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B. A. Berg

published in

*From Computational Biophysics to Systems Biology (CBSB07),  
Proceedings of the NIC Workshop 2007,*  
Ulrich H. E. Hansmann, Jan Meinke, Sandipan Mohanty,  
Olav Zimmermann (Editors),  
John von Neumann Institute for Computing, Jülich,  
NIC Series, Vol. 36, ISBN 978-3-9810843-2-0, pp. 87-90, 2007.

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<http://www.fz-juelich.de/nic-series/volume36>

# Residual Entropy of Ice I from Multicanonical Simulations

Bernd A. Berg<sup>1,2</sup>

<sup>1</sup> Department of Physics, Florida State University,  
Tallahassee, FL 32306-4350, USA

<sup>2</sup> School of Computational Science, Florida State University,  
Tallahassee, FL 32306-4120, USA  
*E-mail: berg@scs.fsu.edu*

We introduce two simple models with nearest neighbor interactions on 3D hexagonal lattices. Each model allows one to calculate the residual entropy of ice I (ordinary ice) by means of multicanonical simulations. This gives the correction to the residual entropy derived by Linus Pauling in 1935. Our estimate is found to be within less than 0.1% of an analytical approximation by Nagle which improved on Pauling's result. In biological applications at room temperature small, ice-like clusters are of importance. Their entropy can be computed by the same method.

## 1 Introduction

In this talk I report on a novel calculation<sup>1</sup> of the residual entropy of ice I. The approach can as well be used to calculate the entropy of arbitrary cluster of hydrogen bonds of known geometry. This is of importance for the interaction of water with proteins and other biomolecules, because the liquid phase of water differs from simple fluids in that there is a large qualitative remnant of ice structure in the form of local tetrahedral ordering<sup>2</sup>. The next section reviews briefly the residual entropy of ice and in section 3 our calculation is sketched.

## 2 Residual Entropy of Ice

In contrast to liquid water the properties of ice are relatively well understood. Most of them have been interpreted in terms of crystal structures, the forces between its constituent molecules, and the energy levels of the molecules themselves<sup>3</sup>. A two-dimensional projection of the hexagonal crystal structure of ordinary ice (ice I) is depicted in Fig. 1 (other forms of ice occur in particular at high pressures). Each oxygen atom is located at the center of a tetrahedron and straight lines (bonds) through the sites of the tetrahedron point towards four nearest-neighbor oxygen atoms. Hydrogen atoms are distributed according to the ice rules: (A) There is one hydrogen atom on each bond (then called hydrogen bond). (B) There are two hydrogen atoms near each oxygen atom (these three atoms constitute a water molecule).

By experimental discovery it was found that ice has a residual entropy<sup>4</sup>  $S_0 = k \ln(W) > 0$  for temperature  $T \rightarrow 0$  and moderate relaxation times. Here  $W$  is the number of configurations for  $N$  molecules. Subsequently Linus Pauling<sup>5</sup> derived estimates of  $W = (W_1)^N$  by two approximate methods based on the ice rules, obtaining

$$W_1^{\text{Pauling}} = 3/2 \tag{1}$$

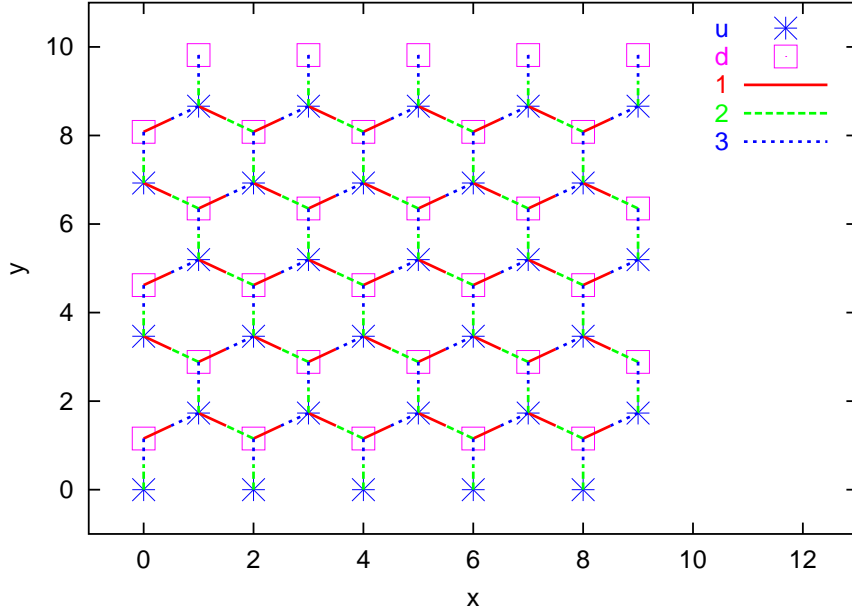


Figure 1. Lattice structure of one layer of ice I. The up (u) sites are at  $z = 1/\sqrt{24}$  and the down (d) sites at  $z = -1/\sqrt{24}$ . The dimensions are explained in Ref. [1]. For each site three of its four pointers to nearest neighbor sites are shown.

in each case. Twenty five years later it was shown by Onsager and Dupuis that  $W_1 = 1.5$  is in fact only a lower bound. Onsager's student Nagle used a series expansion method to derive the estimate<sup>6</sup>

$$W_1^{\text{Nagle}} = 1.50685 (15). \quad (2)$$

The error bar is not statistical but reflects higher order corrections of the expansion, which are not entirely under control. The only independent theoretical value appears to be one for cubic ice, which is obtained by numerical integration of Monte Carlo data<sup>7</sup> and in good agreement with Nagle.

### 3 Multicanonical Calculation

Our calculations are based on two simple statistical models. Each model is defined on the hexagonal lattice of Fig. 1. In the first model, called 6-state H<sub>2</sub>O molecule model, ice rule (B) is always enforced and we allow for six distinct orientations of each H<sub>2</sub>O molecule. Its energy is defined by

$$E = - \sum_b h(b, s_b^1, s_b^2). \quad (3)$$

Here, the sum is over all bonds  $b$  of the lattice and ( $s_b^1$  and  $s_b^2$  indicate the dependence on the states of the two  $\text{H}_2\text{O}$  molecules, which are connected by the bond)

$$h(b, s_b^1, s_b^2) = \begin{cases} 1 & \text{for a hydrogen bond,} \\ 0 & \text{otherwise.} \end{cases} \quad (4)$$

In the second model, called 2-state H-bond model, ice rule (A) is always enforced and we allow for two positions of each hydrogen nucleus on a bond. The energy is defined by

$$E = - \sum_s f(s, b_s^1, b_s^2, b_s^3, b_s^4), \quad (5)$$

where the sum is over all sites (oxygen atoms) of the lattice and  $f$  is given by

$$f(s, b_s^1, b_s^2, b_s^3, b_s^4) = \begin{cases} 2 & \text{for two hydrogen nuclei close to } s, \\ 1 & \text{for one or three hydrogen nuclei close to } s, \\ 0 & \text{for zero or four hydrogen nuclei close to } s. \end{cases} \quad (6)$$

The groundstates of each model fulfill the ice rules. At  $\beta = 0$  the number of configurations is  $6^N$  for the 6-state model and  $2^{2N}$  for the 2-state model. Because the normalizations at  $\beta = 0$  are known, multicanonical (MUCA) simulations allow us in either case to estimate the number of groundstate configurations<sup>8</sup>. Using periodic boundary conditions (BCs), our simulations are based on a lattice construction similar to that set up in Ref. [9] for Potts model simulations, while the thermodynamic properties found are entirely different from those of Potts models.

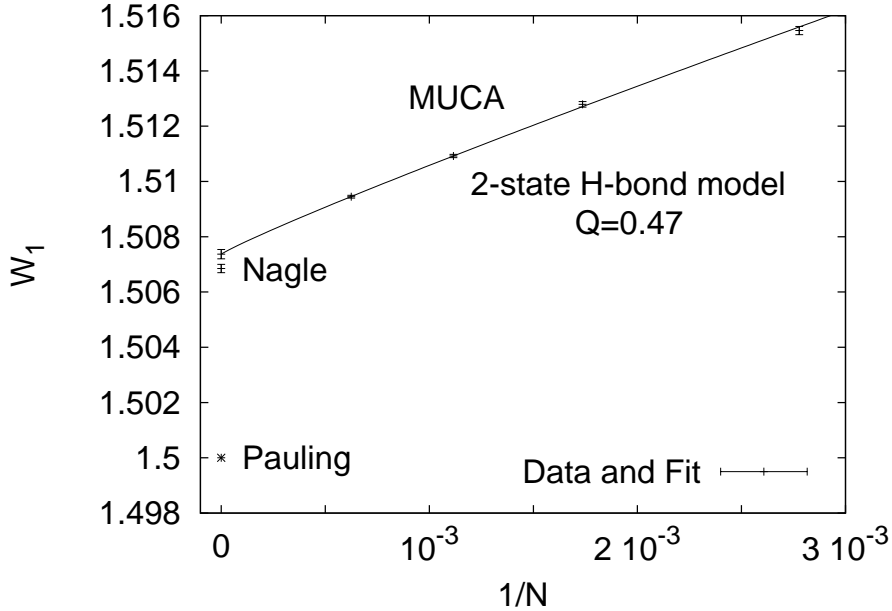


Figure 2. Fit and estimates of  $W_1$ .

The results from the 2-state model are more accurate than those from the 6-state model. Apparently, the reason is that the  $\beta = 0$  entropy of the 2-state model is smaller. In Fig. 2 a fit for the data of the 2-state H-bond model to the form

$$W_1(x) = W_1(0) + a_1 x^\theta, \quad x = 1/N \quad (7)$$

with  $\theta = 0.920$  (25) is shown together with the estimates by Nagle and Pauling. The goodness of fit (chapter 2.8 of Ref. [9]) is  $Q = 0.47$  as given in the figure. That we have  $\theta \neq 1$  reflects bond correlations in the groundstate ensemble.

Combining this fit with that from the 6-state model leads to our final estimate

$$W_1^{\text{MUCA}} = 1.50738 \quad (16).$$

The difference with the estimate of Nagle is 0.035% of  $W_1$ . However, the Gaussian difference test<sup>9</sup> between the two estimates yields  $Q = 0.016$ . As the error bar in (8) covers only statistical and no systematic errors due to finite size corrections from larger lattices, the small discrepancy may be explained in this way. The precision of experimental work<sup>10</sup> has remained insufficient to resolve the difference with Pauling's original estimates and its theoretical improvement. Experimental verification of the difference would be an outstanding confirmation of structures imposed by the ice rules.

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