Aspects of the percolation process for hydrogen-bond networks in water[a]

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Sets of configurations selected from three molecular dynamics simulations for liquid water have been analyzed for the distribution of hydrogen-bond clusters. Two simulations correspond to water at 1 g cm^{-3}, while the third corresponds to highly compressed water at 1.346 g cm^{-3}. An energy criterion was adopted for existence of a hydrogen-bond between two molecules. As the cutoff value for bonding increases (becomes more permissive), a bond percolation threshold is encountered at which initially disconnected clusters suddenly produce a large space-filling random network. At least for the model studied, any chemically reasonable definition of "hydrogen-bond" leads to this globally connected structure though a few disconnected fragments inhabit its interior. Although some polygonal closures can exist, the critical percolation threshold is apparently well predicted by Flory's theory of the gel point for dendritic polymerization.

I. INTRODUCTION

Over the last few years, it has become apparent that the structural and dynamical correlations in pure water can be studied with profit by postulating rather simple pairwise additive potentials between rigid water molecules and using Monte Carlo or molecular dynamics techniques on a system of a few hundred molecules. The result of all these studies has been to show that the water structure can be thought of as a network of hydrogen bonds; however, as against the perfect ice crystal, these hydrogen bonds are not perfectly formed and the resulting network has to be analyzed and understood in terms of the connectivity and clustering that the imperfectly formed hydrogen bonds engender in the assembly of water molecules. Thus, a percolation threshold phenomenon arises when the clustering encompasses the whole system. In this paper, we present the analysis of three molecular dynamics runs from the above point of view.

Unlike the case of ice crystals, in liquid water, one is required to set down a "definition" of a hydrogen bond. As in previous papers,[1-4] we shall use the potential energy of interaction between two molecules as a criterion to decide whether the pair is hydrogen bonded or not. If V_{HB} is put down as the energy upper bound for the definition of a hydrogen bond, two molecules i and j with energy of interaction $V_{ij} < V_{HB}$ are designated as bonded, otherwise nonbonded. One of the major themes of this paper is to investigate the dependence of the properties of the hydrogen bond network on the value of V_{HB}.

II. POTENTIAL FUNCTION AND SYSTEMS ANALYZED

The potential of interaction used for the molecular dynamics runs analyzed here was the ST2 potential given explicitly for instance in Ref. 1. As stated there, 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 the ST2 model. In what follows, we shall at times use $\epsilon_1 = 0.07575$ kcal/mole as an energy unit to facilitate comparison with previously published work on water using the ST2 potential. The three water systems analyzed in this paper are designated I, II, and III and are summarized below:

(I) see Ref. 1; 216 water molecules at 1 g cm^{-3} and 284 K. 620 configurations were analyzed for the present paper. These cover the first third of the total molecular dynamics run reported in Ref. 1.

(II) see Ref. 2; 216 molecules at 1.346 g cm^{-3} and 371 K. 528 configurations were analyzed for the present paper; these span the complete molecular dynamics run reported in Ref. 2.

(III) 1728 molecules at 1 g cm^{-3} and 272 K. The results of this molecular dynamics run have not been reported before. Only 21 configurations of this system were analyzed for the present purpose.

III. DEFINITION OF A CLUSTER AND RELATED QUANTITIES

As mentioned above, once V_{HB} is designated, a pair of molecules is either hydrogen bonded or it is not. Thus, given a configuration of water molecules, one can construct for each molecule i a list of its directly bonded partners j, k, ... Of course, in the list belonging to the molecule called j, i itself has to appear as a member of the list.

These lists allow one to construct clusters of bonded molecules such that stepping along successive hydrogen bonds keeps one confined to a cluster. The "size" of a cluster is defined to be the number n of molecules that form the cluster. This will be referred to as an n net.

In the definition of clusters as above, we have treated the molecular dynamics system as an isolated system, i.e., we have not used the identical repetitions that are generated by periodic boundary conditions. The reason for this and a schematic two dimensional example explaining the construction procedure are given in Appendix A.

Keeping in view the ideas that have been studied in the theory of gelation and condensation (Flory[5] and Stockmayer[6]) and in developing the "gel model" of water,[7,8] we have analyzed the molecular dynamics data by using the definitions that follow.

Let N denote the size of the molecular dynamics system under consideration; in a given configuration of molecules, let m_n denote the number of n nets. Then, obviously

$$N = \sum_{n \geqslant 1} n m_n .$$

The weight fraction ($\equiv$ mole fraction) of water molecules bound into n nets is

$$W_n = n m_n / N .$$

W_n is thus the probability that any molecule will be a member of an n net.

Let $M = \sum_{n \geqslant 1} m_n$ denote the total number of nets in a configuration. Since n is the number of molecules in an n net, the average cluster size $\langle n \rangle$ is given by N/M ($= \sum_{n \geqslant 1} n m_n / \sum_{n \geqslant 1} m_n$).

The fluctuation of the cluster size has been monitored by calculating $\langle n^2 \rangle / \langle n \rangle = \sum_{n \geqslant 1} n W_n$; it is denoted by $\langle n_w \rangle$. If m_n as a function of n is visualized as a histogram, then M is the total "area" under the histogram, $\langle n \rangle$ is the mean, and $\langle n_w \rangle - \langle n \rangle$ is a measure of the fluctuation from the mean.

In the limiting case where $m_1 = N$, $m_n = 0$ for $n > 1$, we get $\langle n \rangle = \langle n_w \rangle = 1$. Similarly, for $m_N = 1$, $m_n = 0$ for $n < N$, $\langle n \rangle = \langle n_w \rangle = N$. In both cases, the fluctuation vanishes. The nature of the maximum in the fluctuation is obviously of interest in this context.

The summation $\sum_{n \geqslant 1} n m_n$ when separated into the one term $n = 1$ and the rest ($n > 1$) allows one to define the number of "unbonded" molecules N_u and the number of "gel" molecules N_g, respectively:

$$N_g = \sum_{n > 1} n m_n, \quad N_u = N - N_g = m_1 .$$

$M_g = M - m_1$ gives the total number of "gel clusters" and by analogy with $\langle n \rangle$ defined above

$$\langle n_g \rangle = N_g / M_g$$

is the average gel cluster size.

Finally, the average number of hydrogen bonds emanating from a molecule is defined as in Ref. 4 (in Ref. 3, this quantity is denoted as $\langle b \rangle$) as

$$\bar{n}_{HB} = \sum_{n_{HB} \geqslant 0} n_{HB} \, p(n_{HB}) ,$$

where $p(n_{HB})$ is the probability that a molecule is hydrogen bonded exactly to n_{HB} other molecules.

IV. VALUES OF V_{HB} CONSIDERED

The values of V_{HB} chosen for consideration were $V_{HB} = -k \epsilon_1$, were $k = 20, 24, \ldots, 72$ and ϵ_1 is as defined in Sec. II.

When k is small, nearly all water molecules will be found to be interconnected forming one single gel molecule; a few "free" molecules or "decoupled" small clusters may sometimes be present. In the opposite extreme where k is so large that V_{HB} is close to the absolute minimum of the ST2 potential (Sec. II), bonds will exist rather exceptionally (contrary to the crystalline case) and only small disconnected nets will be present in the system; the majority of molecules will be classified as belonging to 1 nets. The absolute minimum of the ST2 potential corresponds to $k \sim 90$.

Only in an intermediate interval of values of V_{HB} will medium sized nets be found to exist. The investigation reported here is concerned, among other things, with the width of this band of V_{HB} values where clusters of intermediate size are found.

V. NETWORK SIZE DISTRIBUTIONS

For various choices of k (i.e., of V_{HB}, Sec. IV), system I yields the distribution of W_n (i.e., the probability of a molecule being a member of an n net) shown in Fig. 1(a). It is immediately obvious that the region of interest lies near $k = 60$, as the distribution shifts suddenly from the extreme right to the extreme left as a function of n. This interesting region of Fig. 1(a) is shown in Fig. 1(b) on a larger scale. It signifies the percolation threshold for hydrogen bonding, and is expected to become infinitely sharp for the infinite system size limit.

System II yields similar distributions. The difference between I and II is that the latter shows the same distribution as I at a lower k value, i.e., for a less stringent definition of a bond. This implies that the highly compressed water of II has a less precisely defined structural pattern of hydrogen bonds. Figure 1(c) shows the results for system III; the transition is sharper here because the system is larger than I and II and it appears that $k = 62$ is a good estimate of the percolation threshold for water at ordinary temperature and pressure conditions.

The average quantities defined in Sec. III were calculated for the three systems for varying values of the hydrogen bond energy. These are listed in Tables I–III. The corresponding graphs are shown in Figs. 2–8.

VI. DISCUSSION OF RESULTS

Figure 2 shows the data collected in Table I in graphical form. In Fig. 1(a), we saw the rapid change in
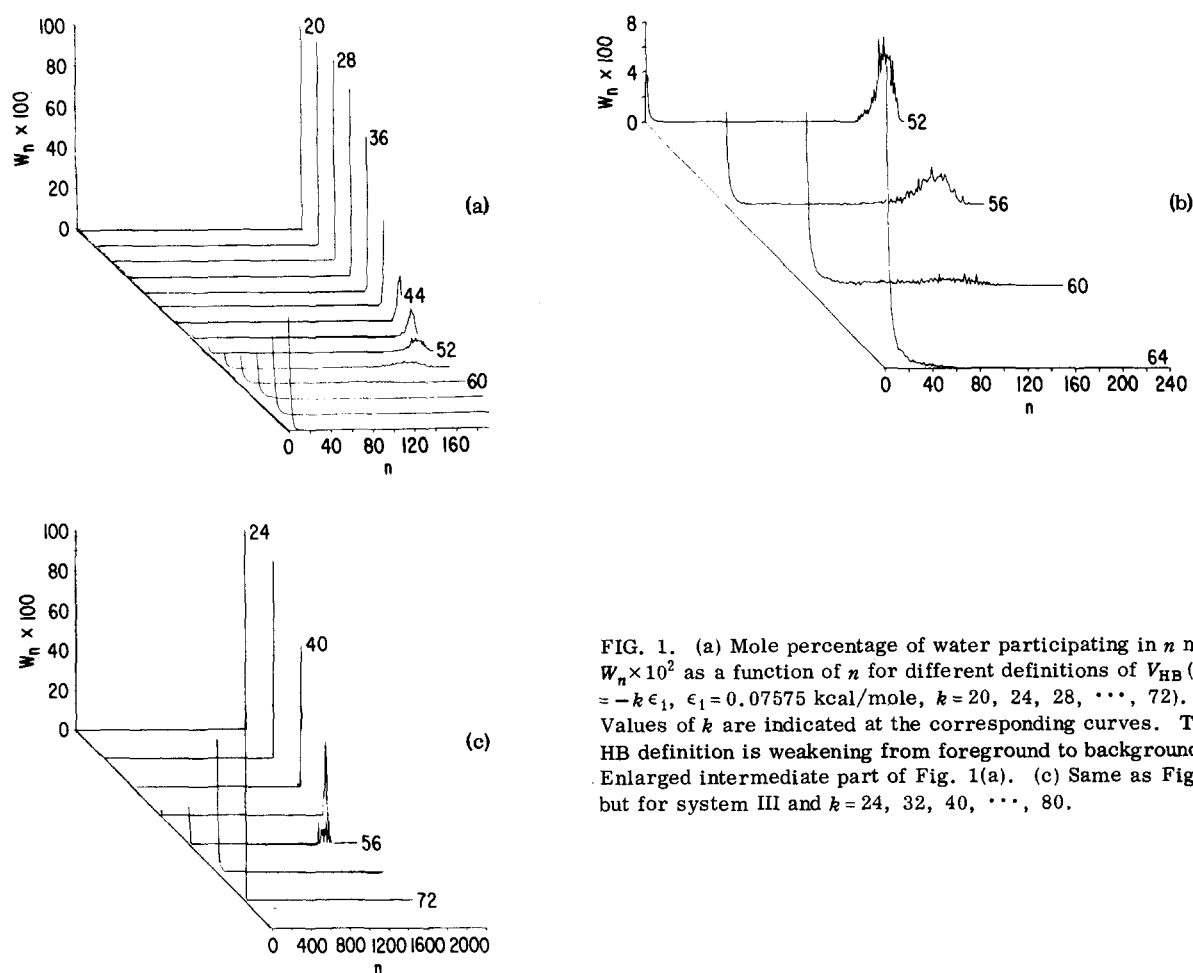
FIG. 1. (a) Mole percentage of water participating in n nets: $W_n \times 10^2$ as a function of n for different definitions of V_{HB} ($V_{HB} = -k\,\epsilon_1$, $\epsilon_1 = 0.07575$ kcal/mole, $k = 20$, 24, 28, $\cdots$, 72). Values of k are indicated at the corresponding curves. The HB definition is weakening from foreground to background. (b) Enlarged intermediate part of Fig. 1(a). (c) Same as Fig. 1(a), but for system III and $k = 24$, 32, 40, $\cdots$, 80.

W_n as a function of V_{HB}. In Fig. 2, we see a consequence of that in the various average properties. The implications of the sharp percolation threshold vary for the different average properties, $\langle n_w \rangle$ showing the most abrupt change. This property will be discussed further in a later section.

Figures for the tabulated results in Tables II and III have not been displayed. They are qualitatively very similar to Fig. 2.

Next we compare equivalent properties calculated for the three systems. We notice that in many cases a reduction to one single curve results when the values are normalized to the size of the system (N) and drawn as a function of $\bar{n}_{HB}$, the average hydrogen bond number

TABLE I. System I.

$-\frac{1}{\epsilon} V_{HB}$	$\bar{n}_{HB}$	M	M_g	N_u	N_g	$\langle n_w \rangle$	$\langle n \rangle$	$\langle n_g \rangle$
12	7.08	1.0	1.0	0.0	216.0	216.0	216.0	216.0
20	4.68	1.0	1.0	0.0	216.0	216.0	216.0	216.0
24	4.21	1.0	1.0	0.0	216.0	216.0	215.3	216.0
28	3.87	1.0	1.0	0.0	216.0	216.0	213.6	216.0
32	3.60	1.1	1.0	0.1	215.9	215.8	200.1	214.9
36	3.34	1.2	1.02	0.2	215.8	215.4	170.0	211.7
40	3.09	1.8	1.12	0.7	215.3	214.0	115.6	191.6
44	2.82	2.1	1.38	1.7	214.3	210.9	69.3	154.8
48	2.54	6.9	2.12	3.8	212.2	203.1	36.3	100.0
52	2.23	12.7	4.45	8.2	207.8	182.3	17.1	46.7
56	1.90	26.5	10.2	16.3	199.7	133.3	8.14	19.6
60	1.54	53.2	22.6	30.6	185.4	46.1	4.06	8.19
64	1.17	90.1	37.1	53.0	163.0	8.09	2.40	4.39
68	0.82	127.2	42.9	84.3	131.7	3.04	1.70	3.07
72	0.53	159.0	37.7	121.3	94.7	1.84	1.36	2.51
80	0.14	201.1	13.4	187.7	28.3	1.15	1.07	2.10

TABLE II. System II.

$-\frac{1}{\epsilon}V_{HB}$	$\bar{n}_{HB}$	M	M_g	N_u	N_g	$\langle n_w \rangle$	$\langle n \rangle$	$\langle n_g \rangle$
12	8.14	1.0	1.0	0.0	216.0	216.0	216.0	216.0
20	5.48	1.0	1.0	0.0	216.0	216.0	215.6	216.0
24	4.73	1.0	1.0	0.0	216.0	216.0	211.2	216.0
28	4.13	1.1	1.01	0.1	215.9	215.8	194.0	214.7
32	3.62	1.4	1.02	0.4	215.6	215.1	149.9	210.8
36	3.16	2.5	1.16	1.3	214.7	212.8	88.1	185.8
40	2.73	5.0	1.73	3.3	212.7	205.9	42.5	122.7
44	2.32	11.7	3.68	8.0	208.0	187.1	18.5	56.5
48	1.93	25.4	8.93	16.5	199.5	141.3	8.49	22.3
52	1.57	50.5	20.5	30.0	186.0	53.7	4.28	9.07
56	1.22	85.1	34.4	50.7	165.3	9.49	2.54	4.81
60	0.91	118.3	41.5	76.8	139.2	3.65	1.83	3.36
64	0.63	147.7	39.9	107.8	108.2	2.18	1.46	2.72
68	0.41	171.5	32.2	139.3	76.7	1.58	1.26	2.38
72	0.24	189.8	22.0	167.8	48.2	1.29	1.14	2.19
80	0.05	210.2	5.68	204.5	11.5	1.06	1.03	2.03

for a molecule:

(A) Figure 3 shows $\langle n_w \rangle/N$ as a function of $\bar{n}_{HB}$; for systems I and II, the curves are essentially coincident in spite of the difference in temperature and density. For large cluster sizes (i.e., for large $\bar{n}_{HB}$), the scaled value is in agreement for all three systems. It is also clear that the large system (III) has a sharper transition than systems I and II (dashed line in Fig. 3 compared to the circles and the triangles).

The dotted line in Fig. 3 exhibits the behavior of $\langle n_w \rangle/216$ for system III, showing clearly that for very strict definitions of hydrogen bonds (i.e., small $\bar{n}_{HB}$), the absolute values of $\langle n_w \rangle$ coincide for all three systems This is as expected since for small cluster sizes the overall system size or the periodic boundary conditions cannot produce large perturbations. The dotted line also shows that for $\bar{n}_{HB}$ close to the transition region, there is a very rapid growth of $\langle n_w \rangle$ in the larger system. We believe that the rapid rise of $\langle n_w \rangle/216$ for III is closely indicative of the infinite system percolation threshold.

(B) The average number of nets M in the system (including 1 nets as mentioned in Sec. III) scaled by N decreases linearly as $\bar{n}_{HB}$ increases up to $\bar{n}_{HB} \sim 1.3$ (see Fig. 4). From Fig. 4, we see that, for all three systems over the whole range of $\bar{n}_{HB}$ values, the depend-

dence of M/N on $\bar{n}_{HB}$ is the same.

Up to $\bar{n}_{HB} \sim 1.3$, we have (within our precision)

$$M/N = 1 - \bar{n}_{HB}/2 .$$

Since $(N/2)\bar{n}_{HB}$ is the total number of bonds in the system, each new bond diminishes M by 1, i.e., two clusters combine to become one cluster. This linear dependence of M on $\bar{n}_{HB}$ reveals that, up to $\bar{n}_{HB} \sim 1.3$, bond ring formations (i.e., intranet bonds) can be neglected.

(C) In Sec. III, we have defined M_g, the number of hydrogen bonded "polymers" (i.e., M_g is the count of clusters of two or more molecules). It is clear that, for $\bar{n}_{HB} \to 0$, all molecules are monomers and $M_g \to 0$. For large $\bar{n}_{HB}$, all molecules will be considered bonded, making $M_g \to 1$. From Tables I–III, we see that M_g passes through a maximum for intermediate values of $\bar{n}_{HB}$ (see also Fig. 2). Moreover (see Fig. 5), M_g/N is the same for all three systems considered in the region of the maximum, the maximum value being ~ 0.2 at $\bar{n}_{HB} \sim 0.8$. For system I, this corresponds to $V_{HB} \sim -68\epsilon_1$ (see Table I) and Fig. 1(a) shows that only small oligomers are present for that value of V_{HB}.

Figure 6 shows the number of unbound molecules N_u normalized to N. Once again, the results for all three systems are the same. Since $N_u = M - M_g$, we see from Figs. 4 and 6 that $M/N \approx 0.6$ and $N_u/N \approx 0.4$ at the value

TABLE III. System III.

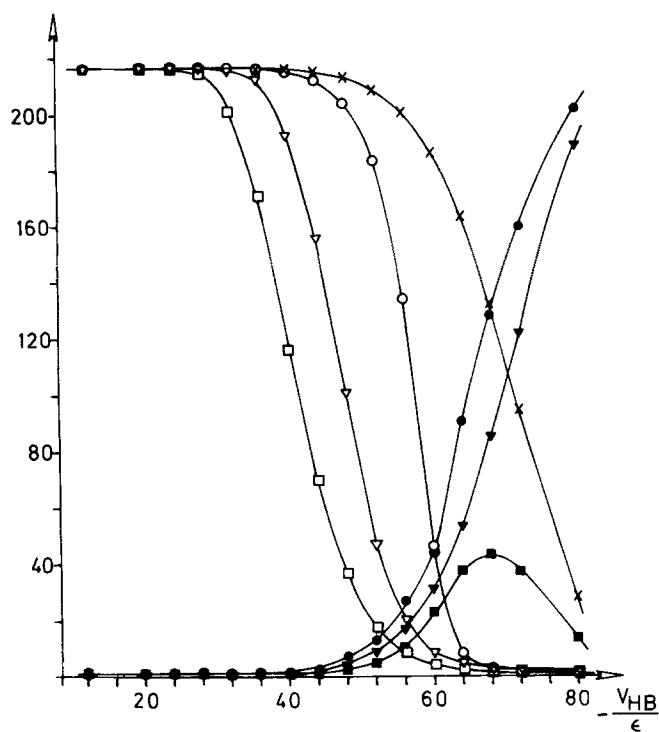| $-\frac{1}{\epsilon}V_{HB}$	$\bar{n}_{HB}$	M	M_g	N_u	N_g	$\langle n_w \rangle$	$\langle n \rangle$	$\langle n_g \rangle$
24	4.20	1.10	1.00	0.1	1727.9	1727.8	1577.7	1727.9
32	3.62	2.05	1.05	1.0	1727.0	1725.7	824.7	1648.5
40	3.14	8.7	1.62	7.1	1720.9	1710.9	197.2	1062.9
48	2.60	39.9	8.71	31.2	1696.8	1628.5	43.25	194.7
56	1.93	198.1	65.9	132.2	1595.8	1101.1	8.72	24.21
64	1.19	704.2	272.2	432.0	1296.0	11.0	2.45	4.76
72	0.54	1265.0	289.1	975.9	752.1	1.94	1.37	2.60
80	0.14	1604.9	110.6	1494.3	233.7	1.16	1.08	2.11

FIG. 2. Collection of the properties of system I, shown as function of the hydrogen–bond energy definition V_{HB}: □: average cluster size $\langle n \rangle$; ∇: average gel cluster size $\langle n_g \rangle$; ○: cluster size weight average $\langle n_w \rangle$; x: number of bound water molecules N_g; ▼: number of unbound water molecules $N_u = N - N_g$; ●: number of nets M; ■: number of gel molecules M_g.
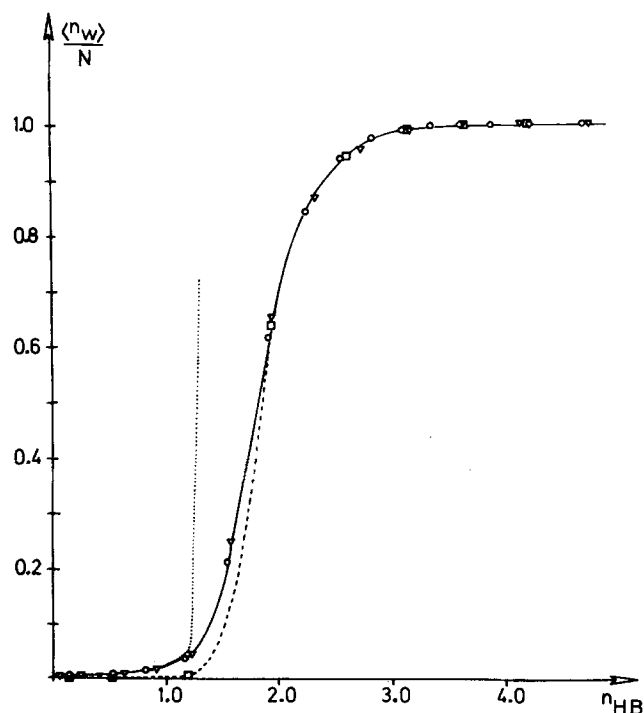
FIG. 3. Weight averaged cluster size $\langle n_w \rangle$ as function of the average hydrogen bond number $\bar{n}_{HB}$, normalized by the number of water molecules N in the system: ○: system I; ∇: system II; □: system III; dashed curve: $\langle n_w \rangle /1728$ of system III; dotted curve: $\langle n_w \rangle /216$ of system III (see text).
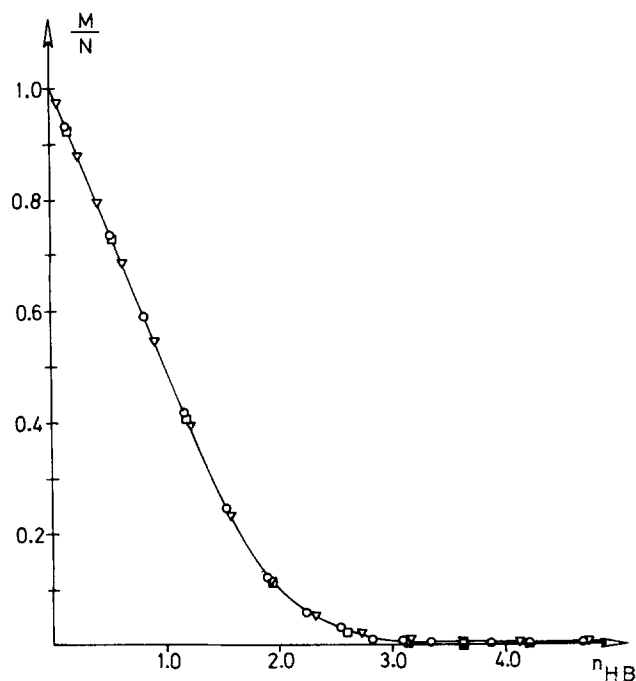
FIG. 4. Average number of nets in the system $M = \sum_{n \geq 1} m_n$, normalized by the system size N. Symbols are as in Fig. 3.

of $\bar{n}_{HB}$ at which M_g/N is a maximum (Fig. 5).

(D) The definition of $\bar{n}_{HB}$ includes unbonded molecules. To take the bias out, we can calculate $\bar{n}_{HB}^*$, which is the average number of hydrogen bonds at a molecule counting only those molecules which have at least one bond. At $\bar{n}_{HB} \sim 0.8$, we get $\bar{n}_{HB}^* \equiv \bar{n}_{HB}(N/N_g) \sim 1.3$. Moreover, $\langle n_g \rangle$, the average gel polymer size, is (from the above values of N_u, M_g, and M at the maximum in Fig. 5) ~ 3.0 at $\bar{n}_{HB} = 0.8$, i.e., $\bar{n}_{HB}^* = 1.3$. This suggests that at the maximum of M_g (Fig. 5), the
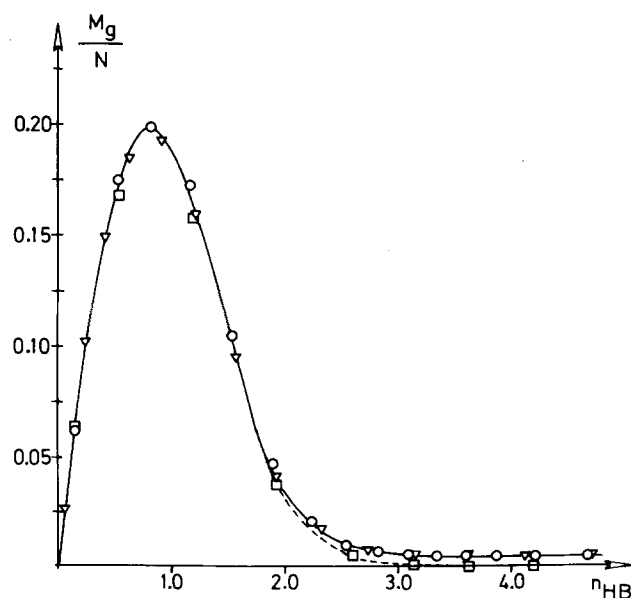

FIG. 5. Number of polymers (gel molecules) $M_g = \sum_{n > 1} m_n$ as a function of the average hydrogen-bond number $\bar{n}_{HB}$, normalized by N. Symbols are as in Fig. 3.
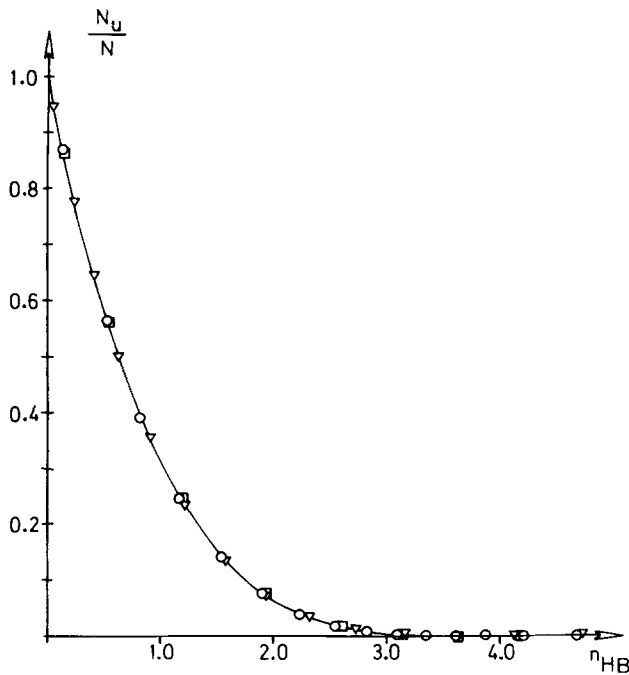
FIG. 6. Number of "unbound" (free) water molecules $N_u \equiv m_1$. The number of bound molecules $N_g = \sum_{n>1} nm_n$. Then, $N_u = N - N_g$. Symbols are as in Fig. 3.

FIG. 8. Number averaged polymer (gel molecule) size. Otherwise, see Fig. 7.

most frequently occurring polymers are "linear" trimers formed by two bonds for which $\langle n_g \rangle = 3$ and $\bar{n}^*_{HB} = 4/3$.

(E) Finally, in Figs. 7 and 8, we show the dependence of $\langle n \rangle$ and $\langle n_g \rangle$ on $\bar{n}_{HB}$, respectively. We notice that the transition region is broader and shifted to larger values of $\bar{n}_{HB}$ (compare Fig. 3). Also, the different
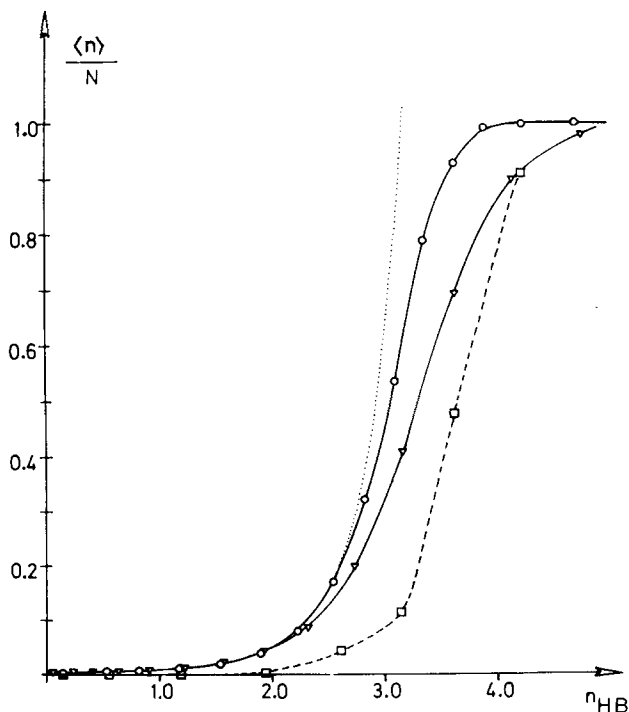

FIG. 7. Number averaged cluster size $\langle n \rangle$ for the different systems as a function of $\bar{n}_{HB}$, scaled to the system size N. Symbols and lines are as in Fig. 3.
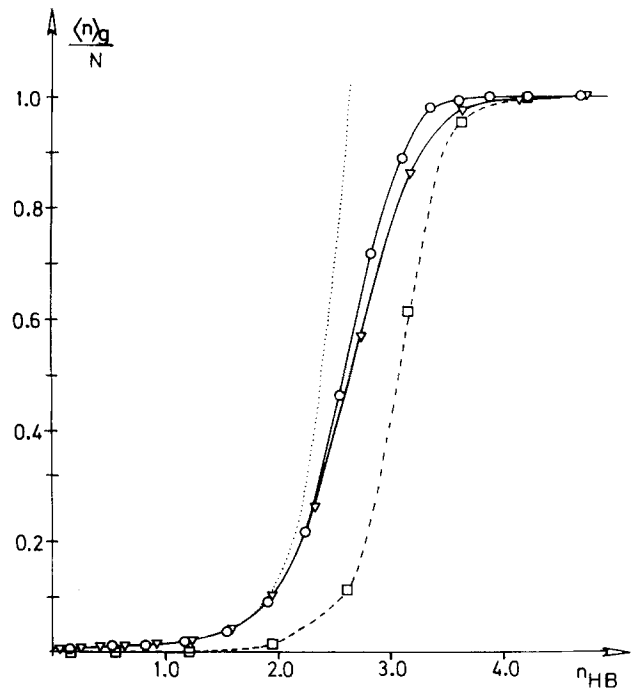
systems show coincidence only in the unscaled values at small $\bar{n}_{HB}$ but not in the transition region.

VII. $\bar{n}_{HB}$: AVERAGE NUMBER OF HYDROGEN BONDS PER MOLECULE

The values of $\bar{n}_{HB}$ derived from various theoretical considerations and from experimental data are uncomfortably diverse. For temperature between 0 and 10 °C and density 1 g cm^{-3} (systems I and III), a list of attempts to obtain $\bar{n}_{HB}$ is given below. The list is ordered according to decreasing values of $\bar{n}_{HB}$:

(a) The lattice gas model of Fleming and Gibbs[9] gives $\bar{n}_{HB} = 3.9$ in this temperature range.

(b) King and Barletta[10] used isotope fractionation experiments to infer a value in agreement with molecular dynamics results[11] for $V_{HB} = -40\epsilon_1 = -3.03$ kcal/mole, giving $\bar{n}_{HB} = 3.1$.

(c) The "bond lattice" model of Angell[12] suggests a value $\bar{n}_{HB} = 2.96$.

(d) Weres and Rice[13] with a "cell model" obtained $\bar{n}_{HB} = 2.7$ (note that their p_h is $\bar{n}_{HB}/2$).

(e) A temperature invariant point in the distribution of pair interaction energies seen in the analysis[1] of molecular dynamics data suggests $V_{HB} = -52.8\epsilon_1 = -4.0$ kcal/mole. For this value of V_{HB}, we get $\bar{n}_{HB} = 2.2$.

Figure 9 shows the dependence of $\bar{n}_{HB}$ on V_{HB} in the three systems considered in this paper. The influence of system size and of temperature and density is seen to be small.

(f) The cluster model of Lentz, Hagler, and Scheraga[14] uses $\bar{n}_{HB} = 1.84$ with negligible temperature dependence. This value, in our calculation, requires $V_{HB} = -56.6\epsilon_1 = -4.3$ kcal/mole. From Figs. 1 and 3, we find large
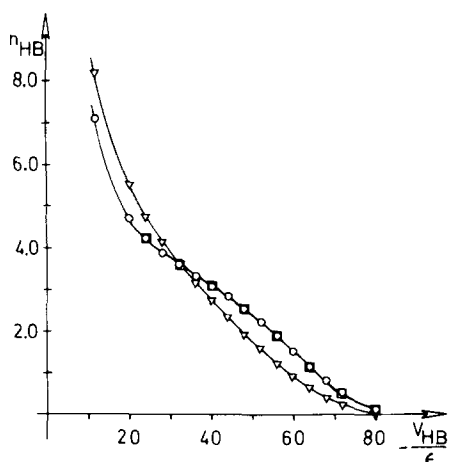
FIG. 9. Average number of hydrogen bonds per water molecule $\bar{n}_{HB}$ as a function of the HB energy definition V_{HB}: o: system I; ∇: system II; □: system III.

clusters $\langle n_w \rangle \sim N/2$ for this V_{HB}. This contradicts the supposition of the cluster model of these authors that only small clusters (of size < 10) are present. Moreover, in this model, W_n increases in going from $n = 1$ to 6 whereas all distributions we obtain show a monotomic *decrease* of W_n in the small cluster size region.

VIII. LIQUID H_2O AS A GEL

The gel model of Cohen, Gibbs, and Fleming[8] is based on the analogy between vapor condensation and gelation in chemical polymerization developed by Stockmayer.[6] The same problem has been treated by Gordon and Temple[15] using graph theory.

Stockmayer[6] showed that the weight average $\langle n_w \rangle$ diverges (in an infinite system) as soon as the "degree of polymerization" α approaches a critical value α_c given by

$$\alpha_c = 1/(f-1) \ ,$$

where f is the "functionality" of the monomer units, i.e., the number of possible bonds of each monomer. For water, $f = 4$ is a natural choice, giving $\alpha_c = 1/3$. The critical number of hydrogen bonds per molecule $n_c \ (= f \times \alpha_c)$ is then $4/3$.

For a finite system, $\langle n_w \rangle$ will not diverge but will undergo a sudden but continuous increase when $\bar{n}_{HB}$ exceeds n_c; this behavior was seen in Fig. 3. We have noticed already that the transition is sharper for the larger system. We also need to remark that the transition occurs for $\bar{n}_{HB} > 4/3$; the main reason for this is that the gelation model excludes intrapolymeric bond ring formation so that clusters with rings are always smaller than the clusters calculated in the model for the same number of hydrogen bonds.

IX. PERCOLATION IN THE WATER SYSTEM

The questions of connectivity between various parts of our system of water molecules is naturally related to the broad class of percolation phenomena. We need to consider a critical bond concentration x_c beyond which percolation paths occur throughout the system;

in obtaining a bond concentration, it is of course desirable not to neglect the formation of rings inside the connected clusters.

Kirkpatrick[16] has given the description of a percolation process which applies to our system nearly literally: When the concentration x of bonds is low ($x \ll x_c$), small isolated clusters occur. The weight average of clusters increases monotonically with x. As x approaches x_c from below, the larger clusters merge and in a macroscopic system the mean cluster size diverges at x_c. For a finite system, this implies one or more connected paths along bonds covering the volume of the whole system. For $x > x_c$, one main cluster remains with possibly several very small ones scattered in various positions.

Regarding x_c, a "rule of thumb" says[17] that, in a three dimensional network, an average of at least 1.5 unblocked steps (bonds) are needed out of every node (molecule).

If f is the functionality of the monomers, Shante and Kirkpatrick[18] pointed out that this rule is valid for a wide range of values of f. The rule continues to be valid when bonds to other than immediate neighbors are also present. In the context of hydrogen bond networks, the possibility of more than four bonds is thus allowed.

More accurate theoretical calculations give $x_c = 1.56$ for the ice (wurtzite) lattice[19] and 1.55 for the diamond lattice.[20]

X. CONCLUSIONS

Molecular dynamics results clearly demonstrate the presence of the percolation threshold, at $k \approx 62$, $\bar{n}_{HB} \approx 1.3$ for water under ordinary conditions. We note, from statements in Secs. VII, VIII, and IX, that estimates of the average number of hydrogen bonds in water all lie beyond the percolation limit.

In an extensive tabulation, Falk and Ford[21] give estimates of the average number of hydrogen bonds in water derived from very different experimental observations. With the exception of two extreme cases, all estimates yield $\bar{n}_{HB} > 1.6$. Hence, water has to be considered as a large macroscopic space-filling network enclosing a few small bonded but isolated clusters.

In the work reported here and in an already published analysis of molecular dynamics results, liquid water appears as a uniform space-filling random network; it should be mentioned however that the conclusions are based on an "energetic" definition of a bond. The possibility cannot be ignored however that, with a different prescription for the existence or absence of a bond, a different picture can emerge of connectivity in liquid water.

## APPENDIX A: SCHEMATIC EXAMPLE FOR CLUSTER SIZE DETERMINATION

The model system is nine molecules in two dimensions, periodic boundaries, and hydrogen bonds are indicated by lines:
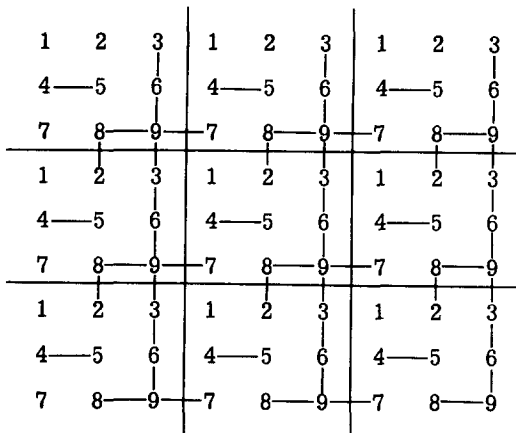
The resulting list of partners is as follows:

reference molecule #	# of hydrogen-bonded partners
1	no HB partner
2	8
3	6 9
4	5
5	4
6	3 9
7	9
8	2 9
9	3 6 7 8

The resulting cluster lists are as follows:

1

2	8	9	3	6	7

4	5
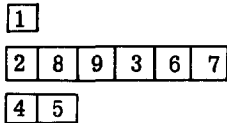
Thus, we find

$$
\left.\begin{array}{l}
1 \quad 1 \text{ net} \\
1 \quad 6 \text{ net} \\
1 \quad 2 \text{ net}
\end{array}\right\}
\begin{array}{l}
m_1 = 1 , \\
m_2 = 1 , \\
m_3, \ldots, m_5 = 0 , \\
m_6 = 1 , \\
m_7, \ldots, m_9 = 0 .
\end{array}
$$

and

It is important to recognize that the network size n refers to the number of particles contained in one single box. If one considers the infinite periodic arrangement, the 6 net transforms to an infinitely large net due to periodicity.

There are also possibilities for 6 nets that remain finite in the infinite periodic arrangement, e. g.,
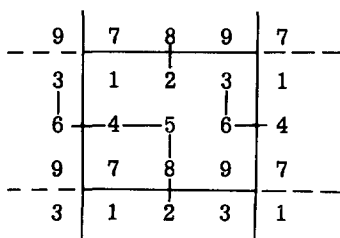
APPENDIX B

For control purposes, several of the results published in Ref. 3 can be compared with the results of the present study (system I): (1) average hydrogen bond number $\bar{n}_{HB} \equiv \langle b \rangle$:

$-\frac{1}{\epsilon} V_{HB}$	$\langle b \rangle$ Ref. 3	$\bar{n}_{HB}$, this paper
28	3.88	3.87
40	3.14	3.09
52	2.26	2.23
64	1.18	1.17

;

(2) fraction of unbonded water molecules $N_u/N \equiv n_0$:

$-\frac{1}{\epsilon} V_{HB}$	n_0, Ref. 3	N_u/N, this paper
28	0	0.00005
40	0.00331	0.00345
52	0.0410	0.0379
64	0.249	0.245

;

(3) fraction of water molecules with exactly one hydrogen bond $p(n_{HB} = 1) \equiv n_1$:

$-\frac{1}{\epsilon} V_{HB}$	n_1, Ref. 3	$p(1)$, this paper
28	0.0026	0.00327
40	0.029	0.0426
52	0.180	0.195
64	0.415	0.420

.

If one takes into consideration that in Ref. 3 only 14 configurations are used for averaging, whereas here 620 configurations are used, the agreement is good, with perhaps one exception: $p(1)$ and n_1 at $-(1/\epsilon)V_{HB} = 28$ and 40 differ by about 50%.

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