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THE "LOCALLY-STRUCTURED TRANSIENT GEL" MODEL OF WATER STRUCTURE

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Résumé - Cette présentation fait une revue sommaire de quelques informations qui viennent en lumière au sujet de la structure de l'eau liquide quand on prête attention aux propriétés de connectivité des liaisons hydrogène. L'évidence appuie généralement l'image que l'eau liquide est un "gel transitoire" caractérisé par la présence de régions localement structurées de dimension caractéristique linéaire de l'ordre de 8 Å.

Abstract - This talk reviews briefly some of the information that comes to light concerning the structure of liquid water when one pays attention to the connectivity properties of the hydrogen bonds. The evidence generally supports the picture that liquid water is a "transient gel" characterized by the presence of locally-structured regions of a characteristic linear dimension of about 8 Å.

It is not easy to give an elementary opening talk to a meeting populated by experts! Hence I've chosen to give a rather brief and parochial overview of the picture of water structure that has been evolving--largely in collaboration with those who kindly consented to join me as co-authors. The details that I will omit can be found in the original papers.¹⁻¹⁴ It is a pleasure to acknowledge at the outset interactions with L. Bosio, P. G. de Gennes, M. Mezei, P. Papon, F. H. Stillinger, and especially C. A. Angell.

I shall organize the talk as follows. First I will present, very briefly, a review of those puzzling features of liquid water that most attract the fascination of a physicist. Then I'll present some clues concerning those features. Thirdly I'll describe the "transient gel" model, and lastly I'll give some tests of the transient gel model on computer water and on real water.

The overall picture that will emerge is that water may be viewed as a gel on time scales smaller than the bond life; i.e., if we took a photograph with a very short shutter speed, water and jello would have something in common. This gel is characterized by many small, locally-structured regions, whose characteristic linear dimension is roughly 8 Å.

I. PUZZLE

We shall start at the beginning with the puzzle of liquid water. Three static properties of water are particularly puzzling to a physicist. The first of these concerns the fluctuations in specific volume ("density"), which are proportional to the isothermal compressibility. For most liquids this function decreases as the

temperature is lowered. This makes intuitive sense: the temperature "drives" density fluctuations. For water, the reverse is true: as T decreases, K_T increases! This is not a 1% effect: K_T increases by almost a factor of two from its minimum at about 50C to its value at the lowest attainable temperatures, about -30C. Thus the explanation of this effect requires some mechanism that operates from +50 to -30!

Analogous behavior occurs for the entropy fluctuations, which are proportional to the constant-pressure specific heat C_p . These are anomalous in the same two respects: the specific heat is larger in magnitude than for most liquids (giving rise to its utility as a coolant), and when one lowers the temperature, the entropy fluctuations increase. This is also counter-intuitive, since we always imagine that the temperature "drives" entropy fluctuations. Again, this is not a small effect: the specific heat at the lowest attainable temperatures is almost a factor of two larger than its value at high temperatures.

One might expect that the thermal expansivity $\alpha_p = (dV/dT)_p$ could not be negative, since it is proportional to the cross fluctuations of entropy and specific volume. When one considers a local region in which the specific volume is larger, then one expects that there are more "arrangements" of the molecules and hence a larger local entropy. Thus the cross fluctuations should be positive. For water the thermal expansivity is anomalous in two respects: firstly, at high temperatures it is only a fraction of its value for typical liquids. Secondly, below about 4C, it is negative!

The dynamic properties are also anomalous. For example, if we examine the dependence upon $1/T$ of the logarithms of characteristic times such as the dielectric relaxation time, inverse diffusion coefficient, or shear viscosity, then we find that these are roughly linear at high T but increase much faster than linearly as T is decreased. Pressure increases the viscosity at high temperatures as for most liquids, but has the opposite effect for T below about 20C.

II. CLUES

The list of strange properties could occupy the entire talk. Perhaps even more striking than the anomalies themselves is the fact that they seem to be "amplified" as one reduces T below the melting temperature. What could be the physical mechanism underlying this amplification?

At first sight, one might seek something special about the supercooled state of matter. This approach has been taken by some workers in an effort to explain the "mysterious behavior of supercooled water." However it is somewhat misleading, since the acceleration in the anomalous behavior in the supercooled regime is already manifest in the normal regime: if one, e.g., fits the behavior of a function in the normal regime to a polynomial (as Kell has done) and then substitutes temperature values corresponding to the supercooled regime then one finds values of K_T remarkably close to the observed behavior (C. A. Angell, private discussions). Thus a major constraint on any possible explanation of the

supercooled behavior is that it must be based on phenomena that are operative in the normal regime. The same physics is controlling the 50C minimum in K_T as the factor of two increase in K_T in the supercooled regime.

What could this mechanism be? Several clues present themselves. Perhaps the foremost clue is that a distinguishing feature of water is the presence of a remarkably high degree of hydrogen bonding when compared to other liquids. It has been known since the classic observations of Pauling that when ice melts at 0C, only a small fraction (perhaps 20%) of the hydrogen bonds break. If one continues to increase the temperature, the fraction of intact bonds, p_B , decreases very slowly--a handy mnemonic formula suggests that for every 2.5C of heating, an additional 1% of the bonds break. Similarly, if one supercools water, p_B increases very slowly--the same 1% for every 2.5C of supercooling. The problem, then, is to go from a very smoothly and slowly varying microscopic parameter-- p_B --to the dramatically varying macroscopic parameters mentioned above. We say that the hydrogen bonds link the water molecules into a network or "gel" because the gelation threshold for a 3-dimensional system is well below 80%. How can we be certain that the hydrogen bond network is responsible for the anomalous properties of water? We can do things to water that are known to weaken the network, and see the anomalies go away. For example, we can apply hydrostatic pressure, or introduce hydrogen-bonding impurities such as H_2O_2 . Alternatively, we may replace part or all of the H_2O by D_2O and find that the anomalies become stronger.

III. LOCALLY-STRUCTURED TRANSIENT GEL MODEL

The qualitative picture of water structure first proposed in Refs. 1-3 is receiving increased quantitative support. In its simplest version, one imagines that water molecules are linked together by hydrogen bonds. Typically there are a maximum of four bonds per molecule. The mean lifetime of a bond is about 1 ps, but at any given instant there will be about 80% of the bonds intact.

All estimates of the gelation threshold for 3-dimensional systems are well below 80% (for example, in Flory theory the gelation threshold occurs at 33% for four-functional monomers). Hence water is certainly above its gelation threshold! This fact has been noted over the years, but by itself does not explain any anomalies since thermodynamic functions are not singular at the gelation threshold. In fact, the anomalies in water occur well above the gelation threshold. Clearly we need additional insight. This additional insight arises from the observation that the local environment of a water molecule is correlated with its degree of bondedness. For example, a molecule situated in a region of the gel where all the molecules have four intact bonds sees a different local environment than a molecule in a region of the network where most of the molecules have broken bonds. Indeed, the statement that a molecule has four intact bonds means that there are four other water molecules located at the correct distance and angle required for hydrogen bonding. The local specific volume would thus be expected to be larger in the vicinity of this molecule, compared to the global specific volume. Similarly, the

local entropy should be smaller than the global entropy. Hence we have a mechanism that makes a positive contribution to the fluctuations in specific volume and entropy and a negative contribution to the cross fluctuations. Moreover, this effect becomes more pronounced as the temperature is lowered. The locally-structured transient gel model would therefore seem to explain the puzzling features of water we mentioned above. It also explains the effect of hydrostatic pressure or hydrogen bonding impurities: the former serve to reduce ρ_B and hence to reduce the probability of finding locally-structured regions while the latter serve to reduce the "structuration" of the local regions since they lack the strong directionality of the tetrahedral bonds in water (Table I). One molecule that does have this strong directionality is D_2O , and for heavy water one finds that the anomalies are more pronounced.

	Pressure	D_2O impurity	other impurities
K_T	↓	↑	↓
C_p	↓	↑	↓
$-\alpha_p$	↓	↑	↓

TABLE I [from Ref. 3]

IV. TESTS

In the remainder of this talk, I will mention some of the recent work devoted to testing the overall picture outlined above. This work naturally falls into two classes, computer simulations carried out for realistic models of water and experiments carried out on real water.

TESTS ON "COMPUTER WATER"

Although there have been many studies of the thermodynamic properties of water, there has been considerably less work on the connectivity peroperties. The most straightforward property to measure is f_j , the fraction of molecules with j intact bonds. This function does not provide a complete description of the connectivity, but is nonetheless useful. We have found that f_j is well described by a simple binomial formula, indicating therefore that the hydrogen bonds are to a good approximation randomly intact or broken. This finding seems to be independent of what model is used. For example, our work has used the famous Rahman-Stillinger tapes on ST2 water as input, while Mezei and Beveridge has carried out analogous calculations of the f_j using other models--and even other definitions of a hydrogen bond (we use an energetic definition, while they use both energetic and geometric definitions. Indeed, in the literature of MD (and MC) calculations on water, one finds many examples of histograms of f_j plotted against j . We find that these data are well fit by simple binomial expressions (cf. Fig. 1).

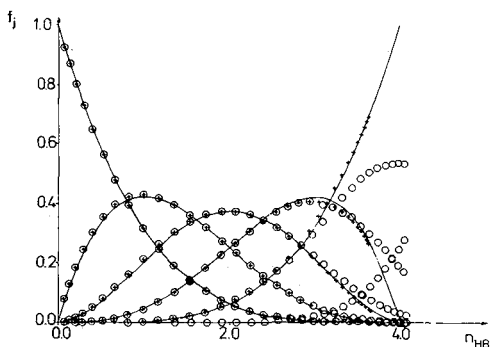


FIG. 1 [Ref. 14]

Suppose we accept the possibility that to a zeroth order approximation, we can describe the hydrogen bonding as random--cooperativity effects certainly are present, but are perhaps not so strikingly important as to require consideration at the present time. Then we can actually obtain a completely quantitative "network analysis" of this transient gel, by simply carrying over to water the ideas developed by Flory and Stockmayer for polyfunctional condensation. Here the water molecules play the role of four-functional monomers in Flory theory, and the short-lived hydrogen bonds are responsible for the network properties. Flory worked out simple analytic formulae for the complete statistical distribution--the weight fraction $W(M,p)$ of molecules belonging to an M -molecule "network" when a fraction p_B of the hydrogen bonds is intact,

$$W_M[\text{Flory theory}] = MA(M)p^{M-1}(1-p)^{2M+2}, \quad (1a)$$

where

$$A(M) = 4(3M)!/M!(2M+2)! \quad (1b)$$

is a combinational factor. Flory's calculation has no adjustable parameters, so its predictions can be directly compared with MD calculations on ST2 water. One finds excellent agreement for small networks. For larger networks, discrepancies arise, presumably due to the fact that Flory theory neglects "cycles," the possibility that one can form a loop or cycle of hydrogen-bonded water molecules. These cycles are rare for small networks but they become increasingly important for larger networks--indeed, it is difficult to imagine a network of, say, 100 molecules without the presence of at least a few cycles. In short, Flory theory assumes a tree-like connectivity and therefore should fail for large networks. To obtain better agreement for larger networks, we have carried out extensive calculations for the network properties for gelation on an ice I_h lattice. We find much better agreement with the MD simulations, but of course this does not mean that the water molecules actually reside on a lattice! Rather, it only

suggests that the connectivity properties are similar to those of a lattice. This is a topological matter, not a geometrical matter. There has been some confusion on this point in previous descriptions of our work, so one cannot make this point too emphatically: we analyze the topological properties of water by making reference to the ice lattice, which says nothing at all about the geometrical properties of water. We found excellent agreement between Flory theory and the MD simulations provided M is not too large; for larger M the simulations agreed better with calculations on a lattice with the topological connectivity of ice I_h . Although we are limited by the small size of the MD water system, we may predict that for even larger M the agreement with the ice lattice calculations will certainly break down. The main point is that on a scale of a few \AA the hydrogen bond network of water is topologically similar to the I_h lattice.

LOCALLY-STRUCTURED REGIONS

We mentioned above that the transient gel of connected water molecules is not sufficient to explain the unusual behavior of liquid water below about 50°C . We also suggested that the anomalies could be understood in terms of locally-structured regions consisting of four-bonded molecules. For this reason, we have carried out the analogous "quantitative network analysis" on the four-bonded molecules. Although typically the hydrogen bonding is so extensive that water is well above the gelation threshold, the fraction of four-bonded molecules is much smaller--if $p_B = 0.8$, then $f_4 = 0.4096$. Thus the four-bonded molecules can be near or even below their percolation threshold. We have studied in detail the analogous distribution functions W_s^* giving the weight fraction of four-bonded molecules belonging to a "patch" of the gel, all of whose members are connected to one another and all of whose members are four-bonded. We generalized the Flory theory to this problem, with the result

$$W_s^* [\text{Flory theory}] = sA(s)p^{3s+1}(1-p^3)^{2s+2}. \quad (2)$$

In analogy with our study of the network functions W_M , we found excellent agreement between Flory theory and the MD simulations provided s is not too large; for larger s the simulations agreed better with calculations on a lattice with the topological connectivity of ice I_h . Thus the MD simulations support the picture that water is a locally-structured hydrogen-bonded network well above its gelation threshold.

What is needed next is evidence that the local regions of four-bonded molecules have a different specific volume. This question was first addressed in the following fashion: an imaginary balloon was inflated around each water molecule, and the number of other molecules residing inside the balloon was calculated. If the local specific volume around four-bonded molecules were indeed larger (as conjectured above), then one would expect to find fewer molecules inside the

balloons centered on four-bonded molecules. This was indeed found to be the case (Fig. 2), with some caveats for those cases in which the balloon radius corresponded to the separation distance between nearest neighbors in an ice lattice (these details are described in Ref. 10).

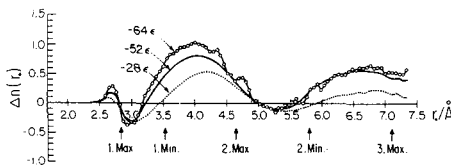


FIG. 2 [from Ref. 10]

It would be nice to make the above conclusions independent of any definition of hydrogen bond, since this is somewhat arbitrary in MD calculations. Hence we have studied the relationship between the number n of neighbors j found within a sphere of radius r_c around some reference molecule i , and the sum u_i of the corresponding pair interaction energies v_{ij} ,

$$u_i = \sum_{j \neq i}^n v_{ij}. \quad (3)$$

Here u_i is the binding energy of the reference molecule i with respect to its n neighbors in the sphere of radius r_c ; it is a measure of the local connectivity, which is more general than the hydrogen bond picture and which avoids the arbitrary definitions of a hydrogen bond.

Due to the fluctuation of the local density, we observe a range of numbers n , the neighbors in the sphere. We calculated the average binding energy as a function of the number of neighbors n

$$u = \langle u_i \rangle_{n=\text{const.}} \quad (4)$$

These values are shown in Fig. 3 for four different choices r_c ; the vertical bars indicate the mean square deviations from the averages u .

These deviations are smallest in the central part of the graphs, because we find those numbers of neighbors n most frequently and therefore we have many contributions to the corresponding averages. Through these more reliable points a dashed guidance line has been drawn. Averages from less than 100 contributions, which occur at the outermost wings of the distributions (very high and very low n) are not considered in these graphs.

We see that for $r_c = 5.5\text{\AA}$ the average binding energy u decreases with an increasing number of neighbors within the sphere of regarded interactions. This is what we would expect from a "normal" liquid like a Lennard-Jones liquid at not too high packing densities, because the addition of another interaction partner will add a negative (attractive) contribution v_{ij} . However, in the cases $r_c = 3.5\text{\AA}$, 4.5\AA

and 6.5A, we observe exactly the opposite behavior: u increases with increasing local density. This means that a less dense local arrangement of the water molecules is energetically favorable over more dense structures; a behavior that we regard as typically "waterlike" is related to the occurrence of the anomalies.

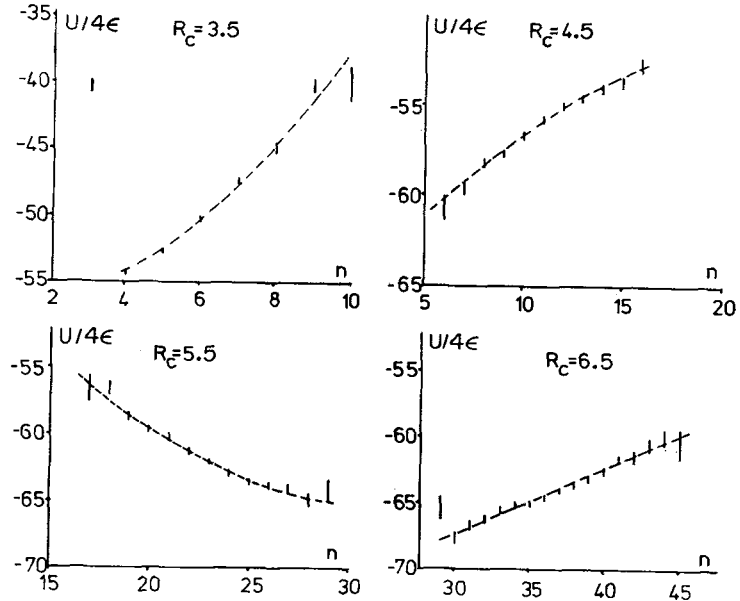


FIG. 3 [from Ref. 14]

The observation that for some choices of r_c we get the picture of a normal liquid can be explained by the oscillatory nature of the pair correlation functions, which describe the local structure of water. Figure 3 indicates a decreased local density around four-bonded water molecules when using $r_c = 3.5, 4.5$ or $6.5A$, whereas for the choice $r_c = 5.5A$ no such difference can be observed.

Thus the present results shown in Fig. 3 confirm and also generalize our previous finding of a correlation between increased connectivity and decreased local density.

Furthermore, concentrating on the graph for $r_c = 3.5A$ (a value which had been used before as the limiting distance for hydrogen bonds), Fig. 3 indicates a marked minimum of u at $n=4$. This indicates again a strong energetic preference for four-coordinated local structures.

TESTS ON REAL WATER

By now you may be convinced that "computer water" conforms quite nicely to the picture presented above. What about real water? This is the real challenge!

It is not easy to design an experiment that is sensitive to the detailed hydrogen bond connectivity of water. However one can test the consequences of the existence of a locally-structured hydrogen-bonded regions of the transient gel: the

characteristic size of such regions is predicted to be about 8Å by molecular dynamics calculations, and the local density of water is smaller in the vicinity of such regions. Accordingly, we might anticipate that the length scale of density fluctuations would also be about 8Å. This quantity can be measured by small-angle x-ray scattering. The structure factor $S(q)$ is known to give an accurate estimate of the length $\xi(T)$ for fluids near their critical point, where $\xi(T)$ becomes quite large. Indeed, data are often fit by a simple Lorentzian function

$$S(q) = 1/(q^2 + \xi^{-2}). \quad (5)$$

Thus the width of the Lorentzian is a direct measure of the inverse correlation length, and can be readily obtained from an "Ornstein-Zernike-Debye plot" in which $1/S(q)$ is plotted against q^2 .

Early experiments of $S(q)$ in water did not attain extremely low q or extremely low T , and no increase of $S(q)$ near $q=0$ was observed. Bosio et al succeeded in obtaining accurate measurements of $S(q)$ for low q and low T and the data indicate a clear increase, as indicated in Fig. 4. The observed behavior can be fit to a Lorentzian, and the characteristic value of ξ from the data is 8Å, in agreement with the MD simulation studies.

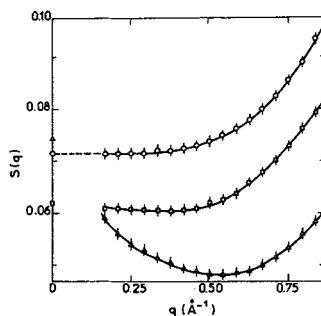


FIG. 4 [from Ref. 6]

In summary, available MD simulations and direct experiments support the possibility that liquid water is a hydrogen bonded network, characterized by many tiny locally-structured regions whose density is less than the global density and whose characteristic linear size is roughly 8Å at low temperatures.

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