

Quantum Ice: A Quantum Monte Carlo Study

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Ice states, in which frustrated interactions lead to a macroscopic ground-state degeneracy, occur in water ice, in problems of frustrated charge order on the pyrochlore lattice, and in the family of rare-earth magnets collectively known as spin ice. Of particular interest at the moment are “quantum spin-ice” materials, where large quantum fluctuations may permit tunnelling between a macroscopic number of different classical ground states. Here we use zero-temperature quantum Monte Carlo simulations to show how such tunnelling can lift the degeneracy of a spin or charge ice, stabilizing a unique “quantum-ice” ground state—a quantum liquid with excitations described by the Maxwell action of $(3 + 1)$ -dimensional quantum electrodynamics. We further identify a competing ordered squiggle state, and show how both squiggle and quantum-ice states might be distinguished in neutron scattering experiments on a spin-ice material.

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Ice is one of the strangest substances known to man. In the common forms of water ice, protons occupy the space between tetrahedrally coordinated oxygen ions, and each oxygen obeys the “ice rule” constraint of forming two long and two short bonds with neighboring protons [1,2]. It was quickly realized that these ice rules did not select a single, unique proton configuration [1], but rather a vast manifold of classical ground states, with an entropy *per water molecule* of $s_0 \approx k_B \log(3/2)$ [2]. This prediction proved to be in good agreement with measurements of entropy at low temperatures [3], but stands in clear violation of the third law of thermodynamics—at zero temperature we expect water ice to be described by a single, unique, ground-state wave function.

The same ice rules, and the same extensive ground-state degeneracy, arise in (i) problems of frustrated charge [4,5] and orbital [6] order; (ii) proton-bonded ferroelectrics [7]; (iii) statistical descriptions of polymer melts [8]; and (iv) a family of rare-earth magnets collectively known as “spin ice” [9–12]. In each case, the ice rules have nontrivial consequences for the properties of the system, notably an algebraic decay of correlations [7,13–15] and excitations with “fractional” character [1,5,8,16,17]. These exotic features of the ice state have been extremely well characterized in spin ice, where the algebraic decay of correlation functions is visible as “pinch points” in the magnetic structure factor [18], and the fractional excitations have the character of magnetic monopoles [19–22].

All of these systems beg the obvious question—how is the degeneracy of the ice manifold lifted at zero temperature? The simplest way for an ice to recover a unique ground state at zero temperature is for it to order. This is exactly what happens in KOH-doped water ice, where the protons order below 70 K [23]. However in many spin-ice

materials, *no* order is observed [12]. This raises the intriguing possibility that there might exist a zero-temperature “quantum-ice” state, in which a single quantum mechanical ground state is formed through the coherent superposition of an exponentially large number of classical ice configurations. Such a state could have a vanishing entropy at zero temperature, and so satisfy the third law of thermodynamics, without sacrificing the algebraic correlations and fractional excitations (magnetic monopoles) associated with the degeneracy of the ice states.

In this Letter, we use zero-temperature quantum Monte Carlo simulations to establish the ground state of the minimal microscopic model of a charge or spin ice with tunnelling between different ice configurations. We find that the ground state is a quantum liquid, with an emergent $U(1)$ gauge symmetry, and excitations described by the Maxwell action of $(3 + 1)$ -dimensional quantum electrodynamics. This state is the exact, quantum, analogue of the spin-liquid phase realized in “classical” spin ices such as $Dy_2Ti_2O_7$, and exhibits the same magnetic monopole excitations. We also explore how quantum effects in this novel liquid modify the “pinch-point” singularities seen in neutron scattering experiments on spin ices.

The best systems in which to look for a quantum ice are those which are able to tunnel from one ice configuration to another. In water ice, in the absence of mobile ionic defects [24], this tunnelling occurs through the collective hopping of protons on a 6-link loop. In spin ice, it is the cyclic exchange of Ising spins on a hexagonal plaquette [25], illustrated in Fig. 1. In both cases, the ice rules can be written as a compact lattice $U(1)$ -gauge theory in which the displacement of protons—or orientation of magnetic moments—are associated with a fictitious magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, in the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$ [13,15].

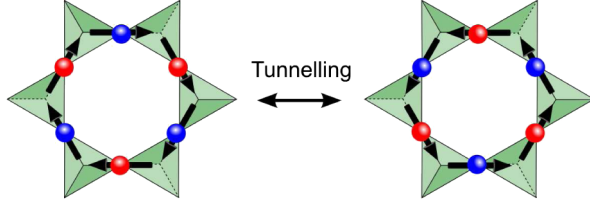


FIG. 1 (color online). Quantum mechanics enters ice physics through the tunnelling of the system from one ice configuration to another. The leading tunnelling matrix element for spin ice is the reversal of a set of Ising spins with closed circulation on a 6-link hexagonal plaquette.

Tunnelling between different ice configurations introduces dynamics in the gauge field \mathbf{A} , and the minimal description of a quantum ice is the Maxwell action of conventional quantum electromagnetism

$$S = \int d^3x dt [\mathbf{E}^2 - c^2 \mathbf{B}^2], \quad (1)$$

where c is the effective speed of light and, in the absence of electric charges, $\mathbf{E} = -\partial\mathbf{A}/\partial t$. It follows directly from Eq. (1) that correlation functions have dipolar character, and local defects in an ice configuration act like deconfined magnetic monopoles [26–28].

Field-theoretical arguments alone cannot resolve whether the quantum U(1) liquid described by Eq. (1) is realized in an ice material, or realistic microscopic model. Encouragingly, evidence supporting the existence of such a phase has been found in quantum Monte Carlo simulations of strongly interacting hard-core Bosons on a pyrochlore lattice [29]. However, these simulations are restricted to temperatures comparable with the degeneracy temperature of the ice manifold, and so are mute as to the zero-temperature ground state. In this Letter, we use zero-temperature Green’s function Monte Carlo (GFMC) simulation techniques [30] to provide concrete evidence for the existence of a quantum U(1) liquid ground state in a microscopic lattice model of a quantum ice.

The model we consider was first introduced by Hermele *et al.* [27] as an effective Hamiltonian for an easy-axis antiferromagnet on a pyrochlore lattice. It is defined by the Hamiltonian

$$\mathcal{H}_\mu = -\sum_{\text{plaq}} [|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|] + \mu \sum_{\text{plaq}} [|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|], \quad (2)$$

acting on all possible (spin) ice configurations. The first term in Eq. (2) describes tunnelling from one ice configuration to another, where $|\uparrow\rangle$ should be understood as a closed circulation of \mathbf{B} on a “flippable” hexagonal plaquette [cf. Fig. 1]. The sum \sum_{plaq} runs over all such plaquettes in the lattice. The additional potential energy term μ counts the number of flippable plaquettes in a given

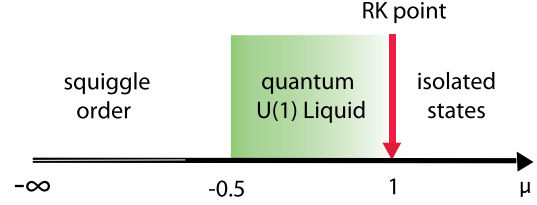


FIG. 2 (color online). Ground-state phase diagram of the quantum-ice model [Eq. (2)] as a function of the ratio μ of kinetic to potential energy. The 3D quantum-ice point $\mu = 0$ exists deep within an extended quantum liquid phase with deconfined fractional excitations and algebraic decay of correlation functions.

ice configuration, and renders the model exactly soluble for $\mu = 1$ [31]. All energies are measured in units of the tunnelling matrix element between ice configurations. For $\mu = 0$, Eq. (2) is the minimal microscopic model for a 3D quantum ice.

We have previously used GFMC simulation to establish the existence of a quantum U(1) liquid in the quantum dimer model on a diamond lattice [32,33]. The quantum-ice model Eq. (2) differs from this only in that the Hamiltonian acts on fully packed loop, rather than dimer coverings of the lattice (cf. Ref. [34]). We can therefore solve it using the methods set out in Ref. [33]. We consider clusters with periodic boundary conditions, and make extensive use of the fact that the “magnetic” flux $\phi = \int d\mathbf{S} \cdot \mathbf{B}$ through *any* periodic boundary is a conserved quantity. This makes it possible to define a series of flux quantum numbers $\vec{\phi} = (\phi_x, \phi_y, \phi_z)$ for each cluster [33]. Our findings are summarized in Fig. 2.

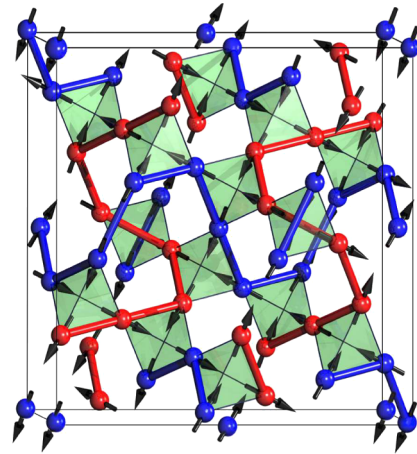


FIG. 3 (color online). The ice configuration possessing the most flippable plaquettes is the squiggle state, shown here within a 40-site tetragonal cell. Arrows show the displacement of protons within Ic water ice or, equivalently, the orientation of spins in spin ice. The squiggle state possesses a net magnetic flux, $\vec{\phi} = \vec{\phi}_{\text{squiggle}}$, orientated along a [100] axis of the crystal. In a spin-ice material this would correspond to a net magnetization of 1/5 the value at saturation, directed along a [100] axis.

For $\mu \rightarrow -\infty$, the ground state of Eq. (2) is the ice configuration which maximizes the number of flippable plaquettes. This is the 60-fold degenerate squiggle configuration shown in Fig. 3. It is ordered, and therefore exhibits Bragg peaks in diffraction experiments [35]. A good measure of squiggle order is the relative density of flippable plaquettes $\nu = N_f(\mu)/N_f(-\infty)$. In Fig. 4(a), we compare GFMC calculations of ν for a series of finite-size clusters, carried out in the squiggle-flux sector, with Padé approximants to a series expansion in $1/\mu$ about perfect squiggle order. The agreement between the two calculations is essentially perfect for $\mu < -0.75$, and the marked suppression in the number of flippable plaquettes for $\mu \geq -0.3$ is strongly suggestive of the melting of squiggle order. However, perturbation theory about the exactly soluble Rokhsar-Kivelson (RK) point $\mu = 1$ dictates that the ground state of Eq. (2) should be in the zero-flux sector for $\mu \rightarrow 1$ [27,33]. And in fact, the gentle demise of squiggle order is preempted by a ground-state level crossing between the squiggle and zero-flux sectors at $\mu = -0.50 \pm 0.03$, shown in Fig. 4(b).

These results are consistent with a first order phase transition out of the squiggle state at $\mu = -0.5$, but do not yet confirm the existence of the quantum U(1) liquid we are seeking. Fortunately Eq. (1) also makes specific predictions for how the quantum U(1) liquid phase evolves

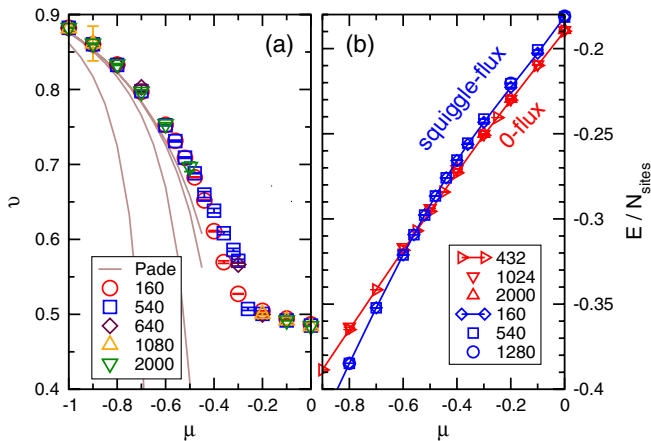


FIG. 4 (color online). Evidence for a phase transition out of the squiggle state. (a) Melting of squiggle order within the squiggle-flux sector $\vec{\phi} = \vec{\phi}_{\text{squiggle}}$. The relative number of flippable plaquettes $\nu = N_f(\mu)/N_f(-\infty)$ is calculated using quantum Monte Carlo simulations for clusters of 160 to 1080 sites. The solid lines show different Padé approximants to the series expansion about a perfectly ordered squiggle state. (b) Ground-state level crossing between the flux sector associated with the squiggle state, and the zero-flux sector associated with the quantum U(1) liquid. The ground-state energy per site is calculated for clusters of 432, 1024, and 2000 sites (squiggle-flux sector) and 160, 540, and 1280 sites (zero-flux sector), using quantum Monte Carlo simulation. A clear crossing is observed for $\mu = -0.50 \pm 0.03$.

out of the RK point at $\mu = 1$ [26,27,33]. Specifically, the finite-size energy gaps $E_\phi - E_0$ should grow as $E_\phi - E_0 \sim c^2 \phi^2/L$ where E_ϕ is the energy of the ground state with flux $\vec{\phi}$ and $c^2 \propto 1 - \mu + \dots$ [27,33]. In Fig. 5(a), we present simulation results for $E_\phi - E_0$ for $\mu \lesssim 1$. We find good agreement between GFMC simulations and perturbation theory about the RK point [27,33], and a near-perfect collapse of both data sets according to the prediction of Eq. (1). This confirms the existence of a quantum U(1) liquid bordering the RK point, as proposed in [27].

However, so far as real materials are concerned, the most interesting point in the parameter space is the “quantum-ice” point $\mu = 0$. Does this also conform to the behavior expected of a quantum U(1)-liquid? In Fig. 5(b), we present simulation results for the finite-size energy gaps of Eq. (2) at $\mu = 0$. We extract the leading dependence on system size by plotting $(E_\phi - E_0)/N_{\text{sites}}$ as a function of $(\phi/\phi_{\text{squiggle}})^2$. Once again, the collapse of the data is excellent, confirming the existence of a quantum U(1) liquid.

The ground-state phase diagram of the quantum-ice model Eq. (2) is summarized in Fig. 2. For $\mu < -0.5$, the ground state is the complex squiggle order shown in Fig. 3. For $\mu > -0.3$ we find unambiguous evidence for a quantum liquid phase which is well-described by the U(1) (lattice) gauge theory of quantum electromagnetism, and so will exhibit both algebraic decay of correlations and deconfined fractional excitations [26,27]. This quantum

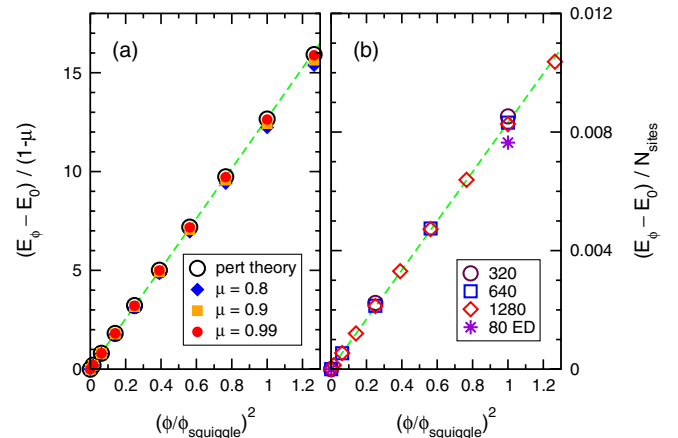


FIG. 5 (color online). Evidence for the existence of a quantum U(1) liquid. (a) Flux dependence of finite-size energy gaps $E_\phi - E_0$ for parameters bordering the RK point, $\mu = 1$. Results are plotted for quantum Monte Carlo simulation of a 1280-site cluster (solid points) and perturbation theory about the RK point (open black circles). The dashed line indicates the scaling expected for a quantum U(1) liquid, following Eq. (1). (b) Flux dependence of finite-size energy gaps at the quantum-ice point, $\mu = 0$. Results are obtained using quantum Monte Carlo simulation for 320-, 640-, and 1280-site clusters, and in exact diagonalization for an 80-site cluster. The dashed line indicates the scaling expected for a quantum U(1) liquid.

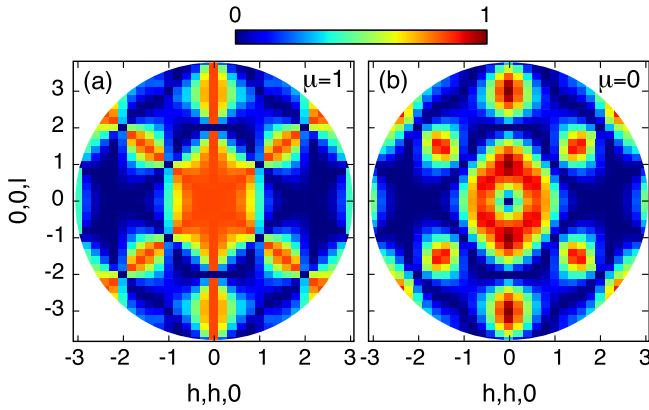


FIG. 6 (color online). (a) Static structure factor $S(\mathbf{q})$ in the spin-flip channel for a classical spin ice, as measured by Fennell *et al.* [18], calculated here from the microscopic model Eq. (2), with $\mu = 1$. Results are plotted in the (h, h, l) plane, and show the pinch-point structure associated with $1/r^3$ dipolar correlations in 3 dimensions. (b) Equivalent static structure factor $S(\mathbf{q})$ for a quantum spin ice described by Eq. (2) with $\mu = 0$. In this case, correlations between spins show the $1/r^4$ behavior characteristic of dipoles in $(3 + 1)$ dimensions, and the pinch points are eliminated. All simulations were performed for a cubic cluster with 2000 lattice sites.

U(1) liquid phase terminates in an RK point at $\mu = 1$, and therefore the quantum-ice point $\mu = 0$ lies deep within it. For $-0.5 < \mu < -0.3$ simulation results depend in detail on the geometry of the cluster chosen. However, we tentatively conclude that a single, first order phase transition takes place between the squiggle and U(1)-liquid phases for $\mu = -0.5$. This phase diagram should be contrasted with those for bosonic [36] and fermionic [37] quantum-ice models on the 2D square lattice, where all phases are ordered and confining for $\mu < 1$. In short—2D quantum-ice models are ordered and confining, but the 3D quantum-ice model solved here is not.

So far as electronic charge ices are concerned, this work should be regarded as a “warm-up” exercise, since Eq. (2) does not allow for the spin or Fermi statistics of the electrons [5,33,37,38]. Similarly, the application of these ideas to hexagonal water ice depends crucially on the generalization to a different lattice, and the role of more general ionic defects [24]. However, the model we have solved may give a good account of “quantum spin-ice” materials such as $\text{Tb}_2\text{Ti}_2\text{O}_7$ [39–42], $\text{Pr}_2\text{Sn}_2\text{O}_7$ [43,44], and $\text{Yb}_2\text{Ti}_2\text{O}_7$ [45–48], where quantum fluctuations of magnetic moments provide a route to tunnelling between spin-ice states. And in this context it is interesting to ask how a quantum ice might be distinguished in experiment on a spin-ice material?

The signal feature of a classical ice state is the presence of pinch-point singularities in the static structure factor $S(q)$ [18]. These reflect the fact that the spins or charges which make up the ice state have correlations of 3-dimensional dipolar form [7,13,15]. In contrast, in a quan-

tum ice, static correlations take on the form of dipoles in $(3 + 1)$ dimensions [27,28] and as a result, the pinch-point singularities in $S(q)$ are eliminated. To illustrate this, in Fig. 6 we present GFMC simulation results for $S(q)$ for a quantum spin ice, calculated directly from Eq. (2). Results for the RK point $\mu = 1$, where the correlations are classical, clearly show pinch points at reciprocal lattice vectors. However, at the quantum-ice point, $\mu = 0$, there is a marked suppression of spectral weight around the same reciprocal lattice vectors. As a consequence, the angle-integrated structure behaves as $S(|\mathbf{q}| \rightarrow 0) \propto |\mathbf{q}|$, while in a classical spin ice $S(|\mathbf{q}| \rightarrow 0) \rightarrow \text{const}$. This linear- $|\mathbf{q}|$ behavior at small $|\mathbf{q}|$ is consistent with published results for $\text{Pr}_2\text{Sn}_2\text{O}_7$ [43]. It might also be interesting to reexamine elastic neutron scattering data on other pyrochlore antiferromagnets in the light of these results [49]. These issues will be explored further elsewhere [50].

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