Residual entropy of ice: a manifestation of the fractional exclusion statistics in real three-dimensional space

LETTER TO THE EDITOR

Residual entropy of ice: a manifestation of the fractional exclusion statistics in real three-dimensional space

Jisoon Ihm

Department of Physics and Center for Theoretical Physics, Seoul National University, Seoul, Korea

Abstract. We report here a tangible example of the fractional exclusion statistics in three spatial dimensions. We identify the chemical constraint of O–H bonds in ice, the so-called ice rule, as the origin of this novel statistics. Then the residual entropy of the crystalline ice is recognized as arising from the fractional exclusion with the statistical interaction parameter $\alpha = 0.867$. Assuming the residual entropy of ice reflects true accessibility to a macroscopic number of states through quantum tunnelling, we propose the possibility that Berry's phase suppresses the tunnelling splitting of ground states and maintains the finite residual entropy.

Recently, Haldane [1] reformulated the concept of the fractional statistics as a generalization of the Pauli exclusion principle so that the fractional statistics is realizable in arbitrary spatial dimensions. Under such a generalization, the fractional statistics has been identified, beyond the well known case of the quasiparticles or holes in the fractional quantum Hall effect in two dimensions [2], and in some one-dimensional model systems [3, 4] as well. Needless to say, the most desired example of this new statistics (now called the 'fractional exclusion statistics') has been its realization in three or higher spatial dimensions, which would unambiguously establish the generality of the fractional exclusion statistics in comparison with the anyon (fractional phase) statistics restricted to two dimensions. In this letter, we would like to report a manifestation of the fractional exclusion statistics in the ordinary crystalline ice, the first example of such statistics in the real three-dimensional world to our knowledge. In ice, each hydrogen atom can occupy one of two equivalent bonding sites between the neighbouring oxygen atoms. However, because of the chemical constraint known as the ice rule to be explained below, the number of allowed configurations is reduced and this reduction will be shown to be describable as the fractional statistics interpolating between the bosonic and fermionic statistics. We will further suggest that there exist similarities, on the fundamental level of physics, between the apparently chemistry-driven statistics presented here and the conventional topology-driven fractional statistics.

The stable structure of ice at low temperatures is known to be hexagonal and each oxygen atom is surrounded by four nearest-neighbour oxygen atoms as shown in figure 1(*a*). There are two chemical constraints for the hydrogenic configurations, namely, (i) that there is one hydrogen atom between any pair of neighbouring oxygen atoms, and (ii) that there are two hydrogen atoms near to (and two hydrogen atoms away from) a given oxygen atom. Consequently, the local configuration around an oxygen atom in ice is H_2O-molecule-like. For convenience of presentation, we assume that the first constraint is already satisfied by
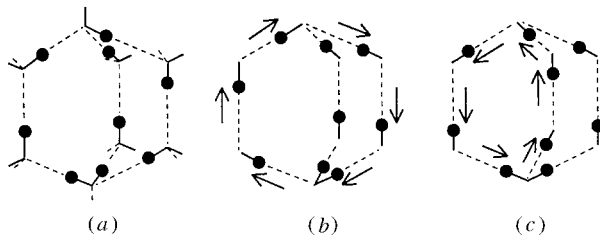
Figure 1. (*a*) Schematic drawing of the structure of the hexagonal ice. Full circles indicate hydrogen atoms. An oxygen atom (not marked) exists at each of eight vertices. Full lines indicate strong O–H covalent bonds and the broken lines weak hydrogen bonds. With other hydrogen atoms residing outside the area shown, the ice rule is always satisfied. (*b*) and (*c*) are obtained from configurations (*a*) and (*b*), respectively, by shifting six hydrogen atoms simultaneously through the tunnel barrier in the arrow directions keeping all outside atoms fixed. Likewise, the configuration (*a*) may be obtained from (*c*). Simultaneous rotation of six O–H covalent bonds by about 105°, respectively, is another possible path to arrive at the configuration (*b*) from (*a*).

the stoichiometric (H_2O) ice (violation of which would cost too much energy), and we will from now on call the second constraint the ice rule. In general, a hydrogen atom located between oxygen atoms I and II can occupy either one of two equilibrium sites, one near to atom I (site A) and the other near to atom II (site B). Therefore, before the ice rule is imposed, the total number of possible hydrogenic configurations is 2^{2N}, where N is the number of oxygen atoms which sets the system size. It was a famous problem in statistical mechanics to count the number of different configurations satisfying the ice rule in the thermodynamic (large-N) limit, and the answer [5] turned out to be $\sim 1.507^N$. On the other hand, it has been known in specific heat (C_p) measurements [6–8] that the crystalline ice exhibits a residual (zero-point) entropy of ~ 0.82 cal/mol·K down to the temperature $T \approx 0.2$K. Since the state degeneracy of 1.507^N is equivalent to 0.815 cal/mol·K in terms of entropy, there exists an excellent agreement between theory and experiment.

Now we can map the statistics of the hydrogenic configuration under the ice rule onto the fractional exclusion statistics. The situation of the maximal degeneracy (2^{2N}) in the absence of the ice rule is mapped to the bosonic statistics, complete vanishing of the configurational degrees of freedom to the fermionic statistics, and the intermediate (realistic) case to the fractional statistics. Following Wu's formalism [9], if there are N_p identical particles occupying G one-particle states of identical energy, the number of N_p-particle states (i.e. the degeneracy of the many-body system) W is

$$W(G, N_p, \alpha) = \frac{[G + (N_p - 1)(1 - \alpha)]!}{[G - \alpha N_p - (1 - \alpha)]! N_p!} \tag{1}$$

where $\alpha = 0$ corresponds to bosons, $\alpha = 1$ to fermions, and $0 < \alpha < 1$ to particles of fractional statistics interpolating between the two limits. On the other hand, with use of the identity $2^{2N} = \sum_{m=0}^{2N} \binom{2N}{m}$ where $\binom{2N}{m} = 2N!/m!(2N - m)!$, the logarithm of the total number of states of ice for N oxygens *without* the ice rule in the thermodynamic limit would be

$$\ln \sum_{m=0}^{2N} \binom{2N}{m} \approx \ln \binom{2N}{N}$$

$$\approx \ln \binom{2N - 1}{N}. \tag{2}$$

In the first line of equation (2), regarding m as the variable number of particles, we retain only the largest term in the summation in the spirit of the equivalence between the grand canonical ensemble and the canonical ensemble. (Or, we simply apply Stirling's formula.) In the second line, $\binom{2N-1}{N}$ may immediately be interpreted as the degeneracy of many-boson states when G (number of one-particle states) $= N$ and N_p (the number of particles) $= N$. With $G = N_p = N$, the number count for a frozen-in state having no configurational degrees of freedom is trivially $\binom{G}{N_p} = \binom{N}{N} = 1$, corresponding to the degeneracy of N fermions occupying N states. In other words, G and N_p of ice are uniquely determined under the two 'boundary conditions', $W(G, N_p, 0) = 2N \ln 2$ and $W(G, N_p, 1) = 0$. Of course, $G = N_p = N$ corresponds to the case where the crystalline ice does not have any deficit or excess of hydrogen atoms or other defects in bonds. The configurational entropy of real ice is $kN \ln 1.507$, a value between the two extremes. α for ice is obtained by substituting $G = N_p = N$ in equation (1) (we neglect 1 compared to N whenever convenient) and comparing it with the residual entropy,

$$N \ln 1.507 \approx (2 - \alpha)N \ln(2 - \alpha) - (1 - \alpha)N \ln(1 - \alpha). \tag{3}$$

We obtain $\alpha \approx 0.867$. To recapitulate, two possible sites (A and B) for each hydrogen atom would be fully available if the presence of other hydrogen atoms in neighbouring bonds would not restrict the freedom of choice between A and B (just as the presence of other particles does not restrict the availability of states in boson statistics), but other hydrogen atoms do impose some statistical constraint (i.e. certain, but not all, states become excluded) in reality and the measure of the constraint in ice is $\alpha = 0.867$. In this formulation, the basic requirement for the fractional exclusion statistics [1] is automatically satisfied: $G(=N)$ is finite and extensive, proportional to the size of the condensed matter region because N is *defined* to be the system size.

We now make a number of observations on the result. Firstly, the 'particles' in the fractional statistics are not necessarily *true excitations* of any kind. In the present case, we are counting the *ground-state* degeneracy of the N-particle system. The distinction is immaterial because the particles in the degenerate ground states may be regarded as being created from the null state just as excitations are created from the ground state. When the reduction of the degeneracy by the chemical constraint is converted into the statistics of the non-interacting particles of fractional α, the meaning of the 'particles' and 'one-particle states' becomes rather abstract. Suppose we assign A and B to two possible hydrogenic sites for every bond between oxygens as before. Any hydrogenic configuration of the whole system can be described by a sequence of A's and B's (with $2N$ of them in total) representing the sites actually occupied by hydrogens. Then we identify A with a 'particle' and B with a 'wall dividing one state from another' (so that the number of B's is equal to $G - 1$). The most probable values for the number of A's and B's are both N. We can easily check that the aforementioned mapping to the fractional exclusion statistics is accomplished this way. More discussions on the nature of the particles from the viewpoint of phase statistics will be given later. Secondly, on the question of the rationality of α, the configurational entropy in the thermodynamic limit may be calculated by means of a series expansion and the resulting α need not be a rational number because the limit of the sequence of rational numbers can be irrational. Thirdly, we can conceive of expanding the case to more than one species and invoking the mutual statistics by Haldane [1]. Our attempt to apply the mutual statistics to a mixture of the protons and deuterons ($H_{2-x}D_xO$) has turned out to be not very meaningful. Another step we can take is to regard the states of different energies (excited states) as different species following Wu [9]. If, in

violation of the ice rule, a hydrogen atom on, say, site A were to move towards site B, a nearest-neighbour pair of H_3O^+ and HO^- would be created at some energy cost ϵ. We could consider the finite-temperature statistics for such excitations. However, state-of-the-art *ab initio* pseudopotential calculations using the gradient-corrected density functional theory [10] indicate that such a single-proton movement to the other side is quite unstable and should not occur in real ice. There is no experimental evidence for it, either. Furthermore, the energy cost $\epsilon(\gtrsim 0.5$ eV$)$ is much greater by far than energies of other excitations such as phonons. Since the low-lying excitations are practically dominant in the finite-temperature statistics, the study of the high-lying configurational excitations will not be pursued here. For such a study on *model systems* rather than real ice, standard methods called the vertex models are available [11] and the viewpoint of the fractional exclusion may be helpful.

Other possibilities of the fractional exclusion statistics lie in polymers and glasses. It can be shown that the excluded volume parameter v in polymer solutions [12] is related to α of the two-dimensional ideal gas through

$$v = a^3(2\alpha - 1) \tag{4}$$

where a is the monomer size. Therefore, α is identified with $(1 - \chi)$ where χ is the Flory interation parameter [12]. On the other hand, macroscopic degeneracy of the ground-state configurations occurs frequently in spin glasses or any frustrated systems in general and the fractional exclusion is again conceivable. (Ordinary structural glasses probably do not have such macroscopic degeneracy.) For instance, the fully-frustrated triangular Ising spin system exhibits a residual entropy of $0.3383kN$ and the corresponding α is 0.717. But there exists a problem of ergodicity here. At low temperatures, the tunnelling time (whether thermal or quantum mechanical) to other low-energy states is practically infinite and the very definition of the (equilibrium) statistics among these states becomes ambiguous. This raises an interesting question why the residual entropy of ice is measured so reproducibly and coincides with the theoretical calculation so precisely. This seems to be an issue separate from the fraction exclusion statistics considered so far, but below we give a sketch of our quantum mechanical calculation on this question beyond the classical configuration-counting method. In doing so we find that the topological excitation may, in general, play an important role in the fractional exclusion statistics just as in fractional phase statistics. More detailed calculations will appear elsewhere [13].

We have stated, in terms of the Born–Oppenheimer energy surface, that there are 1.507^N potential minima of equal well depth corresponding to ice-rule-satisfying configurations. What we have so far neglected is the kinetic part, namely, the quantum mechanical tunnelling and the corresponding energy-level splitting. Of course, the tunnelling splitting of energy levels decreases as the barrier height increases and the states become practically degenerate. However, if the potential barrier becomes too high, a particular hydrogenic configuration is frozen-in and other configurations are inaccessible. It was Ma [14] who correctly stated, on the question of the residual entropy of glasses, that 'as $T \to 0$, motion stops and entropy also tends to zero. The third law (of thermodynamics) cannot be violated'. The often-claimed residual entropy of glasses obtained by integrating C_p/T is an artefact of the irreversibility of the thermal process which causes the inequality

$$\int_0^T C_p/T \ \mathrm{d}T \ < \ \Delta S(= S(T) - S(0)) \,. \tag{5}$$

This explains why the measured residual entropy of glasses is not unique or reproducible (sample- and history-dependent). The situation in the crystalline ice, however, is quite different. Careful experiment always produces the same residual entropy and it coincides

precisely with the theoretically anticipated value. The crystalline ice, despite its random hydrogenic configuration, does not, in general, exhibit characteristics of glasses (e.g. glass transition, hysteresis, or frustration). If we regard $(\Delta S - \int_0^T C_p/T \, dT)$ as a measure of irreversibility, this quantity for ice must be negligibly small. In this context, we note Ma also mentioned in the same reference [14] that the residual entropy can be non-zero if the ground state is degenerate (as opposed to being frozen as in glasses). The measured residual entropy of ice is likely to reflect the truly accessible states down to the experimental temperature (0.2K) and the following development is based on this assumption.

We first pay attention to the fact that the hydrogen tunnelling time must be significantly shorter than the specific heat measurement time-scale (say, 1000 s) in order for a macroscopic number of states to be accessible. In fact, there exists a much more stringent requirement in ice. Since the deuterium ice (D_2O) turned out [15] to show the same residual entropy as the hydrogen ice, the tunnelling time of deuterons is limited by the same measurement time-scale and the proton tunnelling time is expected to be several orders of magnitude shorter than that of deuterons. We have tried the state-of-the-art *ab initio* gradient-corrected pseudopotential total energy calculations similar to [10] for a limited number of configurations to evaluate this rate. Combined with information available in the literature, we roughly estimate that the minimum barrier height occurs between the configuration in figure 1(*a*) and that in figure 1(*b*) (equivalently, between (*b*) and (*c*), or between (*c*) and (*a*)), and its value is ~ 2 eV for a simultaneous movement of six hydrogen atoms (equivalent to ~ 7.5 kcal/mole of H). Since the zero-point vibration energy ($\frac{1}{2}\hbar\omega$) of the O–H stretching mode is 0.2 eV, the actual barrier is reduced to ~ 0.12 eV per hydrogen atom. The overlap integral I across the barrier per hydrogen is ~ 0.3 and the off-diagonal matrix element β connecting the two configurations is

$$\beta \approx \tfrac{1}{2}\hbar\omega \times I^6$$
$$\approx 1.46\times 10^{-4} \text{ eV}. \tag{6}$$

The tunnelling rate goes as the square of the matrix element and turns out to be $\sim$(attempt frequency)$\times (0.3)^{12} \approx 5\times 10^7$ s^{-1}. The tunnelling rate of the D_2O ice is estimated to be $\sim 7\times 10^3$ s^{-1}. Simultaneous rotation of six O–H covalent bonds by about $105°$, respectively, is another way to arrive at configuration (*b*) from (*a*). This tunnelling (hindered rotation) is *not* ruled out, but seems less frequent because of the longer distance of tunnelling. Unfortunately, despite all these estimates, nuclear magnetic resonance (NMR) experiments do not show traces of the hydrogenic motion at low temperatures. Our justification is that, since six hydrogen atoms move in concert without changing relative positions, they may not give rise to NMR signals. (In a strict sense, they should not, because they are in the ground state.) Another (though less likely) possibility is that the tunnelling is faster than the specific heat, but slower than the NMR time-scale. There do exist experimental indications of the hydrogenic tunnelling at higher temperatures, near 90 K in the specific heat measurement [6] and near 250 K in NMR [16]. The lower limit of the potential barrier per *deuterium* for the rotational motion was reported to be 0.15 eV [17] (the barrier per *hydrogen* would be smaller), and the activation barrier of 0.125 eV per hydrogen (with 2×10^{-4} HF added) was quoted in [16]. If the minimum barrier height is really within 0.15 eV as all these numbers suggest, the quantum tunnelling rate of the six hydrogen atoms using a very conservative estimate is still much greater than the specific heat measuring rate, supporting our claim that there exist a collective quantum tunnelling of six hydrogen atoms.

It is ironic, however, that the very existence of quantum tunnelling undermines the finite residual entropy. In the presence of quantum tunnelling between potential minima, a new non-degenerate ground state is formed by the linear combination of these configurations

with equal coefficients and the tunnelling splitting of energy levels follows. If we consider tunnelling among three configurations in figure 1 only and use the off-diagonal matrix element β evaluated previously, the non-degenerate ground-state energy would be -2β and the doubly-degenerate excited-state energy β (with respect to the energy of the state in a single potential well). Therefore, the energy splitting should be $3\beta \approx 0.44$ meV, much too great to pass undetected in the specific heat measurement at 0.2 K. In other words, accessibility to many potential minima does not explain the finite residual entropy.

To overcome this dilemma, we make a rather unusual proposal, namely, that there appear a Berry's phase [18] in ice. A crucial point here is that the ice consists not only of nuclei but also of electrons. As protons move from one configuration to another, electrons follow the protons' motion and the many-electron wavefunction also changes. As the simplest example occurring in ice, we can investigate how the electronic state evolves as the hydrogenic configuration changes from figure 1(*a*) to (*b*) to (*c*) and back to (*a*) in sequence. It has been proved that the electronic state (the fast variable) picks up Berry's phase $\gamma = \pi$ if the trajectory of the ionic configuration (the slow variable) encloses a point at which the electronic states are doubly degenerate. Such phenomena are known to occur at defects in crystals [19] or in Na_3 molecules [20]. In the present case, the spatially extended nature of the crystalline ice with aperiodic hydrogen configurations and the too many structural degrees of freedom prohibit us from drawing definite conclusions yet, although we have some positive calculational results†.

But once we make the conjecture that Berry's phase emerges from the states made out of the three configurations in figure 1, the ground state becomes doubly degenerate [19, 20] as in the spin-$\frac{1}{2}$ system with the degenerate eigenvalue of $-\beta$. One structural unit made of eight oxygen atoms shown in figure 1 can be imbedded without overlap for every 12 oxygen atoms in the hexagonal lattice. Thus the degeneracy for N oxygen atoms coming from this kind of Berry's phase is $2^{N/12}$, accounting for $\sim$14% of the residual entropy of ice. This number is nearly tripled as we include the translation of this structural unit by the Bravais lattice vectors, and the degrees of freedom of hydrogen atoms not residing on this unit also increase the number. On the other hand, by including overlap effects and Berry's phase covering a larger structural unit, we anticipate that some energy splitting takes place. This splitting, however, is a next-order effect and manifests itself as the reduction of the residual entropy only at much lower temperatures $\lesssim 0.01$ K. (At such a low-energy scale, there may be other sources that limit the quantum coherence time.) Therefore, the finite residual entropy and the subsequent violation of the third law of thermodynamics in the practical sense are expected based on the existence of Berry's phase. Notice that Berry's phase considered above is equivalent to the presence of a thin solenoid carrying half the magnetic flux quantum threaded through the loop (still not violating the time-reversal symmetry). The wavefunctions, though representing the lowest-energy states, acquire the 'pseudo'rotational angular momentum $l = \frac{1}{2}$ (rather than 0) because of the unusual boundary condition imposed by Berry's phase and look like *topological excitations* similar to other known cases of the fractional statistics [1–4, 9]. We want to add that topological singularity forms lines or rings in the present case and is equivalent to the conventional point singularity in two-dimensions. The phase change for an individual cyclic motion of a local hydrogenic configuration is either 0 or π (which is *not* fractional!); the phase change can be fractional ($\alpha\pi$) only after statistical averaging.

In conclusion, we have shown that the residual entropy of ice may be interpreted

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† We have found a set of hydrogenic configurations giving rise to quantum mechanical energy degeneracy for the oxygen cluster in figure 1, which is a necessary (but still not sufficient) condition for the existence of Berry's phase.

as a realization of the fractional exclusion statistics in three spatial dimensions. The experimental observation of the residual entropy suggests that a macroscopic number of degenerate configurations may actually be accessible even at low temperatures through quantum tunnelling. The occurrence of quantum tunnelling, however, normally causes an appreciable energy level splitting which would, in turn, make the residual entropy vanish, leaving us in a paradoxical situation. We propose that the emergence of Berry's phase through the topologically non-trivial, collective tunnelling of hydrogen atoms can resolve this puzzle and explain the finite residual entropy. This proposal indicates that the topological excitation may be an essential feature of the fractional exclusion statistics even in the case of ice where the chemical constraint is the source of such an exclusion.

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