

ly decreasing component of  $\Delta_B \rho_s / \rho_s$  in Fig. 1 is described by the  $\exp(-4\Gamma t)$  term of Eq. (7). The experimental quantities  $k$  are given by  $4\Gamma$ , which according to the foregoing discussion of Eq. (4) accounts for the observed field and concentration dependences in Fig. 2.

To our knowledge, this is the first direct optical observation of time-dependent quantum-interference effects in the condensed phase.<sup>12</sup> The present experimental approach should also be a useful tool for spin-lattice relaxation measurements in the nanosecond range.

<sup>1</sup>S. Haroche, J. A. Paisner, and A. L. Schawlow, *Phys. Rev. Lett.* **30**, 948 (1973), and references therein.

<sup>2</sup>B. Brocklehurst, *Chem. Phys. Lett.* **28**, 357 (1974).

<sup>3</sup>D. Paligoric and J. Klein, *Int. J. Radiat. Phys. Chem.* **4**, 359 (1972).

<sup>4</sup>Relevant work includes studies of chemically induced dynamic nuclear and electron polarization [R. Kapstein, *J. Am. Chem. Soc.* **94**, 6251 (1972); F. H. Freed, *Ann. Rev. Phys. Chem.* **23**, 265 (1972)], and of magnetic modulation of dye-sensitized fluorescence in organic crystals [R. P. Groff, A. Suna, P. Avakian, and R. E. Merrifield, *Phys. Rev. B* **9**, 2655 (1974); P. Avakian, *Pure Appl. Chem.* **37**, 1 (1974)].

<sup>5</sup>See Kapstein, Ref. 4, and Freed, Ref. 4. These references contain a careful discussion of the spin Hamiltonian for radical-ion pairs in organic solutions, with a

detailed justification of the expression also used in this work [cf. Eq. (1)].

<sup>6</sup>See Groff *et al.*, Ref. 4, and Avakian, Ref. 4. Following the classification scheme of magnetic-field-sensitive luminescence phenomena, proposed by these authors, the process here reported is a new characteristic example of the hyperfine-modulated processes, to be distinguished from fine-structure-modulated phenomena like delayed fluorescence from triplet-triplet fusion.

<sup>7</sup>A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, London, 1961), Chap. 8.

<sup>8</sup>N. M. Atherton, *Electron Spin Resonance* (Wiley, New York, 1973), Chap. 8.

<sup>9</sup>Examples with field- and/or concentration-dependent relaxation rates of a form similar to  $\Gamma$  are known in NMR (cf. Ref. 7) and for relaxation of polarized atoms by collisions on paraffin-coated walls in optical-pumping experiments [W. Happer, *Rev. Mod. Phys.* **44**, 169 (1972)].

<sup>10</sup>P. B. Ayscough, *Electron Spin Resonance in Chemistry* (Methuen, London, 1968), Sect. 8.16.1.

<sup>11</sup>No ESR data seem to have been published for 2b PPD, but the set of the two equivalent N nuclei may be suspected to dominate hf structure.

<sup>12</sup>Coherent spin properties in condensed molecular materials have also been studied by phosphorescence microwave double-resonance methods with optically detected electron-spin echoes and echo trains in excited triplet states. [W. G. Breiland, C. B. Harris, and A. Pines, *Phys. Rev. Lett.* **30**, 158 (1973); C. B. Harris, R. L. Schlupp, and H. Schuch, *Phys. Rev. Lett.* **30**, 1010 (1973)].

## Spherical Model of a Spin-Glass

J. M. Kosterlitz, D. J. Thouless, and Raymund C. Jones

*Department of Mathematical Physics, University of Birmingham, Birmingham B15 2TT, England*

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A spherical model of a spin-glass is solved in the limit of infinite-ranged interactions with a Gaussian probability distribution. We use the known properties of a large random matrix, and show that the results are identical to those obtained by the  $n \rightarrow 0$  trick. We believe that the solution is exact.

Recently there has been much interest in the problem of magnetic systems with random exchange interactions—spin-glasses.<sup>1-6</sup> Experimentally such systems show definite anomalies similar to those associated with a second-order phase transition.<sup>7,8</sup> Since a real spin-glass is a dilute system of magnetic ions in random but fixed positions interacting via a long-ranged oscillating interaction, we must treat a quenched system in which the free energy is calculated as an average over the interaction configurations of the free energy for a fixed configuration. To date, there have been two main approaches to the

problem of which the most fruitful has been the trick of averaging the  $n$ th power of the partition function and taking the limit  $n \rightarrow 0$  at the end.<sup>1,9</sup> Very recently, Sherrington and Kirkpatrick<sup>5</sup> using this technique have investigated the Ising-like spin-glass analog of the Kac<sup>10</sup> model in which mean-field theory is exact and the statistical mechanics solvable. However, they obtain some odd results in the spin-glass phase, in particular a negative entropy at zero temperature. Otherwise, their results are physically very appealing.

More recently, Thouless *et al.*<sup>11</sup> have investigated this model by resumming the averaged high-

and low-temperature expansions, thereby avoiding the use of the  $n \rightarrow 0$  trick. Using the eigenvalue spectrum of a large random matrix<sup>12</sup> and properties of the corresponding eigenvectors, they find identical high-temperature and critical behavior, but rather different low-temperature properties, in particular a quadratic rather than linear specific heat. This indicates that, in this case, the analytic continuation of the high-temperature results gets one on to the wrong branch of the free energy at low temperatures.

In this Letter, we investigate the same system in the spherical-model limit<sup>13</sup> by both techniques. Although this is even more unrealistic than the Ising case, the thermal averaging is more straightforward and allows us to concentrate on the problem of averaging over the random interactions, and, hopefully, to throw some light on the continuation in  $n$ . In contrast to the Ising case, we find identical results by both methods.

The Hamiltonian we consider is

$$H = - \sum_{(ij)} J_{ij} S_i S_j, \quad (1)$$

where the sum is over all distinct pairs of lattice sites. The interaction  $J_{ij}$  is infinitely long ranged with probability density

$$P(J_{ij}) = (2\pi\sigma^2)^{-1/2} \exp[-(J_{ij} - J_0)^2/2\sigma^2], \quad (2)$$

where the standard deviation  $\sigma = \tilde{J}N^{-1/2}$  and the mean  $J_0 = \tilde{J}_0 N^{-1}$ . We use the intensive variables  $\tilde{J}$  and  $\tilde{J}_0$  in order to obtain a sensible thermodynamic limit. We first consider the case  $\tilde{J}_0 = 0$ . The first step is to diagonalize the matrix  $J_{ij}$  by an orthogonal transformation and introduce new variables  $S_\lambda$  defined by

$$S_\lambda = \sum_i \langle \lambda | i \rangle S_i, \quad (3)$$

where  $\langle \lambda | i \rangle$  is the orthonormal eigenvector of  $J_{ij}$  belonging to the eigenvalue  $J_\lambda$ . Since eigenvalue density  $\rho(J_\lambda)$  obeys the semicircular law<sup>12</sup>

$$\rho(J_\lambda) = (4\tilde{J}^2 - J_\lambda^2)^{1/2}/2\pi\tilde{J}^2 \quad (4)$$

for  $J_0 = 0$  in the limit  $N \rightarrow \infty$ , we can carry out the standard spherical-model manipulations using the spherical constraint  $\sum S_i^2 = N$ . The partition function becomes

$$Z = (2\pi i)^{-1} \int_{c-i\infty}^{c+i\infty} dz \exp\{N[z - (2N)^{-1} \sum_\lambda \ln(z - J_\lambda/2T)]\}, \quad (5)$$

where the contour of integration is to the right of the largest eigenvalue,  $2\tilde{J}$ , and we have omitted the spherical normalization. The only problem which could arise is in the interchange of orders of integration over  $z$  and  $S_\lambda$  before taking the thermodynamic limit because the eigenvalue spectrum is bounded only in the limit  $N \rightarrow \infty$ . However, for sufficiently large  $N$ , the probability of finding an eigenvalue larger than  $2\tilde{J}$  is so small that the error made is negligible.<sup>14</sup>

The standard saddle-point equation for  $z$  is

$$z - (z^2 - \tilde{J}^2/T^2)^{1/2} = \tilde{J}^2/T^2, \quad (6)$$

where we have used  $(1/N)\sum_\lambda \rightarrow \int dJ \rho(J)$ . Equation (6) has the solution  $z = \frac{1}{2}(1 + \tilde{J}^2/T^2)$  for  $T > \tilde{J}$ , so that we can identify the critical temperature  $T_c = \tilde{J}$ . For  $T < \tilde{J}$ , Eq. (6) has no solution, and the saddle-point value of  $z$  sticks at  $\tilde{J}/T$ , the branch point of the integrand of Eq. (5). The free energy per site averaged over the eigenvalue spectrum of Eq. (4) is readily found to be

$$\langle f(T) \rangle_{\text{av}} = \begin{cases} -\tilde{J}^2/4T - \frac{1}{2}T(1 + \ln 2), & T > T_c, \\ \frac{1}{2}T \ln(T/2\tilde{J}) - \tilde{J} + \frac{1}{4}T, & T < T_c, \end{cases} \quad (7)$$

corresponding to a specific heat per site of  $\tilde{J}^2/2T^2$  for  $T > T_c$  and  $\frac{1}{2}$  for  $T < T_c$ , and a negative low-temperature entropy which diverges logarithmically as  $T \rightarrow 0$ . This last is not unexpected since the uniform short-ranged spherical model displays the same pathology.

In the presence of a uniform magnetic field  $h$ , the saddle-point equation is modified to

$$1 = \int dJ \rho(J) \left\{ \frac{1}{2}(z - J/2T)^{-1} + [h^2(J)/4T^2](z - J/2T)^{-2} \right\}, \quad (8)$$

where

$$h(J_\lambda) = h \sum_i \langle i | \lambda \rangle.$$

On the average, using the orthonormality of the eigenvectors, we can replace  $h^2(J)$  by  $h^2$ , in which case it is clear that the solution of Eq. (8) always has  $z > \tilde{J}/T$ . Hence there is no transition in the presence

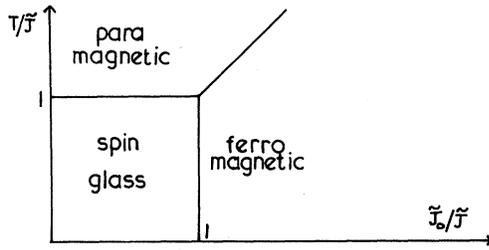


FIG. 1. The phase diagram for the spin-glass.

of a uniform field. The reason for this is that a uniform field has a component  $h(2\tilde{J})$  corresponding to the largest eigenvalue which plays the role of an ordering field. The analogous case in a uniform ferromagnet would be a local field acting at a single site which, in the spherical model, washes out any transition. In the limit  $h \rightarrow 0$  it is straightforward to show that the uniform susceptibility  $\chi$  equals  $1/T$  for  $T > T_c$  and  $1/\tilde{J}$  for  $T < T_c$ , displaying the expected Curie law above  $T_c$  and cusp at  $T_c$ .

From the point of view adopted in this Letter the parameter<sup>1</sup>  $q = \langle m_i^2 \rangle_{av}$  is not the natural order parameter, but the thermal average  $\langle S_{2\tilde{J}} \rangle$  is, i.e., the mode corresponding to the largest eigenvalue, in analogy to a uniform ferromagnet. To evaluate this, we may consider either the system in zero field as in Berlin and Kac<sup>13</sup> or apply an ordering field  $h(2\tilde{J})$  and let  $h(2\tilde{J}) \rightarrow 0$ . Both methods give  $\langle S_{2\tilde{J}} \rangle = N^{1/2}(1 - T/\tilde{J})^{1/2}$  for  $T < T_c$  with all other  $\langle S_\lambda \rangle = 0$ . Since the mean magnetization per site is

$$\langle m_i \rangle_{av} = \sum_\lambda \langle \langle i | \lambda \rangle \rangle_{av} \langle S_\lambda \rangle \quad (9)$$

and  $\langle \langle i | \lambda \rangle \rangle_{av} = 0$ ,<sup>11</sup> but  $\langle \langle i | \lambda \rangle \rangle_{av}^2 = 1/N$ , we see that  $\langle m_i \rangle_{av} = 0$  but  $\langle m_i^2 \rangle_{av} = q = 1 - T/\tilde{J}$  for  $T < T_c$ . It is readily shown that the staggered susceptibility [linear response to  $h(2\tilde{J})$ ] has an exponent  $\gamma = 2$ , in agreement with the scaling laws.

When the mean  $J_0$  of  $J_{ij}$  is positive, allowing the possibility of ferromagnetic ordering, the eigenvalue spectrum is modified and for  $\tilde{J}_0 > \tilde{J}$  an isolated eigenvalue breaks away from the continuum. To see this, we write the interaction matrix  $\hat{J}$  as  $\hat{J}_1 + \hat{J}_2$ , where  $\hat{J}_2$  has elements with mean zero and random Gaussian distribution, while  $\hat{J}_1$  has zeros along the diagonal and all other elements  $J_0$ .  $\hat{J}_1$  can be diagonalized by an orthogonal transformation, which, when applied to  $\hat{J}_2$ , leaves invariant the probability distribution of the indi-

vidual elements.<sup>12</sup> Since  $J_0$  is  $O(1/N)$ , the total interaction matrix is transformed to the same form as the  $J_0 = 0$  case, but with a single extra diagonal element of  $\tilde{J}_0$ . The problem is now formally identical to that of a single local impurity in a crystal,<sup>15</sup> and we can use standard techniques to compute the new eigenvalue spectrum and the properties of the largest eigenvector. As expected, we find

$$\rho(J) = \begin{cases} \rho_0(J), & \tilde{J}_0 < \tilde{J} \\ \rho_0(J) + (1/N)\delta(J - J_m), & \tilde{J}_0 > \tilde{J} \end{cases} \quad (10)$$

where  $\rho_0(J)$  is the  $J_0 = 0$  density [Eq. (4)] and  $J_m = \tilde{J}_0 + \tilde{J}^2/\tilde{J}_0$ .

When  $\tilde{J}_0 > \tilde{J}$ , the isolated eigenvalue at  $J_m$  determines the critical temperature and corresponds to ferromagnetic ordering. Performing the standard spherical-model manipulations, it is clear that for  $\tilde{J}_0 < \tilde{J}$  the results are independent of  $\tilde{J}_0$ , while for  $\tilde{J}_0 > \tilde{J}$  we have  $T_c = \tilde{J}_0$ . The specific heat per site is  $\tilde{J}^2/2T^2$  ( $T > T_c$ ) and  $\frac{1}{2}$  ( $T < T_c$ ), where we see the expected mean-field discontinuity of  $\frac{1}{2}(1 - \tilde{J}^2/\tilde{J}_0^2)$  across the critical isotherm, corresponding to a specific heat exponent  $\alpha = 0$ .

Again, from this point of view, the natural order parameter is  $\langle S_{J_m} \rangle$ , and the mean magnetization per site becomes

$$\langle m_i \rangle_{av} = N^{-1/2} \langle \langle l | J_m \rangle \rangle_{av} \langle S_{J_m} \rangle, \quad (11)$$

where  $\langle l | J_m \rangle$  is the element of the eigenvector belonging to the largest eigenvalue  $J_m$ . The label  $l$  denotes the position of the entry  $\tilde{J}_0$  in the interaction matrix after the first orthogonal transformation. Using the techniques described by Izyumov,<sup>16</sup> we find

$$\langle \langle l | J_m \rangle \rangle_{av} = (1 - \tilde{J}^2/\tilde{J}_0^2)^{1/2} \quad (12)$$

with the average value of all other eigenvectors zero, whence

$$\langle \bar{m}_i \rangle_{av} = (1 - \tilde{J}^2/\tilde{J}_0^2)^{1/2} (1 - T/\tilde{J}_0)^{1/2}. \quad (13)$$

There is a corresponding divergence in the uniform susceptibility for  $T > T_c = \tilde{J}_0 > \tilde{J}$  proportional to  $(1 - \tilde{J}^2/\tilde{J}_0^2)(1 - \tilde{J}_0/T)^{-1}$ , displaying the expected classical exponent  $\gamma = 1$  consistent with the scaling laws. Putting all these results together, we obtain the phase diagram of Fig. 1.

We obtain identical results by using the  $n \rightarrow 0$  trick.<sup>1,9</sup> Making the same assumptions as Sherrington and Kirkpatrick<sup>5</sup> about the evaluation of the average free energy by steepest descents, we find in the limit  $n \rightarrow 0$

$$-\frac{\langle f \rangle_{av}}{T} = \frac{\tilde{J}^2}{4T^2 + z} - \frac{1}{2}x^2 + \frac{1}{4}y^2 - \frac{1}{2} \ln \left( z + \frac{\tilde{J}y}{2T} \right) + \frac{\tilde{J}y}{4T(z + \tilde{J}y/2T)} + \frac{\tilde{J}_0 x^2}{4T(z + \tilde{J}y/2T)}, \quad (14)$$

where  $x = \langle \bar{m}_i \rangle_{av} (\tilde{J}_0/T)^{1/2}$  and  $y = \tilde{J}q/T$  have the same meaning as in Ref. 5 and  $z$  is the variable introduced by the spherical constraint [Eq. (5)]. The extremal values of Eq. (14), corresponding to a minimization of the free energy for  $n > 1$ , but a maximization for  $n < 1$ , give three possibilities: (i)  $m = q = 0$  (paramagnetic phase); (ii)  $m = 0$ ,  $q = 1 - T/\tilde{J}$  (spin-glass phase); (iii)  $m^2 = (1 - T/\tilde{J}_0)(1 - \tilde{J}^2/\tilde{J}_0^2)$ ,  $q = 1 - T/\tilde{J}_0$  (ferromagnetic phase). These yield all the results derived previously, where we have selected the solution which minimizes (maximizes) the free energy for  $n > 1$  ( $n < 1$ ). It is interesting to see that, in contrast to the Ising case,<sup>11</sup> the analytic continuation of the  $n > 1$  results gets us on to the correct branch of the free energy.

It can also be shown that the mean-field equation used by Thouless *et al.*<sup>11</sup> is correct for the spherical model. In the presence of an external field  $h_i$  on the site  $i$  this equation has the form

$$f_i = \sum_j J_{ij} m_j - m_i \tilde{J}^2 (1 - q)/T + h_i. \quad (15)$$

The mean field  $f_i$  is related to the local magnetization by  $f_i = z' m_i$  in the spherical model, and the spherical condition gives  $z' = 1/(1 - q)$ . Solution of Eq. (15) in terms of the eigenvectors of  $J_{ij}$  gives an expression for  $m_i$  which is identical with that obtained from a direct solution of the spherical model, which is

$$m_i = \sum_\lambda \lambda \frac{\langle i | \lambda \rangle h_\lambda}{z - J_\lambda/2T}. \quad (16)$$

To conclude, we have shown that in the spherical-model limit, the spin-glass with infinite-ranged interactions distributed according to a random Gaussian is solvable by using the properties of a large random matrix.<sup>12</sup> Identical results are obtained by the  $n \rightarrow 0$  trick<sup>1,9</sup> and mean-field

theory.<sup>11</sup>

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