Controlling frustrated liquids and solids with an applied field in a kagome Heisenberg antiferromagnet

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Quantum spin-1/2 kagome Heisenberg antiferromagnet is the representative frustrated system possibly hosting a spin liquid. Clarifying the nature of this elusive topological phase is a key challenge in condensed matter; however, even identifying it still remains unsettled. Here we apply a magnetic field and discover a series of spin-gapped phases appearing at five different fractions of magnetization by means of a grand canonical density matrix renormalization group, an unbiased state-of-the-art numerical technique. The magnetic field dopes magnons and first gives rise to a possible $\mathbb{Z}_3$ spin liquid plateau at 1/9 magnetization. Higher field induces a self-organized super-lattice unit, a six-membered ring of quantum spins, resembling an atomic orbital structure. Putting magnons into this unit one by one yields three quantum solid plateaus. We thus find that the magnetic field could control the transition between various emergent phases by continuously releasing the frustration.
It is widely accepted that condensed matter orders at low temperatures by spontaneously breaking some sort of symmetry—translational symmetry in crystalline solids, time-reversal and rotational symmetries in magnets, gauge symmetry in superconductors and so on. Whether they can escape from ordering and instead bear emergent states is a question that has been a topic of study for decades. A possible strategy is to design a model with fine balance of microscopic interactions, where the low-energy states are frustrated and a macroscopic number of quasi-degenerate states compete with each other. When quantum fluctuations between these states prevent a selection of particular order, one ends up with quantum-disordered spin liquids. Modern theories have brought us new insight by identifying spin liquids as topological phases of matter\(^1\).\(^2\) Even if such topological phases are not formed, the resultant phase would also be non-trivial; its smallest disentangled unit could consist of several degrees of freedom—pairs of spins in spin ladders or valence bond solids and so on. Thus, characterizing the regime of such liquids and relevant non-trivial phases has now become an important challenge.

In reality, spin liquids are quite elusive\(^3\). There are experimental studies on a long cylinder\(^8\),\(^9\). In addition, there is a recent study predicting a gapless U(1) liquid\(^10\), and the issue remains unsettled.

Clarifying the nature of the model in an applied field also demands a severe numerical challenge; the magnetization process appears not as a curve but as a staircase of height \(\sim 1/N\) owing to finite size effect. Thus, what is known so far is the highly possible presence of a spin-gapped phase called plateau at a 1/3 magnetization\(^12\),\(^13\) and a jump of the magnetization from 7/9 to 1 at the saturation field\(^13\),\(^16\). Whereas whether a 1/3 plateau is really a plateau\(^12\),\(^13\) or something else\(^14\) was not really concluded.

In the present article, we determine the bulk magnetization process of the kagome Heisenberg antiferromagnet by means of a grand canonical analysis\(^17\),\(^18\). The system turns out to have five different plateau phases, and the magnetic field controls the successive phase transitions between these plateau phases and the gapless liquids in a strikingly analogous manner to the Hall conductivity of the quantum Hall effect\(^19\),\(^20\),\(^21\). Two of the plateaus at the lower fields are the possible spin liquids, which are characterized by the finite topological dimensions. The latter three at the higher fields form a long-range order in a particular unit, a hexagonal plaquette consisting of a six-membered ring of spins. This unit resembles a quantum mechanical atomic orbital that accommodates several magnons in its discrete energy levels. The magnetic field thus transforms the system from the highly frustrated liquid phases to the moderately frustrated solid ones.

**Results**

**Magnetization curve.** To overcome the numerical finite size effect, we apply the grand canonical DMRG, which was developed very recently\(^17\), and was successfully applied to two dimensions\(^18\). This method gives us a numerically exact and unbiased magnetization curve in the thermodynamic limit (see Methods). For example, if we choose the cylinder of a finite circumference and of length \(L\) which is larger than \(\sim 10–20\) lattice spacing, and perform a grand canonical analysis, we obtain a magnetization curve of an infinitely long cylinder of that fixed circumference (see Supplementary Fig. S1). As we need a result of a bulk system, equivalently spanned along three different directions of a kagome lattice, we choose a hexagonal cluster for the present calculation rather than a long cylinder.

Figure 1 shows the whole magnetization curve of the kagome antiferromagnet. Without ambiguity, one finds plateau structures at fractions, \(M/M_{sat} = 0, 1/9, 1/3, 5/9\) and 7/9, as well as a jump from the 7/9 plateau to the saturation value at exactly \(H_{sat}/J = 3.0\), where \(M_{sat}\) is the full magnetization. To verify the accuracy of our grand canonical curve, we perform a set of conventional DMRG calculation, both on a long cylinder with open ends (see Supplementary Fig. S1) and on an open hexagonal cluster. By comparing these results, we confirm that the grand canonical analysis successfully gives the magnetization curve within the typical accuracy of \(10^{-3}\) (see Supplementary Note 1).

**Singlet–triplet spin gap.** The value of the singlet–triplet spin gap of the kagome antiferromagnet at zero field is still unsettled\(^8\),\(^9\),\(^22\). The evaluated spin gaps after the size scaling in the three latest DMRG studies are not fully consistent; as for the cylindrical DMRG, ref. 9 has \(\Delta = 0.13(1)\) (the numerical data of refs 8 and 9 at various fixed circumferences are basically consistent). There, the size scaling is basically given first along the long leg of a cylinder and the extrapolation is given along the circumference of \(L \leq 20\). As for ref. 22, they increased the size within \(N = 36–108\) by keeping the cluster to the square-like shape with periodic boundaries and obtained \(\Delta = 0.055 \pm 0.005\). In fact, we checked these results carefully with the similar scaling and found that the results depend much on the way the size scaling is performed\(^23\) (see Supplementary Notes 1 and 2).
By contrast, in our grand canonical calculation the size dependence becomes negligible (less than $10^{-3}$ in two dimensions, see Methods) once we enter a cluster size of the proper system length. Therefore, one could evaluate the spin gap by the onset value of $H/J$ in the magnetization curve near zero field. In Fig. 1, we find $A = 0.05 \pm 0.02$ (see the red shaded region), which is obtained on a hexagonal cluster.

We briefly mention that our results are fully consistent with the data of the previous conventional DMRG studies: in our grand canonical DMRG on a cylinder with fixed small circumference (see Supplementary Fig. S1), the spin gap gives more than twice as large values as the value mentioned above. This value should be compared with the data in ref. 9 on a long cylinder with the same circumference. For a proper extrapolation of the cylindrical results to a bulk two-dimension, one needs to enlarge both the length and the circumferences simultaneously$^{23}$. In fact, our grand canonical spin gap on a hexagonal cluster is very close to those of ref. 22 on a square cluster.

Zero and 1/9 plateaus. The zero plateau ranging at $0 \leq H/J \leq 0.05$ is the continuation of the zero-field ground state. Correspondingly, in our calculation the spin structure in real space turned out to be completely structureless (see Supplementary Fig. S2). One way to identify the nature of the spin liquid is to calculate the von Neumann entropy, $S = - \text{Tr} (\rho \ln \rho)$, defined on a subsystem of a long open cylinder by the conventional DMRG, where $\rho$ is the reduced density matrix of the subsystem. The value should follow, $S \sim \eta L_y - \gamma$, where $L_y$ is the circumference, $\eta$ is a constant and $\gamma = \text{ln}(D)$ the topological entropy. In ref. 9, the topological dimension, $D$, of the ground state is given as $D \sim 2$, which supports the gapped $Z_2$ spin liquid.

In the 1/9-plateau state, the real space profile of the spin structure is rather intriguing, several geometries breaking the translational symmetry are quasi-degenerate (see Supplementary Fig. S2 and Supplementary Note 3), and their stability is sensitive to the shape and size of the cluster. We consider this to be the good reason that the symmetry-breaking long order is absent. Therefore, we perform the conventional DMRG and calculate the entanglement entropy of the 1/9-plateau state in the same manner as refs 2 and 9, as shown in Fig. 2; to have the 1/9 magnetization, we need to keep the system size at the multiple of nine, and thus the choice of the clusters is limited compared with the calculation on the $MN=0$ ground state. The topological dimension obtained in the $L_y = 0$ limit seemingly gives the value $D = 3$. Thus, the spin-gapped state at 1/9 magnetization is possibly a $Z_3$ spin liquid, and is the first example of a spin-liquid plateau induced by the magnetic field. Even a $Z_3$ spin liquid itself has so far been observed only in a specified bosonic model$^{24}$, and the present model gives a more realistic setup. Further examination is required to identify the detailed nature of this phase.

Long-range ordered plateaus. In contrast to the first two plateaus, the rest of the plateaus have symmetry-breaking long-range orders. Figure 3a–c shows the real space profiles of the magnetization density per site is $M_{sat}/N = 1/2$. The inset shows the geometry of the kagome lattice. The shaded hexagon is the original lattice unit cell including three sites ($Q = 3$). Data points are obtained by the grand canonical analysis on a hexagonal cluster with $N = 114$ and 132, which directly gives the curve of the thermodynamic limit without any size scaling. The range of each plateau is highlighted.

Translation symmetry are quasi-degenerate (see Supplementary Fig. S2 and Supplementary Note 3), and their stability is sensitive to the shape and size of the cluster. We consider this to be the good reason that the symmetry-breaking long order is absent. Therefore, we perform the conventional DMRG and calculate the entanglement entropy of the 1/9-plateau state in the same manner as refs 2 and 9, as shown in Fig. 2; to have the 1/9 magnetization, we need to keep the system size at the multiple of nine, and thus the choice of the clusters is limited compared with the calculation on the $MN=0$ ground state. The topological dimension obtained in the $L_y = 0$ limit seemingly gives the value $D = 3$. Thus, the spin-gapped state at 1/9 magnetization is possibly a $Z_3$ spin liquid, and is the first example of a spin-liquid plateau induced by the magnetic field. Even a $Z_3$ spin liquid itself has so far been observed only in a specified bosonic model$^{24}$, and the present model gives a more realistic setup. Further examination is required to identify the detailed nature of this phase.

Discussion

In spin-1/2 quantum magnets, a conventional (non-topological) non-magnetic state basically comprises a singlet, a unit of spin 0, often represented by the quantum fluctuation between two spins, $(\uparrow \downarrow) - (\downarrow \uparrow)/\sqrt{2}$. A breaking of singlet yields a bosonic elementary particle carrying spin 1, which is called a magnon. The magnetic field controls the density of these bosons, serving as a chemical potential. As in the Mott insulator, there are particular values of the boson densities commensurate with the lattice periodicity$^{25}$, at which the gapped states are strongly pinned.

![Figure 2 | Entanglement entropy of a 1/9 magnetization plateau.](image-url)
In the 1/3 plateau, each triangular unit should hold a net magnetization of 1/2, which consists of one up spin 1/2 and two spins forming a singlet (see Fig. 4a). Similar to the zero-field Ising ground state, there are massive numbers of configuration of the 1/2-magnetized triangular units, which is in fact a typical characteristic of the frustrated system. If these configurations are mixed-up quantum mechanically, a liquid phase should emerge. To realize instead the solid state actually observed, one needs to select a particular configuration, and the problem reduces to how we pave this triangular unit on the kagome lattice to maximally gain energy.

In each configuration, one could draw a string along the singlet bonds of the triangular units as shown in the left panel of Fig. 4a. As every triangle shares its corners with the neighbouring triangles, the string never crosses with other strings, but continues until it meets itself again (otherwise it will extend toward infinity). In addition to the random configuration of strings, the representative two regular patterns are shown in Fig. 4a: a long string forming stripes and a shortest closed loop around the hexagon. One then needs to know which gains the energy, the longer string or the shorter loop, owing to the quantum mechanical resonance of spins along the string. The answer is the latter (see Supplementary Fig. S3a)—the kagome is fully tiled with hexagrams—a symmetry-breaking plaquette order is formed.

Once all the vertices of the hexagram (three sites/nine unit) are filled with a fully polarized up-spin moment ($S_z = 1/2$) at $M/M_{sat} = 1/3$, a further simplified picture may work, focusing on each hexagonal plaquette and isolating it by effectively neglecting the quantum fluctuation between the plaquette and the vertices of the hexagram, as shown in Fig. 4b. This approximation is valid as far as the vertices of the hexagram are fully polarized. The interactions ($J S^z S^z$-term) between the plaquette and vertices work as an internal magnetic field, $H_{int} = -J$ per site on a plaquette. Figure 4c shows the magnetization process of the isolated plaquette in an effective field, $H + H_{int}$, the doping of magnons by the effective chemical potential. Each step of the big staircases corresponds to the increasing $S_z$-value or the number of magnons in the isolated plaquette. Now, notice that the point where the upshift of the staircases crosses the bulk magnetization curve coincides with the inflection point of the curve. This indicates the following scenario: if we condense the massive numbers of hexagrams, the quantum fluctuations between them become coherent throughout the system and works to destroy the staircases from the edge toward the centre of the step. The curve above/below the inflection point is the ruin of the edge of upper/lower staircase. This result thus supports the picture that a hexagon works as a self-organized pseudo atomic orbital consisting of three discrete energy levels. Doping magnons to each level yields a series of plateaus starting from 1/3.

At present, the only other quantum magnet that possibly reveals comparably rich phase transitions is the SrCu$_2$(BO$_3$)$_2$ (refs 31,32). However, the spin-gapped phases of this material are based on a conventional singlet. In forming solids, they expand the unit cell in several ways to allocate the singlets in a regular period in a sea of doped magnons. In contrast, in our kagome a single non-trivial unit based on a hexagram is self-organized by the quantum many-body effect. The doped magnons come into this cell in such a way that the electrons go into the quantum dots in an artificial semiconductor device.

The above picture then gives a strategy to design a system that could control the degree of frustration by the doping of particles; First, prepare an unfustrated unit that could store several numbers of particles (in a kagome, this corresponds to a hexagon that could hold three magnons). Then connect them by the frustrated bonds. For example, this rule gives us a checkerboard lattice and its
relevant pyroclore lattice. Their undoped ground states could be a spin liquid as far as the microscopic interactions are finely balanced. We predict that dopings will also give rise to interesting states of matter similar to the one we find in the kagome.

We further pay attention to the fact that the bose-Hubbard model at zero field and the projected quantum dimer model, both on the same kagome lattice, are considered to have Z₂ liquids. Then, one may also expect the 5/9 and 7/9 plateaus to undergo a solid-to-spin-liquid transition if the additional effect enhancing the quantum fluctuation is added to the Hamiltonian.

The present findings will give some clue to find numbers of such exotic state of matter in kagome and in the above mentioned lattice models, many of which are still unexplored.

Figure 4 | Details of the effective model describing the upper three plateau states. (a) A unit triangle at 1/3 plateau includes one up spin (red circle) and two spins forming singlet bond (blue bond). The left panel gives one snapshot of random configuration of unit triangles, which includes winding singlet loops of several lengths. Other two panels are the regular configurations in which the singlet bonds form stripes and hexagonal plaquettes. The latter plaquette long-range order is formed in the 1/3 plateau. (b) Schematic illustration of the three energy levels in each hexagonal plaquette unit. By putting in magnons from the empty level at 1/3 plateau, the 5/9, 7/9 and the fully polarized states are formed. (c) Solid line is the magnetization step of the isolated hexagon in an effective field, $H + H_{int}$ where $H_{int} = -J$ is from the surrounding six vertex sites indicated in red circles. Broken line is the bulk magnetization curve of Fig. 1. See Supplementary Fig. S3 and Supplementary Note 4 for more details.
results is systematically controlled by the number of basis states kept, \( m \) in the DMRG calculation and the typical error in the energy of the present calculations is around 10^(-4) for \( m = 4000 \). As discussed in the Results section, the aspect ratio closer to 1 gives the results closer to the bulk limit. Therefore, we adopt the hexagonal cluster of \( N = 114 \) and 132, instead of a long cylinder. More details, including the numerical details of the results, are available in the Supplementary Fig S4 and Supplementary Note 5.

Regarding the calculation on the entanglement entropy in Fig. 2, we used the conventional DMRG on a long cylinder with open edges and periodic circumferences. There, the number of states kept are around \( 10^6 \). The typical error in the energy of the present calculations is systematically controlled by the number of basis states kept, \( m \).

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**Author contributions**

S.N. developed a code, carried out the DMRG simulations and analysed the data, with contributions from N.S. and C.H. C.H. brought up the project and wrote the paper, discussing with N.S. and S.N. The project was designed by all three authors and the three are equally responsible for the results.

**Additional information**

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