Exact results for the residual entropy of ice hexagonal monolayer

De-Zhang Li, Wei-Jie Huang, Yao Yao, and Xiao-Bao Yang*
Department of Physics, South China University of Technology, Guangzhou 510640, China

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Since the problem of the residual entropy of square ice was exactly solved, exact solutions for two-dimensional realistic ice models have been of interest. In this work, we study the exact residual entropy of ice hexagonal monolayer in two cases. In the case that the external electric field along the z-axis exists, we map the hydrogen configurations into the spin configurations of the Ising model on the kagome lattice. By taking the low temperature limit of the Ising model, we derive the exact residual entropy, which agrees with the result determined previously from the dimer model on the honeycomb lattice. In another case that the ice hexagonal monolayer is under the periodic boundary conditions in the cubic ice lattice, the residual entropy has not been studied exactly. For this case, we employ the six-vertex model on the square lattice to represent the hydrogen configurations obeying the ice rules. The exact residual entropy is obtained from the solution of the equivalent six-vertex model. Our work provides more examples of the exactly soluble two-dimensional statistical models.

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I. INTRODUCTION

Research of the ice system has been an important theme in the fields of physics and chemistry for a long time. Since the 1930s, the ice rules [1,2] were proposed to explain the nonzero entropy of ice at low temperatures [3,4]. The solution of this residual entropy in various ice systems has been an important and interesting problem in statistical physics and mathematics. The residual entropy arises from the hydrogen configurations obeying the ice rules as $S/k_B = \frac{1}{N_{H_2O}} \ln W = \ln w$, where W is the number of hydrogen configurations, N_{H_2O} is the number of H_2O molecules, and $w = W^{1/N_{H_2O}}$. We list some famous early studies of this problem: Pauling's [2] mean field approximation $w = \frac{3}{2}$ for four-coordinated ice system; DiMarzio and Stillinger's [5] matrix method for square ice and three-dimensional ice; Nagle's [6–8] series expansion for square ice, hexagonal ice (ice Ih), and cubic ice (ice Ic); and Lieb's [9,10] exact result from transfer matrix method for square ice $w = (\frac{4}{3})^{\frac{3}{2}}$. Along with developments in high-performance computational technology, there have been various numerical simulations [11–22] and theoretical evaluations based on computers [23–26] for this problem.

Among the research of the residual entropy problem of ice systems, our interest is the exact solution of the two-dimensional ice models in this work. Since the simple one-dimensional Ising model was solved in the 1920s [27], the studies of exact solutions for various statistical models have been of interest [28,29]. Most of the exactly solved statistical models are in one dimension and two dimensions. For the two-dimensional Ising model on the square lattice, Onsager [30] derived the solution for the case without an external field, and Lee and Yang [31] gave the solution for the case in an imaginary field. Solutions of the Ising models on the honeycomb lattice [32–35], the triangular lattice [36–39], and the kagome lattice [40,41] were also obtained. In particular, the residual entropies from the frustration of the triangular model [36] and the kagome model [41] were exactly solved. It is clear that the residual entropy of ice systems and that of the Ising models on the frustrated lattice have a close relation [42–44]. In 1967, Lieb [9,10] published the famous solution of square ice, which motivated a lot of studies of vertex models such as the six-vertex [45–53], eight-vertex [54–64], and 16-vertex models [65–73]. Square ice can be seen as a special case of the six-vertex model, and the exact residual entropy can be rederived from the low temperature limit of the Ising model with crossing and four-spin interactions on the checkerboard lattice [74–76]. These two-dimensional statistical models, as well as a few others such as the dimer model [77–86], the monomer-dimer model [87–92], and the hard hexagon model [93–95], either solved or unsolved, are briefly reviewed in the introduction of Ref. [73].

In this work, we focus on a two-dimensional ice model—namely, the ice hexagonal monolayer. Two-dimensional ice models have attracted much attention [24,25,96,97] since the research of square ice. Unlike square ice, the ice hexagonal monolayer is a realistic structure in three-dimensional ice, such as ice Ih and ice Ic. Although the exactly solved three-dimensional models are rare [98–101], research of the realistic two-dimensional structure may provide new insights into the physics of real ice. The exact result of the residual entropy of the ice hexagonal monolayer is obtained in two cases. In Sec. II, we consider the case of the presence of an external electric field along the z-axis. The exact residual entropy is derived from the low temperature limit of an equivalent Ising model on the kagome lattice, and is shown to be in agreement with the solution of dimer covering on the honeycomb lattice. In Sec. III, the case of an ice hexagonal monolayer under the periodic boundary conditions in ice Ic is studied, which has not been solved exactly before. In this case, we employ the

*Corresponding author: scxbyang@scut.edu.cn

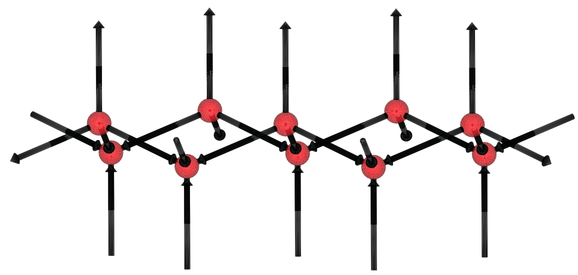

FIG. 1. The standard direction (+1) of the bonds in an ice hexagonal monolayer. The oxygens are marked in red.

mapping of the hydrogen configurations into an exactly solved six-vertex model, and present the exact solution for residual entropy. Discussions and conclusion are presented in Sec. IV.

II. ICE HEXAGONAL MONOLAYER IN AN EXTERNAL FIELD ALONG THE Z-AXIS

The ice hexagonal monolayer consists of the armchair $(H_2O)_6$ rings. All the oxygens are three-coordinated, hence there are three hydrogen bonds and one dangling bond along the z-axis for each oxygen in the layer. $\frac{3}{2}N_{H_2O}$ hydrogens are in the hydrogen bond network, and $\frac{1}{2}N_{H_2O}$ hydrogens are in the dangling bonds. In each hydrogen bond, there are two possible positions for a hydrogen, and in each dangling bond there are also two possibilities: one hydrogen or none. It is natural to introduce the mapping of these two possibilities of each bond into the value +1/–1 of an Ising spin. To do this, we should first define the standard direction (+1) of the bonds, which is shown in Fig. 1. The bond configurations can then be mapped into the spin configurations of the equivalent Ising model, with the value +1/–1 of each spin representing the direction of the corresponding bond. We show the equivalent Ising model in Fig. 2.

One can see from Fig. 2 that the Ising lattice is in a form of ABC, where A and C are two sparse triangular layers and B is the kagome layer. The B layer corresponds to the hydrogen bond network, and the A and C layers correspond to the dangling bonds. Clearly, the configurations with two +1 and two –1 bonds around every oxygen are obeying the ice rules. These configurations correspond to that in the Ising lattice with two +1 and two –1 spins around every tetrahedron. Next let us consider the spins on the kagome, or B, layer. When there are two +1 and two –1 spins around every tetrahedron,

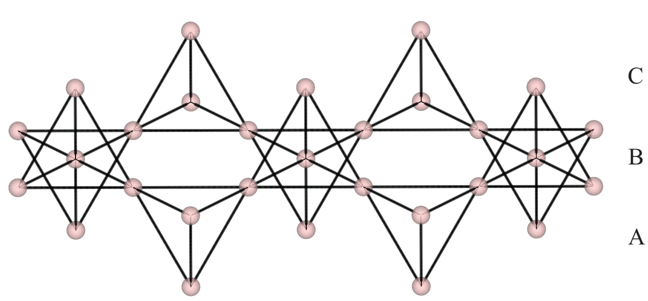

FIG. 2. The equivalent Ising model of the ice hexagonal monolayer.

there must be two +1 and one –1 or two –1 and one +1 spins in every triangle of the kagome layer. These are exactly the ground states of the antiferromagnetic Ising model with nearest-neighbor interactions on the kagome lattice. That is, there is a one-to-one mapping of the configurations obeying the ice rules (in a zero field) to the ground states of the antiferromagnetic Ising model on the kagome lattice. Notice that $N_{H_2O} = \frac{2}{3}N_K$, where N_K is the number of spins on the kagome lattice. Then the residual entropy of the ice hexagonal monolayer in a zero field is simply obtained from that of the antiferromagnetic Ising model on the kagome lattice [41]:

$$\begin{aligned} S/k_B = \frac{3}{2}S_K/k_B &= \frac{3}{2} \times \frac{1}{24\pi^2}\int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \\ &\times \ln\{21 - 4[\cos\theta + \cos\phi + \cos(\theta+\phi)]\} \\ &= 0.752745. \end{aligned} \tag{1}$$

In the presence of an external electric field along the z-axis, the hydrogens in the dangling bonds are pinned parallel to the field. Then, the configurations of the dangling bonds are constrained, i.e., all the spins in the A and C layers are +1. In this case, obviously the residual entropy is reduced. The ice rules force the configurations to those with two –1 and one +1 spins in every triangle of the B layer. The system under this condition is called "kagome ice" [102]. The reduced but still extensive ground state degeneracy was exactly solved by Moessner and Sondhi [103] by mapping the ground states to the configurations of the dimer model on the honeycomb lattice [80,82]. They showed that the residual entropy is one half that of the antiferromagnetic Ising model on the triangular lattice [36] $S = \frac{1}{2}S_{tri}$. Later, Matsuhira *et al.* [102] measured this residual entropy in a pyrochlore spin ice material. Udagawa *et al.* [104] rediscovered the mapping to the dimer model on the honeycomb lattice and rederived the solution using the Pfaffian method. This residual entropy is also discussed by a few other studies, both in the spin ice system [11,17,20,105] and in real ice [106].

Here we will propose an alternative approach to this solution. Noticing the ground states in this case are those with two –1 and one +1 spins in every triangle of the kagome lattice, we consider the low temperature limit of the antiferromagnetic Ising model with nearest-neighbor and three-spin interactions on the kagome lattice. The interaction energy within each triangle surrounded by three spins (s_1, s_2, s_3) is

$$E(s_1, s_2, s_3) = J(s_1s_2 + s_2s_3 + s_1s_3) + \Delta(s_1s_2s_3 - 1), \tag{2}$$

where $J > 0$ is the nearest-neighbor interaction and Δ is the three-spin interaction. The Hamiltonian of this Ising model can then be expressed as

$$H = \sum_{\text{tri}} E(s_1, s_2, s_3), \tag{3}$$

with the summation taken over all triangles. To solve the partition function Z exactly, we follow Refs. [107,108] and map this Ising model into an eight-vertex model on the honeycomb lattice [109]. The vertex weights of this eight-vertex model are given by

$$\begin{aligned} a &= \exp[-\beta E(1,1,1)] = \exp[-3\beta J], \\ b &= \exp[-\beta E(1,1,-1)] = \exp[-\beta(-J-2\Delta)], \\ c &= \exp[-\beta E(1,-1,-1)] = \exp[\beta J], \\ d &= \exp[-\beta E(-1,-1,-1)] = \exp[-\beta(3J-2\Delta)], \end{aligned} \tag{4}$$

where $\beta = 1/k_B T$. It is straightforward to verify that, in choosing $\Delta = -\infty$, the energy within a triangle is in the order $E(1,-1,-1) < E(1,1,1) < E(1,1,-1) = E(-1,-1,-1) = +\infty$. The ground states are exactly the configurations with two –1 and one +1 spins in every triangle. By taking the low temperature limit, the residual entropy can then be obtained from the ground state degeneracy as

$$\begin{aligned} S/k_B &= \lim_{N_{\text{tri}}\to\infty} \frac{1}{N_{\text{tri}}} \ln[g(E_0)] \\ &= \lim_{\beta\to\infty} \left\{ \lim_{N_{\text{tri}}\to\infty} \frac{1}{N_{\text{tri}}} (\ln Z + \beta E_0) \right\} \end{aligned} \tag{5}$$

with the ground-state energy $E_0 = N_{\text{tri}} \times E(1,-1,-1) = -N_{\text{tri}} J$. Here, N_{tri} is the number of triangles and is also the number of vertices on the honeycomb lattice. It is easy to find $N_{H_2O} = N_{\text{tri}}$. Now we may make use of the equivalence with the eight-vertex model on the honeycomb lattice,

$$Z = Z_{8v}(a,b,c,d), \tag{6}$$

in the case of $a = e^{-3\beta J}$, $c = e^{\beta J}$, $b = d = 0$. Fortunately, the eight-vertex model in this case is exactly solved in Ref. [109]. We recall Eq. (17) of Ref. [109], and substitute it into Eq. (5):

$$\begin{aligned} &\lim_{N_{\text{tri}}\to\infty} \frac{1}{N_{\text{tri}}} (\ln Z + \beta E_0) \\ &= \lim_{N_{\text{tri}}\to\infty} \frac{1}{N_{\text{tri}}} \ln Z_{8v}(a,b,c,d) - \beta J \\ &= \frac{1}{16\pi^2} \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \ln\{[a^4 + 3c^4 \\ &\quad + 2c^2(c^2 - a^2)(\cos\theta + \cos\phi \\ &\quad + \cos(\theta+\phi))]e^{-4\beta J}\}. \end{aligned} \tag{7}$$

Inserting $a = e^{-3\beta J}$ and $c = e^{\beta J}$ into Eq. (7) gives the low temperature limit

$$\begin{aligned} \lim_{\beta\to\infty} \left[\lim_{N_{\text{tri}}\to\infty} \frac{1}{N_{\text{tri}}} (\ln Z + \beta E_0) \right] &= \frac{1}{16\pi^2} \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \ln[3 + 2(\cos\theta + \cos\phi + \cos(\theta+\phi))] \\ &= \frac{1}{16\pi^2} \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \ln\left[1 + 4\cos\left(\frac{\theta+\phi}{2}\right)\cos\left(\frac{\theta-\phi}{2}\right) + 4\cos^2\left(\frac{\theta+\phi}{2}\right)\right] \\ &\overset{\sigma_1=\frac{\theta+\phi}{2},\sigma_2=\frac{\theta-\phi}{2}}{=} \frac{1}{16\pi^2} \times 2 \times \int_\Omega d\sigma_1 d\sigma_2 \ln[1 + 4\cos\sigma_1\cos\sigma_2 + 4\cos^2\sigma_1]. \end{aligned} \tag{8}$$

Here, the integral domain Ω is $\{(\sigma_1,\sigma_2) : 0 \leqslant \sigma_1 + \sigma_2 \leqslant 2\pi \text{ and } 0 \leqslant \sigma_1 - \sigma_2 \leqslant 2\pi\}$. It is trivial to verify

$$\int_\Omega d\sigma_1 d\sigma_2 \ln[1 + 4\cos\sigma_1\cos\sigma_2 + 4\cos^2\sigma_1] = \frac{1}{2} \int_0^{2\pi} d\sigma_1 \int_0^{2\pi} d\sigma_2 \ln[1 + 4\cos\sigma_1\cos\sigma_2 + 4\cos^2\sigma_1]. \tag{9}$$

Then Eq. (8) becomes

$$\lim_{\beta\to\infty} \left[\lim_{N_{\text{tri}}\to\infty} \frac{1}{N_{\text{tri}}} (\ln Z + \beta E_0) \right] = \frac{1}{16\pi^2} \int_0^{2\pi} d\sigma_1 \int_0^{2\pi} d\sigma_2 \ln[1 + 4\cos\sigma_1\cos\sigma_2 + 4\cos^2\sigma_1]. \tag{10}$$

Now we examine the residual entropy of the antiferromagnetic Ising model on the triangular lattice. On page 364 of Ref. [36], this entropy was shown in the form of

$$\begin{aligned} S_{\text{tri}}/k_B = \frac{1}{8\pi^2} \int_0^{2\pi} d\omega \int_0^{2\pi} d\omega' \\ \times \ln[1 - 4\cos\omega\cos\omega' + 4\cos^2\omega'] \end{aligned} \tag{11}$$

before the final expression. One can easily see that the integral in Eq. (10) is equal to that in Eq. (11). Hence, the exact solution of the residual entropy in this case is exactly one half that of the antiferromagnetic Ising model on the triangular lattice:

$$S/k_B = \tfrac{1}{2} S_{\text{tri}}/k_B = 0.161533. \tag{12}$$

Then we rederive the result of Refs. [103] and [104] using a different approach of taking the low temperature limit of an Ising model on the kagome lattice.

We remark that, if we consider the Ising model on the kagome lattice with nearest-neighbor interactions $J > 0$ and an external magnetic field $H_{\text{ex}} = 4J$, the ground states will be the configurations with two –1 and one +1 spins or three –1 spins in every triangle. Even in the ground states, the triangles with three –1 spins will disobey the ice rules. This model is equivalent to the monomer-dimer model on the honeycomb lattice [11,20,92], where the triangles with two –1 and one +1 spins can be seen as the sites covered by a dimer, and those with three –1 spins can be seen as monomers. Solving the monomer-dimer model is much more difficult than the dimer covering problem. Nagle [88] obtained the Bethe approximation for the monomer-dimer model on the honeycomb lattice, which was rederived by Isakov *et al.* [11]. Numerical

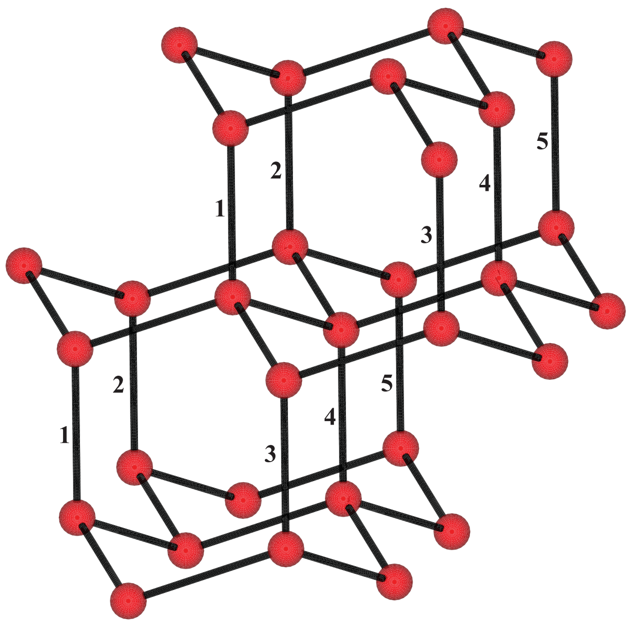

FIG. 3. The diagrammatic representation of the ice hexagonal monolayer in the lattice of ice Ic. The oxygen atoms are marked in red. Five pairs of dangling bonds under the periodic boundary conditions are marked.

results by Wang-Landau Monte Carlo simulation [20] were also studied. The exact solution of the residual entropy in this case has yet to be obtained.

III. ICE HEXAGONAL MONOLAYER UNDER PERIODIC BOUNDARY CONDITIONS

We consider in this case the ice hexagonal monolayer in the lattice of ice Ic. The three-dimensional model of ice Ic is equivalent to the pyrochlore antiferromagnetic Ising model [42]. The residual entropy of this model has been evaluated from various approaches [11,16–20,23,26,110]. Here, we study the ice hexagonal monolayer as a two-dimensional structure from this model.

For the ice hexagonal monolayer in ice Ic, the periodic boundary conditions are taken on the dangling bonds of the layer. In Fig. 3, we show the example of five pairs of dangling bonds under the periodic boundary conditions. It is clear to verify that the dangling bonds of each pair are located on one pair of nearest-neighbor oxygens, and convert into one hydrogen bond under the periodic boundary conditions. Actually, there are double bonds connecting these pairs of nearest-neighbor oxygens. We show the two-dimensional hydrogen bond network in this case in Fig. 4.

The residual entropy of this model can be exactly solved by employing the mapping into a six-vertex model on the square lattice. Consider the direction of each hydrogen bond in the network as an arrow. According to the ice rules, four arrows around each oxygen should be two-in/two-out respective to this oxygen. In Fig. 4, one can easily see that each pair of nearest-neighbor oxygens connected by double bonds can be seen as a single site on the square lattice. It is trivial to find that the double bonds already contribute two-in/two-out of

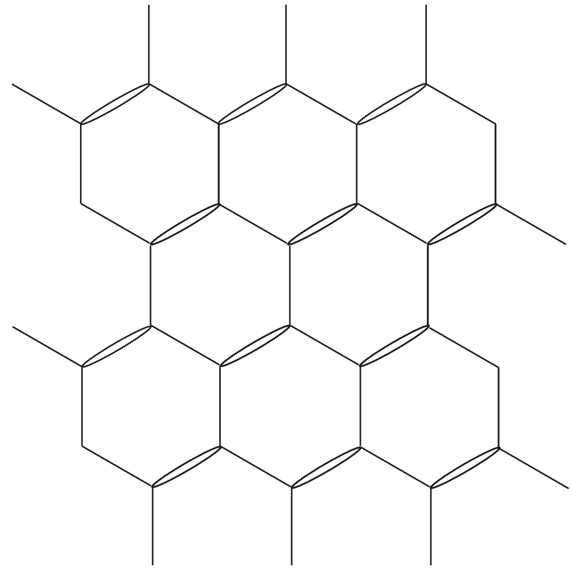

FIG. 4. The hydrogen bond network of the ice hexagonal monolayer under the periodic boundary conditions in ice Ic.

the total four-in/four-out to these two oxygens; then, the four arrows around this site should be two-in/two-out respective to this site. That is, the arrow configurations on the square lattice should be two-in/two-out respective to every site. We then obtain a six-vertex model on the square lattice equivalent to the hydrogen bond network, as shown in Fig. 5.

As shown in Fig. 5, the configuration of vertex (1) allows one hydrogen configuration in the double bonds of this site, and so does vertex (2). Hence, the weights of (1) and (2) should be one. Similarly, the weights of (3), (4), (5), and (6) should be two, as there are two possibilities for the configuration of the double bonds. We list all the vertex weights:

$$\omega_1 = \omega_2 = 1, \quad \omega_3 = \omega_4 = \omega_5 = \omega_6 = 2. \tag{13}$$

The residual entropy is then determined directly by the partition function of this model $S/k_B = \frac{1}{2} \times \lim_{N_{6v}\to\infty} \frac{1}{N_{6v}} \ln Z$, where N_{6v} is the number of vertices on the square lattice and $N_{H_2O} = 2N_{6v}$. Remark that the six-vertex model in the case $\omega_1 = \cdots = \omega_6 = 1$ is the square ice model. To solve our six-vertex model, we should first recall the exactly solved cases in the previous studies. In Refs. [48–50], the solution of a six-vertex model—with the vertex weights and the associated energies

$$\begin{aligned} \varepsilon_1 &= \varepsilon_2 = -\tfrac{1}{2}\delta, \tilde{\omega}_1 = \tilde{\omega}_2 = e^{\frac{1}{2}\beta\delta},\\ \varepsilon_3 &= \varepsilon_4 = \tfrac{1}{2}\delta, \tilde{\omega}_3 = \tilde{\omega}_4 = e^{-\frac{1}{2}\beta\delta},\\ \varepsilon_5 &= \varepsilon_6 = -\varepsilon, \tilde{\omega}_5 = \tilde{\omega}_6 = e^{\beta\varepsilon}, \end{aligned} \tag{14}$$

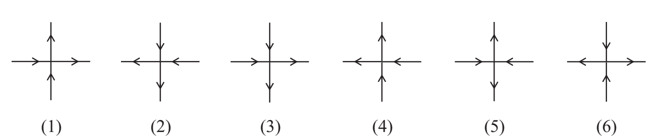

FIG. 5. The arrow configurations of the six-vertex model.

and, in the case $\delta > 0$—was examined. Notice that the solution is invariant under a C_2 symmetry operation along the vertical axis, i.e., under the transformation $\tilde{\omega}_1 \leftrightarrow \tilde{\omega}_4, \tilde{\omega}_2 \leftrightarrow \tilde{\omega}_3$ (see Fig. 5). We may set the vertex energies as $\beta\delta = \ln 2$ and $\varepsilon = \frac{1}{2}\delta$, and redefine the vertex weights as

$$\tilde{\omega}_1 = \tilde{\omega}_2 = e^{-\frac{1}{2}\beta\delta} = \frac{1}{\sqrt{2}}, \tilde{\omega}_3 = \tilde{\omega}_4 = \tilde{\omega}_5 = \tilde{\omega}_6 = e^{\frac{1}{2}\beta\delta} = \sqrt{2}. \tag{15}$$

Then the relation of the partition function of our model with that of the model defined in Eq. (15) is straightforward:

$$Z = \sqrt{2}^{N_{6v}} \times \tilde{Z}. \tag{16}$$

To evaluate the solution of $\tilde{Z}$, we follow the work of Refs. [49,50,111] and determine the quantities

$$\eta = e^{\beta\delta} = 2, \xi = e^{2\beta\varepsilon} = 2$$

and

$$\Delta = \tfrac{1}{2}(\eta + \eta^{-1} - \xi) = \tfrac{1}{4}. \tag{17}$$

Then, we define μ and Φ_0 by

$$\cos\mu = -\Delta$$

and

$$e^{i\Phi_0} = \frac{1 + \eta e^{i\mu}}{\eta + e^{i\mu}}. \tag{18}$$

It is simple to give

$$\mu = \arccos\left(-\tfrac{1}{4}\right), \quad \Phi_0 = \arccos\left(\tfrac{11}{16}\right). \tag{19}$$

Now we recall Eq. (15) of Ref. [50], which is the exact solution of the partition function $\tilde{Z}$, in the case when vertical polarization and horizontal polarization are zero. The vertical and horizontal polarizations are associated with the external electric fields in the vertical and horizontal directions, respectively. In our case, no electric field is employed, and Eq. (15) of Ref. [50] is the expression for $\tilde{Z}$. Then we have

$$\begin{aligned}\lim_{N_{6v}\to\infty} \frac{1}{N_{6v}} \ln Z &= \frac{1}{2}\ln 2 + \lim_{N_{6v}\to\infty} \frac{1}{N_{6v}} \ln \tilde{Z} \\ &= \frac{1}{2}\ln 2 + \frac{1}{2}\beta\delta + \frac{1}{8\mu}\int_{-\infty}^{\infty} \frac{d\alpha}{\cosh(\pi\alpha/2\mu)} \\ &\quad \times \ln\left[\frac{\cosh\alpha - \cos(2\mu - \Phi_0)}{\cosh\alpha - \cos\Phi_0}\right] \\ &= \frac{1}{2}\ln 2 + \frac{1}{2}\beta\delta + \frac{1}{4}\int_{-\infty}^{\infty} \frac{d\alpha}{\cosh(\pi\alpha)} \\ &\quad \times \ln\left[\frac{\cosh(2\mu\alpha) - \cos(2\mu - \Phi_0)}{\cosh(2\mu\alpha) - \cos\Phi_0}\right] \\ &= 0.946954. \end{aligned} \tag{20}$$

The exact residual entropy is

$$S/k_B = \frac{1}{2} \times \lim_{N_{6v}\to\infty} \frac{1}{N_{6v}} \ln Z = 0.473477. \tag{21}$$

We remark that the partition function Z of our model can also be obtained from Ref. [53]. One can easily examine that the same result is achieved from Eq. (6) in Ref. [53] by a different analytic expression from Eq. (20) presented here.

Interestingly, Kirov [24] constructed a digonal hexagonal ice model, in which the hydrogen bond network is very similar to that of our model (see Fig. 5(b) in Ref. [24]). Kirov [24,25] developed a numerical transfer matrix method to enumerate the hydrogen bond configurations completely in finite fragments of various models. For the digonal hexagonal ice model, his result of the largest fragment (140 H_2O molecules) is 0.474497, which is very close to the solution of our model. It is not clear whether the exact residual entropies in the large lattice limit of these two models are consistent though.

IV. DISCUSSIONS AND CONCLUSION

In this work we study the exact residual entropy of the ice hexagonal monolayer, a two-dimensional structure from real ice. We have examined two soluble cases. The case in the presence of an external electric field along the z-axis, also called kagome ice, has been exactly solved in previous studies [103–105]. The model in this case is equivalent to the dimer model on the honeycomb lattice, and the residual entropy is equal to the solution of the dimer covering problem, which is one half the residual entropy of the antiferromagnetic Ising model on the triangular lattice. We give an alternative approach to this solution by mapping the model into an Ising model with nearest-neighbor and three-spin interactions on the kagome lattice. The ground states of this Ising model are exactly the configurations in kagome ice; hence, we take the low temperature limit of this Ising model and obtain the residual entropy. We show that this result is exactly one half that of the antiferromagnetic Ising model on the triangular lattice, thus finishing the rederivation. The advantage of making use of the equivalence of the ice-type model with the Ising spin model is demonstrated in our method.

The second case we consider is the ice hexagonal monolayer under the periodic boundary conditions in ice Ic. In this case, each pair of dangling bonds located on one pair of nearest-neighbor oxygens converts to a hydrogen bond, and then these pairs of nearest-neighbor oxygens are connected by double bonds. The hydrogen bond network can then be mapped into a six-vertex model on the square lattice, with each pair of nearest-neighbor oxygens connected by double bonds seen as a single site. The number of hydrogen configurations in this case has not been studied exactly. For this new system, we transform this six-vertex model to an exactly solved case [48–50] and obtain the solution of residual entropy. Hence, we have presented a new soluble two-dimensional ice model. It is worth comparing this solution with the result of three-dimensional ice Ic. We recall the estimates of the residual entropy of ice Ic in Refs. [16,19,23,26], which are advanced results from thermodynamic integration, Wang-Landau simulation, cluster expansion, and theoretical approximation, respectively. All these estimates—namely, 0.410430 from thermodynamic integration, 0.410081 from Wang-Landau simulation, 0.411014 from cluster expansion, and 0.410423 from theoretical approximation—are significantly smaller than the exact result of the hexagonal monolayer 0.473477 [see Eq. (21)]. This fact confirms that the correlation between layers in three-dimensional ice restricts the hydrogen bond configurations. Anyway, our solution for the hexagonal monolayer under the periodic boundary conditions provides the result of a very simplified version of real ice. Effects of the correlation between layers in three-dimensional ice deserve further study.

In conclusion, for the ice hexagonal monolayer, we rederive the result in a solved case and give the solution in a new soluble case. In this work, we provide more examples of the research of the residual entropy problem in various ice systems. Our work enlarges the set of exactly soluble two-dimensional models in statistical physics.

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