# Low-Density "Patches" in the Hydrogen-Bond Network of Liquid Water: Evidence from Molecular-Dynamics Computer Simulations

Alfons Geiger

*Institut für Physikalische Chemie, Rheinisch-Westfälische Technische Hochschule Aachen,
51 Aachen, West Germany*

and

H. Eugene Stanley

*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215*

The connectivity properties of liquid water are studied with molecular dynamics. It is found that the hydrogen-bonded network includes tiny spatially correlated "patches" of four-bonded molecules, and that the *local* density near a "patch" is lower than the *global* density. The diameter of the finite patches increases with decreasing temperature, and is comparable to the characteristic length scale of density fluctuations recently measured by small-angle x-ray scattering.

Few liquids are more unusual in their physical properties than water.[1] A distinguishing feature of $H_2O$ is the high degree of hydrogen bonding, and this microscopic property has long been suspected to underlie the unusual properties. However, there is very little information on the physical picture of how the bonds conspire to produce the observed macroscopic behavior. Simplistic models, such as those postulating isolated "icebergs" in a sea of dissociated liquid, have been discredited—in large part by information provided from detailed molecular-dynamics computer simulations.[2,3] Rather, it now appears that water consists of a space-filling network formed by hydrogen bonds between water monomers.[4]

In this work, we find a correlation between the local density in the network and the presence of patches of the network where the molecules are completely bonded to four neighbors. This provides a mechanism whereby the hydrogen-bond network can lead directly to the observed anomalies of liquid water. We also calculate the mean square radius of gyration $\langle R_G^2 \rangle$ of the finite (non-spanning) clusters and find it to be comparable to the length scale of density fluctuations obtained by recent small-angle x-ray scattering data.[5]

The input to the present work is a computer tape resulting from a molecular-dynamics simulation[3] of a system consisting of 216 waterlike particles at $T = 284$ K. These interact with one another through an ST2 potential[3] and are confined to a cubic box of edge 18.6 Å that is periodically repeated in space (density 1 g/cm³). ST2 is an effective pair potential designed to reproduce a wide range of properties of real water. Its most prominent feature is a tetrahedral charge distribution around the oxygen atom, with two positive partial charges on the proton location and two negative partial charges representing the lone electron pairs. The absolute minimum of the ST2 potential is $-6.84$ kcal/mole, which can be thought of as the energy of the ideal hydrogen bond in "ST2 water."

There are 38 100 time steps in the simulation; each step represents $2 \times 10^{-16}$ s. After each 300 steps, we created a $216 \times 10$ table which contains for each molecule $i$ ($i = 1, 2, \ldots, 216$) the ten other molecules $j$ that interact most strongly in an attractive way with molecule $i$. We thereby obtain a set of 127 ($= 38\,100/300$) different tables, which are then used as input for the following procedure.

We define two water molecules $i$ and $j$ as "bonded" when their mutual interaction energy $V(i,j)$ is less than a negative cutoff parameter $V_{HB}$.[2-4] Because this choice is not unique, it is customary to make a complete analysis for a sequence of choices for $V_{HB}$. As $V_{HB}$ becomes less negative, the average number $n_{HB}$ of hydrogen bonds per molecule increases. This corresponds in some way to reducing the temperature of the system, since it is possible to "scale" data for systems at different temperatures by $n_{HB}$.[4] If our choice of $V_{HB}$ yields molecules with more than four bonds, we eliminate the weakest bonds until we have a maximum of four bonds per molecule.[6] A typical molecular-dynamics configuration results in a picture like that shown schematically in Fig. 1(a). The bonds are shown in perspective for the constant-volume basic cube. In
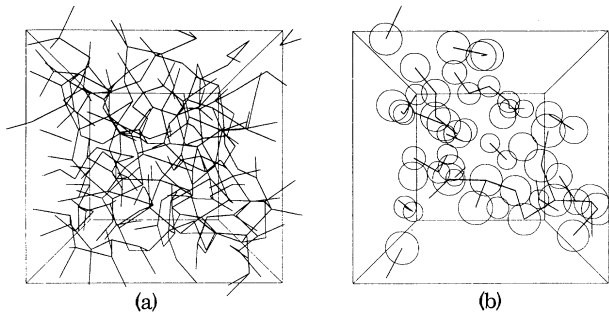
(a)                    (b)

FIG. 1. The results of an instantaneous "snapshot" of a Rahman-Stillinger molecular-dynamics simulation of 216 ST2 waterlike particles constrained to a 18.6-Å cube. (a) Only those "intact bonds" defined by the convention $V_{HB} = -48\epsilon$, $\epsilon = 0.075\,75$ kcal/mole. This value of a cutoff parameter corresponds to $n_{HB} \approx 2.56$. (b) Large open circles indicate those molecules with four intact hydrogen bonds (only the bonds connecting these molecules are drawn to indicate the connectivity of the clusters). The detailed cluster statistics of bond connectivity can be obtained by varying $V_{HB}$ in order to vary $n_{HB}$.

Fig. 1(b) those water molecules with four intact bonds are indicated by circles. Although the fraction $f_4$ of such molecules with four intact bonds is determined by simple statistics, the *connectivity* of the four-bonded molecules is far from trivial.[7] The positions of the four-bonded molecules are strongly correlated—they form tiny ramified clusters or patches in the network.

There is no relation between the patches in the bond network and the observed anomalies of liquid water unless there is some *local* property of the patch—e.g., the density—that is different from the *global* properties of the hydrogen-bonded network as a whole. In order to test this possibility, we count the number of oxygen nuclei $\nu_4(r)$ which we find on the average within a spherical shell of radius $r$ and thickness $dr$ around the oxygen nucleus of the four-bonded molecule (including also the nonbonded neighbors). Clearly $\nu_4(r) = \rho 4\pi r^2 \times g_4(r) dr$, where $\rho$ is the average number density, $r$ is the oxygen-oxygen distance, and $g_4(r)$ is the oxygen-oxygen pair correlation function centered on a four-bonded molecule; $\nu_<(r) = \rho 4\pi r^2 g_<(r) dr$ denotes the same quantity, referring to water molecules with fewer than four intact bonds.

Because we are interested in density differences, we calculate

$$\Delta\nu(r) = \nu_<(r) - \nu_4(r) = \rho 4\pi r^2 [\, g_<(r) - g_4(r)\,] dr.$$

$$(1)$$

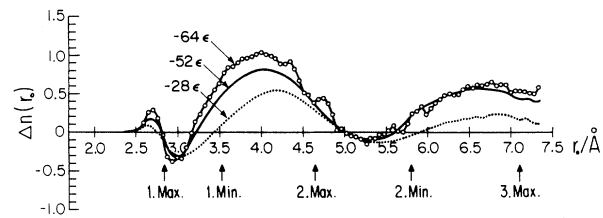If we integrate over all $r$ from $r = 0$ to $r = r_0$, we



FIG. 2. Difference in running coordination numbers between non–four-bonded and four-bonded molecules [Eq. (2)], i.e., the number of molecules within a sphere of radius $r_0$ whose center is a non–four-bonded molecule minus the number in a sphere whose center is a four-bonded molecule. That the function is positive for most choices of $r_0$ means that there are more water molecules in the neighborhood of a non–four-bonded molecule.

get $\Delta n(r_0)$, the difference in the running coordination number[2] (the number of molecules within a sphere of radius $r_0$ around some reference water molecule),

$$\Delta n(r_0) = \int_0^{r_0} \Delta\nu(r) dr. \qquad (2)$$

Figure 2 shows this difference in running coordination numbers for three values of the cutoff parameter $V_{HB}$. If we integrate up to a value $r_0$, we obtain a positive number for most choices $r_0$, which means that there are *more water molecules in the neighborhood of a non–four-bonded molecule compared to a four-bonded molecule*.

The oscillatory behavior of $\Delta n(r_0)$, which leads to two small regions of $r_0$ where $\Delta n(r_0)$ is negative, may be understood as follows: $\nu(r)$ gives the density difference within a spherical *shell* of radius $r$ and thickness $dr$. Thus for $r \cong 2.85$ Å, the most favorable distance for a strong hydrogen bond, $\nu(r)$ is strongly negative since the neighbors of a four-bonded water molecule crowd at that distance. This results in a negative slope, and finally also negative values, of $\Delta n(r)$ itself. However, if one extends the integral a little further out—say to the first minimum of the oxygen-oxygen pair correlation function $g_{OO}(r)$ near 3.6 Å (Ref. 3)—we find a positive value for $\Delta n(r_0)$. There is again a small negative dip near 5.2 Å, which stems from the sphere just including second neighbors which are bound to the reference molecule by a path of two hydrogen bonds. However, if we go further and extend the sphere to the second minimum of $g_{OO}(r)$ near 5.9 Å to include the entire second-neighbor shell, $\Delta n(r_0)$ is again positive. There is good agreement between the locations[3] of the maxima and minima of $g_{OO}(r)$ as indicated by the arrows in Fig. 2, and

the location of the minimum and maximum slopes of $\Delta n(r)$. The magnitudes of the slopes decrease with increasing $r$ leading to decreasing negative dips in $\Delta n(r)$. Note that the curve with the most restrictive definition of a hydrogen bond (largest value of $|V_{HB}|$) has the most pronounced feature of being, on average, positive—and the steepest slopes at the extrema of $g_{00}(r)$.

Frank has shown that compressibility data imply a twofold increase in density fluctuations in water relative to normal liquids.[8] Our calculations associate that increase with the presence of locally structured (four-bonded) regions of the hydrogen-bonded network. Our calculations also permit additional, more microscopic, predictions to be made. For example, we can estimate the characteristic length scale of the density fluctuations. To this end, we calculated the radius of gyration of each cluster $R_G^2 = s^{-1} \sum_{i=1}^{s}(\vec{r}_i - \vec{R})^2$ where $\vec{R} = s^{-1}\sum_{i=1}^{s}\vec{r}_i$, and $\vec{r}_i$ are the oxygen atom positions; the index $i$ labels the atoms in a cluster of size $s$. Figure 3 shows the dependence on $n_{HB}$ of $\langle R_G^2 \rangle$, the average over all finite (non-
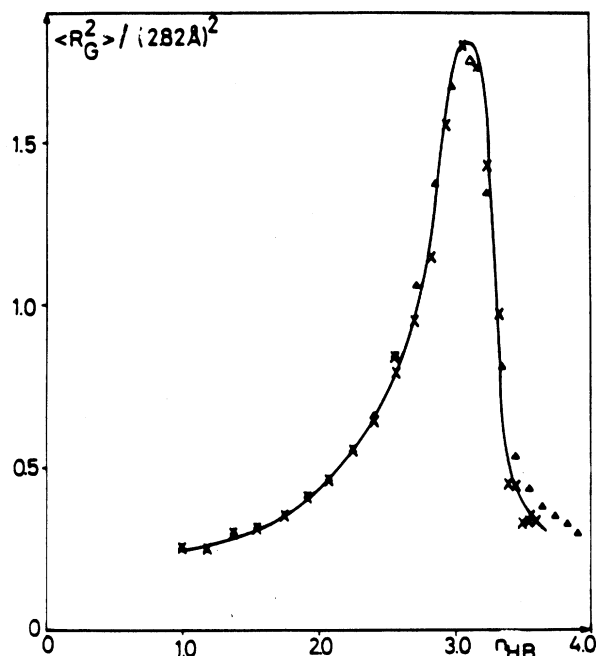


FIG. 3. Dependence on $n_{HB}$ of the mean square radius of gyration of the clusters of four-bonded molecules. The crosses are obtained from the purely energetic criterion for hydrogen bonding described in the text, while the triangles are obtained by neglecting any bonds with bond length greater than 3.5 Å [the first minimum of $g_{00}(r)$]. The curve displays a maximum since the average is over all finite (nonspanning) clusters.

spanning) clusters of four-bonded molecules. We see that $\langle R_G^2 \rangle$ increases very rapidly with $n_{HB}$, attaining a characteristic value of 5–10 Å$^2$ in the region corresponding to $n_{HB} = 2.3$–3.0, which is consistent with recent small-angle x-ray data.[5,9] This range of $n_{HB}$ is thought to be valid for ST2 water from the observation of a temperature-invariant point in the pair energy distribution.[3,4]

In summary, we have considered the density fluctuations in ST2 water by distinguishing the local environments of four-bonded and non–four-bonded water molecules. We found that the local density in the vicinity of a four-bonded molecule is somewhat decreased. Also, we showed that the size of the clusters of four-bonded molecules is comparable to the characteristic length scale of density fluctuations observed by small-angle x-ray scattering.[10] Our analysis supports the following picture of water structure (Fig. 1): When we look at the bond connectivity, water appears as a macroscopic space-filling network (as expected from continuum models of water), while when we look at the four-bonded molecules, water appears as a myriad of tiny ramified lower-density patches (somewhat reminiscent of mixture theories).

[1]*Water, A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972–1977), Vols. 1–7.

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[4]A. Geiger, F. H. Stillinger, and A. Rahman, J. Chem. Phys. 70, 4185 (1979); M. Mezei and D. L. Beveridge, J. Chem. Phys. 74, 622 (1981).

[5]L. Bosio, J. Teixeira, and H. E. Stanley, Phys. Rev. Lett. 46, 597 (1981).

[6]In the case of weak, *purely energetic* definitions (for $V_{HB} > -2.4$ kcal/mole) more than four "bonds" per water molecule may be found. For *realistic* choices of $V_{HB}$ (more negative than $\simeq -3$ kcal/mole) this prob-

lem is negligible. A purely energetic definition of a hydrogen bond becomes unphysical at weak $V_{HB}$, because then electrostatic dipolar interactions with more distant interaction partners have the same magnitude as weak nearest-neighbor interactions. To take these difficulties into account, we also analyzed the tape by eliminating from the list of directly bonded partners of molecule $i$ all molecules $j$ whose separation $|r_i - r_j|$ exceeds 3.5 Å. We found only minor differences between the two approaches.

[7]H. E. Stanley and J. Teixeira, J. Chem. Phys. 73, 3404 (1980); H. E. Stanley, J. Teixeira, A. Geiger, and R. L. Blumberg, Physica (Utrecht) 106A, 260 (1981); H. E. Stanley, J. Phys. A 12, L211 (1979).

[8]H. S. Frank, in Ref. 1, Vol. 1, p. 515.
[9]In comparing the present calculations with small-angle x-ray experiments, one should keep in mind that (i) the "electronic" $R_G$ is presumably larger than our $R_G$ (e.g., our $R_G$ is zero for clusters $s = 1$) and (ii) contributions from the spanning clusters are not included in our calculations. Thus we would expect that the characteristic length scale obtained experimentally would be somewhat larger than that we have calculated.
[10]We have also calculated the Guinier function for clusters of four-bonded molecules, and found, for $n_{HB} > 2$, a strong increase as $q$ decreases below 0.5 Å$^{-1}$; perhaps coincidentally, data for $S(q)$ display a minimum at roughly 0.5 Å$^{-1}$ for $T = 253$ K.

# $(K^-,K^+)$ Reaction and the Dibaryon $H$

A. T. M. Aerts and C. B. Dover

Brookhaven National Laboratory, Upton, New York 11973

Cross sections for the reaction $^3\mathrm{He}(K^-, K^+ n)H$ are estimated. This process affords a promising way of producing the stable six-quark dibaryon $H$ ($0^+$, $I = 0$, strangeness $-2$) predicted by the bag model.

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In the past few years, there has been intense interest in the spectroscopy of multiquark states. Beyond the simplest $Q^3$ baryon and $Q\bar{Q}$ meson configurations, numerous authors have speculated on the existence of long-lived multiquark systems such as the $Q^2\bar{Q}^2$ "baryonium" states,[1] $Q^4\bar{Q}$ baryons (the $Z^*$ resonances,[2] for instance), and $Q^6$ dibaryon[3] configurations. The six-quark ($Q^6$) states which are predicted come with several values of strangeness $S$. For $S = 0$ and $-1$, one predicts a whole spectrum of $Q^6$ composites, all of which are unstable with respect to strong decay into, e.g., nucleon-nucleon or hyperon-nucleon channels. Thus to identify these objects experimentally, one must be able to disentangle the signature of a genuine multiquark state from enhancements[4] due, for example, to the opening up of new strong decay channels, such as $N\Delta$ and $\Delta\Delta$ for $S = 0$ and $\Sigma N$ for $S = -1$. The experimental and theoretical situation on the existence of multi-quark states remains unclear.

For $S = -2$, the situation for dibaryon states is somewhat different. In the bag model, an $S = -2$ particle (called the $H$) was predicted by Jaffe,[5] which is *stable* with respect to strong decay. The $H$, with $J^\pi = 0^+$ and isospin $I = 0$, has a calculated mass $m_H \approx 2150$ MeV, some 80 MeV below the $\Lambda\Lambda$

threshold in Ref. 5; a somewhat smaller binding was found by Aerts, Mulders, and deSwart.[6] The value for $m_H$ is clearly model dependent. A recent evaluation by Liu and Wong,[7] which approximately includes center-of-mass corrections in the bag model, yields a mass for the $H$ some 10 MeV *above* the $\Lambda\Lambda$ threshold. In any case, the $H$ is the lowest-lying $S = -2$ dibaryon. Its configuration $(uuddss)_{0^+,I=0}$, with all six quarks in the $1s$ ground state, takes maximum advantage of the color-magnetic binding forces of quantum chromodynamics (the $H$ is somewhat analogous to the $\alpha$ particle in nuclear physics, but containing *three* different types of constituents). The $H$ could be formed by the fusion of two three-quark bags, corresponding to the $\Lambda\Lambda$, $\Xi N$ or $\Sigma\Sigma$ channels, without the need for any quarks to be promoted to higher orbitals in the composite system.

If the $H$ is indeed stable, it is a unique object in multiquark ($n > 3$) physics, and warrants a high degree of experimental and theoretical attention. Its discovery would provide the first definitive example of an $n$-quark state with $n = 6$. A dibaryon with the quantum number of the $H$ cannot be generated in ordinary potential models involving meson exchange: Using the SU(3) one-boson-exchange models of Nagels *et al.*,[8] we have veri-