

## Gelation models of hydrogen bond networks in liquid water

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Cluster statistics of hydrogen bond networks in water are calculated with the use of molecular dynamics (MD) and are compared with the predictions of gelation models. For small bond networks the MD calculations agree well with Flory theory (which neglects cycles), but they disagree for the larger networks. The MD data for the connectivity of the larger networks agree much better with our ice lattice calculations, providing the first MD test of the ability of Flory theory to describe polyfunctional condensation network statistics.

It is widely agreed that the unusual properties of liquid water are related in some fashion to the hydrogen bond network.<sup>1</sup> However, there is very little information on just how the bonds conspire to produce the observed macroscopic behavior. Computer simulation studies of water afford an opportunity to address this question. Indeed, the first direct information about the hydrogen bond connectivity was obtained from molecular dynamics (MD) studies which revealed the clear existence of a percolation threshold.<sup>2</sup> Shortly thereafter it was established from Monte Carlo simulations that essentially identical results could be obtained for a variety of different intermolecular potentials and bond criteria, so that the main conclusions "network analysis" are independent of the details of the simulation.<sup>3</sup>

Here we examine in much more detail the statistics describing the *microscopic* connectivity. Instead of concentrating on the "macroscopic" functions treated previously,<sup>2-5</sup> we focus on the distribution functions  $W(M,p)$ , the weight fraction of hydrogen bond networks with  $M$  molecules when a fraction  $p$  of the hydrogen bonds are intact. We shall see that the MD data agree well when  $M$  is small with the predictions of the Flory theory of gelation,<sup>6</sup> but that systematic discrepancies occur for larger values of  $M$ . These arise from the fact that Flory theory neglects cycles; therefore, we perform *additional* calculations on the ice lattice which has even-numbered cycles and presumably reflects to some degree the local geometry in water. We shall see that the MD data agree better with the lattice calculations than with the Flory theory for large  $M$ .

## MD CALCULATIONS

The MD results were obtained by analysis of configurations from the simulation<sup>7</sup> of a system of 216 ST2 water particles at  $T = 284$  K and density  $1.0$  g/cm<sup>3</sup>. Periodic boundary conditions are imposed on the basic cubic box of edge  $18.6$  Å. The simulation covers a total period of  $8.1$  ps ( $38100$  time steps). We use two distinct definitions of a hydrogen bond. Definition  $D_1$  defines bonds by a purely energetic criterion: Two molecules  $i$  and  $j$  are considered to be bonded if their pair interaction energy satisfies  $V_{ij} < V_{HB}$ . Definition  $D_2$  combines the energetic definition with a geometric criterion: If the oxygen separation of  $i$  and  $j$  is

greater than  $3.5$  Å, then  $i$  and  $j$  are said to be unbonded even though the energetic criterion may be fulfilled. The parameter  $V_{HB}$  takes on a set of 32 equally spaced values ranging between  $-1.5$  and  $-6.2$  kcal/mole. In the case of more permissive definitions, there sometimes occur molecules having more than four bonds; for the  $D_1$  analysis we eliminate the weakest until there are no more than four bonds per molecule, while for the  $D_2$  analysis we *permit* molecules with more than four bonds. The mean number of hydrogen bonds per molecule  $n_{HB}$  varies roughly between zero and four. We interpret the quantity  $p \equiv n_{HB}/4$  as the fraction of intact bonds.

For each water configuration, we analyze the *complete* hydrogen bond distribution. Networks that span the basic cube in at least one coordinate direction are considered to be infinite, and only the remaining finite nets are used in the analysis procedure described below. Because 127 MD configurations were analyzed for definition  $D_1$  and 800 configurations for  $D_2$ , we expect the data for  $D_2$  to show less statistical fluctuation.

## FLORY THEORY

In 1941, Flory presented the classic analytic results for a random network in the absence of cycles or "polygonal closures."<sup>6</sup> The weight fraction of monomers belonging to a bond network of  $M$  monomers is

$$W(M,p) = A_f(M) p^{M-1} (1-p)^{(f-2)M+2} \quad (1)$$

Here  $p$  is the fraction of all possible bonds that are intact and is interpreted as the extent of reaction,  $f$  is the functionality, and

$$A_f(M) = f(fM - M)! / M!(fM - 2M + 2)! \quad (2)$$

is a combinatorial factor giving the total number of "branched polymer" or "lattice animal" configurations of  $M$  monomers. The most natural choice for water monomers is  $f=4$  as there are two protons and two lone pairs associated with each molecule, and four hydrogen-bonded neighbors in all known modifications of ice.

## HYDROGEN BOND NETWORKS

We have made plots comparing Flory theory and MD calculations on ST2 water for a sequence of  $M$  ranging from 1 to 50; the plots for three selected values,  $M = 5, 15,$  and  $40$ , are reproduced in Fig. 1(a). There are no adjustable parameters in either the Flory theory or the MD calculations and

this comparison provides the *first* MD test of the ability of Flory theory to describe polyfunctional condensation. We find very good agreement for plots with  $1 \leq M \leq 12$ . For still larger  $M$  the positions of the maxima of the Flory curves tend toward a value of  $1/(f-1) = \frac{1}{3}$ , while the MD data approach a larger limit.

Additional quantities of interest in gelation are (a) the to-

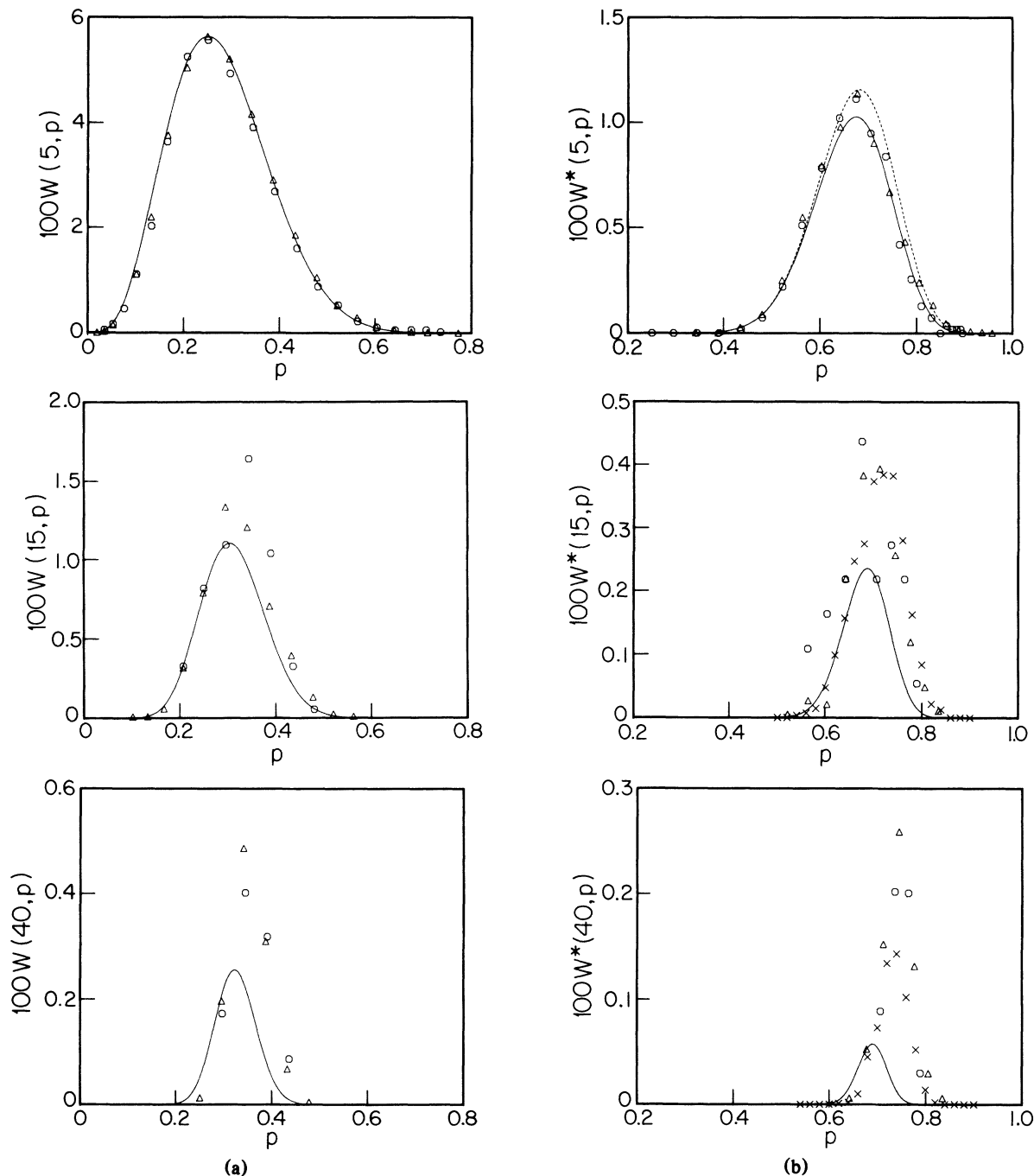


FIG. 1. Dependence on fraction of intact bonds  $p$  of (a)  $W(M,p)$ , the weight fraction of water molecules belonging to an  $M$ -molecule network (for  $M = 5, 15,$  and  $40$ ), and (b)  $W^*(s,p)$ , the weight fraction of molecules belonging to an  $s$ -site patch of four-bonded molecules (for  $s = 5, 15,$  and  $40$ ). Shown are the predictions for the Flory theory as a solid curve and the results of MD calculations using both definitions  $D_1$  ( $\circ$ ) and  $D_2$  ( $\Delta$ ). The crosses indicate the Monte Carlo lattice calculations and the dashed curve represents exact lattice calculations (for the infinite lattice, of course). There are no adjustable parameters, so the decreasing quality of the agreement as  $M$  (or  $s$ ) increases is indicative of the breakdown of Flory theory for large networks.

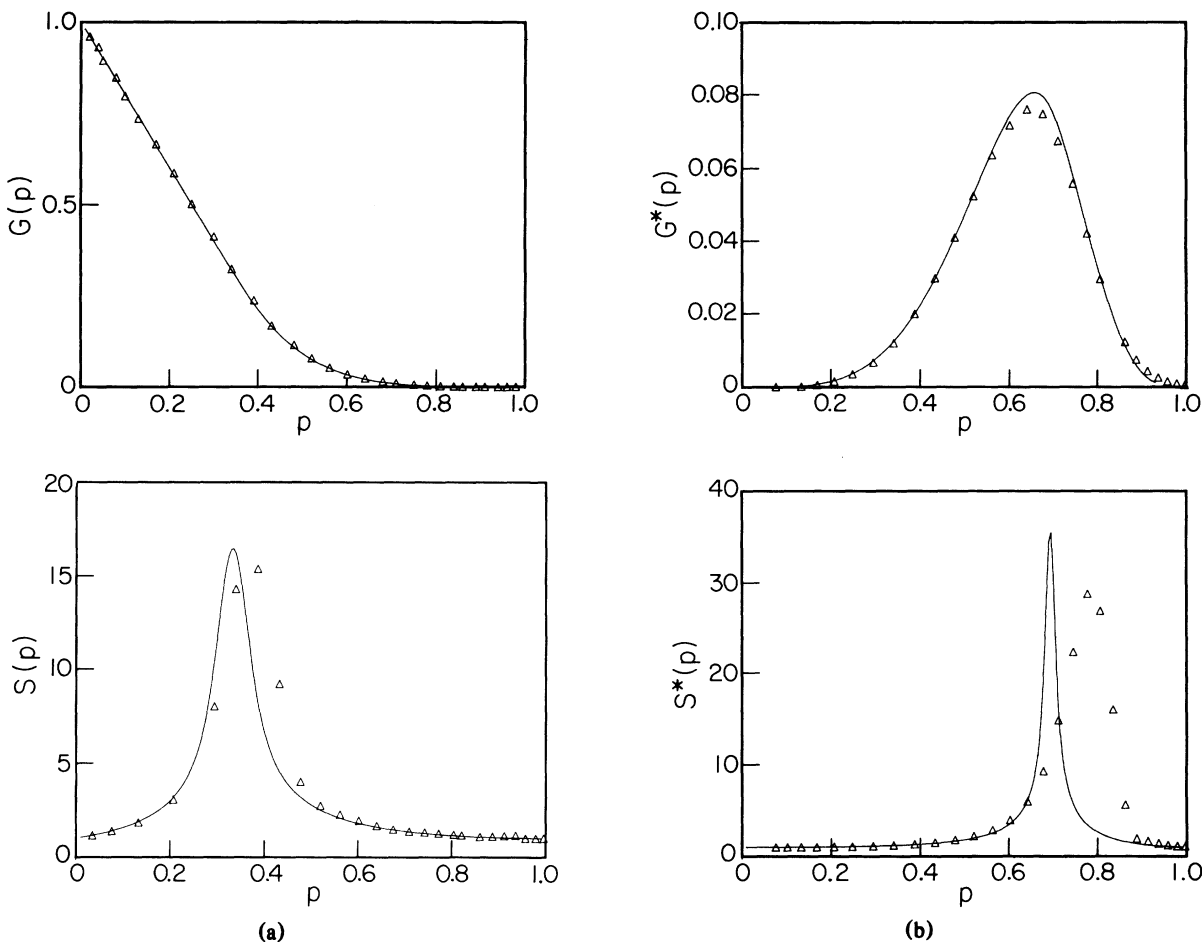


FIG. 2. Part (a) shows the dependence on  $p$  of the total number of bond networks  $G$  and the mean size of a bond network  $S$ , while part (b) shows the corresponding quantities for the patches of four-bonded molecules. The solid curve gives the predictions of Flory theory, while the MD data are shown for definition  $D_2$  (Ref. 8).

tal number of bond networks, regardless of size,

$$G(p) = \sum_{M \geq 1} M^{-1} W(M, p), \quad (3a)$$

and (b) the mean size of a bond network (the mean number of monomers belonging to a network, or "degree of polymerization"),

$$S(p) = \sum_{M \geq 1} MW(M, p). \quad (3b)$$

Figure 2(a) compares these two quantities for the Flory theory and MD calculations. We see that for  $G(p)$  there is excellent agreement for all  $p$ , while for  $S(p)$  there is poor agreement near the percolation threshold. This finding may be understood as follows. Flory theory gives accurate expressions for  $W(M, p)$  at small  $M$ , and  $G(p)$  weights the small networks. Thus Flory theory accurately predicts  $G(p)$ . On the other hand,  $S(p)$  weights the large networks, where Flory theory is no longer a good approximation.<sup>8</sup> The position of the maximum in  $S(p)$  is predicted to approach  $p_c^{\text{Flory}} = \frac{1}{3}$ , while the MD data display a maximum at 0.4—as anticipated from the large- $M$  behavior of  $W(M, p)$ . Note that for any lattice which includes bond cycles, one always finds values for  $p_c$  which are larger than  $p_c^{\text{Flory}}$ .

#### FOUR-BONDED MOLECULES

When  $p$  is very large, the fraction  $p^4$  of four-bonded water molecules is significant. The hydrogen bond networks in liquid water are characterized by many tiny "patches" of four-bonded molecules, and the local density in the vicinity of a patch is lower than the global density.<sup>9</sup> Accordingly, it is of interest to test the extent to which Flory theory provides an adequate description of the corresponding distribution function  $W^*(s, p)$ , the weight fraction of molecules belonging to an  $s$ -site patch of four-bonded water molecules. Equation (1) for bond networks and  $f = 4$  is replaced by

$$W^*(s, p) = A_4(s) p^{3s+1} (1-p^3)^{2s+2}.$$

Figure 1(b) shows the corresponding plots of  $W^*(s, p)$  for  $s = 5, 15$ , and 40. In contrast to the case of bond networks, we see that the Flory theory begins to break down already for  $s = 5$ . This is understandable, since the calculation for  $W^*(s, p)$  for the four-bonded molecules utilizes much more extensively the lattice topology than the calculation of the corresponding  $W(M, p)$  for bond networks, and hence the neglect of rings in Flory theory is more serious.<sup>10</sup>

Figure 2(b) shows the corresponding plots of  $G^*(p)$  and  $S^*(p)$  for the total number of four-bonded patches and the

mean size of a patch, respectively. Again, we see that the MD data agree well for  $G^*(p)$  but not for  $S^*(p)$  near the threshold region. The density of four-bonded molecules  $\rho = p^4$  at the percolation threshold for four-bonded molecules is  $\rho_c = 0.39 = (0.79)^4$ , considerably larger than the corresponding value for the Flory theory  $\rho_c = 0.23 = (0.69)^4$ .

### LATTICE CALCULATIONS

In view of the observed discrepancies between MD data and Flory theory, it is tempting to see if better prediction of the MD data can be obtained by making calculations for a lattice that contains polygonal closures. As noted above, the maximum of  $S(p)$  is near 0.4; perhaps coincidentally, the bond percolation threshold for an ice lattice is 0.39.<sup>11</sup> Accordingly, we have calculated  $W(M,p)$  and  $W^*(s,p)$  for the ice lattice, which perhaps better than other lattices reflects the local geometry in water. For  $M \leq 6$  and  $s \leq 6$  these calculations can be made exactly.<sup>11</sup> For  $s > 6$  we performed Monte Carlo calculations on a sequence of lattice sizes<sup>12</sup> up to a maximum of 21 296 sites. We see that the MD data agree better with the ice lattice calculations than with the Flory theory, indicating that cycles are important in describing hydrogen bond networks in liquid water. Of course, we know that MD simulation results show also the presence of odd-numbered rings<sup>13</sup> while the calculation on an ice lattice includes only even-numbered rings. Hence the better agreement between MD continuum and Monte Carlo

calculations on the ice lattice primarily indicates that rings are important, *not* that the connectivity of water molecules is identical to that of ice.

In summary, we find that both microscopic (Fig. 1) and macroscopic (Fig. 2) results from the MD simulations of water are well described by the Flory theory of gelation, with two important exceptions: (a) the microscopic distribution functions  $W(M,p)$  for bond networks disagree with Flory theory for  $M$  larger than roughly 12. Also, the corresponding distribution functions  $W^*(s,p)$  for clusters of four-bonded molecules disagree for  $s$  larger than about 5. In both cases, the MD data agree better with calculations on an ice lattice, which take into account cycles. (b) Although the macroscopic function  $G(p)$  agrees perfectly with Flory theory, the maximum of  $S(p)$  peaks at a value somewhat closer to the percolation threshold for the ice lattice than the percolation threshold for Flory theory.

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<sup>6</sup>P. J. Flory, *J. Am. Chem. Soc.* **64**, 3083 (1941); W. H. Stockmayer, *J. Chem. Phys.* **11**, 45 (1943).

<sup>7</sup>F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974).

<sup>8</sup>The height of the maximum in  $S(p)$  is very sensitive to the number of terms included in (3b), and is therefore of no significance here. We are primarily concerned with the position of the maximum because this indicates the location of the percolation

threshold. In Fig. 2,  $M_{\max} = 180$  and  $s_{\max} = 800$ .

<sup>9</sup>H. E. Stanley, *J. Phys. A* **12**, L329 (1979); H. E. Stanley and J. Teixeira, *J. Chem. Phys.* **73**, 3404 (1980); A. Geiger and H. E. Stanley, *Phys. Rev. Lett.* **49**, 1749 (1982).

<sup>10</sup>For example,  $W(M=5,p)$  is the same for both the ice lattice and the Flory theory, while  $W^*(s=5,p)$  is quite different for the two systems.

<sup>11</sup>R. L. Blumberg, A. Geiger, and H. E. Stanley (unpublished).

<sup>12</sup>To assure that the deviations of the MD data from Flory theory are not just a result of the system size, we made Monte Carlo lattice calculations for different lattice sizes. These indicate that increasing the system size would actually increase the discrepancy between simulation and Flory theory.

<sup>13</sup>A. Rahman and F. H. Stillinger, *J. Am. Chem. Soc.* **95**, 7943 (1973).