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Exactly Soluble Spin-Glass Model

J. M. Luttinger*

The Rockefeller University, New York, New York 10021

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An exactly soluble model for a spin-glass phase transition is presented. It is essentially a mean-field theory; but instead of "bond" randomness of the exchange interaction (as used by other authors), a "site" randomness is assumed. This enables one to calculate the "quenched" free energy without any uncertain mathematical procedures. Typical results are given for a variety of interesting cases.

There is considerable experimental evidence[1] that in certain magnetically dilute solid solutions ("spin-glasses") a new kind of phase transition takes place. In this spin-glass phase, the moments are frozen into a disordered arrangement with no or little long-range order present. There is now a reasonable model for these transitions[2] due to Edwards and Anderson. The Edwards-Anderson model is essentially a mean-field approximation in which the exchange interaction between different pairs of spins is treated as a random variable. The model, in spite of its clear physical basis, suffers from the fact that in order to solve it, one is reduced to rather complicated and questionable mathematical procedures (the "replication" methods).

In this note another mean-field type of model is proposed which, I believe, is as reasonable physically as the Edwards-Anderson model, but still exactly soluble. The model shows all the essential features of the experiment. As usual, we begin with the following Hamiltonian:

$$\mathcal{3C} = -\tfrac{1}{2}\sum_{i,j} J_{ij} s_i s_j - \mu_0 H \sum_i s_i, \tag{1}$$

where $s_i = \pm 1$ gives the spin orientation of the ith spin, J_{ij} is the exchange interaction between the ith and jth spins, H is the external magnetic field, and μ_0 is the magnetic moment of each spin. (For simplicity we are assuming an Ising model for the spins, although this is not at all necessary.) The J_{ij} are random variables to be specified later. The partition function $Z[J]$ will depend on all the J_{ij}'s and is given by

$$Z[J] = \sum_{\{s_i\}} \exp(-\beta\mathcal{3C}). \tag{2}$$

The corresponding free energy $F[J]$ is

$$F[J] = -\beta^{-1}\ln Z[J]. \tag{3}$$

For this problem, good physical arguments[1] suggest that it is the "quenched" free energy

which we observe. In other words, the free energy F which we observe is given by

$$F = \langle F[J] \rangle, \tag{4}$$

where the angular brackets mean averaging with respect to the random variables which describe the J_{ij}. Edwards and Anderson assume that the different J_{ij} are independent random variables, Gaussianly distributed; we may call this "bond" randomness. We shall assume that instead of bond randomness, we have a kind of "site" randomness. Formally we write

$$J_{ij} = \frac{1}{N}[J_1 + J_2 \xi_i \xi_j + J_3(\xi_i + \xi_j)], \tag{5}$$

where N is the number of spins, J_1, J_2, and J_3 are constants, and the ξ_i are random variables

which only take on the values ± 1.[2] The factor $1/N$ insures mean-field behavior (if $J_2 = J_3 = 0$ and $J_1 > 0$, this gives the usual mean-field theory of ferromagnetism). The J_2 term gives a symmetric distribution of J_{ij} values around the mean value J_1/N; and the J_3 term (which has interesting experimental consequences) makes the distribution somewhat asymmetric. Because of the long-range, very rapidly oscillating interaction between the spins of the Ruderman-Kittel-Kasuya-Yoshida type, the sites would be practically uncorrelated. Therefore the averaging process indicated in (4) is taken to be

$$\langle F[J] \rangle = \frac{1}{2^N} \sum_{\{\xi_i\}} F[J]. \tag{6}$$

Using (5) the partition function becomes

$$Z = \sum_{m_1, m_2} W_N(m_1, m_2) \exp N[\tfrac{1}{2}(K_1 m_1^2 + K_2 m_2^2 + 2K_3 m_1 m_2) + h m_1], \tag{7}$$

where $K_l = \beta J_l$ $(l = 1, 2, 3)$, $h = \beta \mu_0 H$, $m_1 = \sum_i s_i/N$, $m_2 = \sum_i s_i \xi_i/N$, and the summation over m_1 and m_2 is over all possible values of m_1 and m_2. $W_N(m_1, m_2)$ is the number of spin states for a set of given m_1 and m_2.

Obtaining W_N is an elementary problem in combinatorics. Call the number of ξ_i which are equal to $+1$, n_+, and the number equal to -1, n_-. A little reflection yields

$$W_N(m_1, m_2) = \frac{n_+!}{(N_+^{\,+})!\,(N_-^{\,+})!} \frac{n_-!}{(N_+^{\,-})!\,(N_-^{\,-})!}, \tag{8}$$

where $N_+^{\,+}$ is the number of sites with $s_i = +1$ and $\xi_i = +1$, $N_+^{\,-}$ is the number of sites with $s_i = +1$ and $\xi_i = -1$, $N_-^{\,+}$ is the number of sites with $s_i = -1$ and $\xi_i = +1$, and $N_-^{\,-}$ is the number of sites with $s_i = -1$ and $\xi_i = -1$. Using these definitions, we find after an elementary calculation $(\lambda \equiv \sum_i \xi_i/N)$

$$N_+^{\,+} = \tfrac{1}{4}N(1 + m_1 + m_2 + \lambda), \quad N_-^{\,+} = \tfrac{1}{4}N(1 - m_1 - m_2 + \lambda), \quad N_+^{\,-} = \tfrac{1}{4}N(1 + m_1 + m_2 - \lambda),$$

$$N_-^{\,-} = \tfrac{1}{4}N(1 - m_1 + m_2 - \lambda), \quad n_+ = \tfrac{1}{2}N(1 + \lambda), \quad n_- = \tfrac{1}{2}N(1 - \lambda). \tag{9}$$

For large N, (8) becomes

$$W_N(m_1, m_2) = 2^N \exp N\{-\tfrac{1}{4}[(1 + m_1 + m_2 + \lambda)\ln(1 + m_1 + m_1 + \lambda) + (1 - m_1 - m_2 + \lambda)\ln(1 - m_1 - m_2 + \lambda)$$

$$+ (1 + m_1 - m_2 - \lambda)\ln(1 + m_1 - m_2 - \lambda) + (1 + m_1 - m_2 - \lambda)\ln(1 - m_1 + m_2 - \lambda)]$$

$$+ \tfrac{1}{2}[(1 + \lambda)\ln(1 + \lambda) + (1 - \lambda)\ln(1 - \lambda)]\}. \tag{10}$$

Using (10) and (7), we see that Z has the form

$$Z = \sum_{m_1, m_2} \exp[Ng(m_1, m_2, \lambda)], \tag{11}$$

where g is a smooth function of m_1, m_2, and λ independent of the size of the system (N). It is clear from (11) that, as usual, in order to find $\ln Z$ we need only take the maximum term of the summation. That is

$$\ln Z = N \max_{m_1, m_2}[g(m_1, m_2, \lambda)]. \tag{12}$$

The coefficient of N will certainly be an N-independent smooth function of λ.

$$F = -\frac{N}{\beta} \sum_{\lambda} \max_{m_1, m_2} [g(m_1, m_2, \lambda)] P_N(\lambda),$$ (13)

where

$$P_N(\lambda) = \frac{1}{2^N} \frac{N!}{n_+! n_-!} = \frac{1}{2^N} \frac{N!}{[\frac{1}{2}N(1+\lambda)]![\frac{1}{2}N(1-\lambda)]!}.$$ (14)

For large N, $P_N(\lambda)$ has an extremely sharp maximum at $\lambda = 0$,

$$P_N(\lambda) \sim \exp(-\tfrac{1}{2}N\lambda^2) \quad (\lambda \ll 1).$$ (15)

Therefore any smooth function of λ, when averaged over $P_N(\lambda)$, only has an appreciable contribution from the neighborhood of $\lambda = 0$. Thus

$$F = -\frac{N}{\beta} \max_{m_1, m_2} [g(m_1, m_2, 0)].$$ (16)

Writing $m_1 = (a_1 + a_2)/2$ and $m_2 = (a_1 - a_2)/2$, we can summarize our results for the free energy per spin f as follows:

$$f = \frac{F}{N} = \min_{a_1, a_2} [f(a_1, a_2)],$$ (17)

where

$$f(a_1, a_2) = \tfrac{1}{4} \{\beta^{-1}[(1+a_1)\ln(1+a_1) + (1-a_1)\ln(1-a_1) + (1+a_2)\ln(1+a_2) + (1-a_2)\ln(1-a_2) - 4\ln 2]$$
$$- (J_{11}a_1^2 + J_{22}a_2^2 + 2J_{12}a_1a_2) - 2\mu_0 H(a_1 + a_2)\},$$ (18)

and

$$J_{11} = \tfrac{1}{2}(J_1 + J_2) + J_3, \quad J_{22} = \tfrac{1}{2}(J_1 + J_2) - J_3, \quad J_{12} = \tfrac{1}{2}(J_1 - J_2).$$

A necessary condition for the minimum of $f(a_1, a_2)$ is that its first derivatives with respect to a_1 and a_2 vanish, i.e.,

$$(2\beta)^{-1} \ln[(1+a_1)/(1-a_1)] = J_{11}a_1 + J_{12}a_2 + \mu_0 H,$$ (19)

$$(2\beta)^{-1} \ln[(1+a_2)/(1-a_2)] = J_{12}a_1 + J_{22}a_2 + \mu_0 H.$$ (20)

Of the various solutions of (19) and (20) (if there are several), the one which makes $f(a_1, a_2)$ smallest must be taken. Call this solution (a_1^0, a_2^0). Thus we have a system with two order parameters a_1^0 and a_2^0 or the corresponding $m_1^0 = \tfrac{1}{2}(a_1^0 + a_2^0)$ and $m_2^0 = \tfrac{1}{2}(a_1^0 - a_2^0)$. m_1^0 is of course proportional to the mean magnetic moment of the system; and it is the conventional order parameter for magnetic problems. m_2^0 is a new order parameter characteristic of the spin-glass. It is *not* the same as the order parameter used by other authors[3] when employing the replica method.

The complete discussion of (19) and (20) is quite complicated and shall be given elsewhere. (A partial discussion already exists in the literature[4] in connection with the theory of ferrimagnetics.) We shall limit ourselves to the case of no magnetic field and to the calculation of the magnetic susceptibility. Even with this limitation, the enumeration of possibilities is fairly tedious. I will therefore simply give some typical results.

(a) $H = 0$.—If $J_1 + J_2 < 0$, $J_1 J_2 - J_3^2 > 0$, the original quadratic form [in (7), say] is negative definite. The only solution of (19) and (20) is $a_1 = a_2 = 0$ and there is no phase transition.

(b) $H = 0$.—If both the conditions in (a) are not satisfied and $J_1 \neq J_2$, there is always exactly one second-order phase transition at $T = T_C$,

$$k_B T_C = \tfrac{1}{2}(J_1 + J_2) + [\tfrac{1}{4}(J_1 - J_2)^2 + J_3^2]^{1/2} \equiv 1/\beta_C.$$ (21)

For $T > T_C$ the only solution is $a_1 = a_2 = 0$. For T just less than T_C, there is a nonzero solution $a_1 = a_1^0$,

$$a_2 = a_2{}^0,$$

$$a_1{}^0 + \left[\frac{3(J_{12}{}^2 + J_3{}^2)^{1/2}[(J_{12}{}^2 + J_3{}^2)^{1/2} + J_3]}{2J_3{}^2 + J_{12}{}^2} \left(\frac{T_c - T}{T_c} \right) \right]^{1/2}, \tag{22}$$

$$a_2{}^0 = \frac{J_{12}}{(J_{12}{}^2 + J_3{}^2)^{1/2} + J_3} a_1{}^0, \tag{23}$$

$$m_1{}^0 = \frac{1}{2}\left(1 + \frac{J_{12}}{(J_{12}{}^2 + J_3{}^2)^{1/2} + J_3} \right) a_1{}^0, \tag{24}$$

$$m_2{}^0 = \frac{1}{2}\left(1 - \frac{J_{12}}{(J_{12}{}^2 + J_3{}^2)^{1/2} + J_3} \right) a_1{}^0. \tag{25}$$

In general, there is nonvanishing magnetic order $(m_1{}^0 \neq 0)$ and nonvanishing spin-glass order $(m_2{}^0 \neq 0)$ for $T < T_c$. If $J_3 = 0$, however, either $m_1{}^0 = 0$ or $m_2{}^0 = 0$; we get the former if $J_2 > J_1$ or the latter if $J_1 > J_2$. We call the case $J_3 = 0$ and $J_2 > J_1$, the "pure spin-glass." This behavior persists down to $T = 0$. If $J_3 \neq 0$, the behavior at $T = 0$ depends on the signs and relative sizes of the parameters J_1, J_2, and J_3. If $J_2 > |J_3|$ and J_1, the behavior as T approaches zero is simple: $a_1{}^0 \to 1$ and $a_2{}^0 \to -1$, the approach being exponential. Therefore, even if $J_3 \neq 0$ the magnetic order parameter $m_1{}^0 \to 0$ and the spin-glass order parameter $m_2{}^0 \to 1$. That is, there will be a very characteristic rise and fall of $m_1{}^0$ below the transition temperature.

As T decreases through T_c there is a jump (ΔC) in the heat capacity given by

$$\Delta C = \tfrac{3}{2} N k_B (J_3{}^2 + J_{12}{}^2)/(2J_3{}^2 + J_{12}{}^2). \tag{26}$$

(c) $H = 0$.—If $J_1 = J_2$, $J_{12} = 0$ and Eqs. (19) and (20) decouple. The problem is then equivalent to two independent ordinary mean-field problems. If J_{11} and J_{22} are both greater than zero, there will be *two* second-order phase transitions which look very much like ferromagnetic transitions, but the order parameter $m_2{}^0$ will not be zero.

(d) *Zero-field susceptibility*.—Let χ be the susceptibility per spin in units of $\mu_0{}^2/k_B$. Then if we do *not* have the pure spin-glass case $J_3 = 0$ and $J_2 > J_1$, we find near T_c,

$$\chi = \frac{J_{12} + (J_{12}{}^2 + J_3{}^2)^{1/2}}{2(J_{12}{}^2 + J_3{}^2)^{1/2}|T - T_c|}. \tag{27}$$

This is the typical Curie-Weiss behavior. However, as we approach the pure spin-glass case $(J_2 > J_1$ and $J_3 \to 0)$, the coefficient of $|T - T_c|^{-1}$ approaches zero; and it would be very hard to detect the Curie-Weiss behavior unless we were very close to the transition temperature.

(e) For the pure spin-glass case $(J_3 = 0$ and J_2 $> J_1)$, we find

$$\chi(T = T_c{}^+) = \chi(T = T_c{}^-) = k_B/(J_2 - J_1), \tag{28}$$

and

$$\left. \frac{d\chi(T)}{dT} \right|_{T = T_c{}^+} = -\left(\frac{k_B}{J_2 - J_1} \right)^2, \tag{29}$$

$$\left. \frac{d\chi(T)}{dT} \right|_{T = T_c{}^-} = +2\left(\frac{k_B}{J_2 - J_1} \right)^2, \tag{30}$$

displaying the typical cusplike behavior of χ which is seen near the transition temperature for the spin-glasses.

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Electron-Hole Scattering and the Electrical Resistivity of the Semimetal TiS$_2$ †

Carl A. Kukkonen and Pierre F. Maldague

Department of Physics, Purdue University, West Lafayette, Indiana 47907

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We present the first complete theory of the effect of collisions between charge carriers on the electrical resistivity of a simple degenerate semimetal. We find that (i) electron-hole scattering can explain the anomalous T^2 resistivity of *stoichiometric* TiS$_2$, (ii) electron-electron and hole-hole scattering do not contribute to ρ, and (iii) the theory of electron-hole scattering predicts that the resistivity of *nonstoichiometric* TiS$_2$ should fall significantly below T^2 at high temperatures.

In a recent Letter Thompson[1] reported that the a-axis, temperature-dependent electrical resistivity, $\rho(T) - \rho(0)$, of the layered semimetallic compound TiS$_2$ was proportional to T^2 from at least 10 to 400 K. Thompson suggested that this remarkable behavior was due to "general" electron-electron scattering which encompasses electron-electron (e-e), hole-hole (h-h), and electron-hole (e-h) processes. In this Letter we present the first complete theory of the effect of collisions between charge carriers on the electrical resistivity of a simple degenerate semimetal. In TiS$_2$ the electron and hole densities are sufficiently small and the carrier pockets (assumed spherical) are sufficiently isolated that all e-e, h-h, and e-h scatterings conserve momentum. Therefore e-e and h-h processes do not contribute to ρ. For e-h scattering momentum conservation does not imply current conservation; and we find that this mechanism can explain the observed T^2 resistivity. Furthermore, the theory of e-h scattering suggests additional experiments to confirm the validity of this explanation.

Specifically our theory predicts that a compensated (stoichiometric) semimetal has a T^2 term in the resistivity [Eq. (8)] for all T, as has been found in TiS$_2$. An extension of the theory predicts that the resistivity of an uncompensated (nonstoichiometric) semimetal, e.g., Ti$_{1+x}$S$_2$, should fall significantly below T^2 at high T, eventually going linearly with temperature as a result of phonon scattering. The particular behavior we predict for Ti$_{1+x}$S$_2$ is shown in Fig. 1, where we plot the temperature-dependent resistivity versus T^2 for different values of x. For *stoichiometric* TiS$_2$, $x = 0$, the solid curve including e-h and impurity scattering is pure T^2 and the dashed curve

including some phonon scattering shows only a slight deviation. Both are consistent with the data of Thompson. For *nonstoichiometric* TiS$_2$ our predictions are quite different. At low T, ρ is also proportional to T^2, but with a coefficient that decreases with x. At higher T, however, the curves fall far below T^2. The solid curves become constant at high T, while the dashed curve
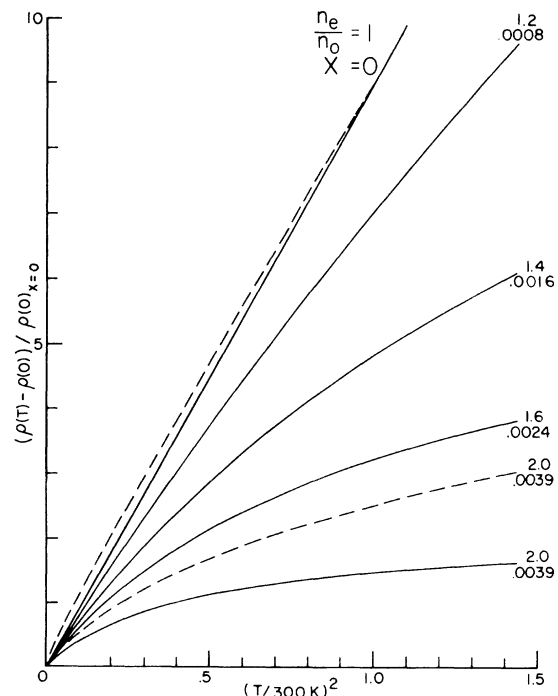

FIG. 1. Theoretical temperature-dependent electrical resistivity of Ti$_{1+x}$S$_2$ for different values of x. The solid curves include electron-hole and impurity scattering. The dashed curves illustrate the changes that occur when phonon scattering is included.