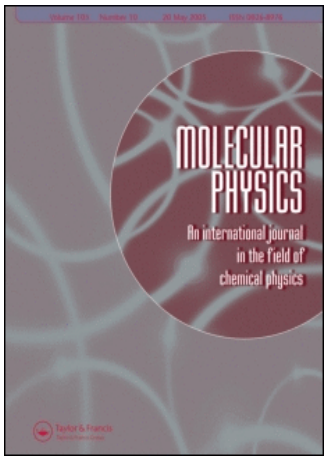

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Comparison of the percolation model with computer simulation results on different water models

Mihaly Mezei [a]
[a] Department of Chemistry, Hunter College of the CUNY. New York, N.Y.. U.S.A.

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Comparison of the percolation model with computer simulation results on different water models

by MIHALY MEZEI
Department of Chemistry, Hunter College of the CUNY,
New York, N.Y. 10021, U.S.A.

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The predictions of the connectivity properties of the hydrogen-bonded networks in liquid water based on the percolation model proposed by H. E. Stanley and co-workers has been compared with Monte Carlo computer simulations using the ST2 and MCY potentials at different temperatures. The comparison is based on a geometric hydrogen-bond definition. Reasons for the good agreement found for the average number of waters with exactly j hydrogen bonds are discussed. Also, the conflicting conclusions on the density of 4-bonded patches were re-examined and were found to be the result of using different water models in the conflicting studies.

1. INTRODUCTION AND BACKGROUND

The percolation model of H. E. Stanley [1] has successfully predicted several thermodynamic anomalies of the supercooled liquid water. The predictions of the model on the molecular level can be checked against computer simulation results, provided an operational definition of the hydrogen bond is adopted. This can be obtained either by setting an energy threshold value such that if two molecules interact stronger than the threshold value then they are considered hydrogen bonded, or by setting limits on the intermolecular geometric parameters. The former is called the energetic hydrogen bond and the latter the geometric hydrogen bond. By changing the respective cutoffs, the strength of the hydrogen bond can be modulated.

Comparison with computer simulation showed good agreement on topological properties of the hydrogen-bonded networks : the distribution of unbonded waters in several simulated systems using a geometric hydrogen-bond definition agreed very well with the prediction of the percolation model [2] ; several cluster distributions were computed by Stanley, Teixeira, Geiger and Blumberg [3] using an energetic hydrogen-bond definition and again good agreement was found. Similar results were found by Okazaki *et al.* [4] in their study of a simple water potential.

The connection between the topological properties of the network and the thermodynamics is based on the assumption that the patches of waters having four hydrogen bonds have lower density than bulk water. The verification of this assumption requires also a definition of the local density or, equivalently, the volume of such a patch. A straightforward definition of the local volume of a patch is the volume of regions composed of points such that the molecule nearest to any point in the region belongs to the patch. This is the union of the Voronoi

polyhedra of the molecules belonging to the patch. A different approach compares the number of neighbours in spheres drawn around the molecules as a function of the radius of the sphere (' running coordination number ') for molecules belonging to a patch with the same function for the rest of the molecules. However, the results obtained using the different approaches gave conflicting results. The study by Geiger and Stanley [5] found the local density of 4-bonded waters to be decreased based on the running coordination number difference function between 4-bonded and other waters, using the ST2 model [6], while the study by Rapaport [7] found a slight increase, based on comparisons between the Voronoi polyhedra of the 4-bonded and other waters, using the MCY model [8].

The results presented in this paper extend the various comparisons discussed above to the MCY and ST2 water models using a geometric hydrogen-bond definition. An analysis is given for the success of the percolation model in predicting quantitatively the connectivity properties of the hydrogen-bonded networks in various water models. Also, the coordination number difference technique is applied to both the MCY and ST2 waters, using both energetic and geometric hydrogen bond definitions.

The basic assumption in the percolation model is that the liquid consists of a hydrogen-bond network that is such that no water can have more than four hydrogen-bonded neighbours. Some applications also use as a computational aid an underlying network with some topological properties assumed. Based on these assumptions, simple combinatorial arguments, given in [1], yield the various distribution treated. A further aim of this note is to examine the effect of the restriction of the maximum number of hydrogen-bonded neighbours on the results.

Comparisons will be done between the percolation model and Monte Carlo results on the following quantities.

(1) The probability f_j^z of having exactly j hydrogen-bonded neighbours, assuming that the maximum number of hydrogen bonded-neighbours is z and the average number of hydrogen-bonded neighbours is n_{HB} :

$$f_j^z = \binom{z}{j} p_{\mathrm{B}}{}^j (1-p_{\mathrm{B}})^{z-j}, \tag{1}$$

$$p_{\mathrm{B}} = n_{\mathrm{HB}}/z.$$

(2) The weight fraction W_s^4 of the isolated patches of s water molecules, each having exactly 4 hydrogen bonds :

$$W_s^4 = n_s c^{(3s+1)/4} * (1-c^{3/4})^{2s+2}, \tag{3}$$

$$c = (n_{\mathrm{HB}}/4)^4, \tag{4}$$

$$n_1 = 1, \quad n_2 = 4, \quad n_3 = 18. \tag{5}$$

The expression for W_s^4, besides assuming that each water can form at most 4 bonds, depends on the topology of the underlying network assumed, and becomes successively more complex for higher s. [3 b] gives W_s^4 up to $s=6$ both for the Ice Ih topology and for the case where it is assumed that the smallest loop in the network contains at least $s+3$ members (for example, the Cayley tree). Equation (5) corresponds to this latter case, that is, the n_s values are

correct assuming that there are no 3, 4 or 5 membered loops in the network for $s=1$, 2 and 3, respectively.

(3) The change in the average number of neighbours within a radius r_0 between 4-bonded and other waters ((1, 2) of [5]) :

$$\Delta n(r_0)=4\pi\rho \int_0^{r_0} r^2[g_<(r)-g_4(r)]\, dr, \tag{6}$$

where ρ is the density of the liquid and $g_<(r)$, $q_4(r)$ are the radial distribution functions for the less than 4-bonded and 4-bonded waters, respectively. The more positive this function is the smaller the density of the 4-bonded clusters. No quantitative conclusion can be drawn, however, since contributions to the integrand come from waters of all kinds, especially when the 4-bonded clusters are small.

2. Calculations

Monte Carlo calculations have been performed on the following systems : 216 ST2 waters [6] at 10°C, 1·000 g/ml ; 125 MCY waters [8] at 25°C, 0·997 g/ml : 216 MCY waters at 37°C, 0·993 g/ml. These calculations have been described in detail earlier [9, 10]. The analysis of the hydrogen bonding on these systems along the lines of Geiger, Stillinger and Rahman [11] was also given earlier, using a geometric definition of the hydrogen bond [2], that places cutoffs on the oxygen–oxygen distance, R_{OO}, hydrogen–oxygen–oxygen angle θ_H, lone pair–oxygen–oxygen angle, θ_{LP} and the hydrogen–oxygen–oxygen–lone pair dihedral angle, δ_D. (The lone pair is the tetrahedrally located site like the negative charges in the ST2 model.) It is to be stressed that this was the sole criterion for hydrogen bonding and it could quite easily yield more than four hydrogen-bonded neighbours. As opposed to the analysis done in [3 a] on the molecular dynamics run on the ST2 water, we did not discard any of these bonds.

Geiger, Stillinger and Rahman found that the essential parameter for the description of the network properties is the average number of hydrogen bonds per molecule, n_{HB}. This result was subsequently confirmed on the analysis of the Monte Carlo results. For this reason, we will always specify n_{HB} only, since the actual combination of cut-offs is of little importance in the network analysis.

The analysis reported in this paper was performed using the history tape of the Monte Carlo runs mentioned above, analysing every 500th configurations. This was shown to cause neglible error only, due to the correlated nature of the Markov chain generated by the Metropolis method.

3. Results and discussion

This section describes the comparisons obtained on the bond percolation represented by (1, 2), on the site percolation represented by (3, 5) and on the density of 4-bonded patches.

3.1. *Bond percolation results*

The $f_j(n_{HB})$ values computed from the different Monte Carlo calculations are compared with $f_j^4(n_{HB})$ in figure 1. The agreement is excellent for $j=0$

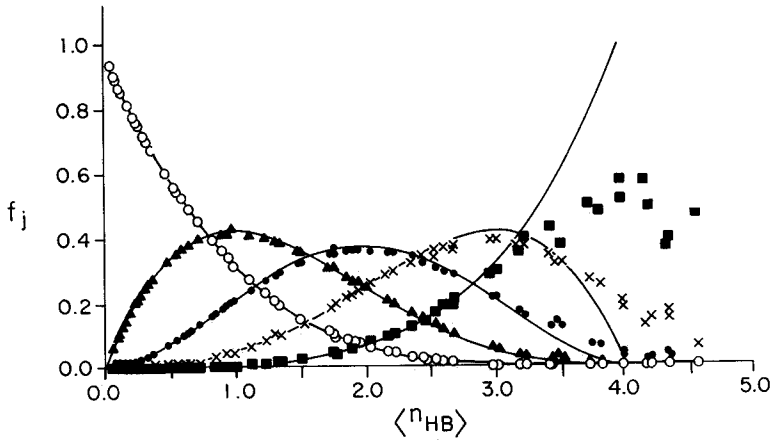

Figure 1. Computed $f_j(n_{HB})$ compared with the $f_j^4(n_{HB})$ obtained from Monte Carlo simulations on the MCY and ST2 waters. Full line: $f_j^4(n_{HB})$; ○, $f_0(n_{HB})$; ▲, $f_1(n_{HB})$; ●, $f_2(n_{HB})$; ×, $f_3(n_{HB})$; ■, $f_4(n_{HB})$.

and 1 for the full range of n_{HB}. For $j=2$, discrepancies start to appear from $n_{HB}=3$, for $j=3$ after $n_{HB}=2{\cdot}5$. For $j=4$, the agreement is still excellent until $n_{HB}=2{\cdot}5$ but for the larger values a qualitative differences appears, since $f_4^4(n_{HB})$ is a monotonously increasing function while the $f_4(n_{HB})$ values obtained from the computer simulation exhibit a maximum, as for $j=1$, 2 and 3. It is to be noted that hydrogen-bond definitions resulting in $n_{HB}>2{\cdot}5$ are already fairly weak [2, 11]. To obtain a better understanding, we prepared a plot of $f_j^z(n_{HB})$ for all possible combinations of $j=0$, 1, 2, 3, 4, 5 and $z=3$, 4, 5, 6 on figure 2. It is rather remarkable that for low n_{HB} or low j values $f_j^z(n_{HB})$ is nearly independent of z. As a consequence, setting $z=4$ is not a serious restriction for these j and n_{HB} values. Comparison of figures 1 and 2 shows that when $f_j^4(n_{HB})$ deviates from $f_j^5(n_{HB})$ (i.e. for $n_{HB}>2{\cdot}5$) $f_j^5(n_{HB})$ is a better approximation to $f_j(n_{HB})$.

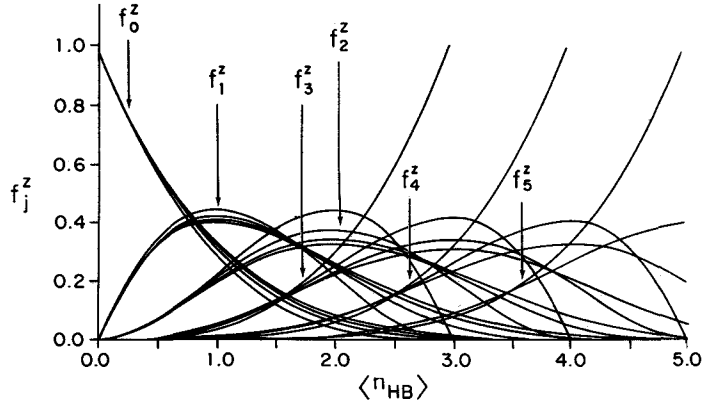

Figure 2. $f_j^4(n_{HB})$ computed for various z values. The location of the maximum defines j and the point where a curve reaches the x-axis, defines z.

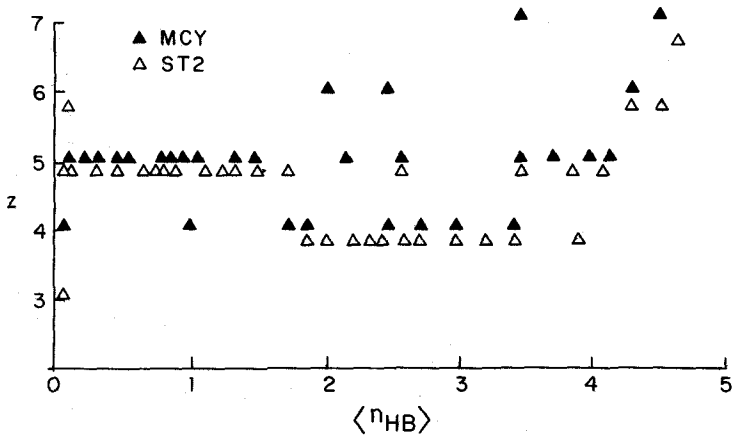

Figure 3. The best z values as a function of n_{HB} for the MCY and ST2 waters.

The question of the best z value was also examined by a numerical comparison of the set of $f_j(n_{HB})$ values obtained from a given hydrogen bond definition with the corresponding $f_j^z(n_{HB})$ values with different zs. The best z value was obtained by minimizing the sum of absolute deviations over j. The values obtained are shown on figure 3 for both the ST2 and MCY waters. For the n_{HB} range 1·5–3·5, $z=4$ gives the best agreement between the computer simulations and the percolation model. As discussed earlier, this range largely coincides with ' reasonable ' hydrogen bonds. As expected, for larger n_{HB}s z values greater than 4 give the best agreement. On the other hand, it is somewhat of a surprise that for $n_{HB}<1{\cdot}5$ $z=5$ is better than $z=4$. However, this latter discrepancy between the simulation and the percolation model is quite insignificant since there is very little difference between $f_j^4(n_{HB})$ and $f_j^5(n_{HB})$ in this range.

There is a simple reason for the success of the (1) to predict $f_j(n_{HB})$. For $j=0$,

$$f_0^z(n_{HB})=1-n_{HB}+O(n_{HB}^2), \tag{7}$$

which approximates the $1-n_{HB}$ line for small n_{HB}. In any event, the dependence of $f_j^z(n_{HB})$ on z is only in the second order. For other j values, consider $f_j^z(n_{HB})/f_j^{z+1}(n_{HB})$. Using (1, 2) we obtained the following expression after straightforward algebraic manipulations :

$$f_j^z(n_{HB})/f_j^{z+1}(n_{HB})=\left(\frac{z+1}{z}\right)^z \frac{z-j+1}{z-n_{HB}+1}\left(\frac{z-j}{z-n_{HB}+1}\right)^{z-j}. \tag{8}$$

Considering $n_{HB}=j$ (that is, at the maximum of $f_j^z(n_{HB})$), the limit of the first factor (as z tends to infinity) is e, the limit of the third factor is $1/e$ and the second factor is identically one. Thus for $z\gg n_{HB}$, this expression approaches one, which expresses z the independence of f_j from z at a smaller j values. In practice, the errors in the two approximations of e largely cancel so even for $z-j>1$ the ratio approaches unity within 5 per cent.

3.2. *Site percolation results*

It was found to be very fruitful in explaining the properties of supercooled water to consider the correlated site percolation problem where water molecules with exactly four hydrogen bonds are specially labelled and then the clusters of these labelled waters are studied.

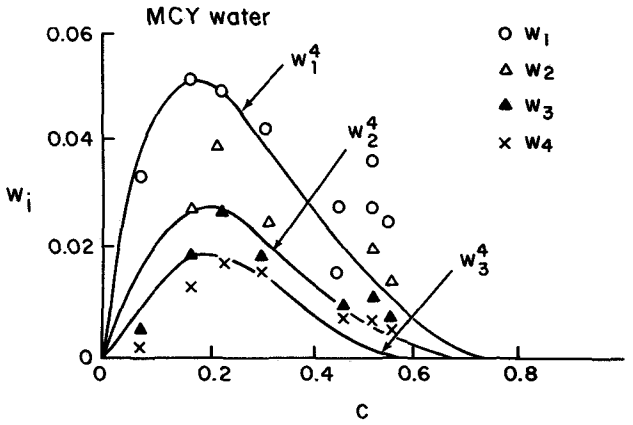

Figure 4. $W_s(c)$ obtained for the percolation model and computer simulation. Full line : $W_s^4(c)$; ○, $W_1(c)$; △, $W_2(c)$; ▲, $W_3(c)$; ×, $W_4(c)$.

The weight fraction of clusters of size 1, 2, and 3, W_s is shown in figure 4, obtained from the computer simulations on the MCY water. The agreement is good for $s=1$ and only qualitative for $s=2$ and 3. Furthermore, unlike for f_j, similar n_{HB} values obtained from different systems may yield different W_s values, showing that this quantity is more sensitive to the finer details of the system than f_j. This is to be expected, since the derivation of W_s^4 not only assumes $z=4$, but also excludes hydrogen-bonded loops of 3, 4 or 5 members for W_1, W_2 and W_3, respectively. Such loops, however, are known to exist in these water models [12, 13]. In particular, [12] found 0·06, 0·16 and 0·35 loops per water molecule of consisting of 3, 4 and 5 waters, respectively, when $n_{HB}=3{\cdot}88$; 0, 0·08 and 0·34 loops per water molecules when $n_{HB}=2{\cdot}26$.

3.3. *Density results*

The running coordination number difference technique of [5] (equation (6)) was used to examine the density difference between 4-bonded patches and bulk water. In this study both the energetic and geometric hydrogen-bond definitions were employed. The energetic hydrogen bonds were defined by $V_{HB}=-14{\cdot}96$ kJ mol^{-1} and $V_{HB}=-12{\cdot}55$ kJ mol^{-1} for the ST2 and MCY models, respectively. These values coincide with one of the cut-offs used in [5] and [6], respectively. The geometric definition used the strong hydrogen bond, as defined in [2]. Other hydrogen-bond definitions were also examined but the results were found to be essentially the same and are not shown here. The resulting running coordination number difference curves are displayed on figure 5 for the ST2 and MCY waters. The ST2 $\Delta n(r_0)$ with the energetic hydrogen-bond definition is similar to the one in [5], although not identical, since they are

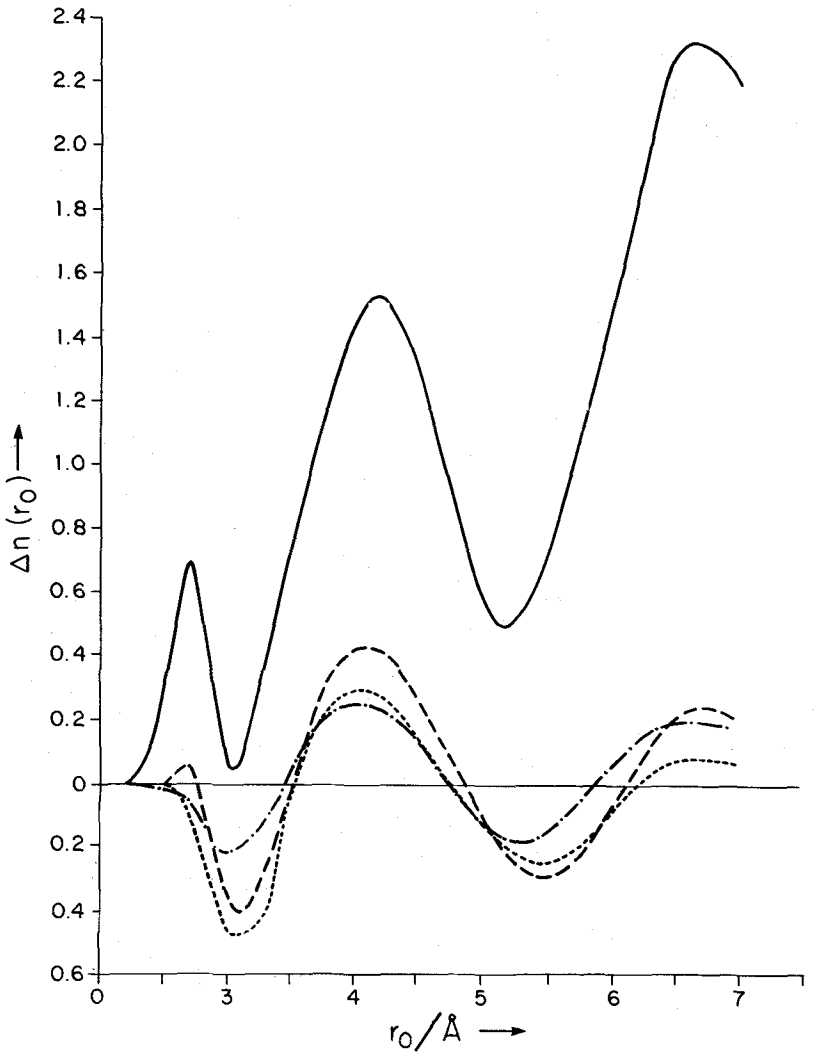

Figure 5. The function $\Delta n(r_0)$ for the ST2 and MCY models. Full line : ST2, energetic hydrogen bond ; — — — —, MCY, energetic hydrogen bond ; — · — · —, ST2, geometric hydrogen bond ; - - - - -, MCY, geometric hydrogen bond.

based on different simulations performed in different thermodynamical ensembles. The $\Delta n(r_0)$s obtained from the energetic hydrogen bond again display the conflicting behaviour reported in [5] and [6]. However, they demonstrate that the conflicting conclusions are simply due to the difference in the water models used. This comparison also serves as a confirmation that the Vornoi polyhedron technique and the coordination number difference technique give essentially the same answer. The comparison of the results using different types of hydrogen-bond definitions gives, however, a surprising result : while for the MCY water no significant difference was found, the predicted density shift of 4-bonded patches occur only with the energetic hydrogen-bond definition. To our knowledge, this is the first example where the two kinds of definitions give a significantly different answer.

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