome only is stated below. The fundamental connectivity expressed by the decomposition (41) involves solely the potential matrix v. The extra connectivity of the diagonal elements is given by (59) and comes into (62). In the combination $\mathrm{tr}H_nP_n$ of (58) the improper projection in $P_n=1-I_n$ effects still further connections. When P_n is multiplied out according to (11), it consists of unity plus a sum of terms each involving a product of one or more factors $\delta(\{\nu\})$, $2S+1\leqq\nu\leqq n$. The arguments of the δ functions belonging to each term are chosen disjointly from among $(1\cdots n)$. When P_n is multiplied by the diagonal H_n, these δ functions provide further "links" between the various C_l's (or $\bar{C}_l$'s). Let us extend the definition of the operations $\mathfrak{C}$ and $\mathfrak{D}$ to include this kind of linkage. The result of Appendix D is that,

$$b_n=(i)^n\,\mathrm{tr}\mathfrak{C}(H_nP_n)=(i)^n[\mathrm{tr}\bar{C}_nP_n-\mathrm{tr}\mathfrak{C}(\bar{D}_nI_n)] \quad (63a)$$

$$=(i)^n[\mathrm{tr}\bar{C}_n-\mathrm{tr}\mathfrak{C}(H_nI_n)]. \quad (63b)$$

Examples are

$$b_n=(i)^n\,\mathrm{tr}\bar{C}_n, \quad 1\leqq n\leqq 2S;$$

$$b_{2S+1}=(i)^{2S+1}[\mathrm{tr}\bar{C}_{2S+1}-NH_{2S+1}(11\cdots)]. \quad (64)$$

The evaluation of the free energy supplied by (50) and (63) is, of course, entirely equivalent to Dyson's,[40] though our derivation has followed a different path and emphasized somewhat different points. The reader is referred to Appendix A for a sketch of Dyson's development.

6. REMARKS ON THE VIRIAL EXPANSION: CONTENT AND USES

General Comments

(i) The formulas (63) for b_n do not contain $E_{\gamma I}$. This is clear, since Q_n of (58) is free of reference to the improper subspace and (55) relates Q_n's and b_n's. This property holds for the exact functions; however, as suggested in Sec. 3, *approximate* evaluations of H_nP_n may contain improper energies. Formula (36) showed that there exist $E_{\gamma I}\leqq E_0$. If these are not exactly projected out, there will be spurious contributions to b_n carrying factors $\exp\beta(E_0-E_{\gamma I})$. If the associated matrix elements are not at least exponentially small, such terms will produce exponentially large errors in the low-temperature thermodynamics. Worse yet, as n becomes of order N, (37) shows the existence of improper states for which the difference $E_0-E_{\gamma I}$ goes as N. Unless these contributions are eliminated, all hope of making sense of the $N\to\infty$ limit is lost. Luckily the situation is not as bad as it might seem. See (viii) below.

(ii) When can the virial expansion be expected to be a useful evaluation of the free energy? So long as (50) converges to the free energy in the vicinity of $\mathfrak{z}=0$, a given finite number of terms—for example, two—approximates W to any desired accuracy, provided $\mathfrak{z}$ is sufficiently small. Unfortunately $\mathfrak{z}$ small requires $\beta\mu$ large. Normally it is the zero-field limit, $\mathfrak{z}\to 1$, which is of the most theoretical interest. Here one must look not to $\mathfrak{z}$ but to the b_n's themselves to provide a practically convergent schema for the free-energy calculation. The schema we shall use in Sec. 8 corresponds to a rearrangement and partial summation of selected terms of the virial expansion. For reasons given in (v)–(viii), it seems feasible only at low temperatures and for $d=3$.

(iii) Equations (63) give two alternatives to the basic expression for b_n. Equivalent in any exact calculation, they emphasize different facets of the problem. In (63a) each separate term contains contributions only from proper states. The price paid is the appearance of the combinatorically complex projections P_n and I_n. In (63b) all the projection is in the second term. The $E_{\gamma I}$ correspondingly appear in each of the two terms separately and, of course, cancellingly. Interpretation of the form (63b) is particularly simple. Equation (62) shows that $(i)^n\,\mathrm{tr}\bar{C}_n$ is just the virial coefficient of the pure boson problem. The expression $(i)^n\,\mathrm{tr}\mathfrak{C}(H_nI_n)$ is the contribution to the virial coefficient from the improper boson states. Its subtraction leaves the property, spin b_n.

(iv) Even in the form (63a), containing only C_l's, $l\leqq n$, and projection operators, there is an arbitrariness, associated with the selection rule (35), by which (as discussed in Sec. 4) all forms $P_{g_1}C_nP_{g_2}$, $g_1\not\subset g_2$, may be eliminated. This seems all that can be said without further narrowing the problem.

Specific Remarks

The three-dimensional Heisenberg model at low temperatures has certain simplifying features.

(v) Let us sketch roughly the relevant physics. For $d=3$ (in contrast to $d=1, 2$) and at temperatures below the Curie point, we do not expect $M/N\to 0$ as $\mu\to 0$ [see discussion after (56)]. In particular for $T=0$, $M/N=-S$, so the spin-deviation density $\langle n\rangle$ is small at low temperatures. Since the spin excitations obey Bose statistics and have a k^2 spectrum,[41] the overwhelming majority of them have very low momenta.

[39] In effect, there is one free coordinate in the trace. The rest are difference coordinates via the connectivity.

[40] Dyson I (157).

[41] Of course, the one-particle spectrum (21) was only derived at $T=0$; however, it is consistent with the low-density picture that its main properties continue to hold at low but finite temperatures.

Now, the scattering of spin waves with low momenta is very weak. Physically this feature is connected with the fact that the zero-momentum mode, involving coherent rotation of all spins through a small angle, is an excitation which, because of the spherical symmetry of the exchange interaction, can never cost any energy. Formally it can be inferred from the structure of the interaction matrix for a process in which two spin waves of total momentum $\mathbf{K}$ scatter from an initial relative momentum $\mathbf{k}$ to a final relative momentum $\mathbf{k}'$ (reading from left to right): the Fourier transform of (25) is

$$\langle \mathbf{k}|V(\mathbf{K})|\mathbf{k}'\rangle = 2J\sum_{i=x,y,z}(\cos\tfrac{1}{2}K_i-\cos k_i)\cos k_i',$$

so that as $\mathbf{K},\mathbf{k}\to 0$ there is no interaction. In effect, then, the $d=3$ low-temperature Heisenberg system exhibits the characteristics of a low-density gas of weakly interacting particles, to which known techniques apply. There are important ways in which this picture must be qualified on closer inspection [see (viii)]; however, the main lines will remain.

(vi) Continuing this thought for the moment, we can anticipate the form of the temperature dependence of the thermodynamics. Equation (21) gives the basic spin-wave spectrum.[41] Thermodynamic factors carry the exponent $-\beta\Omega(\mathbf{k})$. At low temperatures only momenta for which this exponent is order unity can contribute appreciably. This means $|\mathbf{k}|\lesssim(T/SJ)^{1/2}$, thus effectively limiting $\mathbf{k}$ to a region of momentum space of volume proportional to $T^{3/2}$. Corrections bring in further factors of $|\mathbf{k}|$ and, therefore, extra powers of $T^{1/2}$. Similarly, the average energy, $\langle H\rangle-E_0$, has a k^2 factor from the spin-wave energy, in addition to the basic limitation of the effective momentum space, and goes as $T^{5/2}$ plus higher corrections. Actually there are always other corrections due to Brillouin zone edge effects [e.g., (ix)] and to *certain*[42] kinematical effects [see (vii)], which carry factors $e^{-\beta\delta}$, $\delta>0$, and are not, therefore, analytic as functions of $T^{1/2}$. The low-temperature thermodynamic results, which we shall calculate below, will, in summary, have the form of series in powers of $T^{1/2}$ and are to be regarded as at best asymptotically valid, neglecting terms like $\exp(-J/kT)$. Such contributions, while small at low temperatures, render our methods useless in the region of the Curie point [see Sec. 9 (ii)].

(vii) By the definition of Sec. 3, the lowest improper eigenvalue of the n-particle boson problem $n<n_c$ is greater than E_0 by a finite energy gap. Each thermodynamic factor carries this gap, so for $n<n_c$ the improper subtraction in (63b) is exponentially small.[43] As an example, notice that (28) and (36) allow one to write directly

$$H_{2S+1}(11\cdots;1'1'\cdots)\big|_{\mu=0,\ t\to -i\beta} = (2S+1)!(-i)^{2S+1}\exp(-2\beta SdJ(2S+1))\times\delta(11')\eta(l), \quad (65)$$

from which the subtracted term for b_{2S+1} may be evaluated by (64). The energy gap here is $2SdJ(2S+1)$. Equation (38) gives inequalities on n_c. For $1\leqq n\leqq 2S$, there is no improper subspace, and spin and boson virial coefficients are identical [see (64)]. For $2S<n<n_c$, spin and boson virial coefficients are equal to within exponential small terms, which cannot show up in low-temperature asymptotic expansion. Remember that Dyson II obtained this result for all n but only at the expense of drastically modifying H_B (see Appendix A). In our formulation improper subtractions are essential for $n\geqq n_c$ [see (i) and (iii)]. We shall be able to show in Sec. 8 by using the arguments of (iv) and (viii) that a set of apparently large contributions to b_n, $n\geqq n_c$, cancel. This makes it possible to prove in low-temperature series and neglecting certain convergence difficulties [see (viii)] a very limited equivalence between the spin and boson thermodynamics.

(viii) The thermodynamic calculations which follow will be carried out with the aid of perturbation theory. Only in the discussion of b_2 (Sec. 7) will we be able to make statements of any sort of mathematical rigor. Generally we must be content with the summation of a selected subset of diagrams and rough, term-by-term estimates of the remainder.[44] Nevertheless, a few words of *physical* justification for the validity of the perturbation calculation may well be in order. Observe two things: first, that the validity of the asymptotic low-temperature series depends only on the correct form of the dynamics in the immediate neighborhood of E_0 [cf. the energy gap argument of (vii)] and, second, that, generally speaking, the breakdown of perturbation theory is associated with the appearance of bound states.[25]

Now, there are two sorts of bound states here, proper and improper. For $n=2$ proper bound states are absent[14,45] in a region surrounding $\mathbf{K}$ (total pair momentum) equals zero. Consequently, there is a finite positive gap, $E_{\gamma P}-E_0>0$, between the lowest two-particle proper bound-state energy and E_0. It seems likely on the basis of the arguments given in (v) that this result continues to hold for higher n. If so, then the proper states do not, in fact, influence the low-temperature thermodynamics. There remains the possibility that perturbation theory attributes spuriously large contributions to these states. The purely computa-

[42] It seems most unlikely that *all* kinematical effects are of this form. See Secs. 8 and 9(i).

[43] Actually what is obvious is that H_nI_n is small. That this implies $\mathfrak{C}(H_nI_n)$ small can be proved inductively from the relation [see (D.3)], $\mathfrak{D}(H_nI_n)=D_n-\Pi_l[C_l-\mathfrak{C}(H_lI_l)]$.

[44] In this we are no worse off than previous authors. See also footnote 13.

[45] J. G. Hanus, in Quarterly Progress Report, Solid State and Molecular Theory Group (MIT), No. 43, p. 96, 1962; No. 44, p. 38, 1962; No. 46, p. 137, 1962 (unpublished); and Phys. Rev. Letters **11**, 336 (1963).

tional point that all contributions will turn out to involve only low momenta indicates that this is not so.

On the other hand, all improper states, which according to (i) are projected out of the thermodynamics, are bound in the sense that they contain at least one stationary, $(2S+1)$-occupied site. States with $E_{\gamma_I}-E_0<2SdJ(2S+1)$—in particular those with $E_{\gamma_I}\leqq E_0$—involve additional binding. However, it takes a rather large number of particles close together to gain sufficient potential energy to offset the higher momenta necessary for localization and obtain energies below E_0. The number n_c measures the crossover point. The "dangerous" improper bound states only show up in C_n, $n\geqq n_c$. We shall find in Sec. 8 that, to calculate thermodynamics through order T^4, we need deal only[46] with C_1 and C_2 and are, therefore, safely below this limit.

The logic in both cases is the same: The bound states do not influence the vital part of the spin-wave spectrum near E_0 and, correspondingly, the part of the perturbation series which we shall use is, to order T^4, uninfluenced by them. The bound states, in short, neither should nor do affect the low-temperature thermodynamics. Perturbation theory correctly represents the proper, low-lying spin excitations. As a special case, the presence or absence of improper states is irrelevant to order T^4. The question of the order in $T^{1/2}$ up to which this remains so is taken up in Sec. 9.

Simple Calculations

(ix) The form of b_1. Equations (64), (30), and (20) give

$$b_1=\sum_{\mathbf{k}\epsilon F}\exp[-\beta\Omega(\mathbf{k})|_{\mu=0}]. \tag{66}$$

For $N\to\infty$,

$$b_1/N=e^{-2SdJ\beta}\left[\int_{-\pi}^{\pi}\frac{dk}{2\pi}e^{2SJ\beta\cos k}\right]^d$$

$$=e^{-2SdJ\beta}[I_0(2SJ\beta)]^d, \tag{67}$$

where I_0 is the zeroth-order Bessel function of imaginary argument.[47] This is exact. See (70) for low-temperature form.

(x) The simplest approximation to b_n is to consider only the zeroth order of perturbation theory, $H_n=\Gamma_n$, and to neglect altogether the projection P_n. This is equivalent to calculating the thermodynamics of a set of free bosons with the spectrum (21) (i.e., H_B with $v=0$). The connected part of $\mathrm{tr}\Gamma_n$ consists in the $(n-1)!$ cycles, so

$$b_n^{(0)}=(i)^n(n-1)!\,\mathrm{tr}\Gamma_1{}^n=(n-1)!$$

$$\times\sum_{\mathbf{k}\epsilon F}\exp[-n\beta\Omega(\mathbf{k})|_{\mu=0}];\quad b_1^{(0)}=b_1. \tag{68}$$

For $n>1$ this is *not* exact. For $N\to\infty$,

$$b_n^{(0)}/N=(n-1)!e^{-2SndJ\beta}[I_0(2SnJ\beta)]^d. \tag{69}$$

I_0 has an asymptotic expansion for large argument,[48] i.e., low temperature, giving[49]

$$b_n^{(0)}/N=(n-1)!(4\pi SJ\beta)^{-3/2}$$

$$\times\left[\frac{1}{n^{3/2}}+\frac{3}{8(2S\beta J)n^{5/2}}+\frac{33}{128(2S\beta J)^2n^{7/2}}+\cdots\right], \tag{70}$$

which is exact in the asymptotic sense for b_1. The free-particle approximation to the low-temperature thermodynamics is obtained by summing (50):

$$W_0+\beta E_0=N(4\pi S\beta J)^{-3/2}$$

$$\times\left[Z_{5/2}+\frac{3Z_{7/2}}{8(2S\beta J)}+\frac{33Z_{9/2}}{128(2S\beta J)^2}+\cdots\right], \tag{71}$$

where

$$Z_p=Z_p(\mathfrak{z})=\sum_{n=1}^{\infty}\frac{\mathfrak{z}^n}{n^p},\quad \mathfrak{z}\frac{\partial}{\partial\mathfrak{z}}Z_p=Z_{p-1}. \tag{72}$$

The first omitted term in (71) is order $T^{9/2}$.

Formulas (70) and (71) have the anticipated form of power series in $T^{1/2}$. Note that the boson statistics puts the one-particle dynamics into b_n, so *all* virial coefficients have leading $T^{3/2}$ behavior. For general dimensionality the leading term in (70) goes as $n^{-d/2}$, giving a leading $Z_{d/2+1}$ in (71). Thus, for both $d=1,2$, the zeroth approximation to $\langle n\rangle$ is divergent, suggesting that[33] $M/N\to-S$ as $T\to 0$, as mentioned in Sec. 5.

One might be tempted to try to improve on this approximation by using $H_n=\Gamma_n$ but putting in P_n properly, thinking thus to obtain the leading kinematical corrections to the thermodynamics. This is very misleading. For example $S=\frac{1}{2}$, $H_2=\Gamma_2$, gives $b_2=b_2^{(0)}-2b_1^2/N$, an apparent T^3 correction. However, this correction comes from the lowest approximation to $H_2(11;11)$, a function which is actually exponentially small by (65). This pitfall has lead many authors[50]

[46] Roughly speaking, proper n-particle effects contribute as $T^{3n/2}$ (nth power of the spin-deviation density) or smaller.

[47] H. B. Dwight, *Tables of Integrals and Other Mathematical Data* (The Macmillan Company, New York, 1961), formulas 876 and 813.1.

[48] H. B. Dwight, (Ref. 47) formula 814.1.

[49] In this and the following formula the equality sign is used in the asymptotic sense.

[50] Actually, there are two sources of T^3 errors. Erroneous kinematical effects tend to enter as $T^{3(2S+1)/2}$. Also, the random-phase approximation of S. V. Tyablikov [Ukr. Mat. Zh. **11**, 287 (1959)] and others (Ref. 5) misestimates the energy spectrum of the thermodynamic spin waves, neglecting what are essentially exchange corrections to the Hartree spectrum. Improvement of the spectrum [first understood physically by Keffer and Loudon (Ref. 10)] still leaves the kinematical error, T^3 for $S=\frac{1}{2}$ [e.g., H. B. Callen, Phys. Rev. **130**, 890 (1963)].

(notably *not* including Dyson) to believe (wrongly) that T^3 terms are the leading correction to (71). In the next three sections we shall examine in detail the actual form of these corrections.

7. THE $d=3$, $N\to\infty$, LOW-TEMPERATURE SECOND VIRIAL COEFFICIENT

The calculation of the second virial coefficient is free of combinatorical difficulties and depends only on the mechanics of the $n=2$ problem, which can be reduced to quadratures without approximation.[14,45] In Sec. 8 it will turn out that at low temperatures the complete thermodynamics is [in accordance with Sec. 6(v)] dominated by the two-particle mechanics. The correct b_2 is, therefore, a necessary, unambiguous, and nontrivial check on any low-temperature thermodynamic calculation.

Equations (64) and (65) give,

$$b_2=(i)^2\,\mathrm{tr}\bar{C}_2-2N\delta(2S-1)\exp(-2\beta dJ). \quad (73)$$

This is exact at all temperatures. In the spirit of the low-temperature asymptotic calculation, the second term will be omitted henceforth. Knowing H_2, we should in principle simply extract the low-temperature behavior from the relevant integrals. In fact, it turns out to be easier to find the asymptotic behavior of each term in the perturbation expansion and then to sum these contributions. Bound states all have finite total pair momentum $\mathbf{K}$ and energies separated from E_0 by a finite gap. Perturbation theory, therefore, converges rigorously in the region near E_0 contributing to the asymptotic series. In accordance with the logic of Sec. 6 (viii), the perturbation series should and will show contributions only from this region. So much for justification!

The calculation now is of a straight boson b_2 and follows conventional lines. Except for the absence of thermodynamic propagators, it is closely analogous to Dyson's calculation[51] of the complete thermodynamics. It differs in two respects: First, our knowledge of the $n=2$ mechanics makes the use of perturbation theory unambiguous and, second, there are no "supplementary interactions" to be argued away (see Appendix A).

From (30) and (64),

$$b_2=\sum_{n=0}^{\infty} b_2^{(n)};\quad b_2^{(n)}=(i)^2\sum_{1,2}\langle 12|(\Gamma_2(\tfrac{1}{2}iv))^n\Gamma_2|12\rangle, \quad (74)$$

where appropriate intermediate time integrations are left implicit. In analyzing (74) it will be useful to make reference to Eqs. (34)–(44) of Ref. 14. Comparison of (34) there with our (30) establishes the (coordinate representation) correspondences

$$\begin{aligned}&(\text{our})\Gamma_2=\Gamma_2/2S\ (\text{Ref. 14}),\\ &(\text{our})\Gamma_2 v=-K_2J/(2S)^2\ (\text{Ref. 14}).\end{aligned} \quad (75)$$

We shall need the definitions:

$$\mathbf{K}=\mathbf{k}'+\mathbf{k}'',\quad 2\mathbf{k}=\mathbf{k}'-\mathbf{k}'', \quad (76)$$

$$\begin{aligned}S(\mathbf{k},\mathbf{K})&=\Omega(\mathbf{k}')\big|_{\mu=0}+\Omega(\mathbf{k}'')\big|_{\mu=0}\\ &=4SJ\sum_i(1-\cos\tfrac{1}{2}K_i\cos k_i),\end{aligned} \quad (77)$$

and the 3×3 matrix, $l(\mathbf{k},\mathbf{K})$,

$$[l(\mathbf{k},\mathbf{K})]_{ij}=\cos k_i(\cos\tfrac{1}{2}K_j-\cos k_j), \quad (78)$$

where i, j run over the spatial directions. The transforms of Ref. 14 give ($n\geqq1$),

$$\begin{aligned}b_2^{(n)}/N=&\frac{2(2J)^n}{N^{n+1}}\sum_{\mathbf{K},\,\mathbf{k}_1,\,\cdots\mathbf{k}_n\in\bar{F}}\mathrm{tr}\prod_{\alpha=1}^{n}l_\alpha\, i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\\ &\times[(\omega-S_1+i\epsilon)^2\prod_{\gamma=2}^{n}(\omega-S_\gamma+i\epsilon)]^{-1},\end{aligned} \quad (79)$$

where the abbreviations $l_\alpha=l(\mathbf{k}_\alpha,\mathbf{K})$, $S_\alpha=S(\mathbf{k}_\alpha,\mathbf{K})$ have been used and the momentum sums run over the modified Brillouin zone $\bar{F}$ defined by (42) of Ref. 14. For $t>0$ the contour of integration can be closed in the lower half ω-plane. The symmetry of the numerator in the $\mathbf{k}_\alpha$ brings about the cancellation (under the momentum sum) of each of the simple pole contributions with one of the n terms arising from the second-order pole. We are left with

$$\begin{aligned}b_2^{(n)}/N=&\frac{(-2\beta)(2J)^n}{N^{n+1}}\\ &\times\sum_{\mathbf{K},\,\mathbf{k}_1,\,\cdots\mathbf{k}_n\in\bar{F}}[e^{-\beta S_1}\,\mathrm{tr}\prod_{\alpha=1}^{n}l_\alpha/\prod_{\gamma=2}^{n}(S_1-S_\gamma)].\end{aligned} \quad (80)$$

The term-by-term analysis of (80) is tedious but straightforward. We shall summarize the salient logic and proceed to write down the result.[52]

As $N\to\infty$, the momentum sums can be transformed to integrals. The exponential factor forces $\mathbf{K}$ and $\mathbf{k}$ to be small, in accordance with Sec. 6(v) and in confirmation of the expectation that all low-temperature contributions come from the region where perturbation theory is valid. All dependence on the small momenta (aside from the leading exponential) can be expanded in even powers about zero. The finite limits of integration can be extended to infinity with exponentially small error. Phase space arguments [see Sec. 6(vi)] show that the resulting expression is a power series in $T^{1/2}$. The leading dependence might seem to be T^2 (β and two volume elements); however, the weakness of the interaction [Sec. 6(v)] and a certain formal symmetry between the appearances of $\mathbf{k}_1$ and $\frac{1}{2}\mathbf{K}$ give T^4. Denominator singularities occurring when other $\mathbf{k}_\alpha$, $\alpha\neq1$, are small do not contribute before $T^{9/2}$. The leading contribution, which

[51] Dyson II, Secs. 7 and 8.

[52] See Ref. 6 for further details.

is all we shall calculate, is

$$b_2^{(1)}/N=\frac{3}{16\pi^3(2S)}\frac{1}{(2S\beta J)^4}, \tag{81}$$

$$b_2^{(2)}=b_2^{(1)}S^{-1}[\tfrac{2}{3}\Gamma^s+\Lambda-\tfrac{1}{3}], \tag{82}$$

and

$$b_2^{(n)}=\tfrac{4}{3}b_2^{(1)}(\Gamma^s/2S)^{n-1}, \quad n>2, \tag{83}$$

where[53]

$$\Lambda=\frac{1}{\pi^3}\int_0^\pi[(dX)/\sum_{i=1}^3(1-\cos X_i)]\approx 0.505, \tag{84}$$

and

$$\Gamma^s=\frac{3}{\pi^3}\int_0^\pi[(dX)\cos X_1(1-\cos X_2)/\sum_{i=1}^3(1-\cos X_i)] \tag{85}$$

and was proved by Dyson[54] to lie between 0 and $\frac{1}{4}$.

Summation of (74) now gives the complete asymptotic low-temperature b_2 through order T^4,

$$b_2=b_2^{(0)}+b_2^{(1)}[\tfrac{4}{3}(1-\Gamma^s/2S)^{-1}-\tfrac{1}{3}-(1/S)(\Lambda-\tfrac{1}{3})]. \tag{86}$$

The "free" term $b_2^{(0)}$ is given to the same accuracy by (70),

$$b_2^{(0)}/N=(8\pi S\beta J)^{-3/2}\left[1+\frac{3}{2^4(2S\beta J)}+\frac{33}{2^9(2S\beta J)^2}\right]. \tag{87}$$

There are corrections to (86) of order $T^{9/2}$. Our result agrees with the coefficient of $(-2\beta e^{-2\beta L})$ in Dyson's expressions for the free energy.[55]

8. LOW-TEMPERATURE THERMODYNAMICS FOR $d=3$, $N\to\infty$

In this chapter we shall calculate the asymptotic low-temperature free energy through terms of order T^4. The standard of rigor of Sec. 7 cannot, unfortunately, be maintained. The work falls into two parts: first, the qualified elimination of effects due to improper projections; second, the selection and summation of important terms from the resulting boson problem. The central argument of the first part is exact. In the second part we shall rely on perturbative estimates and calculations without justification beyond that given in Sec. 6.

From (32) [or (35)] and Sec. 6(vii) we know that $I_nH_n|_{t\to -i\beta}$ is either zero or exponentially small, so long as $n<n_c$. In the spirit of the low-temperature calculation we may use this fact to derive relations among the C_n, $n<n_c$, which in turn serve to simplify the form of the thermodynamic subtractions, $\mathcal{C}(H_nI_n)$ [cf. Eq. (49) and Sec. 6(iv)]. Let us illustrate for $n=2,3$ and $S=\frac{1}{2}$. The equality sign will be used below in the sense of "equal to within exponentially small terms." Now,

$$H_2(11;1'2')=0 \text{ implies } C_2(11;1'2')+2C_1(1;1')C_1(1;2')=0. \tag{88}$$

This relationship can be used to write

$$H_3(113;1'2'3')=C_3(113;1'2'3')+2[C_2(13;1'2')C_1(1;3')+C_2(13;1'3')C_1(1;2')+C_2(13;2'3')C_1(1;1')]. \tag{89}$$

Of course, $H_3(113;1'2'3')=0$, giving an equality between C_3 and a sum of terms C_2C_1. However, even assuming that we were ignorant of this, (89) can be used to simplify the expression for $\mathcal{C}(H_3I_3)$ occurring in b_3: $I_3^{(1/2)}(123)$ equals $\delta(12)+\delta(13)+\delta(23)-2\delta(123)$, so

$$\mathrm{tr}C_3-(-i)^3b_3=\mathrm{tr}\mathcal{C}(H_3I_3)=3\sum_{1,2}[C_3(112;112)+2C_2(12;11)C_1(1;2)+4C_2(12;12)C_1(1;1)]-2\sum_1[C_3(111;111)+6C_2(11;11)C_1(1;1)], \tag{90}$$

which is actually exact, since it only depends on $I_2H_2P_2=0$. Again, the right-hand side is actually exponentially small by Sec. 6(vii). The point here is that, by using only (88), we have eliminated all $(C_1)^3$ terms from (90). One such term would have been $\sum_{1,2}C_1(1;2)\times C_1(2;1)C_1(1;1)$, an apparent T^3 contribution. This cancellation was first mentioned in Sec. 6(x). It will be shown to be quite general in what follows.

Any improper state has at least one $(2S+1)$-occupied site. Let this site be 1. Remember the symmetry of H_n's and C_n's in left (and right) indices. Write the expansion of $H_n(1\cdots 1(2S+2)\cdots n;1'\cdots n')$, $2S<n<n_c$, in terms of products of C_l's, $l\leqq n$. Pick from this expansion only those terms *each* C_l of which has at least one 1 as a left-hand argument. In particular no such term has more than $(2S+1)$ factors C_l. One can prove by induction that *the sum of such terms is zero.* Equation (88) is a special case. So is (89), when it is set to zero. The heart of the proof is the observation that one may employ a shorthand in which all arguments other than the $(2S+1)$ improper 1's are dropped. Thus (88) becomes $C_2(11;)+C_1(1;)C_1(1;)=0$, where the second term stands for all (two) terms in the expansion of $H_2(12;1'2')$ which have the indicated form when $1=2$. Similarly

$$H_3(113;1'2'3')=C_3(11;)+C_2(11;)C_1(;)+C_2(1;)C_1(1;)+C_1(;)[C_1(1;)]^2,$$

which immediately yields (89) in the form

$$C_3(11;)+C_2(1;)C_1(1;)=0.$$

The point is that when this notation is used the combinatoric takes care of itself. The general expression for $S=\frac{1}{2}$, $n<n_c$, is

$$C_n(11;)+\sum_{l<n}C_l(1;)C_{n-l}(1;)=0, \tag{91}$$

of which (88) and (89) are special cases. Analogous equations hold for $S>\frac{1}{2}$, $n<n_c$, in accordance with the rule given above.

[53] G. N. Watson, Quart. J. Math. **10**, 266 (1939).
[54] Dyson I, Eq. (89).
[55] Dyson II, (131). The extra factors arise because of slight definitional differences.

Now let us use these results to rewrite

$$H_n(1\cdots1(2S+2)\cdots n;1'\cdots n') \quad \text{for} \quad n\geqq n_c.$$

Again employ the shorthand to expand in terms of successively more complicated connected parts:

$$[C_1(1;)]^{2S+1}[C_1(;)]^{n-2S-1}+C_2(11;)[C_1(1;)]^{2S-1}\times[C_1(;)]^{n-2S-1}+C_2(1;)[C_1(1;)]^{2S}[C_1(;)]^{n-2S-2}+C_2(;)[C_1(1;)]^{2S+1}[C_1(;)]^{n-2S-3}+\cdots.$$

By using (91) or its analog for higher spins, we may cancel all terms in which the sum of the orders of those C_l's containing the argument 1 is less than n_c. If, as conjectured, n_c is actually equal to the upper limit provided by (38), then every term in the remaining expression for $H_n(1\cdots1(2S+2)\cdots n;1'\cdots n')$ must contain at least one C_l with $l\geqq(2S+1)^3$. The same is true generally of I_nH_n and, therefore, of $\mathrm{tr}\mathcal{C}(H_nI_n)$. We do not emphasize the precise value of n_c or the precise degree of cancellation.[56] What is important is that the improper subtractions in (63b) do not involve terms $\prod_l C_l$ with all low l's.

Note that we do *not* argue that the terms remaining in $\mathrm{tr}\mathcal{C}(H_nI_n)$, $n\geqq n_c$, are actually small. On the contrary there are exponentially large improper contributions [Sec. 6(iii)]. The point is that the large improper terms in $\mathrm{tr}\mathcal{C}(H_nI_n)$ exactly cancel corresponding terms in $\mathrm{tr}\bar{C}_n$. Appreciable contributions to the low-temperature thermodynamics come from processes involving in an intrinsic way only a small number of particles, i.e., from terms involving C_l's with only low l. What we have proved is that there are no such terms in $\mathrm{tr}\mathcal{C}(H_nI_n)$.

We expect perturbation theory to be valid for the low-order C_l's, which do contribute. In fact, perturbation terms involving higher numbers of particles seem to get smaller roughly as $T^{3l/2}$ [Sec. 6(vi)]. Despite these term-by-term estimates, it is likely [Sec. 6(viii)] that there are divergences for $l\geqq n_c$ due to bound improper states. We need not worry, however, since the improper divergences of the two terms in (63b) must cancel, while associated proper contributions for large l remain small.[13]

We have arrived at what we shall call the "Dyson prescription" for calculating the low-temperature free energy: treat the problem as a set of true bosons governed by H_B, calculate in perturbation theory, and do not worry about higher-order divergences. This receipt certainly works through order T^4 and almost certainly does *not* work to all orders in $T^{1/2}$. The limit on its validity is discussed in Sec. 9. In the remainder of this section we shall accept it without further question.

There are many elegant methods for treating the low density, weakly interacting Bose gas, with which we are now faced.[57] This is exactly the problem which Dyson solved.[58] Our formulation in terms of the virial expansion is not economical at this point. Rather than be either apish or cumbersome, we choose to sketch the virial procedure and jump immediately to an intermediate point which can be attained by any one of the several methods.

The terms in the free energy involving only C_1 were summed in Sec. 6(x) to give W_0, Eq. (71). The class of terms next in importance consists of traces of products of C_2's and C_1's linked sequentially as "ladders": $C_2(;ab)\langle a|C_1^{\alpha}|c\rangle\langle b|C_1^{\beta}|d\rangle C_2(cd;)$. Each C_2 is now expanded perturbatively in v. Terms of each order in v are summed in the virial expansion (50) with appropriate multiplicity and fugacity factors. The resulting free-energy contributions are

$$W_1^{(n)}/N=(-\beta)(2J)^n(1/N^{n+1})\sum_{\mathbf{K},\,\mathbf{k}_1,\,\cdots,\,\mathbf{k}_n\epsilon\Gamma'} n(\tfrac{1}{2}\mathbf{K}+\mathbf{k}_1)n(\tfrac{1}{2}\mathbf{K}-\mathbf{k}_1)\,\mathrm{tr}\prod_{\alpha=1}^{n} l_\alpha \prod_{\gamma=2}^{n}\left[\frac{1+n(\frac{1}{2}\mathbf{K}+\mathbf{k}_\gamma)+n(\frac{1}{2}\mathbf{K}-k_\gamma)}{(S_1-S_\gamma)}\right], \quad (92)$$

$$W_1=\sum_{n=1}^{\infty} W_1^{(n)}, \quad (93)$$

where

$$n(\mathbf{k})=[e^{\beta\Omega(\mathbf{k})}-1]^{-1}=\{\mathfrak{z}^{-1}\exp[\beta\Omega(\mathbf{k})|_{\mu=0}]-1\}^{-1}. \quad (94)$$

This expression should be compared with (80). The asymptotic evaluation proceeds as previously. There is an over-all factor of two different, since it is $\mathfrak{z}^2b_2/2!$ that is a term in the free energy. The $n(\frac{1}{2}\mathbf{K}\pm\mathbf{k}_\gamma)$ in the numerator of the product all lead to contributions of order higher than T^4. The factors $n(\frac{1}{2}\mathbf{K}\pm\mathbf{k}_1)$ play the role of $\exp(-\beta S_1)$ in keeping $\mathbf{K}$ and $\mathbf{k}_1$ small. They introduce an extra factor of $(Z_{5/2})^2$ in each term of (92) as compared to (80). The final result is

$$W_1=\tfrac{1}{2}[Z_{5/2}(\mathfrak{z})]^2(b_2-b_2^{(0)}), \quad (95)$$

which is accurate through order T^4.

Terms in the virial expansion having C_2's and C_1's not in the ladder configuration and terms including one or more C_l, $l>2$, are all smaller than T^4 in perturbation estimate. The author cannot claim to have made a systematic and rigorous examination of the general term; however, the arguments of Secs. 6 and 7 are easy to apply to any given term.[59] The divergences associated with $n\geqq n_c$ are probably a property of sums of

[56] Equation (35) is valid for all n. Much of it remains unused so far and may provide further cancellation.

[57] For example, see L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

[58] Dyson II, Secs. 5–10.

[59] This is, of course, consistent with Dyson's estimates of higher-order regular terms.

terms rather than individual terms. In any case we have already dealt with them.

The upshot of our evaluation, valid through T^4, is

$$W=\beta E_0+W_0+W_1, \tag{96}$$

where (71), (72), (86), and (95) are the needed references. This agrees with Dyson.[55] The corresponding magnetization follows from (51) and (52).

9. CONCLUDING DISCUSSION

(i) Up to what order in $T^{1/2}$ can the "Dyson prescription" for calculating the low-temperature thermodynamics be expected to remain valid? It is mathematically conceivable that the failures of perturbation theory are such as miraculously to ignore all (bound) improper states, while treating proper states correctly. If so, then the prescription is asymptotically exact. This seems unlikely. We adopt the more pedestrian philosophy that there is no reason to trust boson results beyond the point at which $\mathrm{tr}\mathcal{C}(H_nI_n)$ starts contributing.[60] There is no reason to believe that perturbation theory does not err in treating processes involving more than n_c particles. Furthermore, finite kinematical effects may show up even before this point. In either case we assume that the perturbatively calculated boson terms are in error. At what order in $T^{1/2}$ do these terms first enter? Three factors conspire to help the "Dyson prescription": (a) Improper projections tend to discourage "ladder" structure, thus making temperature dependence additive over the various connected parts; (b) Sec. 8 uses only a small part of the full (35); there may well be further cancellations in $\mathrm{tr}\mathcal{C}(H_nI_n)$; (c) the weakness of the interaction v gives powers of $T^{1/2}$ beyond those due simply to density factors. All in all it seems likely that the "Dyson prescription" is asymptotically valid up to roughly $T^{3n_c/2}\approx T^{\frac{3}{2}(2S+1)^{d+1}}$ but not beyond. This is, evidently, a very strong statement.

(ii) The fact that the "Dyson prescription" is asymptotically valid to a high order in the temperature does *not* mean that it can be expected to be good near the Curie point. There are several reasons. Most simply, contributions which we have neglected as exponentially small are appreciable at T_c. More importantly, the physical picture on which we have based our arguments fails to hold: when $M=0$, $\langle n\rangle=S$, so there is a very large density of spin deviations, and low momenta do not necessarily dominate the mechanics.[61] Interactions are strong at higher momenta, so the system is no longer effectively weakly-interacting. Stated otherwise, one has no rationale for believing that spin waves remain the dominant excitations of the system. Furthermore, regardless of dynamical interactions, $I_nH_nI_n$ may no longer be neglected even for $n<n_c$, so $\mathcal{C}(H_nI_n)$ subtractions are important. The finiteness of individual spin magnitudes must make itself felt at high spin-deviation density.

(iii) The consequences of the close relation between the Heisenberg and corresponding boson problems can also be translated into the language of thermodynamic Green's functions.[57] Note, for example, that the spectrum of the Green's function, $(-i)\langle(S^-(1;t)S^+(1';0))_+\rangle$, consisting of energy differences between n- and $(n\pm1)$-spin-deviation states, must differ from the spectrum of the corresponding boson Green's function (with H_B) only through the omission of those differences involving improper energies. The singularities in the energy variable of the spin and boson functions are the same. The difference in kinematics only affects the relative weightings. At low temperatures and for small momenta and energies sharper statements are presumably possible, corresponding to the simplifications we have noted in the thermodynamically important features of the behavior.

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APPENDIX A: DYSON'S CALCULATION

Let us sketch the logic of Dyson's calculation,[2] comparing it at each stage with ours. There are three steps:

(i) Dyson manufactures a boson Hamiltonian [Dyson I (57)] whose action (in an occupation number representation) onto right-hand boson states simulates the action of (1) onto right-hand spin states. Our operator $(i(\partial/\partial t)-\mathcal{L}_n)$, which was used in Sec. 3, acts on left-hand indices, so it is not surprising that Dyson's boson Hamiltonian turns out to be $H_B^\dagger$. With the aid of a "kinematical Green's function," which plays a role closely analogous to our I_n, Dyson formulates the free energy of the spin system as [Dyson I (157)]

$$W=W_B-W_I, \tag{A1}$$

where W_B is the complete boson free energy and W_I corresponds to our improper subtractions. This is a precise parallel to our (50) and (63b).

(ii) Dyson observes that the peculiar properties of the improper energies for $n\gtrless n_c$ [e.g., our (36)–(38)] means that W_B and W_I contain (cancelling) exponentially large contributions at low temperatures. He chooses, therefore, to add to his Hamiltonian an infinite set of "supplementary interactions," H_s [Dyson II (26)

[60] Note that Dyson's proof of the smallness of kinematical effects is for a different Hamiltonian and does not apply here. See Appendix A.

[61] The author feels that this and the following points cast doubt on Kittel's argument that the magnon description is valid near the Curie Temperature [C. Kittel, in *Proceedings of the Eleventh Colloque Ampère, Eindhoven, 1962*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1963), p. 80.

and (123)], with the properties that (a) they have no effect on the proper spectrum of $H_B^\dagger$ and (b) all improper eigenenergies of $(H_B^\dagger+H_s)$ are separated from E_0 by a positive energy gap. The spin free energy can now be written,

$$W=W_B'-W_I', \tag{A2}$$

corresponding to the boson free energy with $(H_B^\dagger+H_s)$ minus associated improper subtractions. Property (b) now allows Dyson to prove (Dyson II Sec. 4) that W_I' is exponentially small at low temperatures, so the spin problem is asymptotically exactly equivalent to a boson problem with $(H_B^\dagger+H_s)$.

By contrast, we use the fact that property (b) holds for H_B so long as $n<n_c$. This and the selection rule (35) allow us to demonstrate (without introducing any supplementary interactions) the low-temperature cancellation of all terms in W_I involving only connected parts C_l with low l. Higher terms in W_I cancel against terms in W_B whose proper parts are small.[13] We are left with the task of computing terms in W_B involving C_l with only low l. Dyson also arrives at essentially this point, as we shall now see.

(iii) Dyson solves the boson problem $(H_B^\dagger+H_s)$ by perturbation theory away from free spin waves [Sec. 6(x)]. There are two kinds of interaction, H_s and the four-point matrix $v^\dagger$ in $H_B^\dagger$. Dyson denotes as "regular" all those perturbation terms involving only $v^\dagger$. Terms including one or more H_s are called "irregular." Thus,

$$W_B'=W_0+W_R+W_S, \tag{A3}$$

corresponding to free, regular, and irregular terms, respectively. Dyson now argues [Dyson II Sec. 9] that W_s is exponentially small at low temperatures and is lead to conclude that (W_0+W_R) is the asymptotically exact Heisenberg free energy. He accordingly sums terms to T^4.

Now, there is clearly an inconsistency: $W_B=W_0+W_R$, so comparison of (A1)–(A3) gives

$$W_S+W_I=0 \tag{A4}$$

at low temperatures to within exponentially small terms. W_I, however, contains exponentially large terms, so W_s cannot be small. Of course, W_R contains exponentially large counterterms from improper states, since (A1) holds and E_0 is the true ground state of the spin system. The extent to which finite terms remain from this cancellation is not made clear. Dyson was aware of this inconsistency [Dyson II after (125)] but conjectured that it would not affect T^4 results.

The author discusses in Sec. 9(i) the limit of validity of the "Dyson prescription" $(W=W_0+W_R)$. It seems likely that the prescription fails somewhere near $T^{3n_c/2}$. The fact that it is good to such a high order in $T^{1/2}$ testifies to the validity of the physical picture on which it is based [Sec. 6(v)]. However, Dyson's introduction of H_s is certainly unnecessary and can be argued to pose more difficulties than it solves.

APPENDIX B: THE CORRESPONDING BOSON PROBLEM

The fact that H_B is not Hermitian will make it difficult unambiguously to exclude certain types of pathological behavior in what follows. Our purpose here is merely to delineate the structure of the connection between the boson and spin problems; therefore, we shall assume at the outset a number of hypotheses sufficient to prohibit anomalies. Should these hypotheses prove wrong upon closer examination, it is hoped that the relevant structure will persist. In any case the boson subspace related to H_nP_n must by (29) be well behaved.

Assume, then, that H_B possesses complete sets of linearly independent left and right n-particle eigenvectors,

$$\langle\gamma|H_B=E_\gamma\langle\gamma|,\ H_B|\gamma\rangle=E_\gamma|\gamma\rangle. \tag{B1}$$

Neglect problems of degeneracy and note that the left and right eigenvectors corresponding to the same eigenvalue can be paired.[62] Remember that in (B1) $|\gamma\rangle$ is *not* generally the Hermitian adjoint of $\langle\gamma|$. An elementary argument shows that $\langle\gamma|\gamma'\rangle=0$ for $\gamma\neq\gamma'$. The possibility $\langle\gamma|\gamma\rangle=0$ is excluded by the assumption of linear independence, so we can normalize according to

$$\langle\gamma|\gamma'\rangle=\delta(\gamma\gamma'). \tag{B2}$$

The completeness assumption implies that an arbitrary left or right vector has a unique expansion in the corresponding basis of eigenvectors, so the unit operator can be exhibited as usual,

$$1=\sum_\gamma|\gamma\rangle\langle\gamma|. \tag{B3}$$

Wave functions for the boson system are defined by [cf. (14)]

$$\begin{aligned}\langle 0|\prod_{i=1}^{n}\psi(i)|\gamma\rangle&=\varphi_\gamma(1\cdots n),\\ \langle\gamma|\prod_{i=1}^{n}\psi^\dagger(i)|0\rangle&=\varphi_\gamma^\dagger(1\cdots n)\end{aligned} \tag{B4}$$

and satisfy (15) and (16) with the projections omitted. Of course, $\varphi_\gamma^\dagger$ is not the adjoint of φ_γ.

The boson Green's function H_n has the representation,

$$H_n(1\cdots n;1'\cdots n';\omega)=(-i)^n\sum_\gamma\frac{\varphi_\gamma(1\cdots n)\varphi_\gamma^\dagger(1'\cdots n')}{[\omega-(E_\gamma-E_0)+i\epsilon]}. \tag{B5}$$

This should be compared to (17). The energies $E_{\gamma I}$ do not appear in (17), so

$$P_n\varphi_{\gamma_I}^\dagger=0. \tag{B6}$$

Equations (B5), (17), and (29) relate the spin and boson

[62] Left- and right-eigenvalue equations are identical.

wave functions belonging to proper eigenenergies:

$$\varphi_{\gamma P}=(h_n)^{1/2}\psi_{\gamma P}, \quad P_n\varphi_{\gamma P}{}^{\dagger}=(h_n)^{-1/2}\psi_{\gamma P}{}^{\dagger}. \quad \text{(B7)}$$

Equations (B6) and (B7) may also be obtained by writing the Schrödinger equation in the matrix form (31).

APPENDIX C: THE CONNECTED KERNEL FOR H_n

The proof of Eqs. (35)–(37) of the text may be approached in several different ways. Weinberg's paper[27] contains a very general constructive demonstration. We shall here adopt the far more pedestrian philosophy of simply observing that the H_n which solves (35) with the definitions (36) and (37) does, in fact, satisfy the original differential equation of motion.

It is convenient to use not (26) but the corresponding right-hand equation of motion, which may be written symbolically

$$H_n(i(\partial/\partial t)-\mathfrak{L}_n)=(-i)^{n-1}\delta(t)1_n. \quad \text{(C1)}$$

A couple of remarks are required. H_B is non-Hermitian, so the Heisenberg representation boson field operators, $\psi(t)$ and $\psi^{\dagger}(t)$, are *not* Hermitian conjugates. To get equations of motion for the indices occurring in the $\psi^{\dagger}$ operators, one must define a Green's function of two time variables, t and t', associated with ψ and $\psi^{\dagger}$, respectively. After computing equations of motion, one may use the observation that H_n is a function only of $(t-t')$ to eliminate t'. Similarly, when the operator $(i(\partial/\partial t)-\mathfrak{L}_n)$ is applied on the right of a matrix product which includes integration over an intermediate time variable [c.f. after Eq. (25)], it must be understood to take the equation of motion with respect to the farthest right time and then to employ the time difference dependence to involve the integrated, intermediate time. With these provisos, then, take $(i(\partial/\partial t)-\mathfrak{L}_n)$ from the right onto (35) and invoke the symmetry of K_n in its right-hand indices:

$$\tfrac{1}{2}(-i)^{n-1}n!K_n=\tfrac{1}{2}(H_n-D_n)(i(\partial/\partial t)-\mathfrak{L}_n). \quad \text{(C2)}$$

Given (C2) for all orders $l<n$, (C1), and the definition (36), one must verify inductively that (C2) reproduces (37) for order n. By definition D_n always contains Γ_n, so (H_n-D_n) has no discontinuity at $t=0$. The typical term in D_n is a product of connected parts, $\prod C$. Resulting from such a term in D_n, there are two types of contribution to the right-hand side of (C2): (a) terms of the form $(\prod C)v$, where the potential v connects two of the C's appearing in the product, and (b) terms of the form $-(\prod' C)(-i)^{l-1}l!K_l$, where $(i(\partial/\partial t)-\mathfrak{L}_l)$ operating from the right has replaced some given C_l by K_l, according to (C2) for $l<n$. Equation (37) for $l<n$ allows the type (b) terms to be rewritten, $-2(\prod' C)C_mC_{l-m}v$. The (a) and (b) terms now have the same form. Finally, group the terms on the right of (C2) according to the number of C factors. Type (a) terms with two C's give just (37) to order n, where the extra factor of two arises from the symmetry of v in its left-hand indices. There are no type (b) terms with two C's. For each higher number of C's, the reader will readily convince himself that the (a) and (b) type terms exactly cancel one another.

APPENDIX D: VIRIAL COEFFICIENT FOR THE SPIN PROBLEM

In order to establish Eq. (63) we begin by analyzing the structure of the diagonal H_nP_n appearing in (58). Equations (59), (61), and (11) give

$$H_nP_n=\sum_P\Big[\prod_{l\leqq n,\,\Sigma_l lm_l=n}(\bar{C}_l)^{m_l}\Big]\times\prod_{\{2S+1\}}(1-I_{2S+1}(\{2S+1\})), \quad \text{(D1)}$$

where the term $m_n=1$, $m_l=0$ for $l<n$ has been included. A typical term in (D1) involves the product of a number of $\bar{C}_l$ factors with a number of I_{2S+1} factors. The $\bar{C}_l$ factors are, by the definition (59), unlinked. We consider, however, the extended definition [given above (63)], whereby an I_{2S+1} may connect two $\bar{C}_l$'s in the sense $\bar{C}_\alpha(1\cdots)\bar{C}_\beta(2\cdots)I_{2S+1}(12\cdots)$. Take some particular term in the expansion of (D1). Form all linkages. The sets of arguments belonging to factors not connected by a series of links are disjoint. Therefore, the linkage analysis defines a partition of the indices $(1\cdots n)$. Now, collect all terms in (D1) corresponding to each partition P. One such partition consists of complete connectivity of all the arguments. The associated terms in (D1) are $\mathfrak{C}(H_nP_n)$,

$$\mathfrak{C}(H_nP_n)=\bar{C}_nP_n + \text{terms involving two or more } \bar{C}_l\text{'s and associated connecting } I_{2S+1}\text{'s.} \quad \text{(D2)}$$

The result towards which we are aiming is

$$H_nP_n=\sum_P\Big[\prod_{l\leqq n,\,\Sigma_l lm_l=n}\{\mathfrak{C}(H_lP_l)\}^{m_l}\Big]. \quad \text{(D3)}$$

To obtain (D3) from (D1) we need only show that the over-all effect of the projection P_n in (D1) is to turn each $\bar{C}_l$ into the associated $\mathfrak{C}(H_lP_l)$. Let us do this. Choose some partition P. A partial decomposition of (D1) including all but not only those terms conforming to P is performed as follows: let the sets of arguments associated with P be g_i; n_i will denote the number of elements (arguments) in g_i; p_i is the set of partitions of g_i. Pick out from H_n the subset of terms,

$$\prod_i\Big[\sum_{P_i}\prod_{l_i,\,\Sigma_{l_i} lm_{l_i}=n_i}(\bar{C}_{l_i})^{m_{l_i}}\Big]=\prod_i H_{n'}. \quad \text{(D4)}$$

Observe that (i) all terms in (D4) do appear in H_n, because of the $\sum_P$ in the structure of H_n and (ii) no term in H_n and *not* in (D4) can lead to terms in (D1) conforming to P, since all other terms already contain violations of P. Finally, write P_n as

$$P_n=\Big[\prod_i\Big(\prod_{\{P_i\}}P_{2S+1}\Big)\Big]\Big[\prod{}' P_{2S+1}\Big]=\Big[\prod_i P_{n_i}\Big]\Big[\prod{}' P_{2S+1}\Big], \quad \text{(D5)}$$

where $\prod_{\{P_i\}}$ denotes the product over all factors

$P_{2S+1}(\{2S+1\})$ with indices, $\{2S+1\}$, contained in g_i and $\prod'$ is the product over all other $(2S+1)$-tuples of indices. The leading term in the expansion of $\prod'$ in 1 and I_{2S+1} is just unity. All further terms violate P. The full contribution of P to (D1) is thus contained in $\prod_i H_{n_i}P_{n_i}$ and is simply given by $\prod_i \mathcal{C}(H_{n_i}P_{n_i})$. The contribution of any partition P to (D1) may be obtained in this way, so (D3) holds. When the trace of (D3) is taken to evaluate Q_n by (58), the equivalence in the trace of different distributions of the arguments $(1\cdots n)$ for fixed m_l provides the numerical factors necessary to identify b_l from (55). Equation (63) results.

The above argument is general enough to prove the structure (D3) for the full $H_n(1\cdots n;1'\cdots n')\times P_n(1'\cdots n')$. This is of some interest, since it allows (48) to be converted into an integral equation directly for $\mathcal{C}(H_nP_n)$. Note in passing that $\mathfrak{D}(H_nP_n)=\mathfrak{D}(D_nP_n)$, so (48) is certainly consistent with (D3).

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Superconducting and Normal State Properties of Dilute Indium-Tin Alloys: Bulk and Thin Film

A. M. TOXEN, M. J. BURNS,* AND D. J. QUINN†
IBM Watson Research Center, Yorktown Heights, New York
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Measurements are reported of normal-state and superconducting-state properties of bulk and thin-film indium-tin alloys. For the bulk samples, whose compositions were in the range 0–5.8 at.% tin, the residual resistivities, critical magnetic fields, and critical temperatures were measured. It is shown that both similarity conditions are well obeyed for the critical fields of samples containing 0–1.8 at.% Sn, for which detailed data were taken. High-purity films were produced containing up to 5 at.% tin. From resistance measurements, the critical temperatures, critical fields, thicknesses, and residual resistivities of the films were obtained. The formula for boundary scattering due to Fuchs has been recast into a more convenient form from which one may calculate the intrinsic mean free path and intrinsic resistivity directly from the measured resistivity and thickness. From the resistivity measurements, one may infer a value for the product of intrinsic resistivity and mean free path, ρl, of $1.6\times10^{-11}\ \Omega\ \mathrm{cm}^2$. The critical-temperature measurements indicate that bulk and film specimens having the same composition do not have the same critical temperature. On the basis of a model which attributes the shift in critical temperature to stress effects, formulas are derived from which one may calculate the stress in a film as well as the equivalent (i.e., stress-shifted) bulk critical field for any film. However, the stress-shifted bulk critical-field curves obtained in this way for the indium alloy films are nearly the same as one would have obtained under the assumption of similarity. Analysis of the critical-temperature results indicates that while stresses in the most dilute films are probably relieved by ordinary dislocation flow, some other mechanism, perhaps twinning, dominates in the more concentrated alloys. The largest uniaxial stress calculated for the films studied was $2.6\times10^9\ \mathrm{dyn/cm}^2$, which was obtained for a film of indium containing 2.6 at.% tin.

INTRODUCTION

WITH a view to studying and understanding mean-free-path effects upon the critical fields of superconducting alloy films, a study was undertaken of dilute alloys of indium containing tin. The indium-tin system was chosen for several reasons. First, the critical temperatures of the dilute alloys, i.e., 0–5 at.% Sn, lie in a temperature range which is convenient for measurement, 3.4–3.9°K. Second, both constituents have low boiling points, which makes for ease of evaporation. Third, since the self-diffusion of indium and the diffusion of tin in indium are both relatively large at room temperature, well-annealed, homogeneous alloy films are readily obtained. Finally, previous work on indium films[1] had demonstrated that their superconducting properties are well behaved and indicated that indium alloy films might also have well-behaved properties.

To properly analyze film critical-field data, one must know the critical fields of bulk samples having the same compositions as the films. For this reason, a careful study of bulk indium-tin alloys was also undertaken.

The work to be reported falls naturally into two parts: that related to measurements on the bulk specimens, and that pertaining to the evaporated films. Therefore, the paper will be divided into two sections.

In Part 1, measurements of the residual resistivity, critical temperature T_c, and critical field H_c of the bulk alloys are reported. The composition range studied was 0–5.8 at.% tin in indium. The concept of similarity is discussed and it is shown that both similarity conditions are quite well obeyed for samples containing 0–1.8 at.% Sn, for which detailed data were taken.

In Part 2, the film measurements are discussed. The discussion includes the preparation of the films, their compositions, the electrical measurements made upon them, and their critical temperatures. From the electrical measurements, the intrinsic residual resistivity (corrected for boundary scattering) is obtained and together with the critical temperature measurements,

* Present address: IBM Components Division, East Fishkill, New York.
† Present address: United Aircraft Research Laboratory, East Hartford, Connecticut.
[1] A. M. Toxen, Phys. Rev. **123**, 442 (1961).