Numerical calculation of the combinatorial entropy of partially ordered ice

Bernd A. Berg\textsuperscript{a,b,c,[1]} and Wei Yang\textsuperscript{a,d,e}

\textsuperscript{a) School of Computational Science, Florida State University, Tallahassee, FL 32306-4120, USA}
\textsuperscript{b) Department of Physics, Florida State University, Tallahassee, FL 32306-4350, USA}
\textsuperscript{c) John von Neumann-Institut für Computing, Forschungszentrum Jülich, 52425 Jülich, Germany}
\textsuperscript{d) Department for Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA}
\textsuperscript{e) Institute for Molecular Biophysics, Florida State University, Tallahassee, FL 32306-4380, USA}

(August 16, 2007)

Using a one-parameter case as an example, we demonstrate that multicanonical simulations allow for accurate estimates of the residual combinatorial entropy of partially ordered ice. For the considered case corrections to an (approximate) analytical formula are found to be small, never exceeding 0.5%.

The method allows one as well to calculate combinatorial entropies for many other systems.

I. INTRODUCTION

After the discovery of the hydrogen bond it was recognized that the unusual properties of water and ice owe their existence to a combination of strong directional polar interactions and a network of specifically arranged hydrogen bonds\textsuperscript{2–4}. By experimental discovery\textsuperscript{5} it was found that ice I (ordinary ice) has in the zero temperature limit\textsuperscript{6} a residual entropy \( S = k \ln(W_1) > 0 \) where \( W_1 \) is the number of configurations per molecule. Subsequently Linus Pauling\textsuperscript{7} based the estimate \( W_1^{Pauling} = 3/2 \) on the ice rules:

1. There is one hydrogen atom on each bond (then called hydrogen bond).
2. There are two hydrogen atoms near each oxygen atom (these three atoms constitute a water molecule).

Pauling’s combinatorial estimate turned out to be in excellent agreement with subsequent refined experimental measurements\textsuperscript{8}. This may be a reason, why it took 25 years until Onsager and Dupuis\textsuperscript{9} pointed out that \( W_1 = 1.5 \) is only a lower bound, because Pauling’s arguments for disordered ice omits correlations induced by closed loops which are encountered when one requires fulfillment of the ice rules for all molecules. Subsequently Nagle\textsuperscript{10} used a series expansion method to derive the estimate \( W_1^{Nagle} = 1.50685 (15) \), where the error bar is not statistical but reflects higher order corrections of the expansion, which are not rigorously under control.

Groundstate entropy calculations by means of multicanonical (MUCA)\textsuperscript{11} Markov chain Monte Carlo (MCMC) simulations were pioneered by Berg and Celik\textsuperscript{12}. In a recent paper\textsuperscript{13} it was shown that this approach allows rather easily for an accurate finite-size scaling estimate of the residual entropy of ice I, \( W_1^{MUCA} = 1.50738 (16) \), where the error bar is now purely statistical. In view of eventual higher order finite size corrections, which are not included in the MUCA error bar, there is satisfactory agreement with Nagle\textsuperscript{10}.

With the advent of neutron scattering technology, it became possible to measure the actual hydrogen arrangements. Besides fully ordered and disordered ice phases, there is also evidence for partially ordered ice\textsuperscript{14–16}. Based on theoretical groundwork laid by Takagi\textsuperscript{17} and Minagawa\textsuperscript{18}, an extension of Pauling’s results to partially ordered ice was derived by Howe and Whitworth\textsuperscript{19} and greatly generalized by MacDowell et al.\textsuperscript{20}. Comparisons with neutron scattering results are also made in Ref.\textsuperscript{20}. Besides, the combinatorial residual entropy needs to be taken into account when one considers the phases of simple models for water/ice\textsuperscript{21}.

As for disordered ice in Pauling’s work, correlations are neglected in the analytical estimates\textsuperscript{18–20} of the residual entropy of partially ordered ice. The magnitude of corrections is largely unknown. For instance, before the paper by Howe and Whitworth an erroneous equation was used, which was off by up to more than 50% for the entropy per molecule. Nagle’s method appears to be too complicated for these situations. In this article we generalize the MUCA approach of Ref.\textsuperscript{13} to include partial order and calculate numerical corrections to the formula of Howe and Whitworth\textsuperscript{19}. Our method is presented in section II, details of our numerical implementation are given in section III, followed by the entropy estimates in section IV. Summary and conclusion with an outlook on other applications are given in the final section V.

II. THE METHOD AND PRELIMINARIES

As in\textsuperscript{13} we confine our interest to the hexagonal crystal structure of which the \( z = 0 \) layer is is depicted in Fig. 1. 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. Distances in this figure are given in units of a lattice constant \( a (a = 1 \) in the figure\textsuperscript{, which is chosen to be the edge length of the tetrahedra. The distance from the center of a tetrahedron to one of its sites is \( \sqrt{3/8} a \) and, hence, the oxygen-oxygen distance is \( \sqrt{3/2} a \).

This is not the conventional crystallographic definition, but convenient for setting up the computer program (see below). For each molecule shown one of the surface triangles of its tetrahedron is placed in the \( xy \)-plane. The molecules labeled by \( u \) (up) are then at \( z = a/\sqrt{24} \) above,
of configurations which fulfill the ice rules is given by
denote the hydrogen positions in this configuration by
This serves as our ordered reference configuration and we
and the molecules labeled by d (down) at \( z = -a/\sqrt{24} \)
below the xy-plane, at the centers of their tetrahedra.
We define an ordered reference configuration, which
fulfills the ice rules, by arranging the hydrogen atoms on
the bonds in the following way:
1. For \( z = i_z 4a/\sqrt{6} \) and \( i_z \) even (as shown in Fig. 1
for \( i_z = 0 \)): For the up oxygens put the hydrogens
on bonds 2 and 4, for the down oxygens put them
on bonds 1 and 2.
2. For \( z = i_z 4a/\sqrt{6} \) and \( i_z \) odd (as shown in Fig. 2 for
\( i_z = 1 \)): For the up oxygens put the hydrogens
on bonds 3 and 4, for the down oxygens put them
on bonds 1 and 3.
This serves as our ordered reference configuration and we
denote the hydrogen positions in this configuration by \( r_h \).
Following\(^{19}\) we denote the fraction of Hydrogen positions,
which agree with the reference configuration by \( f \).
The analytical approximation\(^{22}\) for the residual entropy
of configurations which fulfill the ice rules is given by
\[
W_1^f(f) = \frac{f^2 f(1-f)^2(1-f)2^3(1-p)}{p^2(1+p-2f)(1+f-2f)^2(1+f-2f)^2} \tag{1}
\]
with \( p = f - 2(1 - \sqrt{3f^2 - 3f + 1})/3 \). The probability
that the position of a hydrogen atom agrees by chance
with the one in the reference configuration is 1/2 for
disordered ice and Eq. (1) reproduces Pauling’s result
for this case, \( W_1^f(1/2) = 1.5 \). For \( f = 1 \) all hydrogen
positions agree with the reference configuration, and
\( W_1^f(1) = 1 \). Correlations due to closed loops of hydrogen
bonds are neglected in the arguments, which lead to
Eq. (1). Here they are included numerically.

The residual entropy of ice I was calculated in\(^{13}\) by
performing MUCA simulations for two discrete statistical
models, which were constructed to satisfy the following
properties \( [\beta = 1/(kT)] \):
1. Their total number states (as sampled at \( \beta = 0 \)) is
known.
2. Generically each model fulfills one of the ice rules,
but not the other.
3. In their energy groundstates (reached at large
enough \( \beta \)) each model fulfills both ice rules.
The model, which fulfills ice rule 2 generically is called
6-state \( H_2O \) molecule model and has for \( N \) molecules
a total number of \( 6^N \) states. The model, which fulfills
ice rule 1 generically is called 2-state H-bond model and
has \( 2^{2N} = 4^N \) states. Both systems have similarities
with Potts models, so that the lattice labeling outlined by
Fig. 1 and 2 allows one\(^{23}\) to employ simulation methods
to do the same for the 6-state model is straightforward, but the
simulations are expected to be less efficient.
In the 2-state H-bond model\(^{13}\) we allow two positions
for each hydrogen nucleus on its bond (close to either
one of the two oxygen atoms, which are connected by the
bond). The energy is defined by
\[
E = - \sum_s f_s(s, b_1^s, b_2^s, b_3^s, b_4^s) \tag{2}
\]
where the sum is over all sites (oxygen atoms) of the
lattice and the function \( f_s \) is given by
\[ f_s(b_1, b_2, b_3, b_4) = \begin{cases} 2 & \text{for two hydrogen nuclei close to } s, \\ 1 & \text{for one or three hydrogen nuclei close to } s, \\ 0 & \text{for zero or four hydrogen nuclei close to } s. \end{cases} \] (3)

We consider now an additional term

\[ Q = \sum_b \delta_{x_b, r_b}, \] (4)

which is the overlap of the actual positions \( x_b \) of the hydrogen atoms on the bonds \( b \) with the reference positions \( r_b \). The canonical ensemble of the extended model is defined by the Gibbs-Boltzmann weights

\[ \exp(-\beta E + h Q). \] (5)

The coupling parameter \( h \) plays pretty much the same role as an external magnetic field does for the Ising model.

At \( \beta = 0 \) the expectation value of the overlap per link is readily computed to be \[ \langle q \rangle_{\beta=0} = \langle q \rangle_0 = \langle Q \rangle_0 / (2N) = \frac{e^h}{e^h + 1}, \] (6)

and the number of states for which the positions of \( K \) hydrogen atoms agree with those in the reference configuration is given by the binomial factor

\[ B(2N, K) = \binom{2N}{K} = \frac{(2N)!}{(2N-K)! K!}. \] (7)

The fraction of correct bonds with respect to the reference configuration is given by \( f = K/(2N) \). For \( K \approx \langle Q \rangle_0 \) there will be sufficient statistics so that reweighting of the simulation to \( \beta = 0 \) can be used to normalize the spectral density via the binomial distribution (7). For that purpose it is convenient to choose \( h \) so that \( \langle Q \rangle_0 \) becomes an integer. Assuming that this is done, we take \( K = \langle Q \rangle_0 \) in the following.

Using a MUCA weight function

\[ W_h^{MUCA} = e^{hQ} W^{MUCA}(E), \] (8)

we can connect the \( \beta = 0 \) region, for which the numbers of states are known, to the groundstate \( E_g = -2N \), for which both ice rules are satisfied, and estimate the number of states \( n(Q, E_g) \) for \( Q \) values encountered in the groundstates with sufficient statistics in \( H^{MUCA}(Q, E_g) \) by reweighting:

\[ \frac{n(Q, E_g)}{B(2N, K)} = \frac{H^{MUCA}(Q, E_g)/w^{MUCA}_h(Q, E_g)}{\sum_E H^{MUCA}(K, E)/w^{MUCA}_h(K, E)}. \] (9)

Here \( H^{MUCA}(Q, E_g) \) is the overlap histogram sampled by the multicanonical updating in the groundstate ensemble and \( H^{MUCA}(K, E) \) is the energy histogram sampled for the fixed value \( Q = K \). The reweighting is to \( \beta = 0 \) with \( h \) unchanged. As the MUCA weights (8) factorize, the storage requirements are of order \( N \) (not \( N^2 \)).

To obtain a working estimate (see chapter 5.1 of \cite{24}) of the MUCA weights we use the Wang-Landau recursion \cite{26} as explained in the next section. The numerical quantities encountered in Eq. (9) are often so large that they are not allowed by a conventional programing language like Fortran’ 77 in Real*8 precision. This is overcome by using consistently logarithmic coding for which technical detail are explained in \cite{24}.

The actually covered \( Q \) range in the groundstate ensemble depends on \( h \). Increasing \( h \) will shift the range to higher \( Q \) values. Doing so in small steps, and repeating the simulation each time,

\[ W_1(f) = \frac{1}{N} \ln[n(Q, E_g)] \] (10)

is obtained for all desired values of \( f = Q/(2N) \).

III. NUMERICAL IMPLEMENTATION

Using periodic boundary conditions (BCs), our simulations are based on the lattice construction of Fig. 1 and 2. Following closely the method outlined in chapter 3.1.1 of \cite{24} four index pointers from each molecule to its nearest neighbor molecules are constructed along the directions of the bonds as outlined in Fig. 1. The lattice contains then \( N = n_x n_y n_z \) molecules, where \( n_x, n_y, \) and \( n_z \) are the numbers of sites along the \( x, y, \) and \( z \) axes, respectively; \( i_x = 0, \ldots, n_x-1, \) \( i_y = 0, \ldots, n_y-1, \) and \( i_z = 0, \ldots, n_z-1. \) The periodic BCs restrict the allowed values of \( n_x, n_y, \) and \( n_z \) to \( n_x = 1, 2, 3, \ldots, n_y = 4, 8, 12, \ldots, n_z = 2, 4, 6, \ldots. \) Otherwise the geometry does not close properly. With the inter-site distance \( r_{OO} = 2.764 \) Å from Ref.4, the physical size of the box is obtained by putting the lattice constant to \( a = 2.257 \) Å, and the physical dimensions of the box are calculated to be \( B_x = 2n_x a, B_y = (n_y \sqrt{3}/2) a, B_z = (n_z 4/\sqrt{6}) a. \) In our choices of \( n_x, n_y, \) and \( n_z \) values we aim within reasonable limitations at symmetrically sized boxes.

The \( h \) values at which the simulations are performed are determined from initially proposed \( h_0 \) values in the following way: From (6) we calculate \( \langle Q \rangle_0(h_0) \) and determine the closest integer \( K. \) Then the relation (6) is inverted to find the value \( h \) for which the relation \( K = \langle Q \rangle_0(h) \) holds. All our simulations use \( h_0 = 0.1, \)
0.2, 0.3, 0.4, 0.5, and 0.6. Additional $h_0$-values are listed in Table I, which gives an overview of our lattices and MUCA production statistics. The statistics is in sweeps (i.e., updates per molecule) and repeated 32 times. For each of the 32 bins histograms are recorded. To calculate error bars they are transformed into jackknife bins along the lines of chapter 5.1 of Ref. 24.

All calculations can be done by running one 2 GHz PC for about four weeks. As the runs at different parameter values are independent, the real time is considerably shorter when several PCs are available. The Wang-Landau recursion consumed never more than a few percent of a run. Cycling and a flatness of $H_{\text{min}}/H_{\text{max}} > 0.5$ was considered sufficient for iterating the Wang-Landau refinement factor. Such a crude flatness is sufficient when one does not intend to converge into a reliable estimate of the spectral density, as originally proposed in Ref. 26, but aims only at obtaining a working estimate of the MUCA weights. To use the Wang-Landau algorithm in this ways as a recursion for the first part of a MUCA simulation was suggested in Ref. 27.

For the $h_0 = 0.5$ run on our largest lattice the MUCA energy histogram of the production part is shown in Fig. 3. The value $h_0 = 0.5$ converts for this lattice to $h = 0.500173$ so that $\langle Q \rangle_0 = 1992 = K$. In Fig. 4 the energy histogram is restricted to entries for which $Q = K = 1992$ holds. It is this histogram, which is reweighted to $\beta = 0$ and then normalized, so that its sum over energies, the denominator of the right-hand side of (9), matches the binomial coefficient (7). To monitor the entire $(Q, E)$ distribution a histogram array $H_{\text{MUCA}}(Q, E)$ of size $N^2$ would be needed. In our simulations we avoided arrays of size $N^2$ by focusing reweighting on one selected $Q$ value, such that an array of size $N$ is sufficient. However, this restriction to a microcanonical state was possibly not a wise decision. Compared to the analysis of Ref. 23 we find spurious fluctuations and increased error bars. Likely that could be smoothed out when the full array is available, which would for our largest lattice still fit into the memory of a PC, and in the analysis allow to sum over $Q$ for the normalization. As this would require to repeat all simulations, we cannot pursue this issue further at this point.

The overlap histogram as measured in the corresponding groundstate distribution ($E_g = -2N = -3200$ for this lattice) is depicted in Fig. 5. Properly normalized the number of configuration per molecule follows from this histogram by using Eq. (9) for $f$ values which are sampled with sufficient statistics. The cut-off values for sufficient statistics for $f$ were determined from one half of the maximum value of $H_{\text{MUCA}} = \max_f [H_{\text{MUCA}}(f, E_g)]$ in the following way:

$$f_1 \leq f \leq f_2$$

with

$$f_1 = \min_f [f; H_{\text{MUCA}}(f, E_g) \geq H_{\text{MUCA}}/2],$$

$$f_2 = \max_f [f; H_{\text{MUCA}}(f, E_g) \leq H_{\text{MUCA}}/2].$$
\[ f_2 = \max_f [f; H_{\text{MUCA}}^\text{MUCA}(f, E_g) \geq H_{\text{max}}^\text{MUCA}/2] \]  

(13)

**IV. ENTROPY ESTIMATES**

Fig. 6 compares the approximation \( W_1^0(f) \) of Eq. (1) with the estimates from our smallest lattice and Fig. 7 with the estimates from our largest lattice. The differences between the numerical results and the analytical approximation are in both cases small, but well outside the range of the numerical error bars. The latter point is demonstrated in Fig. 8, where we plot

\[ \Delta W_1(f) = W_1^{\text{MUCA}}(f; N) - W_1^0(f) \]  

(14)

for \( N = 128 \) and 1600. A feature of Figs. 7 and 8 is that only patches of \( f \) are covered by the \( N = 1600 \) data. Each \( h_0 \) value defines such a patch by means of Eq. (11).

**TABLE II.** Infinite volume extrapolations of \( W_1(f) \) and \( \Delta W_1(f) \) (the error bars of both quantities are the same).

| \( f \)  | \( W_1(f) \)   | \( \Delta W_1(f) \) | \( f \)  | \( W_1(f) \)   | \( \Delta W_1(f) \) |
|-------|-------------|-----------------|-------|-------------|-----------------|
| 0.50  | 1.50620 (32)| 0.00620         | 0.80  | 1.27729 (26)| 0.00350         |
| 0.65  | 1.44166 (26)| 0.00587         | 0.93  | 1.09849 (20)| 0.00085         |

The one corresponding to \( h_0 = 0.5 \) can be read off from Fig. 5: \( 0.7775 \leq f \leq 0.8075 \). By adding simulations for further \( h_0 \) values the uncovered \( f \) regions can be filled. We abstained from doing this, because it is only of academic interest. Our corrections to the analytical approximation (1) show that this approximation is sufficiently accurate for practical applications, because error bars of experimental entropy estimates (e.g.,\(^{28}\)) are much larger than the correction to (1).

Fig. 8 shows also the finite size corrections to \( W_1^{\text{MUCA}}(f, N) \) encountered when moving from \( N = 128 \) to \( N = 1600 \) molecules. These estimates together with those from the \( N = 360, 576 \) and 896 lattices allow one to perform infinite volume extrapolations \( W_1(f) = \lim_{N \to \infty} W_1^{\text{MUCA}}(f, N) \). As in Ref.\(^{13}\) for the case \( f = 0.5 \) we fit to the form

\[ W_1^{\text{MUCA}}(f, N) = W_1(f) + a N^{-\theta} . \]  

(15)

With the present data the 3-parameter fits turn out to be unstable and we reduce them to stable 2-parameter fits by using \( \theta = 0.92 \) from\(^{13}\) on input. For four \( f \) values the thus obtained infinite volume extrapolations \( W_1(f) \) are collected in table II (error bars are given in parenthesis).

For \( f = 0.5 \) the fit is shown in Fig. 9. For the other \( f \) values the shapes of the fits are quite similar. For \( f = 0.93 \) the \( N = 128 \) estimate cannot be included, because it would spoil the consistency of the fit. Remarkable is that finite size corrections for our microcanonically normalized data in Fig. 9 are much smaller than those in
the corresponding figure of Ref.\textsuperscript{13}, where a canonical normalization (summed over all $Q$ values) of the density of states was used. Further the sign of the correction is opposite to that Ref.\textsuperscript{13}. As before, the present estimate is in good agreement with Nagle\textsuperscript{10}, undershooting now his value slightly, whereas the value of\textsuperscript{13} is overshooting Nagle’s estimate somewhat.

The $W_1(f)$ estimates together with their error bars are also plotted in Fig. 8. Besides for $f = 0.93$ they are only visible in the color version of this figure, because they fall within the error bars of the $N = 1600$ data. Interestingly the $f = 0.93$ extrapolation is considerably larger than the $N = 1600$ estimate and the sign of the correction with respect to the approximation $W_0^0(f)$ (1) flipped. While on all our lattices we have for sufficiently large $f$ a crossover of the correction from positive to negative, this feature may disappear in the $N \rightarrow \infty$ limit, so that the corrections are ultimately all positive. To illustrate lattice artifacts in the $f \rightarrow 1$ limit we plot in Fig. 10 the $\Delta W_1(f)$ values for $f \geq 0.8$. It is clear that the closest values to $f = 1$ reflect lattice artifacts and should not be used for the $N \rightarrow \infty$ approximation. Still estimates for all values of $f$ can be obtained, because the $f$ range of the artifacts shrinks $\sim 1/N$.

\section{V. SUMMARY AND CONCLUSIONS}

Our main finding is that the corrections to the analytical approximation (1) are small. As illustrated in table II, they are never larger than Nagle’s\textsuperscript{10} already small correction to Pauling’s\textsuperscript{7} value $W_1^\text{Pauling} = 1.5$. For the entropy this translates into

$$\Delta S < \ln \left( W_1^\text{Nagle} \right) - \ln \left( W_1^\text{Pauling} \right) \approx 0.00685 \frac{1}{1.5} \approx 0.46\% .$$

\begin{equation}
(16)
\end{equation}

This is beyond the accuracy of nowadays measurements. But who knows about twenty years ahead? The verification of the correctness of predicted correlations beyond the Pauling-like approximation would be an ultimate confirmation of our understanding of ice.

It is straightforward to include additional parameters in our approach, as introduced by the equations of MacDowell et al.\textsuperscript{20}. Each choice of parameters requires a simulational effort similar to that of Ref.\textsuperscript{13}. So it would be tedious to map out corrections for the entire parameter space. In particular, we did not pursue this further, as due to our present results one may conjecture that these corrections are also small. If one likes to perform a check for a special choice of parameters, for instance because ongoing experimental measurements, the details given in our paper should allow researchers to set up the necessary simulations.

Finally, there may well be applications of our approach to systems for which corrections to existing approximations are not be small. For example, the method allows one to calculate the combinatorial entropy of small clusters of hydrogen bonds directly. They are observed as formation of ice layers in nanotubes\textsuperscript{29} and expected to be of importance in the interaction of water with peptides, proteins and other biomolecules. Through a better understanding of their entropy insights derived from the study of ice may well lead to a better understanding of models, which have primarily been constructed to reflect interactions of water at room temperature (see\textsuperscript{21} for an overview).

\section{ACKNOWLEDGMENTS}

Bernd Berg would like to thank Uli Hansmann and the computational biophysics group at the John von Neumann Institut für Computing for their kind hospitality.
during his stay at the Forschungszentrum Jülich.

1 Correspondence should be addressed to berg@scs.fsu.edu.
2 J.D. Bernal and R.H. Fowler, J. Chem. Phys. 1, 515 (1933).
3 D. Eisenberg and W. Kauzmann, The Structure and Properties of Water, Oxford University Press, Oxford 1969.
4 V.F. Petrenko and R.W. Whitworth, Physics of Ice, Oxford University Press, Oxford 1999.
5 W.F. Giauque and M. Ashley, Phys. Rev. 43, 81 (1933).
6 A unique groundstate is expected if one allows for, possibly, astronomically long relaxation times. Therefore, the residual entropy of ice is not supposed to violate the third law of thermodynamics.
7 L. Pauling, J. Am. Chem. Soc. 57, 2680 (1935).
8 W.F. Giauque and J.W. Stout, J. Am. Chem. Soc. 58, 1144 (1936).
9 L. Onsager and M. Dupuis, Re. Scu. Int. Fis. ‘Enrico Fermi’ 10, 294 (1960).
10 J.F. Nagle, J. Math. Phys. 7, 1484 (1966).
11 B.A. Berg and T. Neuhaus, Phys. Rev. Lett. 68, 9 (1992).
12 B.A. Berg and T. Celik, Phys. Rev. Lett. 69, 2292 (1992).
13 B.A. Berg, C. Muguruma and Y. Okamoto, Phys. Rev. B 75, 092202 (2007).
14 S.J. La Placa, W.C. Hamilton, B. Kamb, and A. Prakash, J. Chem. Phys. 58, 567 (1973).
15 J.D. Londono, W.F. Kuhs, and J.L. Finney, J. Chem. Phys. 98, 4878 (1993).
16 J.D. Lobban, J.L. Finney, and W.F. Kuhs, J. Chem. Phys. 112, 7169 (2000).
17 Y. Takagi, J. Phys. Soc. Jpn. 3, 271 (1948).
18 I. Minagawa, J. Phys. Soc. Jpn. 50, 3699 (1981).
19 R. Howe and R.W. Whitworth, J. Chem. Phys. 86, 6443 (1987).
20 L.G. MacDowell, E. Sanz, C. Vega, and J.L.F. Abascal, J. Chem. Phys. 121, 10145 (2004).
21 C. Vega, E. Sanz, and J.L.F. Abascal, J. Chem. Phys. 122, 114507 (2005).
22 \[ W_1 = \Omega^{1/N} \] with \( \Omega \) and \( p \) given by Eq. (6) and (7) of\cite{23}.
23 B.A. Berg, 2005 (unpublished).
24 B.A. Berg, Markov Chain Monte Carlo Simulations and Their Statistical Analysis, World Scientific, Singapore, 2004.
25 This is Eq. (3.70) of\cite{24} for \( q = 2 \) and \( h = 2H \). Compare also the simulation of chapter 3.3.4.6.
26 F. Wang and D.P. Landau, Phys. Rev. Lett 86, 2050 (2001).
27 B.A. Berg, Comp. Phys. Commun. 153, 397 (2003).
28 O. Haida, T. Matsuo, H. Suga, and S. Seki, J. Chem. Thermodynamics 6, 815 (1974).
29 N. Giovambattista, P.J. Rossky, and P.G. Debenedetti, Phys. Rev. E 73, 041604 (2006).