Vaporization of quantum spin liquids

Joji Nasu, Masafumi Udagawa, & Yukitoshi Motome

1Department of Physics, Tokyo Institute of Technology, Ookayama, 2-12-1, Meguro, Tokyo 152-8551, Japan and
2Department of Applied Physics, University of Tokyo, Hongo, 7-3-1, Bunkyo, Tokyo 113-8656, Japan

Quantum spin liquid (QSL) is an exotic quantum state of matter in magnets. This is a spin analogue of the liquid helium which does not solidify down to the lowest temperature \(T\) due to strong quantum fluctuations. Several experimental candidates were recently nominated, for which the absence of thermodynamic anomalies is regarded as a hallmark of QSL. There, it is implicitly supposed that a spin “gas” corresponding to the high-\(T\) paramagnet is adiabatically connected with QSL, as they possess the same symmetry. However, it is unknown whether a liquid-gas type transition exists in quantum spin systems. Here we show that QSLs can behave very differently from conventional fluids in the thermodynamics; gapless and gapped QSL phases realized in a three-dimensional (3D) Kitaev model are both always distinguished from the high-\(T\) paramagnet by a phase transition. There is no adiabatic connection between the quantum spin analogues of liquid and gas. The transition is driven by a topological nature of excitations, which is not characterized by a local order parameter. Our results give a counterexample to the conventional “myth” about QSLs based on the absence of phase transition. We anticipate our finding to be crucial for the interpretation
of existing and forthcoming experiments on QSLs.

Thermodynamics of QSLs has not been theoretically investigated in depth thus far mainly due to the following two difficulties. One is the scarcity of well-identified QSLs. It is hard to characterize QSL because spatial quantum entanglement and many-body effects are essential for realizing QSL\textsuperscript{8,9}. The other difficulty lies in less choice of effective theoretical tools. Any biased approximation might be harmful for taking into account strong quantum and thermal fluctuations. We solve these difficulties by investigating a 3D extension of the Kitaev model\textsuperscript{10}, which supports well-identified QSLs as the exact ground states\textsuperscript{11}, by an unbiased numerical simulation for the thermodynamic properties.

The Kitaev model is a quantum spin model with anisotropic exchange interactions for nearest neighbour spins, originally introduced on a honeycomb lattice. The Hamiltonian is given by

\[ \mathcal{H} = -J_x \sum_{\langle ij \rangle} \sigma_i^x \sigma_j^x - J_y \sum_{\langle ij \rangle} \sigma_i^y \sigma_j^y - J_z \sum_{\langle ij \rangle} \sigma_i^z \sigma_j^z, \]

where \( \sigma_i^x, \sigma_i^y, \) and \( \sigma_i^z \) are Pauli matrices describing a spin-1/2 state at a site \( i \); \( J_x, J_y, \) and \( J_z \) are exchange constants (\( J_x + J_y + J_z = 1 \)) defined on three different types of the nearest neighbour bonds (see Fig. 1a\textsuperscript{10}). This model is exactly solvable by introducing Majorana fermions\textsuperscript{10}. The ground state phase diagram consists of gapless and gapped QSL phases\textsuperscript{10}, as shown in Fig. 1c. The model has been studied not only from the mathematical virtue of the exact solvability but also from the experimental relevance to several iridium oxides\textsuperscript{12}. Anyonic excitations and their relation to quantum computation have also been discussed for the anisotropic limit of the model\textsuperscript{10}.

A 3D extension of the Kitaev model is defined on the hyperhoneycomb lattice shown in
This model has relevance to recently-discovered iridates Li$_2$IrO$_3$\cite{13,14}. There are three types of nearest neighbour bonds in this lattice as in the honeycomb lattice. Many fundamental aspects are inherited from the original 2D one, including the exact solvability. In particular, the ground state phase diagram is completely the same as that in 2D in Fig. 1c\cite{11}. On the other hand, the difference in the spatial dimension of the model may matter to finite-$T$ properties; while no phase transition is expected at a finite $T$ for 2D (refs.\cite{15,16} and Supplementary Information), we may anticipate a finite-$T$ phase transition for 3D.

Figure 2a shows the $T$ dependence of the specific heat $C_v$ for the isotropic case with $J_x = J_y = J_z = 1/3$ in the 3D Kitaev model obtained by the quantum Monte Carlo simulation. There are two peaks in $C_v$. While the high-$T$ peak at $T \sim 0.6$ does not show the size dependence, the low-$T$ peak located at $T \sim 0.004$ grows with increasing the system size as shown in Fig. 2b. This is a signature of phase transition between the low-$T$ QSL phase and the high-$T$ paramagnetic phase, as firmly supported by the perturbation arguments below. The size extrapolation of the peak temperature gives the estimate of the critical temperature in the thermodynamic limit as $T_c = 0.00519(9)$ (see the inset of Fig. 2b).

By performing the simulation for various sets of $J_x$, $J_y$, and $J_z$, we elaborate the finite-$T$ phase diagram of the 3D Kitaev model. The results are summarized in Fig. 3. Figures 3a and 3b show $T_c$ as a function of the anisotropy parameters $\alpha$ and $\alpha'$ shown in the insets. The limit of $\alpha \to 0$, corresponding to $J_z \to 1$ with $J_x = J_y = J \to 0$, was previously discussed for the effective model obtained by the perturbation theory in terms of $J/J_z$, and a finite-$T$ transition was
found at $T_c = \tilde{T}_c \times 7J^6/(256J^5_z)$ with $\tilde{T}_c = 1.925(1)$\cite{1}. This asymptotic form of $T_c$ is plotted by the solid lines in Figs. 3a and 3b. It shows fairly good agreement with the present results in the small $\alpha$ region, which strongly supports that $T_c$ estimated from the low-$T$ anomaly in $C_v$ is indeed the critical temperature between the low-$T$ QSL and high-$T$ paramagnet. Meanwhile, in the limit of $\alpha \to 3/2$, by using the perturbation expansion in terms of $J_z/J$, we find that $T_c$ is scaled by $J_z^4/J^3$ (Supplementary Information). The dashed lines in Figs. 3a and 3b represent the fitting by this asymptotic scaling, which also supports the phase transition at $T_c$.

Figure 3c summarizes the estimates of $T_c$ in the 3D plot. In the entire parameter space, the low-$T$ QSL is separated from the high-$T$ paramagnet by the thermodynamic singularity at $T_c$. There is no adiabatic connection between the two states. The value of $T_c$ changes continuously, irrespective of the change of the ground state between gapless and gapped QSLs, and the transition always appears to be continuous within the present calculations. These are in sharp contrast to the situation in conventional fluids, where liquid and gas are adiabatically connected with each other beyond the critical end point in the phase boundary of the discontinuous transition.

Interestingly, the value of $T_c$ becomes maximum at $\alpha \simeq 1$: the QSL phase is most stable against thermal fluctuations in the isotropic case. This indicates that the frustration tends to stabilize the QSL: the competition between the bond-dependent interactions in the Kitaev model becomes strongest at $\alpha = 1$. This frustration effect is opposite to that on conventional magnetically ordered states where frustration suppresses the critical temperatures.

Now let us discuss the reason why the specific heat $C_v$ exhibits two peaks. We show the $T$
dependence of the entropy per site, $S$, in Fig. 4b, obtained by the numerical integration of $C_v$ in Fig. 4a divided by $T$. By decreasing $T$, the entropy decreases from $\ln 2$ corresponding to the high-$T$ peak in $C_v$ and approaches $\frac{1}{2} \ln 2$. After staying at $\simeq \frac{1}{2} \ln 2$, it decreases again corresponding to the low-$T$ peak in $C_v$, and approaches zero toward $T = 0$. By rewriting the Kitaev Hamiltonian into a Majorana fermion system coupled with the $Z_2$ variables $W_p = \pm 1$ (ref. [10] and Supplementary Information), the successive changes of the entropy by $\frac{1}{2} \ln 2$ are ascribed to a separation of the energy scales for the Majorana fermions and the $Z_2$ variables $W_p$. Namely, while decreasing $T$, the entropy of $\frac{1}{2} \ln 2$ associated with Majorana fermions is first gradually released at $T \sim 0.1 - 1$, corresponding to their kinetic energy scale $\sim J_x + J_y + J_z = 1$. Subsequently, the remaining entropy of $\frac{1}{2} \ln 2$, associated with the $Z_2$ variables $W_p$, is released at the phase transition. This lower energy scale is set by the effective interactions between $W_p$ mediated by Majorana fermions, and sensitively depends on the anisotropy of the system. We confirm this picture by calculating $\tilde{W}$ defined as the thermal average of the density of $W_p$ (Supplementary Information). As shown in Fig. 4c, this quantity rapidly increases near $T_c$ as $T$ decreases. Thus, the entropy of $\frac{1}{2} \ln 2$ is released according to the coherent growth of $W_p$ at $T_c$.

However, it is worthy noting that the phase transition at $T_c$ is not caused by the symmetry breaking in terms of the local variables $W_p$. Instead, the phase transition will be understood by the topological nature of excited states as follows. The excited states are generated by flipping $W_p$ from the ground state where all $W_p = +1$. The flipped $W_p = -1$ form loops because of the local constraints originating from the fundamental spin-1/2 algebra [11]. The excitation energy of loops and their configurational entropy compete with each other, which may lead to the phase
transition at a finite $T$, as is discussed by Peierls for the 2D Ising model$^{18}$. This picture was indeed confirmed in the limit of $J_z \gg J_x, J_y$, through the winding number defined for $W_p$ (ref. $^{17}$). The situation is in sharp contrast to the 2D Kitaev model, where the excitation with $W_p = -1$ is allowed independently without local constraints, and consequently, the QSL is adiabatically connected to the high-$T$ paramagnet.

Our results on the topological transition suggest a new paradigm of critical phenomena beyond the Ginzburg-Landau-Wilson (GLW) theory. Due to the lack of local order parameter, the description based on the GLW theory is no longer applicable to the “vaporization” of QSLs. Such nontrivial finite-$T$ phase transitions have been studied by the mean-field approximations for 3D $Z_2$ QSLs on the basis of the $Z_2$ gauge theory$^{19,20}$. To understand the critical properties, however, it is necessary to take into account fluctuations of a topological structure in the excitations beyond the mean-field approach. The current study presents, to our knowledge, the first unbiased results on the finite-$T$ transition to QSLs, which may give birth to a new concept of critical phenomena beyond the conventional GLW theory.

It will also be interesting to consider the “solidification” of QSLs. Indeed, the solid phase (magnetically ordered phase) is accessible in the context of the present 3D Kitaev model, by considering additional interactions which favor a magnetic order, such as the Heisenberg exchange interaction$^{21,22}$. The detailed study of the magnetic three states of matter, liquid, gas, and solid, and their topological nature will provide a new insight in the research area of not only magnetism but also quantum information.
Figure 1: **Lattice structures and the ground state phase diagram for the Kitaev models.**

**a,** Two-dimensional honeycomb lattice. **b,** Three-dimensional hyperhoneycomb lattice. Blue, green, and red bonds denote the exchange couplings $J_x$, $J_y$, and $J_z$ in the Kitaev Hamiltonian, respectively. The shaded plaquette on each lattice represents the shortest loop $p$ for which the $\mathbb{Z}_2$ variable $W_p$ is defined. **c,** Phase diagram of the Kitaev model at zero temperature, common to the models on the honeycomb and on the hyperhoneycomb lattices. This diagram is depicted on the plane where the condition $J_x + J_y + J_z = 1$ is satisfied. There are two kinds of phases distinguished by the excitation gap; the QSL with gapless excitation is stabilized in the center triangle including the isotropic case $J_x = J_y = J_z$, while the QSL with an excitation gap appears in the outer three triangles with anisotropic interactions.
Figure 2: **Temperature dependence of the specific heat in the isotropic case with** $J_x = J_y = J_z = 1/3$ ($\alpha = 1$). **a.** The plot in a wide temperature range. **b.** The enlarged view in the vicinity of the low-temperature peak. The calculations were performed by the quantum Monte Carlo simulation for the systems on the hyperhoneycomb lattice with $N = 4 \times L^3$ spins up to $L = 6$. The inset in **b** shows the peak temperature $T'_c$ of the specific heat as a function of the inverse of the system size $N$. The dotted line represents the linear fit for three largest $N$. The estimated critical temperature in the thermodynamic limit is $T_c = 0.00519(9)$. In contrast, the 2D Kitaev model does not show such growing peak in the specific heat, indicating the absence of the finite-temperature phase transition (Supplementary Information).
Figure 3: Finite-temperature phase diagram of the 3D Kitaev model.  

a, Cut of the phase diagram along the $\alpha$ and $\alpha'$ axes. As shown in the insets, the anisotropic parameters $\alpha$ and $\alpha'$ are defined as $J_z = J_y = \alpha/3$ and $J_z = 1 - 2\alpha/3$, and $J_z = (1 - \alpha')/4$, $J_y = (1 + \alpha')/4$, and $J_z = 1/2$, respectively. 

b, The log-scale plot of the same data. The critical temperature $T_c$ takes the maximum value at $\alpha \simeq 1$ corresponding to the isotropic case, and decreases to zero as $\alpha \to 0$ and $\alpha \to 3/2$. The solid line shows $T_c = 1.925 \times 7J_6/(256J_5^5) (J = J_x = J_y)$, which was obtained for the effective model in the limit of $\alpha \to 0$ (ref.17). The dashed line represents the fitting by $T_c \propto J_z^4/J^3$, which is the asymptotic form in the limit of $\alpha \to 3/2$ obtained by the perturbation in terms of $J_z/J$. 

c, 3D plot of the phase diagram in the whole parameter space with $J_x + J_y + J_z = 1$. The base triangle represents the ground state phase diagram shown in Fig. 1c.
Figure 4: Temperature dependences of physical quantities while changing the anisotropy parameter $\alpha$. a, The specific heat. b, The entropy. c, Thermal average of the $Z_2$ variables $W_p$ per ten-site plaquette. The data are calculated for the hyperhoneycomb clusters with $N = 4 \times 5^3$ and $4 \times 6^3$ spins. $\alpha = 3/4$ corresponds to the ground state phase boundary between the gapless and gapped QSLs, but we find no singularity except for $T_c$ in the temperature dependences. Some anomaly associated with the change of low-energy excitations may happen to be seen at much lower temperature we reached in the present simulation.
Methods

We investigate the thermodynamic properties of the 3D Kitaev model by adopting a Monte Carlo simulation. By the Jordan-Wigner transformation, the Kitaev model can be written as a free Majorana fermion system coupled with the $Z_2$ degree of freedom. Formally, the model is similar to the double-exchange model with Ising localized spins, which allows us to apply the Monte Carlo algorithms developed for the double-exchange type models. Here, we adopt the conventional algorithm in which the Monte Carlo weight for a given configuration of $Z_2$ variables is obtained by the exact diagonalization of the Majorana fermions. Details are given in Supplementary Information. The simulation is free from the fermion sign problem, and numerically exact except for the statistical errors. Also, the method is commonly applicable to the 2D honeycomb and 3D hyperhoneycomb lattices.

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