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Molecular-field theory with correlations

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We derive an improved molecular-field theory for spins $\frac{1}{2}$ from first principles. Formulas are obtained for use in cases when the fields, bonds, or occupation of the sites are random variables.

We report on an improvement of molecular-field theory,[1] one which is suited to the study of "frozen-in" defects such as those that fall under the popular rubric of "spin glasses".[2] Our theory allows for short-range order even above the critical temperature T_c and correctly predicts $T_c=0$ for the linear chain. While it might be feared that such improvements are at the expense of computational simplicity, as in the cluster expansions,[3] the opposite is in fact true. Our method obtains the order parameter as the root of an ordinary polynomial, instead of a transcendental function as in traditional mean-field theory (MFT). In the limit that each spin interacts with a large number of neighbors, the expressions reduce to those of MFT, which are known to be correct in that limit.[4] We easily obtain the critical percolation probability p_c and the critical temperature T_c of the Ising model and obtain reasonable agreement with the results of other frequently more complicated methods. Our equations can be applied to the study of random fields, random bonds, and random occupation probabilities.

Our prototype Hamiltonian is the nearest-neighbor Ising model in a specified external field, which may vary from site to site.

$$H=-\sum_i h_i S_i-\sum_{(i,j)} J_{ij} S_i S_j \; . \tag{1}$$

This model has a number of applications, such as to a model spin-glass in which the bonds are separable[5] and to the low-lying degrees of freedom of Anderson's negative U model of electrons in amorphous semiconductors.[6] For the latter, h_i is the energy of an electron pair at the ith site, $S_i=+1$ signifies occupancy of this site by a pair, and $S_i=-1$ signifies unoccupancy. Because single-electron occupancies are at energies $|U|$ higher, with $|U|/k_B \approx 10^4$ °K or so, Eq. (1) is suitable for the calculation of thermodynamic properties such as the specific heat and correlation functions, at all reasonable temperatures.

Let each spin be nominally connected to z nearest neighbors, with $z=2d$ in a simple cubic lattice in d dimensions; later, we will examine the effects of missing spins or broken bonds. Each spin present "feels" a molecular field that we denote $\tilde{h}_i$, given by

$$\tilde{h}_i \equiv h_i+\sum_{j=1}^{z} J_{ij} S_j \; . \tag{2}$$

In conventional MFT this quantity is first averaged, so that subsequent thermodynamic averaging over the ith spin yields the well-known result

$$\langle S_i\rangle \equiv m_i=\tanh \beta\langle\tilde{h}_i\rangle \; . \tag{3}$$

This equation is ill adapted to the study of random fields, bonds, or occupations. Even in the field-free homogeneous case, it incorrectly predicts a phase transition at $T_c=Jz/k_B$ in any number of dimensions, violating theorems by Landau and others[7] concerning the absence of long-range order in one dimension. The error comes from subjecting the ith spin to a unique field $\langle\tilde{h}_i\rangle$. In our method, each spin is subjected to *all* the allowed values of $\tilde{h}_i$ and to *no others,*

$$\begin{aligned} &h_i+zJ \text{ (probability } R_z) \; , \\ &h_i+(z-2)J \text{ (probability } R_{z-2}), \ldots, \\ &h_i-zJ \text{ (probability } R_{-z}) \; . \end{aligned} \tag{4}$$

Our immediate goal is to obtain the set of probabilities R_n. The original studies of the distribution of molecular fields (rather than of their averages) is found in the works of Marshall and of Klein and Brout,[8] and is also implicit in the more modern treatment of block spins by renormalization-group methods.[9] It is an approach well suited to the introduction of random fields, bonds, etc. without additional hypotheses or difficulties.

We cast our results in terms of the given distribution of random fields $P(h)$ or, more conveniently, by Fourier transform methods. Define $F(t)$, the Fourier transform of $P(h)$, as

$$F(t)=\int_{-\infty}^{\infty} dx\, P(x)e^{-ixt}$$

or

$$P(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, F(t)e^{ixt} \; . \tag{5}$$

For a constant field, $P(x)$ is a δ function. For a distribution of width γ centered at $h=0$, $F(t) = \exp[-(\gamma t)^2]$ for the Gaussian, and $\exp(-\gamma|t|)$ for the Lorentzian.

We next express the (as yet unknown) $R(\tilde{h})$ in terms of itself, starting with

$$R(\tilde{h}_i) = \left\langle P\left(\tilde{h}_i - \sum_j J_{ij} S_j \right) \right\rangle ,$$

in which all quantities except $\tilde{h}_i$, random or thermal, are to be averaged. The ensemble over which the average is performed must be carefully determined. Using Eq. (5) we shall find it necessary to evaluate averages of the kind

$$\left\langle \exp - it \sum_{j=1}^{z} J_{ij} S_j \right\rangle = \left\langle \prod_{j=1}^{z} \exp - it J_{ij} S_j \right\rangle . \tag{6}$$

The essence of molecular-field theory is embodied in the assumption that the nearest neighbors are uncorrelated, to justify replacing the above average product by the product of the averages. Writing this out with the help of Eq. (5) we have

$$R(\tilde{h}_i) \approx \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, F(t) e^{i \tilde{h}_i t} \prod_{j=1}^{z} \int_{-\infty}^{\infty} d\tilde{h}_j\, R(\tilde{h}_j) \frac{\mathrm{Tr}\left(e^{-(\beta \tilde{h}_j + itJ_{ij}) S_j}\right)}{\mathrm{Tr}\left(e^{-(\beta \tilde{h}_j) S_j}\right)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, F(t) e^{i \tilde{h}_i t} \prod_{j=1}^{z} \Lambda_j(t) . \tag{7}$$

We distinguish several cases. For uniform bond strength J and perfect occupation of each lattice site by a spin, and approximating the ensemble of $z-1$ neighbors to each site j by z neighbors as in the central site case, we have

$$\Lambda_j(t) = \cos Jt - i m_j \sin Jt . \tag{8a}$$

In the bulk all $m_j = m$, the bulk magnetization. But near a surface our equations can be used to obtain the spatial variation of the magnetization or to derive the appropriate Landau-Ginzburg equations. For random bond strengths we obtain in Eq. (7)

$$\Lambda_j(t) = \langle \cos Jt \rangle - i \langle m_j \sin J_{ij} t \rangle , \tag{8b}$$

where the $\langle\ \rangle$ indicate averages with respect to the distribution of J_{ij}'s. Finally, for random occupation of the sites (with p the probability of a spin being present, $q=1-p$ the probability that it is replaced by a nonmagnetic atom) we have in Eq. (7)

$$\Lambda_j(t) = q + p(\langle \cos Jt \rangle - i \langle m_j \sin J_{ij} t \rangle) , \tag{8c}$$

the most general result. When m_j is constant we shall simply write $\Lambda(t)$.

Next, we derive an equation which, while bearing some superficial resemblance to the MFT result of Eq. (3), is nevertheless rigorously exact and permits the calculation of m_i in terms of the neighboring m_j's alone. First, we take the thermodynamic average

$$m_i = \langle S_i \rangle = \left\langle \frac{\mathrm{Tr}\left[S_i e^{-\beta(S_i \tilde{h}_i + H')}\right]}{\mathrm{Tr}\left[e^{-\beta(S_i \tilde{h}_i + H')}\right]} \right\rangle , \tag{9a}$$

where H' is the part of the Hamiltonian which does not involve S_i. Performing the traces,

$$m_i = \left\langle \frac{\sinh \beta \tilde{h}_i}{\cosh \beta \tilde{h}_i} \right\rangle = \langle \tanh \beta \tilde{h}_i \rangle . \tag{9b}$$

It remains to perform the averages over the $\tilde{h}_i$.

$$m_i = \int d\tilde{h}_i\, R(\tilde{h}_i) \tanh \beta \tilde{h}_i , \tag{9c}$$

which is the desired result. We now substitute the product approximation to R, our Eq. (7), into this equation and obtain the principal result,

$$m_i = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, F(t) \phi_0(T,t) \prod_{j=1}^{z} \Lambda_j(t) , \tag{10}$$

in which we use ϕ_0, a special case of the function ϕ_n defined by

$$\phi_n(T,t) = \int_{-\infty}^{\infty} d\tilde{h}\, \tilde{h}^n \tanh \beta \tilde{h} \exp(i \tilde{h} t) . \tag{11}$$

For the special case of uniform magnetization, $m_i = m_j$ and Eq. (10) becomes

$$m = \frac{1}{2\pi} \int dt\, F(t) \phi_0(T,t) \Lambda^z(t) . \tag{12}$$

The right-hand side is a polynomial in m of degree z, the number of nearest neighbors, and the solution of Eq. (12) requires only finding the roots of this polynomial. The coefficients are integrals of the type

$$\int dt\, F(t) \phi_0(T,t) \langle \cos Jt \rangle^{n_1} \langle \sin Jt \rangle^{n_2} ,$$

with n_1, n_2 integers. Further specializing to the case of constant bonds, zero applied magnetic field $[P(h) = \delta(h)]$ but random occupation of sites

$(0 \leq p \leq 1)$, we see that the integrations over t in Eq. (12) yield only δ functions at discrete values of the molecular field $R_n \delta(nJ - \tilde{h})$ with $n = z, \ldots, -z$ and appropriate weights R_n.

We have calculated the curve $T_c(p)$ which the above yields. This curve separates ferromagnetic and paramagnetic phases in the T-p plane. For $z=2$, the line shrinks to a point $T_c=0$, $p_c=1$. For $z=3$ we obtain for the equation of the line

$$\begin{aligned} 1 = 3p\,[\,(q^2 + \tfrac{1}{4}p^2)\tanh K + pq\,\tanh 2K \\ + \tfrac{1}{4}p^2 \tanh 3K]\ , \end{aligned} \tag{13}$$

where $K = J/k_B T$. At $T=0$ it has the solution $p_c = 0.557\,51$, while at $p=1$ it yields the critical temperature $T_c = 2.103\,73\ (J/k_B)$. This is closer to the exact result for the honeycomb lattice[10] 1.518 65 than MFT, which yields 3.0, but not quite as close as Bethe's cluster method which yields[11] 1.8205.

For $z=4$, the critical line has the equation

$$\begin{aligned} 1 = 4p\,[\,(q^3 + \tfrac{3}{4}qp^2)\tanh K + (\tfrac{3}{2}q^2 p + \tfrac{1}{4}p^3)\tanh 2K \\ + \tfrac{3}{4}qp^2 \tanh 3K + \tfrac{1}{8}p^3 \tanh 4K]\ . \end{aligned} \tag{14}$$

This yields $p_c = 0.428$, which compares reasonably with the exact result for critical percolation in the square lattice,[12] 0.5. The solution $T_c = 3.090$ at $p=1$ is not as close to Onsager's result 2.2692 as Bethe's cluster method, which yields[11] 2.8854. Both, however, are much better than the MFT value of 4.0. At $z=6$, we obtain 5.073 vs 4.933 for the Bethe method and 4.5 for the series value for the sc lattice.[13]

Applications to $z > 6$ involve increasing algebra but no essential new complications. In the limit of large z, proceeding to the limit $J \to 0$ and $z \to \infty$ in such a way that $Jz =$ finite, we note that

$$[q + p(\langle \cos Jt \rangle - im\,\langle \sin Jt \rangle)]^z \to \exp -(imp\,\bar{J} zt)\ , \tag{15}$$

hence Eq. (12) reduces precisely to MFT and Eq. (3) is our "correspondence limit."

To obtain the internal energy in the absence of applied fields, we must include a factor of $\frac{1}{2}$ to correct for double counting of bonds. Thus, the energy per spin is

$$\begin{aligned} E_0 &= -\tfrac{1}{2} \int d\tilde{h}\ R(\tilde{h})\tilde{h}\tanh \beta\tilde{h} \\ &= -\frac{1}{4\pi} \int dt\ F(t)\phi_1(T,t)\ \Lambda^z(t)\ , \end{aligned} \tag{16}$$

with ϕ_1 defined in Eq. (11). If we wish the energy per site in the case of missing spins, this expression must be multiplied by p. When an external field h is applied, the situation is not so simple. In order to express everything in terms of the molecular-field parameter $\tilde{h}$ it is necessary to double the interaction bonds, then to subtract out the excess explicitly. Thus, the energy per spin becomes

$$\begin{aligned} E &= -\int d\tilde{h}\ R(\tilde{h})\tilde{h}\tanh \beta\tilde{h} + \tfrac{1}{2}\bar{J} z\,\langle S_i S_j \rangle \\ &= 2E_0 + \tfrac{1}{2}\bar{J} z\,\langle S_i S_j \rangle\ . \end{aligned} \tag{17}$$

Evaluating the new average quantity with the help of Eq. (7) we obtain

$$\begin{aligned} \langle S_i S_j \rangle = \frac{p}{2\pi} \int dt\ F(t)\phi_0(T,t)\ \Lambda^{z-1}(t) \\ \times (m\,\langle \cos Jt \rangle - i\,\langle \sin Jt \rangle)\ . \end{aligned} \tag{18}$$

The specific heat is dE/dT.

To generalize this theory to spins one, $\frac{3}{2}$, etc. it is required to obtain the generalization of the identity, Eq. (9c), on which the principal results, Eqs. (10)–(12) and (16)–(18) are based. It does not appear possible merely to replace "tanh" by the Brillouin function, as one might have guessed, for in the Λ_j there now appear terms such as $\langle S_j^2 \rangle$, $\langle S_j^3 \rangle$, etc., and equations must be obtained for these. However, we have already been able to extend our procedure to the three-state Potts model, for which we find some interesting results.

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