GenIce: Hydrogen-Disordered Ice Generator
Masakazu Matsumoto, Takuma Yagasaki, and Hideki Tanaka

GenIce is an efficient and user-friendly tool to generate hydrogen-disordered ice structures. It makes ice and clathrate hydrate structures in various file formats. More than 100 kinds of structures are preset. Users can install their own crystal structures, guest molecules, and file formats as plugins. The algorithm certifies that the generated structures are completely randomized hydrogen-disordered networks obeying the ice rule with zero net polarization. © 2017 The Authors. Journal of Computational Chemistry Published by Wiley Periodicals, Inc.

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Methods
Stillinger first introduced an algorithm for making hydrogen-disordered ice structures. The initial structure is a hydrogen-ordered ice with no net polarization. The algorithm searches for unidirectional cyclic paths (homodromic cycles) of hydrogen bonds by random walk on the network and introduces randomness to the network by reversing the cyclic paths one after another. In this algorithm, the search stops when the random walk intersects its own trajectory. This makes a small cyclic path and, therefore, the algorithm is called the short-loop algorithm.

Barkema proposed a different method in this algorithm, first, a structure that completely satisfies the ice rule is prepared, and a $H_3O^+$ ion and an OH$^-$ ion are generated by moving a hydrogen atom along the hydrogen bond. Next, a hydrogen atom of the $H_3O^+$ ion is moved along the hydrogen bond to transfer the protonic defect by the Grotthuss mechanism. The random proton transfer is continued until the protonic defect reaches the OH$^-$ ion generated initially. Since a long distance transfer of $H_3O^+$ is required to annihilate the defect pair, this algorithm is called the long-loop algorithm.

Both of these algorithms start from a hydrogen-ordered structure and invert the orientation of the hydrogen bonds randomly to obtain a hydrogen-disordered structure. These methods may yield a nonisotropic and nonuniform structure due to improper selections of the initial configuration and insufficient randomization. Therefore, separate tests are necessary to certify that the generated structure is indeed sufficiently disordered.

Unlike the conventional methods, GenIce uses totally randomized structures as initial states. An initial random structure is converted so that it obeys the ice rule (step 1). Then,
the net polarization is removed by an efficient algorithm which can be used for large systems (step 2).

**Step 1: Ice rule**

We first generate a four-regular undirected graph based on the hydrogen bond network topology of the ice phase, and make a directed graph from the undirected graph by replacing undirected edges with randomly oriented directed edges. Since the obtained randomly directed graph does not satisfy the ice rule, defects are purged by the following algorithm.

1. Push all vertices that do not have two incoming bonds, which correspond to defects in ice, into a FIFO (first-in, first-out) queue.
2. Pop a vertex from the queue and count the number of incoming bonds for the vertex, \( N_i \).
3. If \( N_i \) is less than 2, choose an outgoing edge of the vertex randomly. If \( N_i \) is greater than 2, choose an incoming edge of the vertex randomly. Otherwise, go to 7.
4. Invert the chosen edge.
5. If the original vertex is still a defect, push it back to the queue.
6. If the neighbor vertex becomes a defect by the inversion, push it to the queue.
7. Go to 2 unless the queue is empty.

Essentially, this algorithm is similar to the procedure proposed by Buch.\(^{[14]}\)

**Step 2: Removal of the net polarization**

The procedure in step 1 certifies the uniformity of the obtained hydrogen bond network. However, usually, there remains a nonzero net polarization in the resultant hydrogen bond network. A component of the net dipole vector parallel to the direction of one of the primitive translational vectors, \( a \), \( b \), or \( c \), is always an integral multiple of a certain constant value for the hydrogen bond network that obeys the ice rule under periodic boundary conditions, and the polarization can be removed only by inverting homodromic cycles of hydrogen bonds spanning the cell. Random inversion of homodromic cycles is a common method to introduce randomness to hydrogen bond networks so as not to violate the ice rule. However, a randomly generated homodromic cycle hardly spans the cell neither by the short- nor by the long-loop algorithm when the system is large. Therefore, more efficient algorithm is necessary to find cell-spanning homodromic cycles.

In GenIce, the following algorithm is employed to remove the net polarization efficiently. Here, we explain the way to reduce the dipole moment along the \( c \) axis as an example.

1. Choose a vertex of the network, say \( i \), randomly.
2. When the fractional coordinate of a given point in the cell is written as \((a,b,c)\), the \( c \)-antipode of the given point is \((a,b,c+0.5)\). Find the vertex, say \( j \), that is closest to the \( c \)-antipode of \( i \).
3. The shortest path from \( i \) to \( j \) in the directed graph is obtained by Dijkstra’s algorithm.\(^{[15]}\)
4. The shortest path from \( j \) to \( i \) is obtained in the same manner.
5. Merge the two paths to make a cycle. It can be a homodromic cycle spanning the cell along the \( c \)-axis.
6. If the polarization along the \( c \) axis decreases by inverting the homodromic cycle, invert it. Otherwise, go back to 1.
7. Repeat inversion of homodromic cycles until the net polarization vanishes.

The procedure is applied to the \( a \), \( b \), and \( c \) axes of the cell independently. The processing time depends on the initial

| Symbol | Description |
|--------|-------------|
| 1h, 1c | Most popular ice I (hexagonal or cubic). |
| 1 | Hydrogen-ordered ice II. |
| 20 | Hypothetical hydrogen-disordered counterpart of ice II.\(^{[16]}\) |
| 2, 3, 4, 5, 6, 7, 12 | Conventional high-pressure ices III, IV, V, VI, VII, and XII.\(^{[17]}\) |
| 16 | Negative-pressure ice XVI.\(^{[18]}\) |
| 17 | Negative-pressure ice XVII.\(^{[19]}\) |
| 0 | Hypothetical ice “0” \(^{[18]}\) |
| 1 | Hypothetical ice “1” \(^{[18]}\) |
| C0-II | Hypothetical ice “C0-II” \(^{[18]}\) |
| C1 | Hypothetical ice “C1” \(^{[18]}\) |
| C2 | Hypothetical ice “C2” \(^{[18]}\) |
| Cr | Hypothetical ice “Cr” \(^{[18]}\) |
| MTN | Hypothetical ice “MTN” \(^{[18]}\) |
| RHO | Hypothetical ice “RHO” \(^{[18]}\) |
| FAU | Hypothetical ice “FAU” \(^{[18]}\) |
| CRN1, CRN2, CRN3 | Hypothetical ice “CRN1”, “CRN2”, “CRN3” \(^{[18]}\) |
| Struct01 – Struct84 | Hypothetical ice “Struct01” to “Struct84” \(^{[18]}\) |
| A15, sigma, Z | Hypothetical ice “A15”, “sigma”, “Z” \(^{[18]}\) |
| M12 | Hypothetical ice “M12” \(^{[18]}\) |
| C20 | Hypothetical ice “C20” \(^{[18]}\) |
| C1 | Hypothetical ice “C1” \(^{[18]}\) |
| C0-II | Hypothetical ice “C0-II” \(^{[18]}\) |
| T | Hypothetical ice “T” \(^{[18]}\) |

It will be updated over time (see the latest online manual). Ice names with double quotations have not been verified experimentally.
configuration, but it is almost linear against the number of molecules in the simulation cell for practical system sizes (up to the tens of thousands of molecules).

**Typical usage of GenIce**

To create a $3 \times 3 \times 3$ unit cell replica of hydrogen-disordered ice IV (4) in the Gromacs format with the TIP4P water model, enter the following command:

```
genice 4 --water tip4p --rep 3 3 3 > ice4.gro
```

See Table 1 for the preset ice structures. Note that the same structure may have different names in different structure frameworks. They are listed in Table 2. One can make a new ice structure by preparing a lattice plugin.

Different hydrogen order can be obtained by specifying the random seed with the -s option.

```
genice 4 -s 1234 --water tip4p --rep 3 3 3 > ice4.gro
```

By default, the hydrogen bonds are appropriately arranged to make the polarization be zero. The option --nodep avoids the depolarization process.

The density of ice is set automatically according to the shortest distance between water molecules. It can be specified by the --dens $x$ option where $x$ is the density of water in ice given in g cm$^{-3}$ (the mass of guest molecules is not included for clathrate hydrates and filled ices).

```
genice T --rep 1 1 1 --format o > T.scad
```

One can also prepare clathrate hydrates filled with guest molecules. For example, to stuff CO$_2$ molecules in all “12” cages (512) and 50% of “14” cages (51262) of CS1 hydrate, add the “-g” options as follows:

```
genice CS1 -g 12 5 co2 -g 14 5 co2*0.5 > cs1.gro
```

The option also accepts compositions for mixed hydrates. The syntax is (cage type) $5$ (guest name)*fill ratio$1$ (guest name)*fill ratio$1$ ... , for the -g option.

```
genice -g 16 5 me*0.9 CS2 -g 12 5 me*0.5 14=co2*0.5 > cs1.gro
```

There are only a few types of guest molecules prepared by default. They are listed in Table 4. One can define new molecular types by writing molecule plugins.

**Designing semiclathrate hydrates** is complicated. Refer to the manual.

**Plugins**

GenIce offers extensions by plugins. There are three types of plugins: molecular plugin, lattice plugin, and format plugin. Users can install their own plugins to serve new kind of guest.
and water molecules, crystal lattices, and output formats for specific applications.

**Incorporating Zeolite Structures**

It is possible to make ice structures from porous SiO$_2$ zeolite frameworks. Such structures can be candidates for stable ice polymorphs ([29]), and makes lattice modules for GenIce. This tool obtains CIF files of zeolites from the zeolite database web site ([29]) and makes lattice modules for GenIce.

**Summary**

We introduce a tool for generating hydrogen-disordered ice structures, GenIce. The algorithm employed in GenIce certifies the uniformity of hydrogen-disorder and the zero net polarization. Various ice and clathrate hydrate structures are preset. Users can install new host (water) molecules, guest molecules, lattice structures, and output formats as plugins.

The uniformity of hydrogen-disorder may affect the quality and reliability of computer simulations of ices and clathrate hydrates. Nowadays, the system size of computer simulations is getting larger and larger, and there is a great need for preparing many hydrogen bond networks of different orderliness efficiently. GenIce has already been used in our researches ([10], [16]-[34]) and we will continue to improve the tool to generate more complex structures such as ice including various types of defects which play important roles in dynamic properties ([35]).

**Appendix**

GenIce is served at the GitHub (https://github.com/vitroid/GenIce) as an open source software since 2015. Feedbacks, proposals for improvements and extensions, and bug fixes are sincerely appreciated. Developers and test users are also welcome. The latest users’ manual is available at the website. GenIce is written in Python 3, and can be obtained as the “genice” package from the PyPI (Python Package Index) repository using the easy_install or pip commands. Extension plugins should also be written in Python 3.

**Keywords:** hydrogen-disordered ice · lattice generator · ice polymorphs · clathrate hydrates · zeolite

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[1] V. F. Petenko, R. W. Whitworth, *Physics of Ice*; Oxford University Press: Oxford, U.K., 2002.
[2] C. G. Salzmann, A. Hallbrucker, J. L. Finney, E. Mayer, *Phys. Chem. Chem. Phys.* 2006, 8, 3088.
[3] C. G. Salzmann, A. Hallbrucker, J. L. Finney, E. Mayer, *Chem. Phys. Lett.* 2006, 429, 469.
[4] C. G. Salzmann, P. Radaelli, E. Mayer, J. Finney, *Phys. Rev. Lett.* 2009, 103, 105701.
[5] A. Falenty, T. C. Hansen, W. F. Kuhs, *Nature* 2014, 516, 231.
[6] L. del Rosso, M. Celli, L. Ullivi, *Nat. Commun.* 2016, 7, 13394.
[7] J. D. Bernal, R. H. Fowler, *J. Chem. Phys.* 1933, 1, 515.
[8] L. Pauling, *J. Am. Chem. Soc.* 1935, 57, 2680.
[9] P. Englezos, *Ind. Eng. Chem. Res.* 1993, 32, 1251.
[10] W. L. Voi, L. W. Finger, R. J. Hemley, H. Mao, *Phys. Rev. Lett.* 1993, 71, 3150.
[11] D. Londono, W. F. Kuhs, J. L. Finney, *Nature* 1988, 332, 141.
[12] A. Rahman, F. H. Stillinger, *J. Chem. Phys.* 1972, 57, 4009.
[13] G. T. Barkema, M. Newman, *Phys. Rev. E* 1998, 57, 1155.
[14] V. Buch, P. Sandler, J. Sadlej, *J. Chem. Phys.* 1998, 102, 8641.
[15] E. W. Dijkstra, *Numer. Math.* 1959, 1, 269.
[16] T. Nakamura, M. Matsumoto, T. Yagasaki, H. Tanaka, *J. Chem. Phys.* 2015, 120, 1843.
[17] C. Lobban, J. L. Finney, W. F. Kuhs, *Nature* 1998, 391, 268.
[18] J. Russo, F. Romano, H. Tanaka, *Nat. Mater.* 2014, 13, 733.
[19] C. J. Fennell, J. D. Gezelter, *J. Chem. Theory Comput.* 2005, 1, 662.
[20] G. S. Smirnov, V. V. Stegailov, *J. Phys. Chem. Lett.* 2013, 4, 3560.
[21] V. I. Kosyakov, T. M. Polyanyskaya, *J. Struct. Chem.* 1999, 40, 239.
[22] G. A. Jeffrey, *Inclusion Compounds*; J. L. Atwood, J. E. D. Davies, D. D. Mac Nicol, Eds.; Academic Press: London, 1984; Vol. 1, Chap. 5.
[23] Y. Huang, C. Zhu, L. Wang, X. Cao, Y. Su, X. Jiang, S. Meng, J. Zhao, X. C. Zeng, *Sci. Adv.* 2016, 2, e1501010.
[24] Y. Huang, C. Zhu, L. Wang, J. Zhao, X. C. Zeng, *Chem. Phys. Lett.* 2017, 671, 186.
[25] N. Mousseau, G. T. Barkema, *Curr. Opin. Solid State Mater. Sci.* 2001, 5, 497.
[26] M. Dutour Sikirić, O. Delgado-Friedrichs, M. Deza, *Acta Crystallogr.* A 2010, 66, 602.
[27] A. J. Karttunen, T. F. Fässler, M. Linnolahti, T. A. Pakkanen, *Inorg. Chem.* 2011, 50, 1733.
[28] F. C. Frank, J. Kasper, *Acta Crystallogr.* 1959, 12, 483.
[29] Ch. Baerlocher, L.B. McCusker, *Database of Zeolite Structures*. Available at: http://www.iza-structure.org/databases/ (Accessed on July 4, 2017).
[30] T. Yagasaki, M. Matsumoto, H. Tanaka, *Phys. Rev. B* 2016, 93, 054118.
[31] T. Yagasaki, M. Matsumoto, H. Tanaka, *J. Phys. Chem. C* 2016, 120, 21512.
[32] T. Yagasaki, M. Matsumoto, H. Tanaka, *J. Phys. Chem. C* 2016, 120, 3305.
[33] T. Yagasaki, M. Matsumoto, H. Tanaka, *Phys. Chem. Chem. Phys.* 2015, 17, 32347.
[34] T. Yagasaki, M. Matsumoto, H. Tanaka, *J. Am. Chem. Soc.* 2015, 137, 12079.
[35] S. Klotz, K. Komatsu, F. Pietrucci, H. Kagi, A. A. Ludl, S. Machida, T. Hattori, A. Sano-Furukawa, L. E. Bove, *Sci. Rep.* 2016, 6, 32040.