

INTERPRETATION OF THE UNUSUAL BEHAVIOR OF H₂O AND D₂O AT LOW TEMPERATURE: ARE CONCEPTS OF PERCOLATION RELEVANT TO THE “PUZZLE OF LIQUID WATER”?

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Abstract

This talk will summarize the present status of an ongoing research program designed to answer the question posed in the title. Since a snapshot of liquid water with a subpicosecond shutter speed reveals that this system (a hydrogen-bonded liquid) is above its percolation threshold, it is tempting to imagine that connectivity concepts of the sort encompassed in percolation theory may prove useful. We find that the traditional approach of random-bond percolation theory – developed to describe the onset of gelation – is not sufficient, since water is well above its gelation threshold. Hence we develop a new correlated-site percolation model, whose predictions are found to be in quantitative agreement with molecular dynamics calculations and in qualitative agreement with a wide range of experimental data on low-temperature water.

The picture that emerges is that of an “infinite” hydrogen-bonded network subject to continuous restructuring. At any instant of time, there are many strained and broken bonds. Tiny patches of this network have a local density and local entropy lower than the global density and global entropy of the network. These patches – described by correlated-site percolation theory – are all possible sizes and are characterized by highly ramified (“tree-like”) shapes, just as in random-site percolation.

In particular, this model explains the paradoxical facts that at sufficiently low temperature, the isothermal compressibility $K_T \propto \langle (\delta \bar{V})^2 \rangle_{TPN}$ and the constant-pressure specific heat $C_P \propto \langle (\delta S)^2 \rangle_{TPN}$ increase as T decreases, while the thermal expansivity $\alpha_P \propto \langle \delta \bar{V} \delta S \rangle_{TPN}$ is negative. Finally, we discuss some ongoing calculations and experiments designed to provide additional tests of the overall picture.

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Résumé

Cet exposé va résumer l'état actuel d'un programme de recherche en cours se proposant de résoudre la question posée dans le titre. Depuis qu'un cliché d'eau liquide effectué à l'aide d'un obturateur à vitesse ultra-rapide (<picoseconde) a montré que ce système (liquide avec liaisons hydrogène) est au-dessus de son seuil de percolation, il est tentant de croire que les concepts de connectivité de la sorte de ceux rencontrés en théorie de la percolation peuvent se révéler utiles. Nous trouvons que l'approche traditionnelle de la théorie de la percolation avec liens aléatoires – développée en vue de décrire les débuts de la gélation – est insuffisante, étant donné que l'eau est bien au-dessus de son seuil de gélation. Nous développons alors un nouveau modèle de corrélation entre les sites dont les prédictions s'avèrent être en accord quantitatif avec les calculs de la dynamique moléculaire et en accord qualitatif avec un large échantillon de données expérimentales recueillies pour l'eau à basse température.

L'image qui en ressort est celle d'un réseau "infini" de liaisons hydrogène sujet à restructuration continue. A chaque instant, il y a plusieurs liens sous tension ou brisés. Les petites mailles de ce réseau ont une densité locale ainsi qu'une entropie locale inférieure à la densité et l'entropie globale du réseau. Ces mailles – décrites par la théorie de la percolation avec corrélation entre les sites – sont de toutes les grandeurs possibles et sont caractérisées par des formes hautement ramifiées (type arbre généalogique) juste comme en percolation avec sites aléatoires.

En particulier, ce modèle explique les faits paradoxaux qu'à température suffisamment basse, la compressibilité isothermique $K_T \propto \langle (\delta \bar{V})^2 \rangle_{TPN}$ et la chaleur spécifique à pression constant $C_P \propto \langle (\delta S)^2 \rangle_{TPN}$ croissent comme T décroît, pendant que l'expansivité thermique $\alpha_P \propto \langle \delta \bar{V} \delta S \rangle_{TPN}$ est négative. Finalement nous discutons quelques calculs et expériences présentement en cours désignés à fournir des tests additionnels à l'ensemble.

When the Organizing Committee asked if I would present a progress report on some relatively recent ongoing research on the relevance of percolation to water, I happily accepted. I can never resist the opportunity to lecture on the possibility that a relatively abstract and formal topic of statistical physics – percolation – may in fact turn out to have an unexpected application to the real world. It is these unexpected applications that serve to justify years of research in basic theory.

At the beginning, it is appropriate to state my own degree of indebtedness to a number of individuals. In addition to my collaborators who join me as co-authors, many individuals played key roles in influencing the direction of this research program. First and foremost, C.A. Angell should be thanked for extensive interactions at every stage of this work. Insightful remarks of R. Bansi, L. Bosio, A. Coniglio, H. Frank, P.G. de Gennes, W. Klein, J. Leblond, P. Papon, S. Redner, P.J. Reynolds, and F.H. Stillinger have strongly influenced the directions this program is taking.

This program had its genesis in large part due to my poor command of the French language. When I arrived at the Laboratoire de Physique Thermique to spend a few months as the "Joliot-Curie Visiting Professor" I found that the French I had studied from language tapes bore little resemblance to that heard in the laboratory. Either I had to learn French overnight, or speak English. The decision was made easily: José Teixeira spoke perfect English. He was in the process of making measurements on supercooled water, a

subject I knew nothing about¹). His data²), as well as data from a variety of other laboratories, pointed to the fact that almost every property of liquid H_2O and D_2O has paradoxical behavior. Some properties are anomalous at relatively high temperatures³), while others become anomalous only at low temperature¹). All the anomalies are greatly accentuated as one lowers the temperature into the supercooled region.

What are these anomalies? Simply put, the fluctuations are (i) much larger than one would anticipate and (ii) depend upon temperature T , pressure P , and mole fraction x of impurity in a fashion that runs counter to our intuition. For example, three commonly-studied static correlation functions are the following:

(a) *Density fluctuations.* One might expect that the isothermal compressibility K_T could not decrease with T , since K_T is proportional to the density-density correlation function, and density fluctuations should not decrease as T increases. Although K_T does indeed increase with T at high temperature, it decreases with T for $T < 46^\circ\text{C}$ (fig. 1).

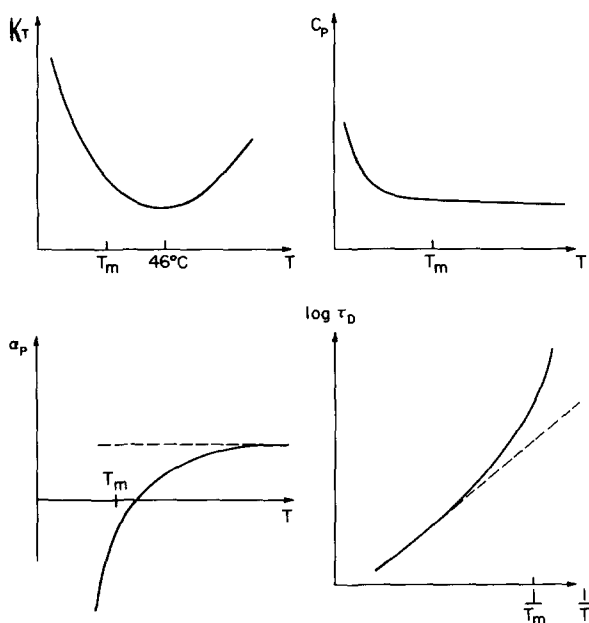


Fig. 1. Schematic dependence on temperature of (a) the isothermal compressibility $K_T(T, P_0, x_0)$, (b) the constant-pressure specific heat $C_P(T, P_0, x_0)$, the thermal expansivity $\alpha_P(T, P_0, x_0)$ for either H_2O or D_2O . For all functions, the pressure P_0 is atmospheric, and the impurity concentration x_0 is zero. The behavior of a typical liquid is indicated by the dashed line, which very roughly is an extrapolation of the high-temperature behavior of liquid water. Note that the anomalies displayed by liquid water become more striking as one supercools below the melting temperature T_m ²¹).

(b) *Entropy fluctuations.* One might expect that the constant pressure specific heat C_P could not decrease with T , since C_P is proportional to the entropy-entropy (or enthalpy-enthalpy) correlation function, and entropy (enthalpy) fluctuations should not decrease as T increases. In fact, C_P also decreases with T for $T < -10^\circ\text{C}$.

(c) *"Cross-fluctuations" of entropy and specific volume.* One might expect that the thermal expansivity α_P could not be negative, since α_P is proportional to the cross-fluctuations of entropy and specific volume. When there is a density fluctuation to lower density and hence larger specific volume, we would expect that the entropy would increase, so that $\alpha_P > 0$. In fact, one finds that $\alpha_P < 0$ for $T < 4^\circ\text{C}$ (H₂O) and for $T < 11^\circ\text{C}$ (D₂O).

The dynamic properties are also anomalous. For example, if we examine the dependence upon $1/T$ of the logarithm of characteristic times such as τ_D (dielectric relaxation time), D_s^{-1} (D_s = coefficient of self-diffusion), or η/T (η = shear viscosity), we find that these are roughly linear at high T , but increase much faster than linearly at low T . Pressure increases the viscosity at high temperatures (as for other liquids), but has the opposite effect for $T < 20^\circ\text{C}$.

Most liquids undergo a glass transition when supercooled sufficiently rapidly. No glass transition has ever been observed in liquid water, even at remarkably high quenching rates.

The list of strange properties could occupy this entire talk. Moreover, all the anomalies seem to be greatly accentuated on reducing T below T_m , the normal melting temperature. The important point is that despite tremendous accomplishments of recent years in obtaining experimental information on the detailed properties of water – even down to the lowest attainable temperatures (roughly -38°C) – no physical picture has emerged that even qualitatively encompasses all the experimental facts. What is the physical mechanism (or mechanisms) underlying these unusual phenomena?

The first place to look for a physical mechanism is the microscopic properties. The principal difference, microscopically, between water and most other liquids is that water has an intermolecular potential that is believed to strongly favor a highly directional (tetrahedral) network of hydrogen bonds. However the properties of these bonds – their relative fraction⁴) p_B and their lifetime⁵) τ_{HB} – vary smoothly with temperature (fig. 2).

We conclude therefore that the "puzzle of liquid water" will require some sort of mechanism (i) whereby the hydrogen bonds among the four-functional monomers play a dominant role, and (ii) which can amplify the smoothly varying bond properties p_B and τ_{HB} . When one considers bonding among four-functional monomers, one immediately thinks of Flory's theory of gelation⁶) – which is essentially equivalent to random bond percolation⁷).

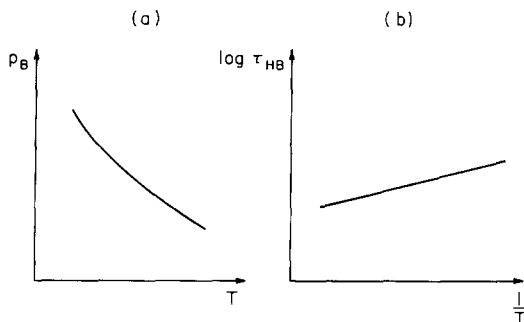


Fig. 2. Schematic dependence on temperature of the two microscopic parameters emphasized in the present percolation approach. (a) the fraction of intact hydrogen bonds, $p_B(T, P_0, x_0)$, and (b) the characteristic hydrogen-bond lifetime $\tau_{HB}(T, P_0, x_0)$. The fact that these functions do not display any striking "non-linear" behavior motivates the need for an amplification mechanism – such as that provided by eq. (1) – to explain the highly non-linear behavior of functions such as those plotted in fig. 1.

However there are at least two problems with the possibility⁸⁾ that the unusual properties of liquid water are associated with its "gelation threshold" (or bond percolation threshold):

(i) There is ample evidence that the fraction of intact hydrogen bonds, p_B , is well in excess of the bond percolation threshold even at relatively high temperatures⁹⁾, and

(ii) The observed anomalies in thermodynamic functions, such as the unusual density and entropy fluctuations mentioned above, are not associated with the gelation (or random-bond percolation) threshold, with which are associated increased connectivity fluctuations.

It is thus necessary to go beyond conventional models of percolation if one is to find a physical mechanism germane to the unusual behavior displayed by the hydrogen-bonded "gel", liquid water. The first model I thought of¹⁰⁾ is extremely simple, yet potentially useful in providing a "zeroth order" description of the essential physical mechanism underlying water behavior. I will first describe this model¹⁰⁾, and then discuss some recent tests using molecular dynamics data on ST2 water¹¹⁾ and experimental data on real water¹⁰⁾. Finally, I will mention some improvements on the simple model that may be appropriate.

Fig. 3 shows a small section of the infinite hydrogen-bonded network for $p_B = 0.8$ (a very rough estimate^{4,9)} for low-temperature water). Each vertex represents an oxygen, and each line segment an intact hydrogen bond. Of course, the oxygens in *real* water are not situated on the vertices of a lattice, but the essential features of percolation theory appear to be generalizable from lattice systems to continuum systems^{11,12)}. Every "oxygen" with four

intact bonds incident upon it is indicated by a heavy black dot. The study of the connectivity of these "black oxygens" constitutes a novel sort of *correlated-site* percolation problem ("correlated" – e.g., it is impossible that the four neighbors of an oxygen are all black unless the oxygen itself is black).

In what follows we shall summarize the evidence that (i) this simple picture is supported by *quantitative* calculations – without adjustable parameters – on ST2 water¹¹) and that (ii) this picture provides a *qualitative* interpretation of essentially all of the experimental anomalies of low-temperature water of which we are aware¹⁰).

Calculations on ST2 water. In many computer calculations on the properties of water-like particles, one defines two water molecules as "bonded" when their mutual interaction energy $V(r)$ is less than a cutoff parameter V_{HB} (fig. 4). Thus a typical molecular dynamics calculation results in a picture like that shown schematically in fig. 5. The bonds are shown in perspective for the $18.6\text{\AA} \times 18.6\text{\AA} \times 18.6\text{\AA}$ constant-volume cube within which reside 216 water-like particles whose motion is studied. Note that there are "networks" of every shape and size. Percolation theory gives the weight fraction $W(M, p_B)$ of networks with M molecules. The comparisons between molecular dynamics and percolation theory are shown in fig. 6 for the case $M = 5$.

For the sake of computational facility, we have made two assumptions in carrying out the percolation calculations: (i) The water molecules on average have the connectivity of an ice I_h lattice, and (ii) the hydrogen bonds are randomly distributed – the presence of three bonds incident upon a given oxygen does *not* make a fourth any more likely. The x -axis, the bond probability p_B , is obtained by calculating for each choice of V_{HB} the mean number of intact hydrogen bonds per molecule n_{HB} , and then setting $p_B = n_{HB}/4$. Thus there are no "adjustable parameters" in fig. 6, so the agreement is indeed rather remarkable, especially in light of assumptions (i) and (ii).

Next we direct our attention to the water molecules themselves. Extensive molecular dynamics and Monte Carlo information exists on f_j , the fraction of water molecules with j intact bonds (note that $n_{HB} = \sum_j j f_j$). Assumptions (i) and (ii) suggest that one might usefully compare with the binomial distribution:

$$f_j = \binom{4}{j} p_B^j (1 - p_B)^{4-j}. \quad (1)$$

The predictions of eq. (1) are shown in fig. 7, together with results based on analysis of the Rahman–Stillinger molecular dynamics tapes. Note that eq. (1) reduces for $j = 4$ to $f_4 = p_B^4$, so that there is a built-in amplification mechanism for the weight fraction of four-bonded atoms.

The agreement shown in fig. 7 is not limited to molecular dynamics calculations using the ST2 potential:

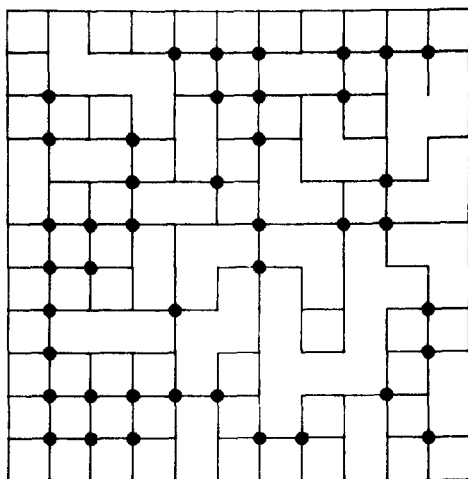


Fig. 3. A subsystem consisting of 100 oxygen atoms, situated (for convenience only) on the vertices of a square lattice. Of course, the detailed connectivity of this square lattice is different from the connectivity in water or ice (cf. figs. 6–8). Intact hydrogen bonds – randomly present with probability $p_B(T, P, x) = 0.8$ – are indicated by solid line segments. Oxygens with four intact bonds are shown as heavy black dots. The “black oxygens” form patches in the hydrogen-bonded network. The site percolation problem defined by the connectivity of these black oxygens is a correlated one: if a given oxygen A is black, there is a greater probability that the neighbors of A are also black.

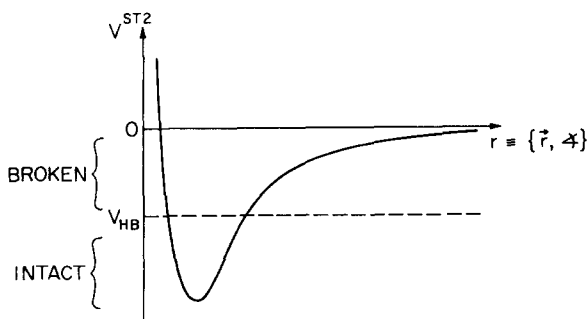


Fig. 4. Schematic illustration of a water–water interparticle potential $V(r)$. The fact that the water molecule is highly asymmetric implies that this curve depends not only on the molecule–molecule separation vector r , but also on the relative orientation of the two waters. Also shown is the concept of a cutoff parameter V_{HB} , as used extensively in molecular dynamics calculations. When the mutual energy of interaction is stronger than V_{HB} , we say that the two molecules have a bond between them; otherwise no bond is said to exist. This imposition of a discrete symmetry upon a continuous physical function can be avoided by the extension of our present model to a “continuum, polychromatic” case²⁴).

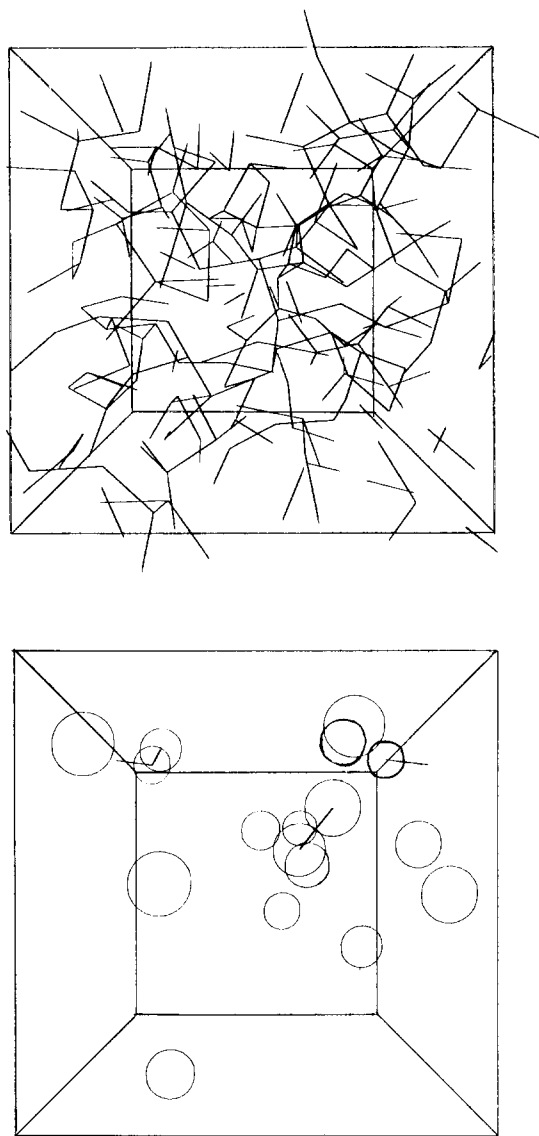


Fig. 5. The results of an instantaneous "snapshot" of a Rahman–Stillinger molecular dynamics simulation of 216 ST2 water-like point particles constrained to a 18.6 Å cube. In (a) are shown only those "intact bonds", as defined by the convention of fig. 4, with $V_{HB} = -56\epsilon$, and $\epsilon = 0.07575$ kcal/mole. This value of a cutoff parameter corresponds to $n_{HB} = 1.92$ and $p_B = 0.48$ (above the bond percolation threshold). In (b) are shown as large open circles those "black oxygens" with four intact hydrogen bonds. The detailed statistics of bond connectivity can be obtained by varying V_{HB} in order to vary p_B ; these are exemplified by the results of fig. 6. The details of the connectivity of the patches of four-bonded oxygens are exemplified by the results of fig. 8. Adapted from ref. 11.

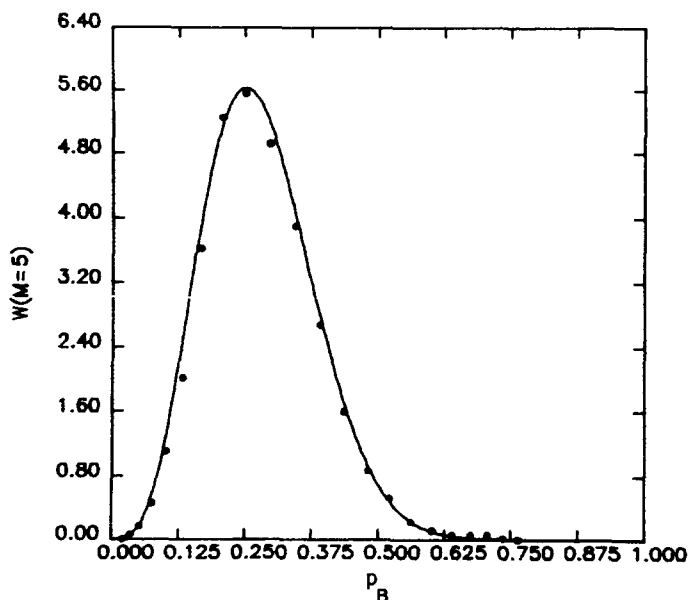


Fig. 6. Dependence upon p_B of the weight fraction of oxygens belonging to finite-size networks containing M molecules, for $M = 5$. Incidentally, the case $M = 1$ is identical to f_0 , plotted in fig. 7. The points represent the bond connectivity analysis of the Rahman–Stillinger molecular dynamics tapes for ST2 water, while the solid curves represent the results of random-bond percolation calculations for an ice I_h lattice. Adapted from ref. 11.

(i) Jorgensen¹³) has calculated the hydrogen-bonding statistics for STO-3G water using Monte Carlo methods, with the results $100 f_j = 0, 2, 11, 36, 50, 2$ for $j = 0, 1, 2, 3, 4, 5$. Eq. (1) predicts $100 f_j = 0, 2, 11, 38, 50$ for $j = 0-4$ using $p_B = 0.84$ ($n_{HB} = 3.36$).

(ii) Pengali et al.¹⁴) have calculated f_j for several different system sizes, and we find full agreement between their Monte Carlo calculations and eq. (1).

(iii) Mezei and Beveridge¹⁵) have analyzed the network properties for a variety of separate Monte Carlo and molecular dynamics calculations on both ST2 and MCY potentials. Altogether four different values of temperature are considered. For all cases, they find network properties depend only on n_{HB} , and not on the interparticle potential, the temperature, or the definition of a hydrogen bond (“energetic criterion” or “geometric criterion”). Their analysis thereby supports a principal assumption of our work that $p_B = n_{HB}/4$ is the primary determinant of network properties: all their data collapse upon the same curve if plotted against p_B (cf. fig. 10 of ref. 15).

Although the fraction of molecules f_j belonging to each class is determined by simple statistics, the connectivity of each of the five species of molecules is far from trivial. In fact, the positions of the four-bonded “black oxygens”

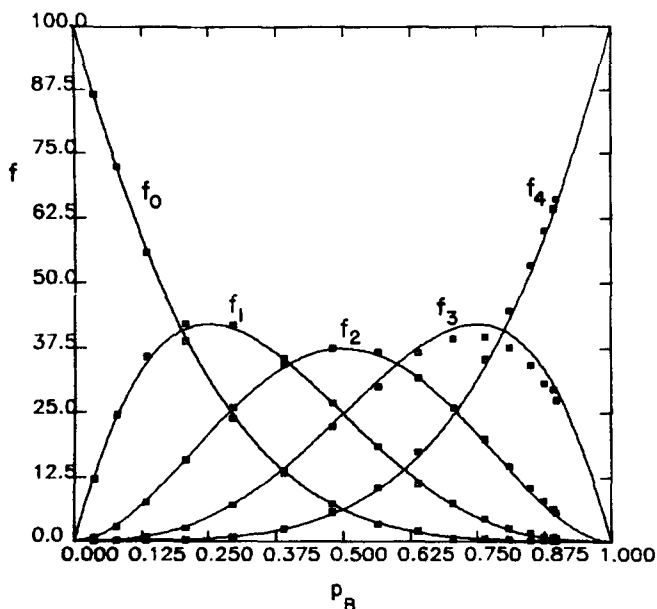


Fig. 7. Dependence upon p_B of the fraction of oxygen atoms having j intact bonds, for $j = 1-4$. The points represent the results from the Rahman-Stillinger tapes for ST2 water, while the solid curves represent the results of eq. (1). Adapted from ref. 11.

are strongly correlated, just as if there were an energy term leading to a tendency to clump together¹⁶). At first sight this is a subtle and extremely surprising point: "random bonds lead to correlated sites." This "clumping" is most clearly seen if we calculate the weight fraction $W(s, p_B)$ for s -site patches of four-bonded oxygens. This calculation can be done exactly for s up to 5, and it can be done with about 1% accuracy by Monte Carlo methods for s up to about 15 or 20. The remarkable agreement between $W(s, p_B)$ and the results of molecular dynamics calculations on ST2 water is illustrated for $s = 5$ in fig. 8. Thus there is ample reason to believe that we may regard water as an infinite hydrogen-bonded network, tiny patches of which are four-bonded.

The functions $W(s, p_B)$ have also been calculated for the much simpler case of *random* site connectivity¹⁷), and the results are shown in fig. 9. We find that the ratio of "random" to "correlated" weight function increases as p_B increases. Since p_B increases when T decreases, we have a "clumping effect" which increases as T decreases, just as might have been expected were there present an explicit "energy term." For example, if $p_B = 0.8$, then we find the ratio of "random" to "correlated" $W^R(1, 0.8)/W(1, 0.8) = 2.1$ for 1-site patches, and $W^R(2, 0.8)/W(2, 0.8) = 2.5$ for 2-site patches. This is intuitively

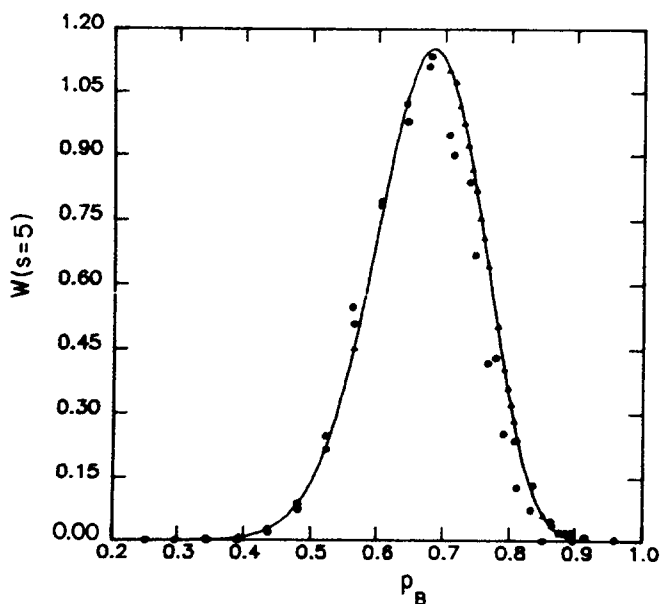


Fig. 8. Dependence upon p_B of the weight fraction of oxygens belonging to finite-size "patches" of s molecules, characterized by the fact that every oxygen in a patch is bonded to precisely four other oxygens. Shown is the representative case, $s = 5$. The points represent the molecular dynamics results for ST2 water, and the solid curve represents exact calculations for the ice I_h lattice. Adapted from ref. 11.

plausible, since small patches occur much less frequently due to their tendency to "clump together" in larger patches (fig. 9).

To summarize thus far: When looking at the bond connectivity problem, water appears as a large macroscopic space-filling hydrogen-bond network, as expected from continuum models of water⁸). However when we focus on the four-bonded molecule ("sites"), we find that water can be regarded as having certain clustering features – the clusters being not isolated "icebergs" in a sea of dissociated liquid (as postulated in mixture models dating back to Roentgen¹⁸)) but rather patches of four-bonded molecules embedded in a highly connected network or "gel".

At this stage, one can ask "So what?" That is, "What is the relation between the patches in the infinite bond network and the observed anomalies of liquid water?"

The answer to this question must be "Nothing whatsoever!" unless there is some *local* property of the patch that is different from the *global* properties of the hydrogen-bonded network as a whole. It is our *Ansatz* that (i) the local density and (ii) the local entropy of the patch are less than the global density and the global entropy of the network. If this intuitively-plausible assumption

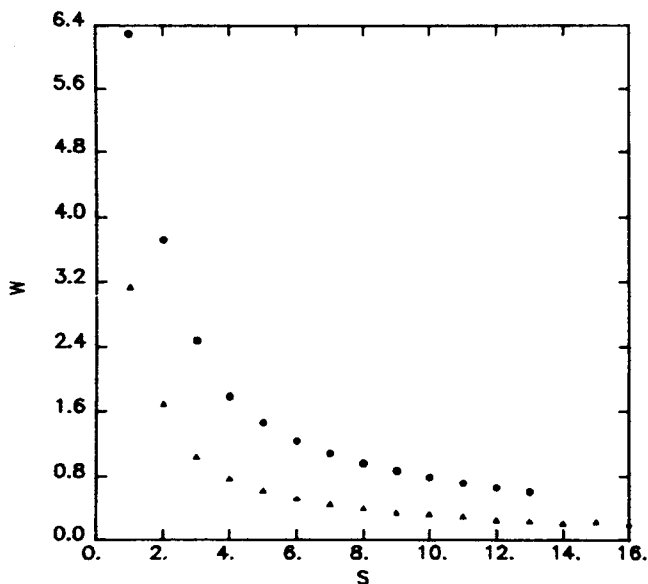


Fig. 9. Histograms showing the dependence upon s of the weight fraction of oxygen atoms belonging to a patch of size s . Note that this distribution is monotonically decreasing, so that there are always more 1-site patches than 2-site patches, etc. The triangles are correlated-site percolation calculations on an ice I_h lattice with 35,152 sites. Shown for comparison are the results of random-site percolation theory (ref. 17).

is correct, it would provide a mechanism for the observed anomalies in static properties.

(i) *Local density associated with a patch.* The assumption that the local density in a patch should be smaller than the global or mean density of the network has recently received support from the molecular dynamics analysis of ST2 water¹¹), and it is certainly intuitively plausible that if all molecules in a given patch are tetrahedrally bonded, the local density should be different than in a region of space in which this is not true.

(ii) *Local entropy associated with a patch.* The assumption that the local entropy in a patch should be smaller than the mean entropy of the network requires more explanation. The water molecule is extremely non-spherical, and hence its tendency to form hydrogen bonds is highly directional. Thus the angular degrees of freedom are greatly reduced (i.e., the angular range is much smaller) in a patch where all molecules are four-bonded.

Assumption (i) implies that the existence of tiny patches gives rise to an additional contribution to the fluctuations $\delta\bar{V} \equiv \bar{V} - \langle\bar{V}\rangle_{TPN}$ in the specific volume, where $\langle\cdots\rangle_{TPN}$ is an ensemble average with temperature, pressure, and particle number fixed. Hence there is an "anomalous" contribution K_T^A to

the compressibility, since

$$K_T \equiv -(1/\bar{V})(\partial\bar{V}/\partial P)_T \propto \langle(\delta\bar{V})^2\rangle_{TPN}. \quad (2a)$$

Indeed, it is known that the density fluctuations of liquid water are roughly twice as large as those of a typical liquid¹⁹).

As the temperature is lowered, K_T^\wedge would be predicted to increase initially, since the patches become more numerous as p_B increases (cf. fig. 8). This behavior is in contrast to that of most liquids, as mentioned at the beginning of this talk. Of course, if we could lower the temperature sufficiently, we would expect K_T^\wedge to become smaller, so that the overall compressibility might again decrease. There are recent indications that this might be the case for the adiabatic compressibility K_S^{20}).

Assumption (ii) implies that analogous statements may be made concerning the fluctuations $\delta S \equiv S - \langle S \rangle_{TPN}$ in the entropy, and hence we anticipate an anomalous contribution C_P^\wedge to the constant-pressure specific heat,

$$C_P \equiv (1/T)(\partial S/\partial T)_P = k\langle(\delta S)^2\rangle_{TPN}. \quad (2b)$$

Thus we correctly predict that C_P for water should be larger than C_P for most liquids, and should increase at sufficiently low T .

One might imagine that whereas the density of a very small patch (e.g., 2–3 molecules) might be significantly reduced from the global density, one would require rather larger patches in order to obtain a significant entropy reduction. If this intuitive hunch is correct, it would explain why K_T begins to display anomalous behavior at much higher temperatures than $C_P^{1)}$.

Incidentally, one may replace the above discussion concerning entropy fluctuations by an analogous discussion concerning fluctuations in the enthalpy H , since C_P is also given by $C_P = kT^2\langle(\delta H)^2\rangle_{TPN}$.

Finally, we consider the thermal expansivity, which is proportional to the cross-fluctuations of volume and entropy:

$$\alpha_P \equiv (1/\bar{V})(\partial\bar{V}/\partial T)_P \propto \langle\delta\bar{V}\delta S\rangle_{TPN}. \quad (2c)$$

For most liquids, when there is a local volume fluctuation with a positive $\delta\bar{V}$, there is a corresponding *increase* in the local entropy ($\delta S > 0$). However for the patches in question, $\delta S < 0$ when $\delta V > 0$, so that there is an anomalous negative contribution α_P^\wedge to the thermal expansivity. The normal and anomalous contributions balance at $T = 4^\circ\text{C}$.

Thus the effect of the hydrogen bonds is predicted to “correct” the basic response functions K_T , C_P , and α_P in the fashion summarized in the first line of table I. As the temperature is lowered, p_B increases, and these corrections would be expected to change in magnitude, in the directions indicated by the arrows given in the second line of table I. If hydrostatic pressure is applied to

the system, the patches decrease in size and number – on average – and we predict the changes summarized on the third line. However if we dilute H₂O with a mole fraction x of the “impurity” D₂O, then we expect that the patches increase in characteristic size and number – with the predictions summarized on the fourth line. If instead we dilute H₂O with “patch-breaking” impurity – such as ethanol, which can form essentially 3 bonds per molecule rather than 4 – we make the predictions given on the bottom line of table I²¹).

All 15 qualitative predictions summarized in table I are borne out by experiment^{1,3}). A more quantitative discussion of the predictions, together with detailed references to the experimental results, is provided in ref. 10.

Summary and outlook. In a talk of finite length, it has been impossible to discuss all the experimental facts and the extent to which percolation theory may be relevant. Hence I have concentrated on (i) the evidence from molecular dynamics for the existence of patches whose statistics are described quantitatively by correlated-site percolation theory, and on (ii) the qualitative implications of the existence of such patches for the three response functions just discussed. Other functions can be approached in the same spirit. For example, we (correctly) predict that the *constant-volume* specific heat C_V has no anomalies, since an essential feature of the tiny patches of four-bonded oxygens is that their local density is slightly smaller

TABLE I

Summary of the qualitative predictions of the simple bichromatic discrete percolation model for the behavior of three static response functions: the isothermal compressibility K_T defined in eq. (2a), the constant-pressure specific heat C_P defined in eq. (2b), and the thermal expansivity α_P defined in eq. (2c).

	K_T	C_P	α_P
Sign of anomaly	+	+	–
Lower T	↑	↑	↓
Increase P	↓	↓	↑
Dilute with D ₂ O	↑	↑	↓
Dilute with a “patch-breaking” impurity	↓	↓	↑

than the global density. Also, we (correctly) predict that there will be no glass transition in liquid water, since the tiny low-entropy patches of the random hydrogen-bonded network create an irreversible situation tending toward crystallization. However relatively few molecules of a "patch-breaking" impurity should restore the transition, and this is indeed found to be the case²²). We further predict that less impurity will be required when measurements are made under pressure, and this prediction is also borne out²³). By the way, various pictures of liquid water that resemble glassy water would seem to have difficulty in explaining the absence of a glass transition⁸).

It is clear that the present picture is based on an assumption: the existence of tiny patches of the hydrogen-bonded network. While this assumption has been strikingly verified by molecular dynamics calculations¹¹), what is most urgently needed is a direct experimental confirmation in real water. One possible experiment would be measurements of the X-ray structure factor $S(q)$ at very small momentum transfer vectors q and at very low temperatures T . One would predict that the very small reduction in electron density associated with a patch would provide sufficient contrast to be detectable²⁴). Previous measurements of $S(q)$ did not attain extremely low q or extremely low T , but did suggest a slight increase^{25,26}). Further work is planned using synchrotron radiation to provide high X-ray flux²⁶). We are especially optimistic, since preliminary molecular dynamics analysis¹¹) suggests a non-negligible effect.

Theoretical elaborations are also called for, if the present heuristic picture is to become sufficiently developed to provide a fully quantitative description of low-temperature water. Among the most important is the creation of an appropriate Hamiltonian that describes simultaneously (i) the interactions and (ii) the connectivity between water molecules²⁷). Approaches analogous to that used for describing solvent effects on gelation²⁸) are under study at the present time. Also important is a study of how serious an approximation is made by the imposition of a discrete symmetry – the assumption of two bond states (fig. 4) – upon a physical function, $V(r)$, that is certainly not discrete. Here one can hope that the essential physical features of the present "discrete" picture are not altered, just as the discrete lattice-gas adequately describes the essential physics of a fluid near its critical point. However a more refined "polychromatic continuum percolation" is a natural and quite feasible extension²⁴).

Thus much remains to be done, both experimentally and theoretically. However we are optimistic that the simplicity and elegance of the present picture will not be lost by the sort of elaborations that will perforce arise. In particular, it is our hope – as physicists – that whatever the solution may be to the "puzzle of liquid water", it is sufficiently economical that only a single

physical mechanism remains to be discovered to encompass the entire range of phenomena – ranging from the compressibility minimum at +46°C to the Angell singularity¹⁾ at about –46°C. It would be most unsatisfactory if we would require *one* mechanism for, say, $T > T_m$ and a *second* mechanism for $T < T_m$.

What, then, does the future hold? The most optimistic possibility is that we can answer “yes” to the question posed by the title, and our program may possibly lead to a useful foundation on which to further understanding of liquid water. At the least optimistic, percolation concepts will prove to be irrelevant to the behavior of liquid water, but nevertheless we will have learned a great deal about a simple model in which sites become correlated as a result of a random process. Even the least optimistic possibility is not without some satisfaction, however, since any well-understood model is likely to have some application in the complex physical world. This seems to be the case here, also: Brodsky of IBM Research Laboratories has recently succeeded in applying the model to hydrogenated amorphous silicon, aSiH_x²⁹⁾, a prototype material for energy conversion. Specifically, he proposes that pure Si corresponds to our model with $p_B = 1$. Hydrogenation corresponds to breaking covalent Si–Si bonds, and therefore corresponds to increasing temperature, pressure, or patch-breaking impurity concentration. By doing calculations on the system of “disconnected Si patches,” Brodsky succeeds in predicting the results of several hitherto inexplicable experiments. Who knows – given the energy crisis facing every country represented at this meeting – if the “least optimistic” possibility is not sufficient justification for continuing our research program in polychromatic correlated-site percolation?

References

- 1) A recent and comprehensive review of the experimental anomalies displayed by supercooled water is C.A. Angell, in *Water: A Comprehensive Treatise*, F. Franks, ed. (Plenum, New York, 1981) Vol. 7.
- 2) See, e.g., J. Teixeira and J. Leblond, *J. Phys. Lett. (Paris)* **39** (1978) L83; O. Conde, J. Teixeira and J. Leblond, *J. Phys. (Paris)* **41** (1980) 997.
- 3) See, e.g., the classic monograph D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, New York, 1969). Briefer but more recent reviews include F.H. Stillinger, *Adv. Chem. Phys.* **31** (1975) 1; *Philos. Trans. Roy. Soc. London* **B278** (1977) 97; *Science* **209** (1980) 541; S.A. Rice, *Topics in Current Chemistry* **60** (1975) 109; J.T. Edsall and H.A. McKenzie, *Adv. Biophys.* **10** (1978) 137; E.H. Trinh, *Tech. Memorandum No. 2*, Yale University (1977); M.S. Jhon and H. Eyring, *Ann. Rev. Phys. Chem.* **27** (1976) 45; W. Luck, *Angewandte Chemie* **92** (1980) 29.
- 4) See, e.g., W. Luck, in *The Hydrogen Bond*, P. Schuster, G. Zundel and C. Sandorfy, ed.

- (North-Holland, Amsterdam, 1976) Ch. 28;
G. Walrafen, in ref. 1, Vol. 1.
- 5) C.J. Montrose, J.A. Bucaro, J. Marshall-Croakley and T.A. Litovitz, *J. Chem. Phys.* **60** (1974) 5025.
 - 6) P.J. Flory, *J. Am. Chem. Soc.* **63** (1941) 3083, 3091, 3096;
W.H. Stockmayer, *J. Chem. Phys.* **11** (1943) 45.
 - 7) M.E. Fisher and J.W. Essam, *J. Math. Phys.* **2** (1961) 609;
H.L. Frisch and J.M. Hammersley, *J. Soc. Ind. Appl. Math.* **11** (1963) 894;
P.G. de Gennes, *J. Phys. (Paris)* **36** (1975) 1049;
D. Stauffer, *Chem. Soc. Faraday Trans.* **72** (1976) 1354.
 - 8) J.D. Bernal and R.H. Fowler, *J. Chem. Phys.* **1** (1933) 515;
J.A. Pople, *Proc. R. Soc. London* **A205** (1951) 163;
J.D. Bernal, *Proc. R. Soc. London* **A280** (1964) 299;
J.H. Gibbs, C. Cohen, P.D. Fleming and H. Porosoff, *J. Solution Chem.* **2** (1973) 277;
M.G. Sceats and S.A. Rice, *J. Chem. Phys.* **72** (1980) 3236, 3248, 3260, 6183.
 - 9) A. Geiger, F.H. Stillinger and A. Rahman, *J. Chem. Phys.* **70** (1979) 4185.
 - 10) H.E. Stanley, *J. Phys.* **A12** (1979) L329.
A more detailed description and development of the model, together with extensive comparison to experimental data, is in H.E. Stanley and J. Teixeira, *J. Chem. Phys.* **73** (1980) 3404. Detailed Monte Carlo calculations have been carried out by R.L. Blumberg, G. Shlifer and H.E. Stanley, *J. Phys.* **A13** (1980) L147, while renormalization group calculations have been performed by A. Gonzales and P.J. Reynolds, *Phys. Lett.* (in press).
 - 11) A. Geiger et al., work in progress (to be published).
The classic "Rahman-Stillinger tapes" that we used are described in F.H. Stillinger and A. Rahman, *J. Chem. Phys.* **60** (1974) 1545; potentials other than ST2 are described in D.W. Wood, in ref. 1, Vol. 6.
 - 12) E. Gawlinski and H.E. Stanley, *J. Phys. A* (submitted).
 - 13) W.L. Jorgensen, *Chem. Phys. Lett.* **70** (1980) 326.
 - 14) C. Pengali, M. Rao and B.J. Berne, *Mol. Phys.* **40** (1980) 661.
 - 15) M. Mezei and D.L. Beveridge, *J. Chem. Phys.* (in press).
 - 16) The detailed calculations concerning the "clumping" of small patches were motivated by questions of F.H. Stillinger. We wish to thank Dr. Stillinger for discussions on the sort of "effective attraction" exhibited by our model.
 - 17) M.F. Sykes, D.S. Gaunt and M. Glen, *J. Phys.* **A9** (1976) 1705.
 - 18) W.C. Roentgen, *Ann. Phys.* **45** (1892) 91.
 - 19) H.S. Frank, in ref. 1, Vol. 1.
 - 20) E. Trinh and R.E. Apfel, *J. Chem. Phys.* **72** (1980) 6731;
See also O. Conde et al., work in progress (to be published).
 - 21) A particularly simple but striking example is the dependence of the adiabatic sound velocity $v_s \propto K_s^{-1/2}$ upon the mole fraction x of ethanol. Although v_s for pure ethanol ($x = 1$) is much smaller than v_s for pure water ($x = 0$), one finds a substantial *increase* in v_s as ethanol is added to pure water. We would interpret this finding as follows: ethanol is "breaking up" the patches, and thereby reducing the compressibility. When v_s is plotted against x for a range of temperature from 5°C to 45°C, one finds that all the isotherms intersect at a single "isobestic point" with $x = 0.17$ and $v_s = 1.6$ km/s (A. Giacomini, *J. Acoustical Soc. Am.* **19** (1947) 701; see also G.W. Willard, *J. Acoustical Soc. Am.* **19** (1947) 235. Thus at 17% ethanol, increasing T from 5°C to 45°C serves to decrease the fluctuations due to the patches, but this is precisely compensated for by an increase in the fluctuations of the normal regions of the network. It would be desirable to extend these observations to a wider range of temperature and pressure, to other impurities, and to properties other than v_s . It is my opinion that careful study of judiciously-chosen two-component systems will serve to provide useful clues relevant to the "puzzle of liquid water."

- 22) I.V. Yannas, *Science* **160** (1968) 298;
C.A. Angell and E.J. Sare, *J. Chem. Phys.* **52** (1970) 1058.
- 23) C.A. Angell, private communication.
- 24) Strictly speaking, we cannot talk about "contrast": the density and entropy fluctuations are continuously distributed in space. But in reality there is no sharp distinction between bonded and non-bonded molecules, since V_{HB} is but a fiduciary parameter. A more refined model would be one in which we replace our discrete bichromatic picture with a continuum polychromatic picture. Each bond can be in a continuum of states – not just intact and broken – and each oxygen can see a continuum of different possible local densities and local entropies. Such a model could be formalized, I suppose, by making a one-to-one correspondence between the energy of each bond and a "wavelength". Wavelengths in the violet end of the spectrum would correspond to "strong" bonds, $V(r) < V_{HB}$, while wavelengths in the red end of the spectrum would correspond to "weak" bonds $V(r) > V_{HB}$. A snapshot of the system would reveal a rainbow of colors. A Maxwell demon situated on a given oxygen would see a local density which depends, to lowest order, on the sum of the wavelengths of the incident bonds. The essential feature of the present discrete bichromatic model would be preserved in the continuum polychromatic model: there is a spatial correlation between the density fluctuations. Thus we preserve the simple physical mechanism of creating correlated enhanced fluctuations that *increase* as temperature is decreased.
- 25) R.W. Hendricks, P.G. Mardon and L.B. Shaffer, *J. Chem. Phys.* **61** (1974) 319 and references therein.
- 26) L. Bosio, J. Teixeira and H.E. Stanley, *Phys. Rev. Lett.*
- 27) We wish to thank D. Chandler for emphasizing this need.
- 28) A Coniglio, H.E. Stanley and W. Klein, *Phys. Rev. Lett.* **42** (1979) 518; *Phys. Rev. B* (submitted).
- 29) M.H. Brodsky, *Solid State Commun.* **36** (1980) 55.