Properties of a Classical Spin Liquid: The Heisenberg Pyrochlore Antiferromagnet

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We study the low-temperature behavior of the classical Heisenberg antiferromagnet with nearest neighbor interactions on the pyrochlore lattice. Because of geometrical frustration, the ground state of this model has an extensive number of degrees of freedom. We show, by analyzing the effects of small fluctuations around the ground-state manifold, and from the results of Monte Carlo and molecular dynamics simulations, that the system is disordered at all temperatures T and has a finite relaxation time, which varies as T^{-1} for small T. [S0031-9007(98)05655-5]

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In recent years, geometrically frustrated antiferromagnets have been identified as a distinct class of materials, separate both from unfrustrated antiferromagnets and from conventional spin-glasses [1]. Most characteristically, they remain in the paramagnetic phase, down to a freezing temperature T_F, which is small on the scale set by the interaction strength, as measured via the magnitude of the Curie-Weiss constant Θ_{CW}. This behavior appears to be a consequence of their structures, with magnetic ions arranged in corner-sharing frustrated units—triangles or tetrahedra—favoring high ground-state degeneracy.

Compounds in this class include $SrCr_8Ga_4O_{19}$ (SCGO) [2], in which a proportion of the magnetic ions occupy the sites of a kagomé lattice, and the oxide [3,4] and fluoride [5,6] pyrochlores, in which the magnetic ions form tetrahedra, as illustrated in Fig. 1. Magnetic correlations in these materials, determined from neutron scattering [2,3,5,6] and muon spin relaxation [4,7] measurements, are short ranged, with fluctuations that slow down as T is reduced towards T_F [1]. An important step towards a theory of geometrically frustrated antiferromagnets is to understand the behavior of the classical Heisenberg model defined with nearest neighbor interactions on the appropriate lattices. This simplified description may be sufficient in the paramagnetic phase, and is a natural starting point for the treatment of various additional features of real materials (anisotropy, disorder, dipolar interactions, and quantum fluctuations) that might be relevant, especially below T_F. For the lattices concerned, the Heisenberg antiferromagnet has ground states with extensive numbers of degrees of freedom. Properties in the temperature range $T \ll |\Theta_{\mathrm{CW}}|$ are controlled by small amplitude fluctuations around the ground-state manifold: the free energy of fluctuations may select specific ground states, a phenomenon known as *order by disorder* [8], while the long-time dynamics results from coupling between these fluctuations and the ground-state coordinates. Dynamical correlations, in particular, are potentially one of the most interesting aspects of these systems, but have so far received only limited attention [9,10].

In this paper we analyze the low-temperature statistical mechanics and dynamics of the classical pyrochlore Heisenberg antiferromagnet, and place our results in a broader setting. Most importantly, we show that the system is, as proposed in early work by Villain [11], an example of a cooperative paramagnet or classical spin liquid. It does not display order by disorder, and at small T the spin autocorrelation function (with precessional dynamics) decays in time t as $\langle \mathbf{S}_i(0) \cdot \mathbf{S}_i(t) \rangle = \exp(-cTt)$, where c is a constant. This behavior is in striking contrast to that of the kagomé Heisenberg antiferromagnet, previously the best-studied example of geometric frustration, in which fluctuations select coplanar spin configurations in the limit $T \to 0$ [12]. Additionally, we find, in agreement with Reimers [9], that the freezing transition observed experimentally in most pyrochlore antiferromagnets [13] is absent from the Heisenberg model.

We take, as a general starting point, n-component classical spins, $\mathbf{S}_i$, with $|\mathbf{S}_i| = 1$, arranged in q site, corner-sharing units: the kagomé and pyrochlore lattices have $q = 3$ and $q = 4$, respectively [14]. An antiferromagnetic exchange interaction, of strength J, couples each

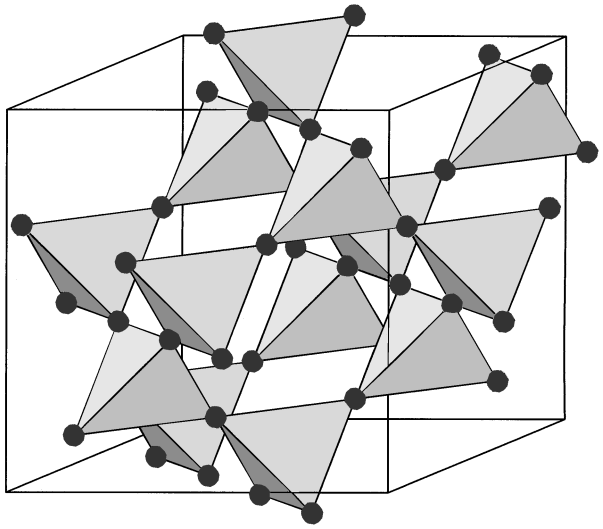

FIG. 1. The pyrochlore lattice.

spin with its $2(q-1)$ nearest neighbors in the two units to which it belongs, so that the Hamiltonian is

$$H = J\sum_{\langle i,j\rangle} \mathbf{S}_i \cdot \mathbf{S}_j \equiv \frac{J}{2}\sum_{\alpha} |\mathbf{L}_\alpha|^2 - \frac{J}{2}Nq\,, \qquad (1)$$

where the sum on $\langle i,j\rangle$ runs over all neighboring pairs, the sum on α runs over the N units making up the system, and $\mathbf{L}_\alpha$ is total spin in unit α.

The ground-state degeneracy can be demonstrated using a Maxwellian counting argument, as follows [15]. From Eq. (1), a configuration is a ground state provided $\mathbf{L}_\alpha = 0$ for each unit separately. The system has in total $F = N(n-1)q/2$ degrees of freedom, and the requirement that $\mathbf{L}_\alpha = 0$ for all α imposes $K = Nn$ constraints. The ground-state manifold has $D = F - K$ dimensions if these constraints are independent. Of the physically realizable cases ($q \le 4, n \le 3$), it is only for $q = 4, n = 3$ that $F - K = N[n(q-2) - q]/2$ is positive and extensive (taking the value $F - K = N$), and it is partly for this reason that the pyrochlore Heisenberg antiferromagnet is particularly interesting. In other systems, an extensive ground-state dimension can arise only if the constraints are not all independent, as happens starting from coplanar spin configurations of the kagomé Heisenberg model.

The ground-state manifold has two simple properties which should have direct physical consequences. First, the same counting argument shows, for a system in which $F - K$ is positive and extensive, that there exist degrees of freedom within the ground state which are strictly local. That is, for a region of the system which is sufficiently large, the ground state remains degenerate even if spins at the surface of the region are held fixed, since $F - K$, proportional to volume, is larger than the number of additional constraints, proportional to surface area. It seems likely that such local modes will cause rapid relaxation of spin correlations. Second, restricting attention to the pyrochlore lattice with $n = 2$ or 3 and open boundary conditions, we have been able to prove that the manifold is connected. The central idea is that any ground state can be deformed continuously into a reference state, without leaving the manifold; details will be given elsewhere [16]. An implication is that the system does not have internal energy barriers: if it were to freeze, it could do so only because of dynamical bottlenecks or free-energy barriers.

At low but nonzero temperature, $0 < T \ll J$, all accessible configurations lie close to the ground-state manifold, and thermal fluctuations generate a probability distribution for the system on this manifold. The question of whether the system shows order by disorder is a question about the limiting form of this distribution as $T \to 0$. To specify the problem more precisely, let $\mathbf{x}$ denote coordinates on the ground-state manifold, and let $\mathbf{y}$ be (locally defined) coordinates in the remaining orthogonal directions in configuration space. The leading term in the energy, sufficient for $T \ll J$, is quadratic in $\mathbf{y}$. Choosing axes that diagonalize this quadratic form, we have

$$H \approx H_2 = \sum_l \epsilon_l(\mathbf{x}) y_l^2. \qquad (2)$$

Retaining only quadratic terms in H and integrating over $\mathbf{y}$, the (unnormalized) ground-state probability distribution is

$$Z(\mathbf{x}) = \int d\{y_1\}\, e^{-\beta H_2} \propto \prod_l [k_B T/\epsilon_l(\mathbf{x})]^{1/2}. \qquad (3)$$

If $Z(\mathbf{x})$, calculated in this way, is normalizable, the system does not show order by disorder; instead, it explores all ground states in the limit $T \to 0$, with a probability density proportional to $Z(\mathbf{x})$. Alternatively, for a particular ground state, $\mathbf{x}_0$, some of the $\epsilon_l(\mathbf{x}_0)$ may vanish. Then $Z(\mathbf{x})$ will diverge as $\mathbf{x}$ approaches $\mathbf{x}_0$. If any such divergences are nonintegrable, one should keep higher order terms from Eq. (2) when calculating $Z(\mathbf{x})$. The result of doing so will be, in the limit $T \to 0$, a distribution concentrated exclusively on the subset of ground states for which $Z(\mathbf{x})$ is divergent: these are the configurations selected by thermal fluctuations.

To decide whether there is, in fact, order by disorder, it is necessary to know the number M of ϵ_l that vanish, and the dimension S of the subspace on which this happens. Close to this subspace, we separate $\mathbf{x} \equiv (\mathbf{u}, \mathbf{v})$ into an S-dimensional component $\mathbf{u}$, lying within it, and a $(D-S)$-dimensional component $\mathbf{v}$, locally orthogonal to it. Then, transforming $\mathbf{v}$ into radial and angular variables, v and Ω, we have, at small v, the behavior $\epsilon_l(\mathbf{x}) \propto v^2$ for M of the ϵ_l's. Hence, $Z(\mathbf{x})$ diverges as v^{-M} for small v, at fixed Ω and $\mathbf{u}$, and the potentially divergent contribution to its normalization is

$$\int Z(\mathbf{u},\mathbf{v})\, d\mathbf{v} \propto \int v^{D-S-M-1}\, dv\,. \qquad (4)$$

The integral is actually divergent at small v, and the system has order as $T \to 0$, if $D - S - M \le 0$; otherwise, the subspace is not selected.

In principle, one should calculate the value of $D - S - M$ for all possible ordering patterns. In fact, we examine only the simplest candidates, and obtain for these only the extensive part of $D - S - M$, checking our conclusions using Monte Carlo simulations. Specifically, we test for collinear spin order in tetrahedra, and coplanar order in triangles. We find [16] that $D - S - M$ increases with n, passing through the marginal value, zero, at $n = 3$ in the first case, and $n = 4$ in the second case. Simulations of both marginal systems—the Heisenberg model on the pyrochlore lattice (Refs. [9,17] and as described below), and four-component spins on the kagomé lattice [18]—indicate that they are disordered. We conclude that the only models of this kind which display order by disorder are the XY-pyrochlore and Heisenberg kagomé antiferromagnets.

We next present the results of Monte Carlo simulations of pyrochlore antiferromagnets with two- and three-component spins, which extend pioneering calculations by Reimers [9] and Zinkin [17], and confirm the above conclusions. We treat systems of size varying from $2N = 4$ to $2N = 19\,652$ spins, over a temperature range extending down to $T/J = 5 \times 10^{-5}$. We use run lengths of order 10^6 Monte Carlo steps per spin and check that the same results are obtained from both random and ordered initial configurations.

If order by disorder occurs, it leaves a signature in the heat capacity per spin C of the classical model at low temperature, which can be identified without advance knowledge of the ordering pattern [12]. The value of C reflects the nature of fluctuations in the system: each coordinate y_l for which ϵ_l is nonzero contributes $k_B/2$ to the total heat capacity, while coordinates for which $\epsilon_l = 0$, so that the associated energy varies as y_l^4, make contributions of $k_B/4$. Since there are in total $n/2$ coordinates $\{y_l\}$ per spin, and since collinear order introduces one such quartic mode per tetrahedron, or half a mode per spin, we expect values of C, in units of k_B, of $n/4$ without order, and $(n/4 - 1/8)$ with collinear order. At $T/J \sim 10^{-4}$, we find $C = 0.376 \pm 0.002$ for the XY model, and $C = 0.747 \pm 0.002$ for the Heisenberg model. For XY spins, this confirms that there is one quartic mode per tetrahedron, and hence ordering. For Heisenberg spins, it sets an upper limit of 0.04 quartic modes per tetrahedron: there is no order by disorder.

To show explicitly that ordering in the XY model is collinear and that there is no such order in the Heisenberg model, we introduce a measure of collinearity

$$P(r_{ij}) \equiv \frac{n}{n-1}\left(\langle(\mathbf{S}_i \cdot \mathbf{S}_j)^2\rangle - \frac{1}{n}\right), \qquad (5)$$

defined so that $P = 1$ for collinear spins and $P = 0$ in the high-temperature limit. As illustrated in Fig. 2, for the Heisenberg model the associated correlation length is very short even at low temperature. By contrast, for the XY model, P approaches 1 as $T \to 0$ (Fig. 2, inset), providing unequivocal evidence of order. Deviations vary as $1 - P \propto (T/J)^{1/2}$, behavior that can be understood on the basis of the analysis of Ref. [12].

Finally, we turn to the low-temperature dynamics of the Heisenberg pyrochlore antiferromagnet. Since different ground states are separated neither by energy barriers (the ground-state manifold is connected) nor by large free-energy barriers (the system does not display order by disorder), one might expect correlations to relax rapidly even at low temperature. We find that they indeed do, in the sense that the relaxation time increases at low temperature only as T^{-1} and not exponentially. The equation of motion is

$$\frac{d\mathbf{S}_i}{dt} = \mathbf{S}_i \times \mathbf{H}_i(t) \equiv -J\mathbf{S}_i \times (\mathbf{L}_\alpha + \mathbf{L}_\beta), \qquad (6)$$

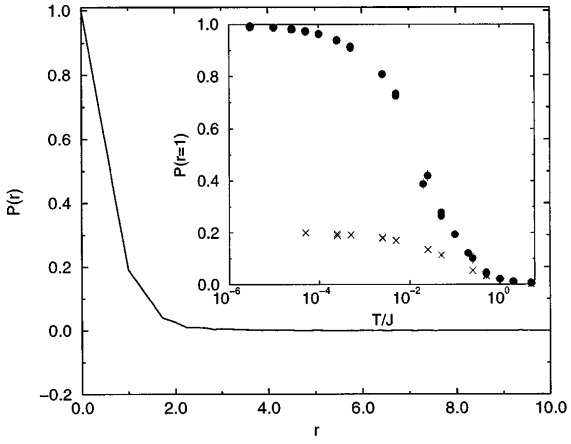

FIG. 2. Dependence of the collinearity parameter, $P(r)$, on separation, r, in units of the nearest neighbor distance, for the Heisenberg model at low temperature [$T/J = 5 \times 10^{-4}$]. Inset: temperature dependence of $P(r = 1)$ in the Heisenberg model (lower points) and the XY model (upper points).

where $\mathbf{H}_i(t)$ is the exchange field acting at site i, which can be expressed in terms of $\mathbf{L}_\alpha$ and $\mathbf{L}_\beta$, the total spins of the two tetrahedra to which $\mathbf{S}_i$ belongs. Solving this equation in the harmonic approximation, by linearizing around a ground state, yields $2N$ normal modes. If the ground state is a generic one, in the sense that none of the ϵ_l of Eq. (2) are zero, then $3/4$ of these modes have finite frequencies and the remaining $1/4$ have zero frequency. The canonical coordinates for the zero modes represent displacements in phase space that lie within the ground-state manifold. In order to study nontrivial aspects of the long-time dynamics, it is, of course, necessary to go beyond the harmonic approximation. At low temperature, anharmonic effects are small, and there is a separation of time scales: the periods of finite-frequency modes are temperature independent, and the shortest of these sets a scale of order J^{-1}, while the long time scale for motion around the ground-state manifold increases as T decreases. For short times, the exchange field, $\mathbf{H}_i(t)$ consists simply of oscillatory contributions from each of the finite-frequency modes. Over long times, the amplitudes of these modes vary, because of anharmonic coupling, and $\mathbf{H}_i(t)$ is a randomly fluctuating function. Its relevant properties on these scales are its mean, $\langle \mathbf{H}_i(t)\rangle = 0$, and its low-frequency spectral density

$$\int_{-\infty}^{\infty} dt' \,\langle \mathbf{H}_i(t) \cdot \mathbf{H}_i(t')\rangle \equiv 2\Gamma\,. \qquad (7)$$

Noting that (i) $\langle|\mathbf{H}_i(t)|^2\rangle \sim J^2\langle|\mathbf{L}_\alpha|^2\rangle \sim Jk_BT$ and (ii) only the lowest frequency modes contribute to the time integral in Eq. (7), we find [16] $\Gamma \propto Jk_BT\rho(0^+)$, where $\rho(\omega)$ is the density in frequency ω of the finite-frequency modes. We have checked, by diagonalizing the linearized equations of motion numerically, that $\rho(0^+)$ is nonzero; we conclude that $\Gamma = cT$ where c is a constant.

We can therefore calculate long-time spin correlations from Eq. (6), by treating $\mathbf{H}_i(t)$ as Gaussian white noise with the correlator $\langle \mathbf{H}_i(t) \cdot \mathbf{H}_i(t') \rangle = 2\Gamma\delta(t - t')$. Solving the resulting Langevin equation, we obtain

$$\langle \mathbf{S}_i(0) \cdot \mathbf{S}_i(t) \rangle = \exp(-cTt). \tag{8}$$

To test these ideas, we have carried out molecular dynamics simulations in which we compute the spin autocorrelation function $A(t) \equiv \langle \mathbf{S}(t') \cdot \mathbf{S}(t + t') \rangle$. Similar calculations for the kagomé Heisenberg antiferromagnet have been described by Keren [10]. A Monte Carlo simulation is used to generate uncorrelated, thermalized initial configurations, from which the equation of motion, Eq. (6), is integrated using a fourth-order Runge-Kutta algorithm. The integration time step is chosen so that energy is conserved to at least one part in 10^8. Finite size effects are suppressed by constraining the total spin of the entire system to be near zero.

We expect at low temperature, from Eq. (8), that $A(t)$ should depend on T and t only through the scaling variable Tt. $A(t)$ is shown in Fig. 3 as a function of the rescaled time, Tt, at eight different temperatures in the range $5 \times 10^{-4} \leq T/J \leq 0.5$, for a system of size 2048 spins. There are no adjustable parameters in the construction of this plot. Except at the highest temperatures, the data collapse onto a single curve, which is exponential to the precision of our calculations. To examine quantitatively the accuracy of the temperature scaling, we extract a decay time τ from $A(t)$ at each temperature $T/J < 0.15$, and fit the temperature dependence of τ to the power law $\tau \propto T^{-\zeta}$ (Fig. 3, inset), obtaining $\zeta = 0.998 \pm 0.012$. These results agree with and confirm our predictions.

Some experimental properties of pyrochlore antiferromagnets are consistent with our findings, although a detailed comparison is not yet possible. Inelastic neutron scattering from $CsNiCrF^6$ [6] for $T > T_F$ has been fitted to a Lorentzian in energy, appropriate to the time dependence of Eq. (8), with a width that decreases as T is lowered below Θ_{CW}. Similar behavior has been observed in SCGO, in the temperature range $T_F < T \lesssim \Theta_{CW}$ [19].

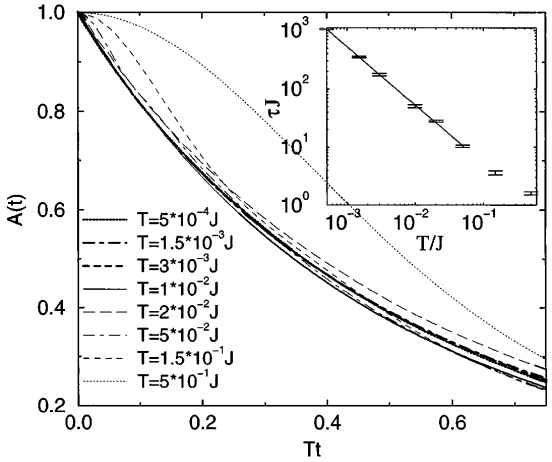

FIG. 3. The autocorrelation function as a function of the rescaled time $t \times T$ over one and a half decay times. Inset: the decay time τ as a function of temperature.

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[1] For reviews, see A. P. Ramirez, Annu. Rev. Mater Sci. **24**, 453 (1994); P. Schiffer and A. P. Ramirez, Comments Condens. Mater. Phys. **18**, 21 (1996).
[2] A. P. Ramirez *et al.*, Phys. Rev. Lett. **64**, 2070 (1990).
[3] B. D. Gaulin, J. N. Reimers, T. E. Mason, J. E. Greedan, and Z. Tun, Phys. Rev. Lett. **69**, 3244 (1992).
[4] S. R. Dunsiger *et al.*, Phys. Rev. B **54**, 9019 (1996).
[5] M. J. Harris, M. P. Zinkin, Z. Tun, B. M. Wanklyn, and I. P. Swanson, Phys. Rev. Lett. **73**, 189 (1994).
[6] M. J. Harris, M. P. Zinkin, and T. Zeiske, Phys. Rev. B **52**, R707 (1995).
[7] Y. J. Uemura *et al.*, Phys. Rev. Lett. **73**, 3306 (1994).
[8] J. Villain *et al.*, J. Phys (Paris) **41**, 1263 (1980); E. F. Shender, Zh. Eksp. Teor. Fiz. **83**, 326 (1982) [Sov. Phys. JETP **56**, 178 (1982)]; C. L. Henley, Phys. Rev. Lett. **62**, 2056 (1989).
[9] J. N. Reimers, Phys. Rev. B **45**, 7287 (1992).
[10] A. Keren, Phys. Rev. Lett. **72**, 3254 (1994).
[11] J. Villain, Z. Phys. B **33**, 31 (1979).
[12] J. T. Chalker, P. C. W. Holdsworth, and E. F. Shender, Phys. Rev. Lett. **68**, 855 (1992); I. Ritchey, P. Chandra, and P. Coleman, Phys. Rev. B **47**, 15 342 (1993).
[13] M. J. P. Gingras *et al.*, Phys. Rev. Lett. **78**, 947 (1997), and references therein.
[14] We assume that the n-component spin spaces are the same for every lattice site. This need not be the case. A Heisenberg model with easy-plane anisotropy orientated according to the local symmetry directions at each site has been studied in S. T. Bramwell, M. J. P. Gingras, and J. N. Reimers, J. Appl. Phys. **75**, 5523 (1994).
[15] J. N. Reimers, A. J. Berlinsky, and A.-C. Shi, Phys. Rev. B **43**, 865 (1991).
[16] R. Moessner, J. T. Chalker, and M. P. Zinkin (unpublished).
[17] M. P. Zinkin, D. Phil. thesis, University of Oxford, 1996.
[18] A. D. Rutenberg and D. A. Huse, Phys. Rev. B **45**, 7536 (1992).
[19] S.-H. Lee, Ph.D. thesis, Johns Hopkins University, 1996; S.-H. Lee, C. Broholm, G. Aeppli, T. G. Perring, B. Hessen, and A. Taylor (unpublished).