Dynamics and Transport of the Z_2 Spin Liquid: Application to κ-$(ET)_2Cu_2(CN)_3$

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We describe neutron scattering, NMR relaxation, and thermal transport properties of Z_2 spin liquids in two dimensions. Comparison to recent experiments on the spin $S = 1/2$ triangular lattice antiferromagnet in κ-$(ET)_2Cu_2(CN)_3$ shows that this compound may realize a Z_2 spin liquid. We argue that the topological ''vison'' excitations dominate thermal transport, and that recent thermal conductivity experiments by M. Yamashita *et al.* have observed the vison gap.

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Much attention [1–7] has recently focused on the organic compound κ-$(ET)_2Cu_2(CN)_3$ because it may be the first experimental realization of a resonating valence bond spin liquid [8,9]. This compound belongs to a class [10,11] of organic Mott insulators which can be described by $S = 1/2$ spins residing on the vertices of a triangular lattice. Experiments have not detected any magnetic order or a structural distortion leading to a doubling of the unit cell in κ-$(ET)_2Cu_2(CN)_3$, and so there is justifiable optimism that the elusive spin liquid state may finally have been found.

The debate then turns to the identification of the precise spin liquid state, among the many possible candidates. Measurements of the electronic specific heat, C_P, by S. Yamashita *et al.* [3] were interpreted to yield a nonzero low temperature (T) value of $\gamma = \lim_{T\to 0} C_P/T$. Such a nonzero γ is characteristic of a Fermi surface, and hence a spin liquid state with a Fermi surface of neutral, $S = 1/2$, fermionic spinons was postulated [3,5,6]. However, it should be noted that the measurement of γ involves a potentially dangerous subtraction of a divergent nuclear specific heat [3].

Very recently, M. Yamashita *et al.* have measured [4] the thermal conductivity, κ, to below $T \approx 0.1$ K. This has the advantage of focusing on the mobile excitations, and not being contaminated by a nuclear contribution. A spinon Fermi surface should yield a nonzero low T limit for κ/T, but this quantity was clearly observed to vanish. Instead, the measured κ was fit reasonably well by the activated behavior $\kappa \sim \exp(-\Delta_\kappa/T)$, with a ''gap'' $\Delta_\kappa \approx 0.46$ K. Furthermore, κ was found to be insensitive to an applied field for $H < 4$ T, suggesting that the gap Δ_κ is associated with a spinless excitation. These observations appear to be incompatible with spinon Fermi surface states at these low T, and we shall present an alternative theory here.

Also of interest are the measurements [2] of the NMR relaxation rate, $1/T_1$. The power-law behavior $1/T_1 \sim T^a$, with the exponent $a \approx 1.5$, was observed for $0.02 < T < 0.3$ K. This requires the presence of spinful excitations with a gapless spectrum at the fields of the NMR experiment, although at zero field there may well be a small spin gap.

In this Letter, we will compare these observations with the Z_2 spin liquid state originally proposed in Refs. [12–14]. The low energy excitations of this state are described by a Z_2 gauge theory, and the spinful excitations are constructed from $S = 1/2$ quanta (the spinons) which carry a Z_2 electric charge. Crucial to our purposes here are vortex-like spinless excitations [15] which carry Z_2 magnetic flux, later dubbed ''visons'' [16]. A number of solvable models of Z_2 spin liquids, with spinon and vison excitations, have been constructed [16–22]. We propose here that it is the visons which dominate the thermal transport in κ-$(ET)_2Cu_2(CN)_3$, and the gap Δ_κ is therefore identified with a vison energy gap, Δ_v. If our interpretation is correct, the vison has been observed by M. Yamashita *et al.* [4].

Our proposal requires that the density of states of low energy vison excitations is much larger than that of all other excitations. A model appropriate to κ-$(ET)_2Cu_2(CN)_3$ is the triangular lattice $S = 1/2$ antiferromagnet with nearest neighbor two-spin exchange (J_2) and plaquette four-spin (J_4) exchange which was studied by LiMing *et al.* [23]. They found antiferromagnetic order at $J_4 = 0$ (as in earlier work [24]), and a quantum phase transition to a spin liquid state with a spin gap around $J_4/J_2 \approx 0.1$. Notably, they found a very large density of low-lying spin singlet excitations near the transition. We propose here that κ-$(ET)_2Cu_2(CN)_3$ is near this quantum phase transition, and identify these singlets with visons which have a small gap and bandwidth, both much smaller than the spin exchange $J_2 \sim 250$ K. We will argue below that at $T \ll J_2$, and comparable to the vison bandwidth, visons will dominate the thermal transport.

Further support for the proximity of a magnetic ordering quantum-critical point comes from [11] the closely related series of compounds $X[Pd(dmit)_2]_2$. By varying the anisotropy of the triangular lattice by varying X, we obtain compounds with decreasing magnetic ordering critical temperatures, until we eventually reach a compound with a spin gap and valence bond solid order [25]. In between is the compound [26] with $X = EtMe_3P$ (Et and Me denote C_2H_5 and CH_3, respectively) which has been proposed to be at the quantum-critical point [11], and has properties similar to κ-$(ET)_2Cu_2(CN)_3$. Finally, series expansion studies [27] also place the triangular lattice antiferromagnet near a quantum-critical point between magnetically ordered and valence bond solid states.

A description of the NMR experiments requires a theory for the spinon excitations of the Z_2 spin liquid. The many models of Z_2 spin liquids [12–22] have cases with either fermionic or bosonic spinons. While we do not find a satisfactory explanation for the NMR with fermionic spinons, we show that a model [12–14] of bosonic spinons in a spin liquid close to the quantum phase transition to the antiferromagnetically ordered state (as found in the model of Liming *et al.* [23]) does naturally explain the T dependence of $1/T_1$. We shall show below that the quantum-critical region for this transition leads to $1/T_1 \sim T^{\bar{\eta}}$ with the exponent [28,29] $\bar{\eta} = 1.37$, reasonably close to the measured value $a = 1.5$. It is important to note that the vison gap, Δ_v, remains nonzero across this magnetic ordering critical point [30]. Consequently, our interpretation of the experiments remains valid even if the system acquires a small antiferromagnetic moment, as may be the case in the presence of the applied magnetic field present in the NMR measurements.

The remainder of the Letter presents a number of computations of the physical properties of Z_2 spin liquids, and uses them to elaborate on the experimental interpretation sketched above.

We begin with a theory [31] of the spinon excitations near the quantum-critical point between the magnetically ordered state and the Z_2 spin liquid. Here the low energy spinons are $S = 1/2$ complex bosons z_α, with $\alpha = \uparrow, \downarrow$ a spin index, and the low energy imaginary time action is

$$\mathcal{S} = \frac{1}{g}\int d^2r d\tau [|\partial_\tau z_\alpha|^2 + c^2|\nabla_r z_\alpha|^2], \tag{1}$$

where (r, τ) are spacetime coordinates, g is a coupling which tunes the transition to the spin liquid present for some $g > g_c$, and c is a spin-wave velocity. We impose the local constraint $\sum_\alpha |z_\alpha|^2 = 1$ in lieu of a quartic self-interaction between the spinons. This theory has an emergent O(4) global symmetry [29,32] (which becomes manifest when z_α is written in terms of its real and imaginary components). This symmetry is an enlargement of the SU(2) spin rotation symmetry, and we will neglect the irrelevant terms which reduce the symmetry to SU(2).

Dynamic spin susceptibility.—The dynamic spin correlations of $\mathcal{S}$ near the quantum-critical point can be computed by the $1/N$ expansion on the O(N) model, which has been described elsewhere [33]. With an eye towards possible future neutron scattering measurements, we first describe the dynamic spin susceptibility $\chi(k, \omega)$ as a function of momentum k and real frequency ω. Here the momentum k is measured as a deviation from the ordering wave vector, Q, of the antiferromagnetically ordered state. At $g = g_c$ and $T = 0$, this has the quantum-critical form

$$\chi(k, \omega) = \frac{\mathcal{A}}{(c^2k^2 - \omega^2)^{1-\bar{\eta}/2}}, \tag{2}$$

where the exponent $\bar{\eta}$ is related to the scaling dimension of the composite spin operator $\sim z_\alpha \sigma^y_{\alpha\gamma} \vec{\sigma}_{\gamma\beta} z_\beta$ ($\vec{\sigma}$ are the Pauli matrices), and is known with high precision from field-theoretic studies [28] [$\bar{\eta} = 1.374(12)$] and Monte Carlo simulations [29] [$\bar{\eta} = 1.373(2)$]. The overall amplitude $\mathcal{A}$ is nonuniversal, but the same $\mathcal{A}$ will appear in a number of results below. Integrating Eq. (2) over all k, we obtain the local susceptibility $\chi_L(\omega)$, which is also often measured in scattering experiments, again at $g = g_c$ and $T = 0$:

$$\mathrm{Im}\,\chi_L(\omega) = \frac{\mathcal{A}\,\mathrm{sgn}(\omega)}{4c^2}\frac{\sin(\pi\bar{\eta}/2)}{\pi\bar{\eta}/2}|\omega|^{\bar{\eta}}. \tag{3}$$

Let us now move into the spin liquid state, with $g > g_c$, where the spinons have an energy gap Δ_z. The critical results in Eqs. (2) and (3) will apply for $|\omega| \gg \Delta_z$, but for $|\omega| \sim 2\Delta_z$, we will have spectra characteristic of the creation of a pair of spinons (we set $\hbar = 1$, although it appears explicitly in a few expressions below). Computing the pair creation amplitude of noninteracting spinons, we obtain a step-discontinuity threshold at $\omega = \sqrt{c^2k^2 + 4\Delta_z^2}$ (at $T = 0$). However, the spinons do have a repulsive interaction with each other, and this reduces the phase space for spinon creation at low momentum, as described in the supplementary material; the actual threshold behavior is [34]

$$\mathrm{Im}\,\chi(k, \omega) = \frac{\mathcal{A}\mathcal{C}\mathrm{sgn}(\omega)}{\Delta_z^{2-\bar{\eta}}}\frac{\theta(|\omega| - \sqrt{k^2 + 4\Delta_z^2})}{\ln^2(\frac{|\omega^2 - k^2 - 4\Delta_z^2|}{16\Delta_z^2})}, \tag{4}$$

where $\mathcal{C}$ is a universal constant; to leading order in the $1/N$ expansion, $\mathcal{C} = N^2/16$. We can also integrate the k-dependent generalization of Eq. (4) to obtain a threshold behavior for the local susceptibility at $2\Delta_z$: $\mathrm{Im}\chi_L(\omega) \sim \mathrm{sgn}(\omega)(|\omega| - 2\Delta_z)/\ln^2(|\omega| - 2\Delta_z)$.

NMR relaxation.—Turning to the NMR relaxation rate, we have to consider $T > 0$, and compute

$$\Gamma = \lim_{\omega \to 0} \frac{k_B T}{\omega}\mathrm{Im}\chi_L(\omega). \tag{5}$$

This is far more subtle than the computations at $T = 0$, because we have to compute the damping of the quantum-critical excitations at $T > 0$ and extend to the regime $\omega \ll T$. From general scaling arguments [33], we have

$$\Gamma = \frac{\mathcal{A}}{c^2}(k_B T)^{\bar{\eta}}\Phi(\Delta_z/(k_B T)), \tag{6}$$

where Φ is a universal function. The computation of Φ for undamped spinons at $N = \infty$ is straightforward and, unlike the case for confining antiferromagnets [33], yields a reasonable nonzero answer: $\Phi(y) = [4\pi e^{y/2}(1 + \sqrt{4 + e^y})]^{-1}$. However, the $1/N$ corrections are singular, because Γ has a singular dependence upon the spinon lifetime. A self-consistent treatment of the spinon damping is described in the supplementary material, and leads to the quantum-critical result ($\Delta_z = 0$):

$$\Phi(0) = \frac{(\sqrt{5}-1)}{16\pi}\left(1 + 0.931\frac{\ln N}{N} + \ldots\right). \quad (7)$$

Thermal conductivity.—We now turn to the thermal transport coefficient measured in the recent revealing experiments of Ref. [4]. We consider the contribution of the spinons and visons in turn below, presenting further arguments on why the vison contribution can dominate in the experiments.

(i) Spinons. For agreement with the NMR measurements of $1/T_1$ [2], we need the spinons to be in the quantum-critical regime, as described above. Therefore, we limit our considerations here to the quantum-critical thermal conductivity of the spinons, κ_z, with $\Delta_z = 0$. This can be obtained from the recent general theory of quantum-critical transport [35] which yields

$$\kappa_z = sc^2\tau_z^{\text{imp}}, \quad (8)$$

where s is the entropy density of the spinons, and $1/\tau_z^{\text{imp}}$ is the spinon momentum relaxation rate, with the T dependence

$$\tau_z^{\text{imp}} \sim T^{2/\nu-3}. \quad (9)$$

Here ν is the critical exponent of the O(4) model [36], $\nu = 0.749(2)$, and so $\tau_z^{\text{imp}} \sim T^{-0.33}$. The two-dimensional entropy density can be obtained from the results of Ref. [33]:

$$s = \frac{3N\zeta(3)k_B^3T^2}{2\pi\hbar^2c^2}\left[\frac{4}{5} - \frac{0.3344}{N} + \ldots\right], \quad (10)$$

where ζ is the Riemann zeta function. We estimate the coefficient in Eq. (9) in the supplementary material using a soft-spin theory with the spinons moving in a random potential, $V(r)|z_\alpha|^2$, due to impurities of density n_{imp} each exerting a Yukawa potential $V_q = V_z/(q^2+\mu^2)$; this leads to [34]

$$\kappa_z \sim \frac{Nc^2\hbar k_B^4\mu^4T^2T_z}{an_{\text{imp}}V_z^2}\left(\frac{T}{T_z}\right)^{2/\nu-3}. \quad (11)$$

Here a is the spacing between the layers, and T_z is the spinon bandwidth in temperature units and is proportional to the spinon velocity c.

(ii) Visons. The visons are thermally excited across an energy gap, Δ_v, and so can be considered to be a dilute Boltzmann gas of particles of mass m_v. We assume there are N_v species of visons. The visons see the background filling of spins as a magnetic flux through the plaquette on the dual lattice, and hence the dynamics of visons can be well described by a fully frustrated quantum Ising model on the honeycomb lattice. Detailed calculations show that there are four minima of the vison band with an emergent O(4) flavor symmetry at low energy [17]; therefore $N_v = 4$. As with the spinons, the visons are assumed to scatter off impurities of density n_{imp} with, say, a Yukawa potential $V_q = V_v/(q^2+\mu^2)$. We use the fact that at low T, and for a large vison mass m_v, the visons are slowly moving. So each impurity scattering event can be described by a T matrix $= [m_v \ln(1/k)/\pi]^{-1}$ characteristic of low momentum scattering in two dimensions. Application of Fermi's golden rule then yields a vison scattering rate $1/\tau_v^{\text{imp}} = \pi^2 n_{\text{imp}}/[m_v \ln^2(1/k)]$. This formula becomes applicable when $\ln(1/k)V_v/(\hbar^2\mu^2/2m_v) \gg 1$; i.e., the impurity potential becomes nonperturbative. We can now insert this scattering rate into a standard Boltzmann equation computation of the thermal conductivity $\kappa_v = 2k_B^2 T n_v \tau_v^{\text{imp}}/m_v$, where n_v is the thermally excited vison density and the typical momentum $k \sim (m_v k_B T)^{1/2}$, to obtain

$$\kappa_v = \frac{N_v m_v k_B^3 T^2 \ln^2(T_v/T)e^{-\Delta_v/(k_BT)}}{4\pi\hbar^3 n_{\text{imp}} a}. \quad (12)$$

Here T_v is some ultraviolet cutoff temperature which can be taken as the vison bandwidth. Note that for a large density of states of vison excitations, i.e., a large m_v, the prefactor of the exponential can be large. Similar calculations will not lead to a logarithmic divergence for the critical spinon z due to the positive anomalous dimension of $|z|^2$, and therefore the impurity scattering of spinons is perturbative for $V_z/(c\mu\hbar)^2 < 1$.

Using Eq. (12), we fit the thermal conductivity measured by M. Yamashita *et al.* in Ref. [4] by tuning parameters T_v and Δ_v. The best fit values are $T_v = 8.15$ K, and $\Delta_v \equiv \Delta_\kappa = 0.238$ K, as shown in Fig. 1. For a consistency check, we calculate the ratio between the thermal conductivities contributed by spinons and visons using Eqs. (11) and (12) and assuming moderate spinon impurity strength $V_z/(c\mu\hbar)^2 \sim 1$:

$$\frac{\kappa_z}{\kappa_v} \sim \frac{k_BT_z}{m_vc^2}\left(\frac{T}{T_z}\right)^{2/\nu-3}\frac{1}{(\ln T_v/T)^2}e^{\Delta_v/k_BT}$$
$$\sim \frac{T_v}{T_z}\left(\frac{T}{T_z}\right)^{2/\nu-3}\frac{1}{(\ln T_v/T)^2}e^{\Delta_v/(k_BT)}. \quad (13)$$

We plot this ratio in Fig. 2, with $T_z \sim J_2 = 250$ K and other parameters as above, for the experimentally relevant temperature between 0.1 K and 0.6 K; we find consistency because κ is dominated by the vison contribution. The vison dispersion is quadratic above the vison gap, and this leads to a T-independent $\gamma = C_p/T$ when $T > \Delta_v$, as observed in experiments [3]. Our estimate of the vison

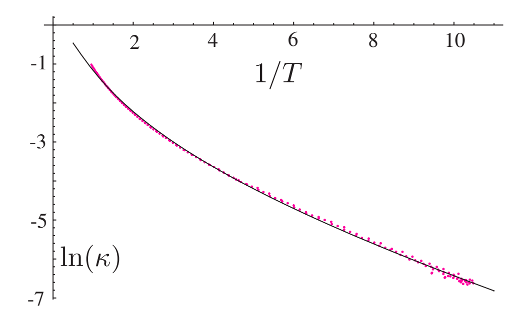

FIG. 1 (color online). Fit of the T dependence of the vison thermal conductivity in Eq. (12) to the thermal conductivity measurements by M. Yamashita *et al.* [4]; T_v, Δ_v and the overall prefactor were the fit parameters.

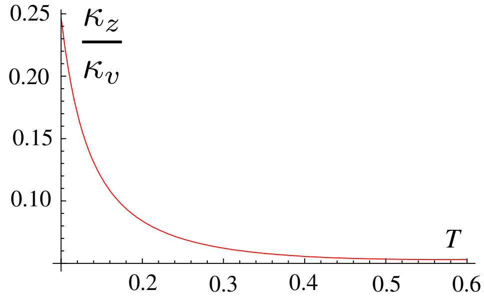

FIG. 2 (color online). Ratio of the thermal conductivity of spinons to visons in Eq. (13).

bandwidth, T_v, is also consistent with a peak in both C_P [3] and κ [4] at a temperature close to T_v.

The vison gap, Δ_v, obtained here is roughly the same as the temperature at which the $1/T_1$ of NMR starts to deviate from the low temperature scaling of Eq. (6) [2]. When T is above Δ_v, thermally activated visons will proliferate. We discuss a theory of the spin dynamics in this thermal vison regime in the supplement, and find a $1/T_1$ with a weaker T dependence compared to that present for $T < \Delta_v$. These observations are qualitatively consistent with the NMR data for $0.25 < T < 10$ K [2].

Reference [4] also measured the thermal conductivity, in an applied field H up to 10 T. There was little change in κ for $H < 4$ T. As H couples to the conserved total spin, it only appears as an opposite "chemical potential" term for z_α, modifying the temporal derivative $[\partial_\tau + (H/2)\sigma^z]z^\dagger[\partial_\tau - (H/2)\sigma^z]z$. At the quantum-critical point, this term will induce a condensate of z, i.e., a noncollinear magnetically ordered state. We do not expect a significant difference in the thermal conductivity of the gapless spinons versus gapless spin waves across this second order transition. We conjecture that the change at 4 T is associated with a vison condensation transition to a valence bond solid, as the field scale is on the order of the energy scales noted in the previous paragraph. This transition is possibly connected to the H-dependent broadening of the NMR spectra [2].

We have described the properties of a Z_2 spin liquid, on the verge of a transition to a magnetically ordered state. We have argued that the quantum-critical spinons describe the NMR observations [2], while the visons (with a small energy gap and bandwidth) dominate the thermal transport [4].

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[1] Y. Shimizu *et al.*, Phys. Rev. Lett. **91**, 107001 (2003).
[2] Y. Shimizu *et al.*, Phys. Rev. B **73**, 140407(R) (2006).
[3] S. Yamashita *et al.*, Nature Phys. **4**, 459 (2008).
[4] M. Yamashita *et al.*, Nature Phys. **5**, 44 (2009).
[5] O. I. Motrunich, Phys. Rev. B **72**, 045105 (2005).
[6] S.-S. Lee, P. A. Lee, and T. Senthil, Phys. Rev. Lett. **98**, 067006 (2007).
[7] Y. Qi and S. Sachdev, Phys. Rev. B **77**, 165112 (2008).
[8] P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 423 (1974).
[9] S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987).
[10] B. J. Powell and R. H. McKenzie, J. Phys. Condens. Matter **18**, R827 (2006).
[11] Y. Shimizu *et al.*, J. Phys. Condens. Matter **19**, 145 240 (2007).
[12] N. Read and S. Sachdev, Phys. Rev. Lett. **66**, 1773 (1991).
[13] R. A. Jalabert and S. Sachdev, Phys. Rev. B **44**, 686 (1991).
[14] S. Sachdev, Phys. Rev. B **45**, 12 377 (1992).
[15] N. Read and B. Chakraborty, Phys. Rev. B **40**, 7133 (1989).
[16] T. Senthil and M. P. A. Fisher, Phys. Rev. B **63**, 134521 (2001).
[17] R. Moessner and S. L. Sondhi, Phys. Rev. B **63**, 224401 (2001).
[18] A. Y. Kitaev, Ann. Phys. (N.Y.) **303**, 2 (2003).
[19] X. G. Wen, Phys. Rev. B **44**, 2664 (1991); Phys. Rev. Lett. **90**, 016803 (2003).
[20] M. Freedman *et al.*, Ann. Phys. (N.Y.) **310**, 428 (2004).
[21] F. Wang and A. Vishwanath, Phys. Rev. B **74**, 174423 (2006).
[22] G. Misguich and F. Mila, Phys. Rev. B **77**, 134421 (2008).
[23] W. LiMing *et al.*, Phys. Rev. B **62**, 6372 (2000).
[24] R. R. P. Singh and D. A. Huse, Phys. Rev. Lett. **68**, 1766 (1992).
[25] M. Tamura, A. Nakao, and R. Kato, J. Phys. Soc. Jpn. **75**, 093 701 (2006); Y. Shimizu *et al.*, Phys. Rev. Lett. **99**, 256403 (2007).
[26] T. Itou, A. Oyamada, S. Maegawa, M. Tamura, and R. Kato, Phys. Rev. B **77**, 104413 (2008).
[27] Z. Weihong, R. H. McKenzie, and R. R. P. Singh, Phys. Rev. B **59**, 14 367 (1999).
[28] P. Calabrese, A. Pelissetto, and E. Vicari, Phys. Rev. B **67**, 054505 (2003).
[29] S. V. Isakov, T. Senthil, and Y. B. Kim, Phys. Rev. B **72**, 174417 (2005).
[30] In the ordered state, the visons have a logarithmic interaction, and the self-energy of an isolated vison diverges logarithmically with system size.
[31] A. V. Chubukov, T. Senthil, and S. Sachdev, Phys. Rev. Lett. **72**, 2089 (1994).
[32] P. Azaria, B. Delamotte, and T. Jolicoeur, Phys. Rev. Lett. **64**, 3175 (1990).
[33] A. V. Chubukov, S. Sachdev, and J. Ye, Phys. Rev. B **49**, 11 919 (1994).
[34] See EPAPS Document No. E-PRLTAO-102-005920 for supplementary information, which includes the $1/N$ derivation of the spin susceptibility, and the vison contribution to susceptibility and thermal conductivity. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[35] S. A. Hartnoll *et al.*, Phys. Rev. B **76**, 144502 (2007); M. Müller and S. Sachdev, Phys. Rev. B **78**, 115419 (2008).
[36] M. Hasenbusch, J. Phys. A **34**, 8221 (2001).