Thermal Quenches in Spin Ice

C. Castelnovo,[1] R. Moessner,[2] and S. L. Sondhi[3]

[1]*Rudolf Peierls Centre for Theoretical Physics and Worcester College, Oxford University, Oxford OX1 3NP, United Kingdom*
[2]*Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany*
[3]*Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*

We study the diffusion-annihilation process which occurs when spin ice is quenched from a high temperature paramagnetic phase deep into the spin-ice regime, where the excitations—magnetic monopoles—are sparse. We find that due to the Coulomb interaction between the monopoles, a dynamical arrest occurs, in which nonuniversal lattice-scale constraints impede the complete decay of charge fluctuations. This phenomenon is outside the reach of conventional mean-field theory for a two-component Coulomb liquid. We identify the relevant time scales for the dynamical arrest and propose an experiment for detecting monopoles and their dynamics in spin ice based on this nonequilibrium phenomenon.

PACS numbers: 75.10.Hk, 75.40.Mg, 87.15.R−

Introduction.—There is intense current interest in the study of strongly correlated systems hosting fractionalized excitations, in fields as diverse as magnetism, quantum Hall physics, quantum computing, or even (topological) band insulators. Such excitations arise against the background of highly unusual ground states.

Recently, we argued that spin ice—an Ising magnet on the pyrochlore lattice—hosts deconfined magnetic monopole excitations, which result from the fractionalization of the high-energy local dipole moments [1]. At the moment, theoretical and experimental studies focus on predicting and detecting signatures of these excitations [2–6].

In spin ice, the ground-state ensemble is unusual in that it exhibits algebraic correlations without representing a conventional critical point: this Coulomb phase—in the sense of the deconfined phase of a U(1) gauge theory—is a consequence of the local constraint that two spins point into each tetrahedron and two point out. Spin ice owes its name to this magnetic version of the Bernal-Fowler ice rules. The Coulomb phase is characterized by an emergent gauge field, rather than an emergent order parameter.

Violating the ice rules by flipping a spin out of a ground-state configuration, at a cost in energy of Δ_{sf}, leads to *a pair* of pointlike defects in the tetrahedra the spin belongs to. These two defects are deconfined: they can be separated to an arbitrarily large distance at a finite cost in energy. In the presence of long-range dipolar interactions—the model referred to as dipolar spin ice below—such defects experience a magnetic Coulomb interaction, $V(r) = \mu_0 Q_m^2/(4\pi r)$, whence the appellation *magnetic monopoles*. Here, μ_0 is the vacuum permeability, and the magnetic charge $Q_m = 2|\vec{\mu}|/a_d$ is related to the dipole moment of the magnetic ions $|\vec{\mu}|$ and the distance between the centers of adjacent tetrahedra a_d.

In addition, there is a Coulomb interaction of entropic origin, with coupling strength $Q_s^2 \propto T$. It is present even in the nearest-neighbor model for spin ice, where the long-range dipolar interactions are omitted and $Q_m = 0$.

Spin-ice compounds, such as $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$, are thus the first instances of three-dimensional magnets which host deconfined fractionalized excitations. The most satisfying detection experiment would consist of a direct visualization of a magnetic monopole in bulk spin ice. However, due to its small magnetic charge and the fact that single quasiparticles are hard to come by in bulk systems—even in quantum Hall physics, a single fractionalized charge has never been imaged—this has so far proven beyond reach. In Ref. [1], we have shown that a thermodynamic signature of the magnetic Coulomb interaction of the monopoles is the presence of a liquid-gas transition in a magnetic-field applied in the [111] direction, which had already been experimentally observed.

In this Letter, we study the evolution of the monopole density after a thermal quench. The description of such nonequilibrium dynamics is a worthwhile enterprise in itself, as thus far there have been no instances of three-dimensional magnets with pointlike elementary excitations, and hence little motivation for their study. Work on the quench dynamics of Coulomb liquids [7,8] shall provide the starting point for our analysis.

Our central result consists of the demonstration that the time dependence of the monopole density after a quench provides a distinct signature of not only their pointlike nature but also of their magnetic Coulomb interaction. For the nearest-neighbor model, we show that mean-field theory applies. We analytically account for the simulated time dependence of the density without free parameters. In dipolar spin ice, monopole bound states appear which can only be annihilated over an energy barrier. This leads to a dynamical arrest at low temperatures. This is again borne out by Monte Carlo (MC) simulations, where the fundamental dynamical move consists of a single spin flip as appropriate for the large Ising spins in spin ice [2].

The outline of the Letter is as follows. We set the stage by briefly summarizing the annihilation-diffusion physics in Coulomb liquids. We address the new features present in

nearest-neighbor spin ice, before presenting our results on the dipolar system. We close with remarks on equilibration in spin ice, and how the freezing of bound pairs could be used as an experimental technique to achieve measurable monopole densities at very low temperatures.

Diffusion-annihilation in Coulomb liquids.—Consider a density $n_\pm(r)$ of positive and negative monopoles. As oppositely charged pairs can annihilate, their density obeys

$$\frac{dn_+(r)}{dt} = \frac{dn_-(r)}{dt} = -\mathcal{K}n_+(r)n_-(r), \quad (1)$$

where $\mathcal{K}$ is an appropriate rate constant. In addition, the monopoles move deterministically in response to their mutual forces, and they are subject to diffusion in the presence of density inhomogeneities.

Neglecting density fluctuations, one obtains the mean-field solution

$$\rho(t) \equiv \frac{n_+ + n_-}{2} = \frac{\rho_0}{1 + \mathcal{K}\rho_0 t} \quad (2)$$

for a quench to $T = 0$, where $\rho_0 \sim a_0^{-3}$ is the initial density: the characteristic time scale for the decay is $\tau_\mathcal{K} \sim a_0^3/\mathcal{K}$. A dynamical bottleneck can arise if there are spatial fluctuations in the relative density of positive and negative monopoles $\sigma(r) = [n_+(r) - n_-(r)]/2$ (which is unaffected by the symmetric annihilation process) that are not smoothed fast enough by the motion of the monopoles. The relevant time scale for a particle to move a distance a_0 is given by $\tau_Q \sim a_0/(\mu E) \sim a_0^3/(\mu q)$, where μ is the monopole mobility and $E \sim q/a_0^2$ is the typical strength of the Coulomb field.

Nearest-neighbor spin ice.—This system presents a number of special features with respect to ordinary Coulomb liquids, which are intricately linked to the existence of the monopoles against a backdrop of spin configurations in spin ice. The first is a constraint on the possible values of σ which follows from the fact that the charge density encodes the change in the magnetization of the sample. The boundedness of the magnetization implies that a cube of volume L^3 can at most accommodate a net charge $\sigma \sim L^2$. Thus the long-wavelength Fourier components are suppressed as $\tilde{\sigma}(q) \sim q^2$.

The other crucial feature is that the interaction between the defects is of a purely entropic nature, due to the weighting of the monopole states by the number of spin configurations they are compatible with. This interaction has a Coulombic form

$$V_s(r) = k_B T \frac{Q_s^2}{r/a_d}, \quad (3)$$

where $Q_s^2 \simeq 0.35 \pm 0.01$ can, e.g., be obtained from the probability distribution of the separation of a lone pair of monopoles in equilibrium Monte Carlo simulations [9,15]. Whereas the strength of this interaction vanishes as $T \to 0$, the mobility $\mu \simeq (Q_m a_d^2)/(6\tau k_B T)$ arising from the single spin-flip Metropolis dynamics diverges, resulting in a regular $T \to 0$ limit of τ_Q. Here τ is the basic unit of time, e.g.,

the inverse of the flip rate of an isolated spin in Monte Carlo simulations. In spin ice materials, ac susceptibility measurements indicate that $\tau \sim 1$ ms [10]. A simple estimate yields $\mathcal{K}/a_d^3 \simeq 2g/\tau$, where $g \in [\frac{3}{4}, \frac{9}{10}]$: the probability of two oppositely charged monopoles on neighboring tetrahedra is proportional to ρ^2, and they annihilate in the next step (after time τ) if flipping the intermediate spin restores the ice rules in both tetrahedra; this probability, which depends on the spin correlations, is estimated by g ($1 - g$ being the probability that the two monopoles do not annihilate upon flipping the intermediate spin).

Our numerical simulations of thermal quenches in nearest-neighbor spin ice down to zero temperature are displayed in Fig. 1. The mean-field solution shows quantitative agreement with the numerics without any fitting parameters: the fact that $\tilde{\sigma}(q) \sim q^2$, together with the entropic Coulomb interaction, effectively suppress fluctuations in the charge density.

Dipolar spin ice.—The presence of a magnetic Coulomb interaction in spin ice leads to further features outside the conventional picture of Coulomb liquids. First of all, a diverging mobility is no longer compensated by a vanishing potential energy, and $\tau_Q \to 0$ in the zero temperature limit. This indicates that the motion of the monopoles does not follow linear response, but rather the monopoles move along the local field direction at the maximum speed permitted by microscopic constraints, namely, one step in time τ. We thus expect monopoles to find each other very efficiently, and therefore a decay of ρ which is at least as fast as in the nearest-neighbor case.

This is, however, not what happens.

The interplay between long-range interactions and constraints imposed by the underlying spin degrees of freedom leads to the formation of *noncontractible* monopole pairs, and the system exhibits a dynamical arrest. Indeed, not all nearest-neighbor monopole-antimonopole pairs can be an-
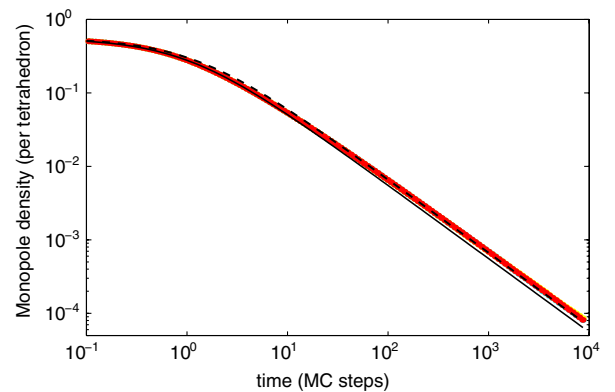

FIG. 1 (color online).   Monopole density evolution in nearest-neighbor spin ice ($J = 1$ K), after a temperature quench from $T = 10$ K down to $T = 0$ K. We simulate systems of size $L = 32, 64, 128$, and finite size effects are absent at these time scales (estimated error bars are smaller than the symbol size). The analytical mean-field result Eq. (2) is shown for $g = 3/4$ (dashed black line) and $g = 9/10$ (solid black line).

nihilated by flipping the shared spin (see Fig. 2, left-hand panel). Annihilation then takes place only if the two monopoles separate and meet elsewhere in the lattice. Because of their magnetic Coulomb interaction, there is an energy barrier for such a process, leading to an activated Arrhenius behavior in the monopole density relaxation.

The smallest possible energy barrier determines the long time behavior in the system. This is given by an elementary move where the monopoles of a bound pair annihilate around one of the adjacent hexagonal loops in the lattice (see Fig. 2, right-hand panel). Two of the five spin flips involved in such a process increase the distance between oppositely charged monopoles. A rough estimate for the concomitant energy gaps (see Ref. [1]) is given by the Coulomb interaction between the magnetic charges, leading to an overall energy barrier $\Delta = 1.47$ K. In practice, the energy cost of a spin flip varies due to the effectively random fields set up by nearby bound pairs, leading to a broadened distribution of Δ.

We ran extensive numerical Monte Carlo simulations treating the long-range dipolar interaction via the Ewald summation technique, [11] and using the waiting time method [12] with single spin flip updates to access the long time regime [13]. We prepare the system at equilibrium at the initial temperature of 10 K. We then set the temperature to its quench value at time $t = 0$, and we start the measurements.

The defect density either reaches its equilibrium value very quickly (for $T \gtrsim 0.4$ K), or a significant deviation from power law decay appears ($T \lesssim 0.4$ K) due to the activated behavior induced by the noncontractible bound pairs, as illustrated in Fig. 3.

A (temperature independent) Gaussian distribution of energy barriers Δ peaked around 1.47 K, with a variance 0.01 K^2, leads to a probability distribution $\mathcal{P}(\Theta)$ of single hexagon decay times Θ, and hence a (normalized) defect density $\rho(t) = 1 - \int_0^t \mathcal{P}(\Theta) d\Theta$. The resulting curves $\rho(t)$ are compared with the numerical ones in the inset of Fig. 3.

Notice the good agreement over more than 20 orders of magnitude in t for the different values of the quench temperature. Clearly, this phenomenological model captures the fundamental physics underlying the dynamical arrest in thermal quenches.

To further confirm this scenario, we explicitly determined the density of monopoles forming noncontractible pairs, as well as the density of contractible defect pairs (i.e., pairs where flipping the intermediate spin lowers the number of defects in the system). The result is illustrated in Fig. 4 for a given quench temperature. One can see that the initial decay ends when there are essentially no contractible pairs left in the system (magenta curve falling below $1/N_t$, where $N_t = 8L^3$ is the total number of tetrahedra in the lattice). From thereon, the total defect density is essentially given by monopoles forming noncontractible pairs.

The defect density decay approaching the plateau is captured by a diffusion process where oppositely charged particles (A, B) either annihilate $(\varnothing)$ or fuse into a noncontractible pair (D) (Fig. 5, left-hand panel). For quenches to low temperatures, the noncontractible pairs can be approximated as frozen unless another single particle annihilates one member of the pair, thus freeing the other one (Fig. 5, right-hand panel). In a simple mean-field model, one finds a surviving population of noncontractible pairs D, provided the single particle density decays faster than $1/t$, as is the case in our simulations. The resulting time dependence of the total and noncontractible particle densities is in qualitative agreement with the numerical results illustrated in Fig. 4 [15]. On the longest time scales,
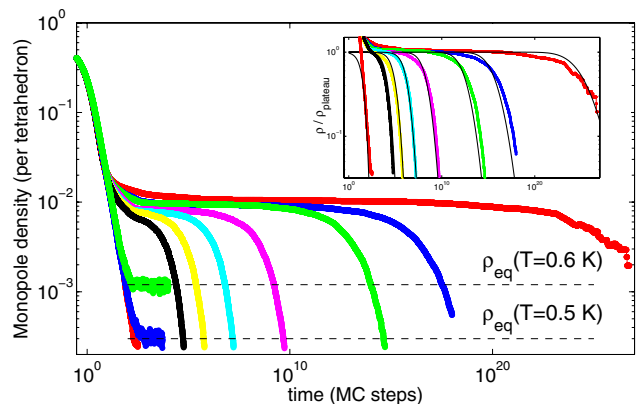
FIG. 3 (color online). Numerical simulations of thermal quenches in dipolar spin ice (system size $L = 8$, i.e., 8192 spins, and simulation parameters for Dy$_2$Ti$_2$O$_7$ as in Ref. [17]). The curves show the total density of defects ρ per tetrahedron as a function of Monte Carlo time in units of Monte Carlo steps (one attempt per spin), for quenches from $T = 10$ K, down to $T = 0.025$ K (red), $T = 0.04$ K (blue), $T = 0.05$ K (green), $T = 0.075$ K (magenta), $T = 0.1$ K (cyan), $T = 0.125$ K (yellow), $T = 0.15$ K (black), $T = 0.4$ K (red), $T = 0.5$ K (blue), and $T = 0.6$ K (green)—appearing in order from right to left. Inset: Long time behavior of ρ normalized by its plateau value ρ_{plateau}, compared to the phenomenological model discussed in the text (thin black lines).
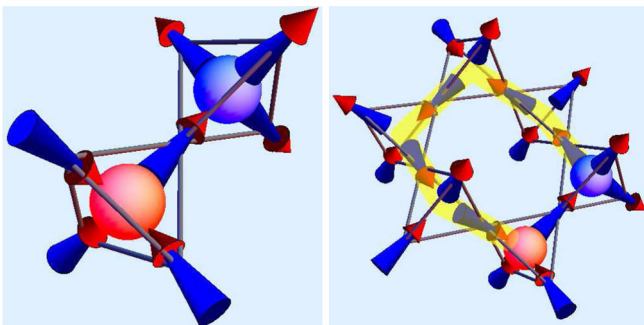

FIG. 2 (color online). Example of a noncontractible monopole-antimonopole pair (left-hand panel). The shortest path that can lead to their annihilation is a hexagonal loop, provided the spins along the path are oriented appropriately (right-hand panel). One can see explicitly that the two monopoles must separate before they are allowed to annihilate, resulting in a Coulomb energy barrier for the process.
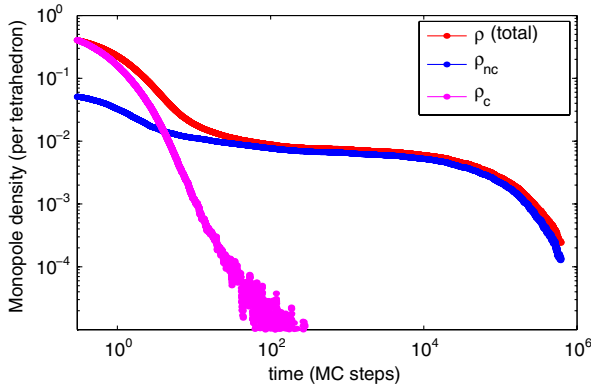
FIG. 4 (color online). Numerical simulation of a thermal quench down to $T = 0.125$ K (system size $L = 8$). The red curve shows the total density of defects per tetrahedron ρ, while the blue and the rapidly decaying magenta curves correspond to the density of defects forming noncontractible pairs ρ_{nc} and contractible pairs ρ_c, respectively.

annihilation of noncontractible pairs $D \to 0$ around hexagonal loops terminates the plateau.

Equilibration time scales and experiment.—The dominant dynamics in spin ice at low temperatures consists of hopping monopoles. These correspond to single spin flips which do not incur a cost for violating the ice rules. As the temperature is lowered to zero, the monopole density vanishes and spin ice freezes completely. At finite temperatures the low density of monopoles leads to an exponentially large time scale (in fact, possibly super-exponentially large [2,10]) which grows faster than the time scale governing the monopole density. Upon cooling, there is a "fast" process responsible for the thermalization of the energy (i.e., the monopole density), and a slower process that equilibrates the spin correlations. We believe that this mechanism explains why certain quantities such as the energy seem to equilibrate at temperatures where the magnetization has long fallen out of equilibrium. It would be on the long time scales of the slower process that any magnetic order is established [14].

We note that noncontractible bound monopoles are practically absent upon heating from an equilibrium state. There is thus an asymmetric approach to equilibrium in the monopole density at a given temperature, depending on the use of heating or cooling thermal quenches.

The most elegant way to measure monopole densities would be via zero-field NMR on the oxygen nuclei at the center of the tetrahedra, which experience different field strengths and corresponding fluctuation rates when the tetrahedra host a monopole [16]. One needs a sufficiently large density of monopoles to yield a measurable signal, while preventing the monopoles from moving around too quickly, thus spoiling the measurement. In thermal equilibrium, temperatures low enough for the second condition to be satisfied result in exceedingly small monopole densities. Our results suggest that a temperature quench on time scales sufficiently shorter than the time to develop the dynamical arrest plateau in Fig. 3 ($\sim$10–100 ms) could be used to induce a monopole-rich state ($\rho \gtrsim 10^{-2}$ per tetrahedron), where motion at short times is obstructed by the formation of noncontractible pairs.

Finally, the method of choice for imaging spin correlations is neutron scattering [3–5]. As the noncontractible monopole pairs remain bound on long time scales, the concomitant short-range correlations should be visible in the neutron scattering cross section.
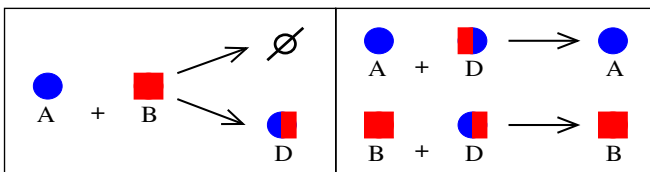
FIG. 5 (color online). Schematic illustration of the reaction processes in the mean-field model used to describe the very low temperature limit of thermal quenches in spin ice.

[1] C. Castelnovo, R. Moessner, and S. L. Sondhi, Nature (London) **451**, 42 (2008).
[2] L. D. C. Jaubert and P. C. W. Holdsworth, Nature Phys. **5**, 258 (2009).
[3] D. J. P. Morris *et al.*, Science **326**, 411 (2009).
[4] T. Fennell *et al.*, Science **326**, 415 (2009).
[5] H. Kadowaki *et al.*, J. Phys. Soc. Jpn. **78**, 103706 (2009).
[6] S. T. Bramwell *et al.*, Nature (London) **461**, 956 (2009).
[7] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).
[8] V. V. Ginzburg, L. Radzihovsky, and N. A. Clark, Phys. Rev. E **55**, 395 (1997).
[9] W. Krauth and R. Moessner, Phys. Rev. B **67**, 064503 (2003).
[10] J. Snyder *et al.*, Phys. Rev. B **69**, 064414 (2004).
[11] S. W. de Leeuw, J. W. Perram, and E. R. Smith, Proc. R. Soc. A **373**, 27 (1980).
[12] J. Dall and P. Sibani, Comput. Phys. Commun. **141**, 260 (2001); P. Sibani and H. J. Jensen, Europhys. Lett. **69**, 563 (2005).
[13] While the simulations, when thermalized using appropriate cluster updates, have been argued to undergo an ordering transition below $T_c \simeq 180$ mK, single-spin dynamics does not take the system across the first-order transition into the ordered phase [14].
[14] R. G. Melko, B. C. den Hertog, and M. J. P. Gingras, Phys. Rev. Lett. **87**, 067203 (2001).
[15] C. Castelnovo, R. Moessner, and S. L. Sondhi (to be published).
[16] K. Kitagawa and M. Takigawa (private communications).
[17] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000).