

A Cellular Automata Model of Water

Lemont B. Kier^{*,†} and Chao-Kun Cheng[‡]

Departments of Medicinal Chemistry and Mathematical Sciences, Virginia Commonwealth University,
Richmond, Virginia 23298

Received August 10, 1993*

A model of liquid water has been created using cellular automata. In particular we use a kinematic, asynchronous, stochastic system to generate, iteratively, configurations simulating water emerging from initial conditions. We vary the cluster-breaking probability to generate variability in the network analysis. The breaking probability is found to have a close relationship to the temperature of liquid water when comparisons are made using the average number of hydrogen bonds, the average cluster size, and the number of free water molecules. A good correlation exists between the viscosity and the average cluster size as well as the number of free water molecules and the vapor pressure. The cellular automata model that we have generated gives a picture of large, extended clusters with very few small clusters or single water molecules. The graphic picture is very similar to the results described by Geiger, Stillinger, and Rahman and also Mezei and Beveridge. We identify this with a random network model of liquid water.

A critical influence on the biological properties of a drug molecule is the presence of and interaction with liquid water. The essential role of water is recognized in all studies of biological phenomena, but it is also appreciated that we know very little about the form or order of water in the bulk phase. A number of theories have evolved which attempt to reconcile some of the measurable properties and anomalies of water. Bernal and Fowler¹ proposed a model of liquid water consisting of molecules hydrogen bonded in a tetrahedral arrangement accompanied by a certain percent of non-hydrogen-bonded molecules interspersed in this array. This model reflects the greater density in the liquid state relative to ice. Samoilov² speculated that single water molecules, released from the ice cluster upon melting, formed residence within the interstitial positions of fragments of the original ice cluster.

Building upon X-ray analysis of liquid water by Morgan and Warren,³ Marchi and Eyring proposed the significant structure theory of water.⁴ This model describes water as being an equilibrium state between two ice-like clusters, each composed of 46 hydrogen-bonded molecules. Later, Pople⁵ proposed that liquid water is essentially a distorted ice lattice in which many hydrogen bonds are merely bent, not broken. Pauling⁶ has proposed that liquid water is a series of water hydrates, molecules entrapped into cage-like complexes. More recent contributions have been made by several investigators,^{7,8} all contributing to the rich variety of models available for our consideration.

Theoretical studies on single water molecules and small clusters have shed some light on the probable structures of these entities, as they might exist in whatever liquid water is ultimately defined to be.¹⁰⁻¹³ The existence of an identifiable, long-lived structural ingredient in liquid water is open to question. One attribute of hydrogen-bonding liquids is the continual changing of partners, persistence being definable at the level of 10^{-10} s.⁹ Multiple hydrogen bonds found in clusters are thought to be broken in cooperative processes at rates different from single hydrogen bonds in small clusters.^{7,14} This recognition leads us to a model of a dynamic system in which clusters may be disintegrating through cooperative hydrogen bond breaking, while a simultaneous process of cluster

formation by hydrogen bond making is occurring. A well-defined cluster of a specified size and shape is not likely to exist for very long in such a medium of dynamic activity.

This rapidly changing mosaic has been recognized by a number of investigators who have sought to model water using dynamical simulations. The first of these by Stillinger and Rahman¹⁵ used molecular dynamics with empirical central force pair potentials to model the hydrogen bond. Plummer¹⁴ has modeled small cluster organization using two different potentials to describe the interaction between atoms. Other studies have focused on selected aspects of water structure.¹⁶⁻¹⁸ Molecular dynamics is developing as a useful method of the synthesis philosophy.¹⁹ It follows three phases in its execution: (1) the construction of a model, (2) the calculation of trajectories of the parts, and (3) the analysis of trajectories of the molecules determined numerically by solving differential equations of motion in the simulation process. A force field provides the intermolecular potentials necessary for the trajectory calculation. The method requires vast amounts of computer time for more than just a few molecules.

Molecular dynamics is an example of the synthesis approach to research, in contrast to the analysis or reductionist philosophy. In synthesis we seek to combine different parts to construct a model of the whole which has an emergent behavior. This behavior is not likely evident from the parts; it cannot be predicted on the basis of what are called fundamental theories. The emergent behavior of water is the pattern of clusters, forming and changing their configurations with temperature and time. Measurable emergent properties would include viscosity, vapor pressure, and certain hydraulic phenomenon such as turbulence.

One alternative to molecular dynamics for the study of liquid water is found in the class of dynamic models called cellular automata (CA). This was introduced by von Neumann to address the question of the logical organization needed for self-reproduction.²⁰ Basically, the elements of a system are represented by cells in n -dimensional space. The physical laws reflecting the state of the cells and their transition from one configuration in time to the next are mimicked by a set of rules. Space and time are independent and discrete. At each time interval, in response to the rules of state or transition functions, a new configuration of the system emerges.

[†] Department of Medicinal Chemistry.

[‡] Department of Mathematical Sciences.

* Abstract published in *Advance ACS Abstracts*, March 1, 1994.

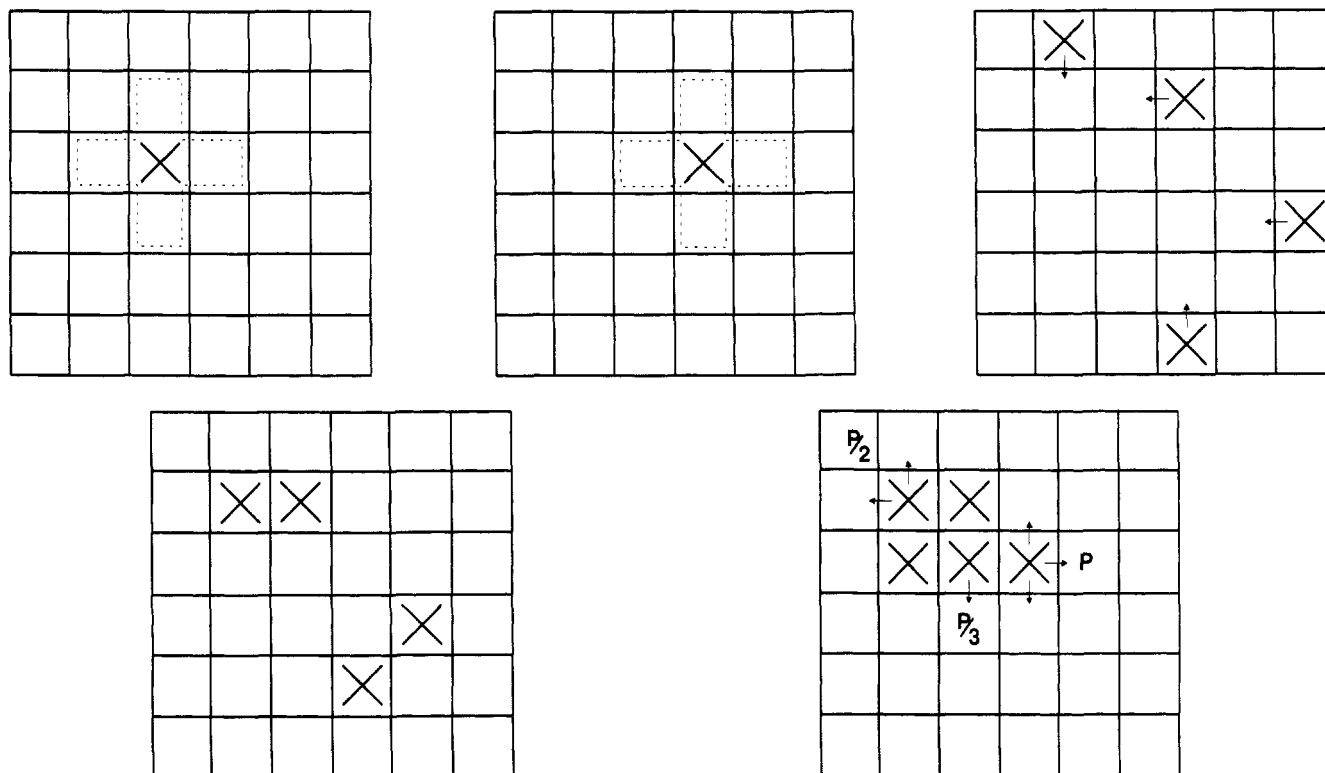


Figure 1. (a, top left) Von Neumann neighborhood of the cell marked \times . The central cell, \times , is occupied with a water molecule, while the other neighborhood cells are vacant. (b, top middle) Configuration after one iteration interval. The central cell, \times , has moved randomly to a vacant cell. The new von Neumann neighborhood is formed. (c, top right) Positions of four water molecules in a particular configuration. Arrows indicate the directions that they will move as a result of random selection. (d, bottom left) Positions of the four water molecules after the movement. The water molecules in the upper left area form a cluster of size 2. The other water molecules are not in a cluster. (e, bottom right) Breaking of a cluster at positions which differ by the number of bonds, n , formed by tessellated unions. The probability of breaking is related to the selected probability, p , divided by n .

Considerable attention has been given to CA in modeling dynamic complex behavior in biological events. Ermentrout and Edelstein-Keshet have recently published a thorough review.²¹ The realization that water is a complex substance, constantly changing because of the nature of the hydrogen bonds, leads us to believe that CA might be a good dynamic modeling method to reveal some emergent behavior. This information in turn may be of considerable value in subsequent studies of drug molecules and their behavior in water.

CELLULAR AUTOMATA MODEL

The model is made up of cells constituting a tessellated space in n -dimensions. The space defined in these studies is boundless since it is a portion of the surface of a torus. The space used here is two dimensional, each cell having four neighbors. This pattern of five tessellated cells is called a von Neumann neighborhood, Figure 1a. The state of each cell reflects whether it is occupied with a water molecule. The configuration of the entire system at any time is defined by the set of state values. At discrete intervals of time, discrete changes in each cell occur according to rules that constitute the transition functions. More information can be found in a review,²² a symposium report,² and a text.²⁴

RULES

In this study, we state rules which govern the movement of each water molecule from one cell to another; thus, this CA is kinematic. The movement of water molecules is based upon probabilities input into the system; thus, the CA is probabilistic or stochastic. The rule for a water molecule in a cell surrounded by four empty cells states that it will move vertically

or horizontally to one of these cells, which one to be determined randomly, Figure 1b. A molecule, i , moving to a position adjacent to a cell occupied by a molecule, j , forms an attachment to that cell, the union producing a cluster (see Figures 1c,d). Clusters of any size above one molecule do not move as a whole.

Clusters larger than one water molecule disintegrate according to a previously determined probability, p . If a molecule, i , which is part of a cluster is bonded to only one water molecule, j in that cluster, then the probability of breaking the union i - j is p . The breaking occurs by the movement of i into one of three adjacent cells currently unoccupied, Figure 1e. If a water molecule i in a cluster is bonded to two other water molecules in that cluster, the probability that molecule i will move to an unoccupied cell is $p/2$. Similarly, if i is bonded to three other water molecules in the cluster, the probability that it will move to the remaining unoccupied cell is $p/3$. A molecule in a cell surrounded by four occupied cells does not move. Each cell responds to its state, environment, and transition function in turn. After all have responded, a complete iteration is achieved. The method we employ is thus a kinematic, asynchronous, stochastic cellular automata. After each iteration a configuration of states results which is studied for several attributes.

INITIAL CONDITIONS

Initialization requires a statement of the domain size, number of water molecules in the domain, and the starting configuration, i.e. a single cluster (ice), a set of isolated water molecules (vapor), or a random distribution of water molecules over the domain. In addition we must select a value of the breaking probability so that $p = 0$ -1.0. Other selections

Table 1. Relationship of Percent Standard Deviation of the Average Cluster Size, N/M , for Several Values of p

p	% std dev of N/M	p	% std dev of N/M
0.03	± 25	0.25	± 11
0.06	± 13	0.50	± 6
0.10	± 12	0.90	± 5

influence the reporting of data, the number of iterations, and the characteristics of the graphic display.

A critical choice must be made concerning the number of water molecules relative to the domain size. For these studies to have any significance the results must bear some relationship to water properties. Our initial choice was to adopt a ratio of water molecules to domain size, mirroring the ratio of space occupied by the van der Waals volume of water molecules relative to the liquid volume.

A series of values of the probability, p , were selected as transition functions for the breaking of clusters. The system was iterated through several series of studies to determine how long it took to achieve an approximate stability in the values of attributes generated by the system. Several attributes were recorded including the distribution of water molecules into various cluster sizes, the average cluster size, the relative frequency of a particular cluster size, and the count of common edges, interpreted as hydrogen bonds. A graphic display revealed the configuration with each iteration.

Several runs at various values of p produced configurations in which the count of the number of free water molecules remained fairly constant after a number of iterations. Using 1100 water molecules in a 40×40 cell domain, stability was achieved after about 1000 iterations for $p = 0.03$ – 0.07 , about 500 iterations for $p = 0.1$ – 0.25 , and about 250 iterations for $p > 0.5$. These same values were also found for lower counts of water molecules in the 40×40 cell domain. The percent standard deviation of the count of the average cluster size exhibited a strong relationship to the value of p . After reaching an approximate equilibrium, this value is related to p as shown in Table 1. Similar results are obtained for other calculated water attributes.

RESULTS

Definition of Terms. We use the definitions described by Geiger, Stillinger, and Rahman²⁵ for their results from molecular dynamics simulations. We let N be the number of water molecules used in our model within a domain of size G . In the present study we use $G = 40 \times 40 = 1600$ cells where the domain is on the surface of a torus to eliminate a boundary condition. In any configuration there are a number m_n of water clusters containing n water molecules. The total number of clusters in a configuration is M , where $M = \sum_{n \geq 1} m_n$. The average cluster size, $\langle n \rangle$, is N/M . The number of free water molecules ($n = 1$) in a configuration is N_u . All other clusters, $n > 1$, called gel clusters, are calculated from $N - N_u = N_g$. The average number of hydrogen bonds in a configuration is n_{HB} .

Evaluation of an Optimum N/G Ratio. The results of several runs using varying values of N in a domain of $G = 1600$ cells produced a series of values for the percent of single water molecules, $(N_u \times 100)/N$ for several values of N as a function of p . See Table 2. Haggis, Hasted, and Buchanan²⁶ have predicted the percent of free water molecules as a function of temperature and have used these values to achieve agreement with the dielectric constant. Walrafen²⁷ has used these same values to calculate the heat capacity of water. These $(100N_u/N)$ values are shown in Table 3. From the data in Tables 2 and 3, we deduce a relationship between p and the temperature

Table 2. Percent of Single Water Molecules, $100N_u/N$, from Several Values of N and p

N	values of p					
	0.03	0.06	0.10	0.25	0.50	0.90
1100	0.14	0.22	0.32	0.61	1.00	1.20
1000	0.30	0.40	0.70	1.20	1.70	2.50
900	0.40	0.80	1.06	1.87	2.90	3.97
800	0.70	1.08	1.36	3.09	4.38	6.47

Table 3. Percent of Free Water Molecules for Several Temperatures, Derived by Haggis et al.,²⁶ to Predict Dielectric Constants

T (°C)	$100 N_u/N$	T (°C)	$100 N_u/N$
0	0.1	60	0.9
25	0.2	100	1.5

Table 4. Calculated Attributes from Several Configurations

p	M^a	N/M	N_u^a
0.03	55	219	27
0.06	94	200	44
0.10	122	162	64
0.25	214	109	134
0.50	313	81	216
0.90	350	67	263

^a Values using 1100 water molecules in a 40×40 domain. The values are averaged over the last 20 iterations.

of water used by Haggis et al. If we combine the two sets of data and assume that $P = 0.01 T$ (°C), the relationship between the temperature and the corresponding $(100N_u/N)$ values have a correlation coefficient of 0.965 for the choice of $N = 1100$. Several attempts to improve this correlation by shifting the values of T (°C) by ± 5 and ± 10 °C produced no statistically significant change in the relationship. In view of the standard deviations encountered for the calculated values shown in Table 1, the estimate $p = 0.01 T$ (°C) is quite a reasonable relationship that we provisionally adopt.

This study revealed that a value of $N = 1100$ when $G = 1600$ (or any comparable ratio) is a system that is close to the ratio of the van der Waals volume of water molecules to liquid volume. It is also a value producing a good prediction of the number of free water molecules in our cellular automata model. Until evidence vitiates this finding, we will use it for subsequent studies.

Cluster Studies. A series of studies were run using 1100 water molecules in a 1600-cell domain. The number of iterations calculated ensured that the various attributes analyzed had reached stable values. Populations of clusters of various sizes and the average cluster sizes, N/M , for several p values were compiled. These are shown in Table 4. Each of these values is derived from averages over the last 20 iterations of a run. Virtually all of the water molecules in each configuration are part of one or a very small number of large clusters. An inspection of one configuration, Figure 2, shows that an extended random network of bound water molecules percolates through the entire domain. With each iteration, it changes shape, forming and breaking extended ramifications constituting a random network of contiguous molecules. The sequence of illustrations in Figure 3 shows the transition of configurations beginning with one solid cluster (ice) and proceeding through iterations using $p = 0.8$ to an approximate equilibrium configuration. These visual representations are very similar to the results described by Geiger, Stillinger, and Rahman²⁵ as well as Mezei and Beveridge.²⁸ These figures depict a model for water compatible with the models proposed by Speedy²⁹ and Rice and Sceats³⁰ for self-replicating structures or a random network model for water.

The average number of hydrogen bonds per molecule, n_{HB} , for 1100 water molecules in a 1600-cell domain is found to range from 2.76 with $p = 0.10$ to 2.66 with $p = 0.90$. These n_{HB} values correspond to the number of unbound water molecules per 1100 water molecules, N_u/N , shown in Table 5. If n_{HB} and N_u/N are plotted against each other, the close group of points fall on the curve shown by Mezei and Beveridge²⁸ to exist for three studies using the Rahman and Stillinger ST2 intermolecular potential function²⁵ and two studies using the Monte Carlo computations using the quantum mechanical MCY potential of Owicki and Sheraga.³¹ These n_{HB} values are over the percolation threshold value of $n_{HB} = 1.3$ proposed by Stockmeyer.³²

PHYSICAL SIGNIFICANCE OF SOME CA RESULTS

Viscosity. We test this cellular automata model for physical significance by evaluating the relationship between certain model attributes and physical properties. The viscosity is one emergent property of water which is dependent on the collective behavior of ensembles of molecules. The average cluster size, N/M , should have some influence on this property. The functional form of this relationship was found to be the log of N/M using the relationship $p = 0.01 T(^{\circ}\text{C})$. A regression analysis gave a good equation:

$$\eta(\text{cP}) = 2.50 \log(N/M) - 4.23 \quad (1)$$

$$r^2 = 0.997, \quad s = 0.03, \quad n = 10$$

Table 6 and Figure 4 show this result. Of course it must be recalled that there is a significant standard deviation in the average cluster size, N/M , particularly for lower values of p . But this result is an achievement for the model and the assumed $p - T(^{\circ}\text{C})$ relationship.

Water Vapor Pressure. The vapor pressure above the surface of water might be viewed as a consequence of the number of single water molecules (or small clusters) in the condensed phase at different temperatures. To test the significance of our model in respect to this property, we have focused attention on the number of single water molecules, N_u . We anticipate that the contribution of this value will be progressively more significant as T (and p) increase. Using an exponential expression for N_u , we have found eq 2 to closely model this property:

$$P_v(\text{mmHg}) = \exp(0.2N_u)^2 + 10 \quad (2)$$

$$r^2 = 0.99, \quad n = 7$$

The predicted values are shown in Table 7 and Figure 5.

DISCUSSION

We have proposed a model of water developed from a cellular automata synthesis. In particular, this is a kinematic, asynchronous, stochastic CA model derived from the representation of individual water molecules as designated cells in a domain. The domain is boundless, being projected on the surface of a torus. The transition functions are simple rules from which the water molecules respond, creating at each complete iteration a new configuration of the system. We find that a stable equilibrium is achieved for each of several calculated attributes after a number of iterations. These attributes include an average cluster size, the number of clusters of any designated size, the number of single water molecules, and the average number of hydrogen bonds. Each set of attributes is a function of the cluster-breaking



Figure 2. A configuration after 1000 iterations for 1100 water molecules in a 1600-cell domain with a p value of 0.85. The white cells are water.

probability, p , selected for a particular transition function. The value of p has an influence on the numerical values of each of these attributes.

We have found that the value of p bears a close relationship to the temperature in the form $p = 0.01 T(^{\circ}\text{C})$ when a comparison is made for a water to grid ratio of 0.69. This ratio corresponds closely to the ratio of the van der Waals volume of water and the volume of the liquid that they constitute. This same ratio also gives a close agreement between the percent of free water molecules, N_u , calculated and the percent calculated by Haggis²⁶ at the same temperatures. Haggis used these percentages to calculate the dielectric constants of water. The number of N_u molecules at various values of p is strongly dependent upon this ratio. This same set of free water percentages were also used by Walrafen to calculate the heat capacity of water.²⁷ These relationships have led us to adopt values of $N = 1100$ and $G = 1600$. The average number of hydrogen bonds in each configuration has been calculated and is shown to be 2.66–2.76, depending upon the p value (temperature) used in the transition function. At several values of p , we have calculated both the average number of hydrogen bonds and the average cluster size. A plot of these two values produces a segment of a curve coinciding to one reported by Mezei and Beveridge²⁸ using five different dynamic simulations. Three of these were derived from the Rahman and Stillinger molecular dynamics potential²⁵ and two of these were derived from the quantum mechanics based Monte Carlo simulation of Owicki and Sheraga.³¹ The correspondence of our results with those from very different methods encourages us to believe that our model has enough validity to continue this line of investigation.

As a test of the attributes calculated from this CA model, we have found an equation relating viscosity of water at various temperatures with the predicted average cluster size at various values of p . The equation is based on the assumption that $p = 0.01 T(^{\circ}\text{C})$. The standard deviation of this equation is only 0.03 cP. A second test of the attributes calculated concerns the vapor pressure above the surface of water. We have conjectured that this property should bear some relationship to the average number of free water molecules in a configuration as a function of the value of p . An exponential function was found that is of the same quality as that developed for the viscosity.

We have thus far interpreted the count of joined or tessellated faces of water molecules as counts of hydrogen bonds. These values are shown in Table 5 and are discussed above. The question arises as to whether this information can be

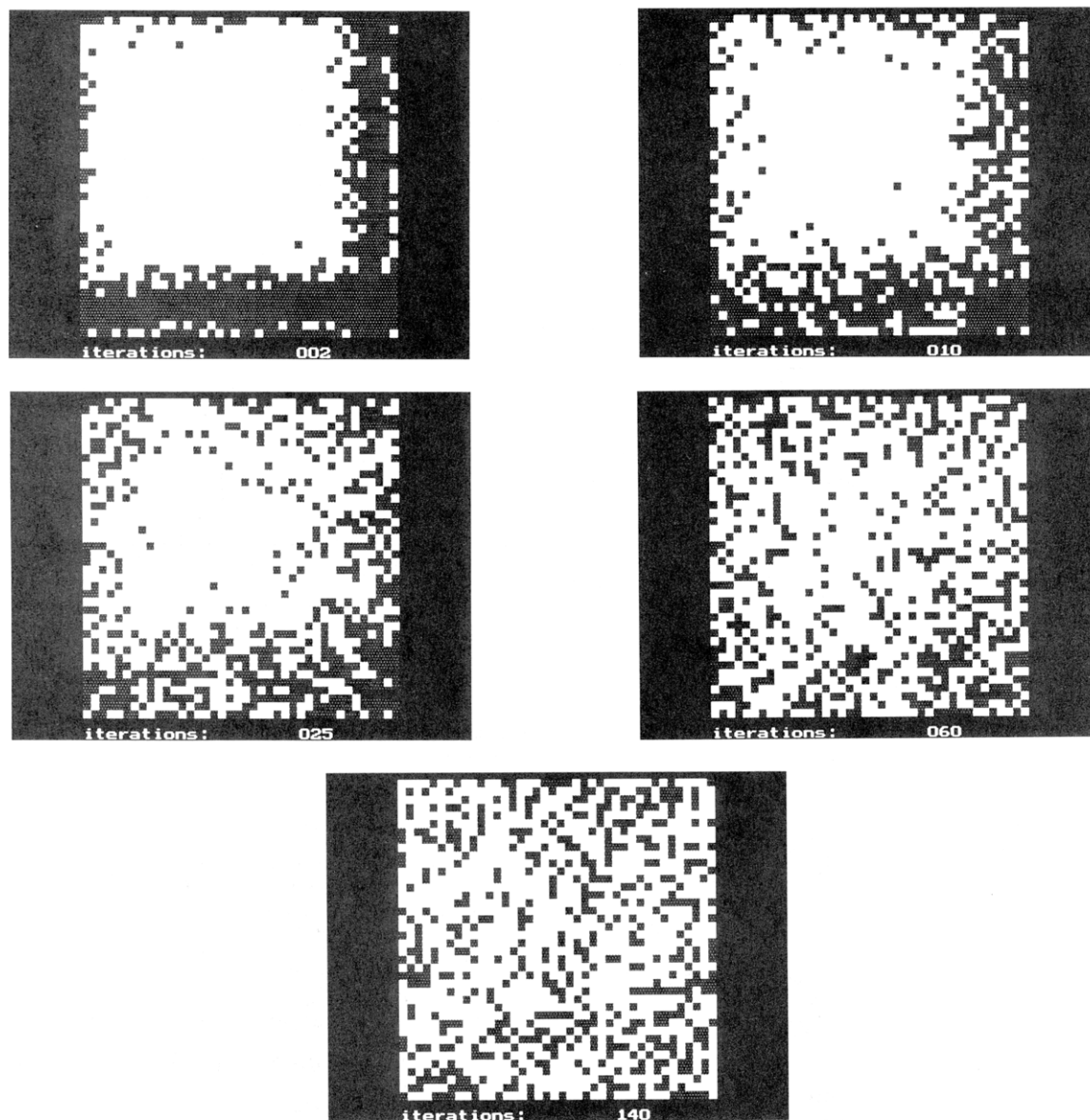


Figure 3. A sequence of configurations beginning with a solid configuration of water molecules. After subsequent iterations the configurations are shown. The white cells are water molecules. It is interesting to note that the cover design of this journal could be interpreted as a CA configuration.

Table 5. Number of Hydrogen Bonds and N_u/N in a Configuration

p	n_{HB}	N_u/N
0.10	2.76	0.004
0.30	2.73	0.006
0.50	2.70	0.010
0.90	2.66	0.012

Table 6. Viscosity of Water and Average Cluster Size

p	$\log N/M$	viscosity (cP)	viscosity (calc)
0.03	2.34	1.62	1.61
0.06	2.30	1.47	1.51
0.10	2.21	1.31	1.29
0.20	2.07	1.00	0.95
0.25	2.04	0.89	0.86
0.30	2.01	0.80	0.80
0.40	1.97	0.65	0.69
0.50	1.91	0.55	0.54
0.70	1.85	0.40	0.42
0.90	1.83	0.31	0.34

translated into an expression of the energy of the system. There is no directly interpretable attribute in this cellular automata model commensurate with energy. Indirectly, however, we can make some initial effort to extract energy

Table 7. Vapor Pressure of Water and Average Number of Single Water Molecules, $\langle N_u \rangle$

p	$\langle N_u \rangle$	P_v (mmHg)	calc P_v
0.10	3.2	9.2	11.5
0.30	7.4	31.8	18.9
0.50	10.4	92.5	85.7
0.60	11.05	149	161
0.70	11.35	233	183
0.80	12.1	355	359
0.90	12.5	526	528

information from the data in Table 5. Consider the tessellation count (hydrogen bond count) at two breaking probabilities, p (temperature in °C), say 10 and 90 °C. A difference of 0.1 tessellation counts per water molecule (hydrogen bond counts per water molecule) is recorded for this range. This is equivalent to $0.1/2.76 = 0.036$ counts per mole. The energy difference per mole for this temperature range is 0.08 kcal/mol. The energy per tessellation count (hydrogen bond) is thus calculated to be 2.21 kcal/mol. This is a reasonable value when we recall that a tessellation count is not necessarily an optimum strength hydrogen bond.

The CA dynamics produces a model of liquid water in which a large cluster dominates each configuration, accompanied

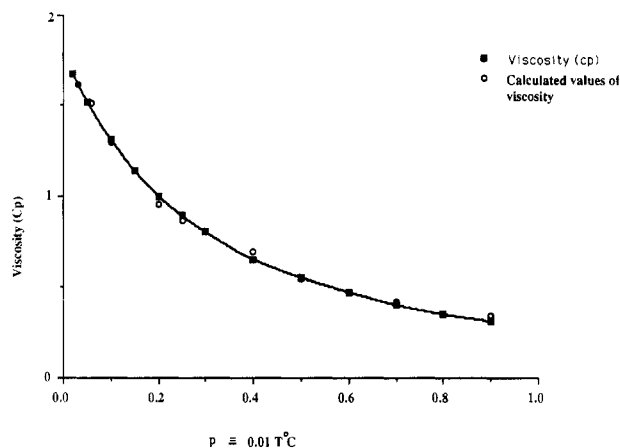


Figure 4. Relationship of the viscosity (cP), —■—, to the predicted value, O, from eq 1. The temperature, T ($^{\circ}\text{C}$), is assumed to be related to the probability, p , as $p = 0.01T$ ($^{\circ}\text{C}$).

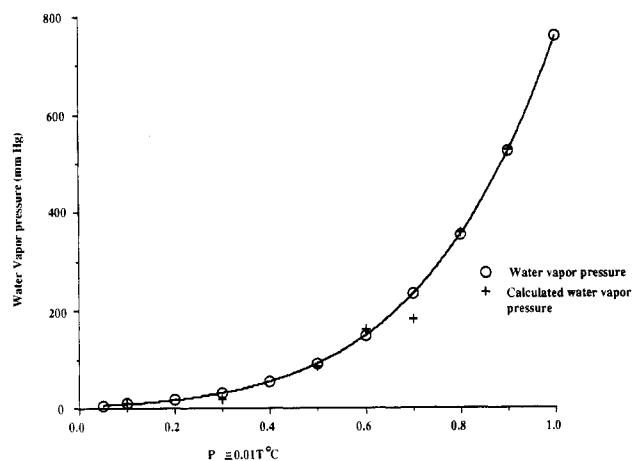


Figure 5. Relationship of the vapor pressure of water (mmHg), —○—, to the predicted value, +, from eq 2. The temperature is assumed to be related to p as $p = 0.01T$ ($^{\circ}\text{C}$).

by a limited number of small clusters and single water molecules. This is very similar to the pattern reported by Mezei and Beveridge²⁸ and Geiger, Stillinger, and Rahman.²⁵ This pattern does not change dramatically from low to high values of p . The average cluster size diminishes with a concurrent increase in the N_0 value. The graphic illustration of the dynamics reveals a percolation model or a random network model, as described by several authors.^{25,29,30,33}

The agreement of our model with that of other models from different methods and the relationship of our calculated attributes to physical properties encourage us to believe that our model has a measure of validity. An interesting nondynamic model of water has just been published which illustrates the utility of two-dimensional representations.³⁴ The advantages of CA models are ease of generation, ability to graphically illustrate results, and the possibility of studying more complex systems. For now we report these results, realizing that further studies are needed to establish the general utility of the results and to improve the various aspects of the method.

ACKNOWLEDGMENT

We have benefitted from discussions with D. Shillady, G. Kellogg, N. Joshi, B. Testa, and J. Venitz. We thank N. Joshi and M. Born for technical assistance.

REFERENCES AND NOTES

- Bernal, J. D.; Fowler, R. H. A Theory of Water and Ionic Solution. *J. Chem. Phys.* **1933**, *1*, 515–548.
- Samoilov, O. Y. Structure of Aqueous Electrolyte Solutions and the Hydration of Ions. *Zh. Fiz. Khim.* **1946**, *20*, 12–21.
- Morgan, J.; Warren, B. E. X-Ray Analysis of the Structure of Water. *J. Chem. Phys.* **1938**, *6*, 666–673.
- Marchi, R. P.; Eyring, H. Application of Significant Structure Theory to Water. *J. Phys. Chem.* **1964**, *68*, 221–228.
- Pople, J. A. Molecular Association in Liquids. II. A Theory of the Structure of Water. *Proc. R. Soc. A (London)* **1951**, *A205* 163–178.
- Pauling, L. In *Hydrogen Bonding*; Hadzi, L., Ed.; Pergamon Press: London 1959; p 1.
- Benson, S. W.; Siebert, E. D. A Simple Two-Structure Model for Liquid Water. *J. Am. Chem. Soc.* **1992**, *114*, 4269–4276.
- Huyskens, P.; Kapuku, F.; Colemonts-Vanderyvere, C. Thermodynamics of H-Bonding in Alcohols and Water. *J. Mol. Struct.* **1990**, *237*, 207–220.
- Kristenmacher, H.; Lie, G. C.; Pople, H.; Clementi, E. Study of the Structure of Molecular Complexes. VI. Dimers and Small Clusters of Water Molecules in the Hartree-Fock Approximation. *J. Chem. Phys.* **1974**, *61*, 546–561.
- Kim, K. S.; Mhin, B. J.; Choi, U. S.; Lee, K. Ab Initio Studies of the Water Dimer Using Large Basis Sets. *J. Chem. Phys.* **1992**, *97*, 6649–6662.
- Mo, O.; Yanez, M.; Elguero, J. Cooperative Nonpairwise Effects in Water Trimers. Ab Initio Molecular Orbital Study. *J. Chem. Phys.* **1992**, *97*, 6628–6638.
- Pillard, J.; Oszewski, K. A.; Piela, L. Theoretically Predicted Lowest Energy Structures of Water Clusters. *J. Mol. Struct.* **1992**, *270*, 277–285.
- Radhakrishnan, T. P.; Herndon, W. C. Graph Theoretical Analysis of Water Clusters. *J. Phys. Chem.* **1991**, *65*, 10609–10617.
- Plummer, P. L. M. Molecular Dynamics Simulations and Quantum Mechanical Studies of the Hydrogen Bond in Water Cluster Systems. *J. Mol. Struct.* **1990**, *237*, 47–61.
- Stillinger, F. H.; Rahman, A. Revised Central Force Potential for Water. *J. Chem. Phys.* **1978**, *68*, 666–670.
- Caldwell, J.; Doug, L. X.; Kollman, P. A. Implementation of Nonadditive Intermolecular Potentials by Use of Molecular Dynamics. *J. Am. Chem. Soc.* **1990**, *112*, 9144–9147.
- Yu, J. Y.; Jhon, M. S. Molecular Dynamics Study on the Properties of Water Clusters. *J. Colloid Interface Sci.* **1991**, *147*, 443–452.
- Belch, A. C.; Berkowitz, M. Molecular Dynamics Simulations of TIPS2 Water Restricted by a Spherical Hydrophobic Boundary. *Chem. Phys. Lett.* **1985**, *113*, 278–283.
- Haile, J. M. *Molecular Dynamics Simulation*; John Wiley & Sons: New York, 1992.
- von Neumann, J. In *Theory of Self-Reproducing Automata*; Burks, A. W., Ed.; Univ. of Illinois Press: Urbana, 1966.
- Ermentrout, G. B.; Edelstein-Keshet, L. Cellular Automata Approaches to Biological Modeling. *J. Theor. Biol.* **1993**, *160*, 97–113.
- Wolfram, S. Statistical Mechanics of Cellular Automata. *Rev. Mod. Phys.* **1983**, *55*, 601–644.
- Cellular Automata*; Farmer, D., Toffoli, T., Wolfram, S., Eds. *Physica* **1984**, *10D*.
- Jackson, E. A. *Perspectives of Non-Linear Dynamics*; Cambridge University Press: Cambridge, England, 1991; Chapter 10.
- Geiger, A.; Stillinger, F. H.; Rahman, A. Aspects of the Percolation Process for Hydrogen Bond Networks in Water. *J. Chem. Phys.* **1979**, *70*, 4186–4192.
- Haggis, G. H.; Hasted, J. B.; Buchanan, T. J. The Dielectric Properties of Water in Solutions. *J. Chem. Phys.* **1952**, *54*, 1452–1464.
- Walrafen, G. E. In *Hydrogen-Bonded Systems*; Covington, A. K., Jones, P., Eds.; Taylor and Francis Publ.: London, 1968.
- Mezei, M.; Beveridge, D. L. Theoretical Studies of Hydrogen Bonding in Liquid Water and Dilute Aqueous Solutions. *J. Chem. Phys.* **1981**, *74*, 622–632.
- Speedy, R. J. Self-Replicating Structures in Water. *J. Phys. Chem.* **1984**, *88*, 3364–3373.
- Rice, S. A.; Sceats, M. G. A Random Network Model for Water. *J. Phys. Chem.* **1981**, *85*, 1108–1119.
- Owicki, J. C.; Sheraga, H. A. Monte Carlo Calculations in the Isothermal-Isobaric Ensemble. 1. Liquid Water. *J. Am. Chem. Soc.* **1977**, *99*, 7403–7411.
- Stockmayer, W. H. Theory of Molecular Size Distribution and Gel Formation in Branched Chain Polymers. *J. Chem. Phys.* **1943**, *45*, 11–18.
- Stanley, H. E.; Teixeira, J. Interpretation of the Unusual Behavior of H₂O and D₂O at Low Temperatures: Tests of a Percolation Model. *J. Chem. Phys.* **1980**, *73*, 3404–3422.
- Yalkowsky, S. H. A Two Dimensional Model for Water. *J. Chem. Educ.* **1993**, *70*, 614–615.