Universality in hydrogen-bond networks

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We present several lattice models for water that belong to the universality class of Angell's independent-bond model. The relevance for real water, the relationship to percolation models for water, and the possible use of these models in simulations of protein-solvent systems is discussed.

Hydrogen bonds play an important part in the structure of liquid water. For example, ir-absorption experiments [1], molecular-dynamics (MD) simulations [2-4], and percolation models [5] suggest that in liquid water there is always a percolating cluster of hydrogen-bonded water molecules. Moreover, in most molecular biological systems hydrogen bonds are responsible for the secondary and tertiary structure [6]. Common to all these cases is that a *network* of hydrogen bonds is present at the temperatures of interest. At nonzero temperatures, these bonds will fluctuate, i.e., they will open and close randomly, due to thermal fluctuations.

We have investigated the thermodynamic properties of several lattice models for water based on water molecules that interact only via hydrogen bonds [7]. The basic one is an extension to nonzero temperatures of the square-ice model by Lieb [8], which we termed, consequently, *square water* (SW). Water molecules, whose allowed conformations are shown in Fig. 1, are placed densely on a square lattice. The conformations of Fig. 1 arise by projecting the almost tetrahedrical hydrogen-bond structure of a water molecule into the plane, while retaining the local connectivity of a diamond lattice [8]. Translational degrees of freedom are disregarded for simplicity. Hydrogen bonds are possible between neighboring water molecules if the O−H bond of one molecule faces the oxygen of the next molecule (see also Fig. 1). We denote the energy of a closed hydrogen bond by −ε. The restriction of the allowed orientations of water molecules to the conforma-

tions of Fig. 1 is motivated by the strongly directional nature of hydrogen bonds [9]. SW was analyzed by Monte Carlo (MC) simulations [7], and the temperature dependence of the average number of hydrogen bonds per molecule, $\langle n_H \rangle$, and of the specific heat due to hydrogen-bond fluctuations, $c_v/k_B = (\beta\varepsilon)^2 \langle \delta n_H^2 \rangle /4$, are shown in Fig. 2 (note that $\delta n_H = n_H - \langle n_H \rangle$, and $\beta = 1/k_B T$, with absolute
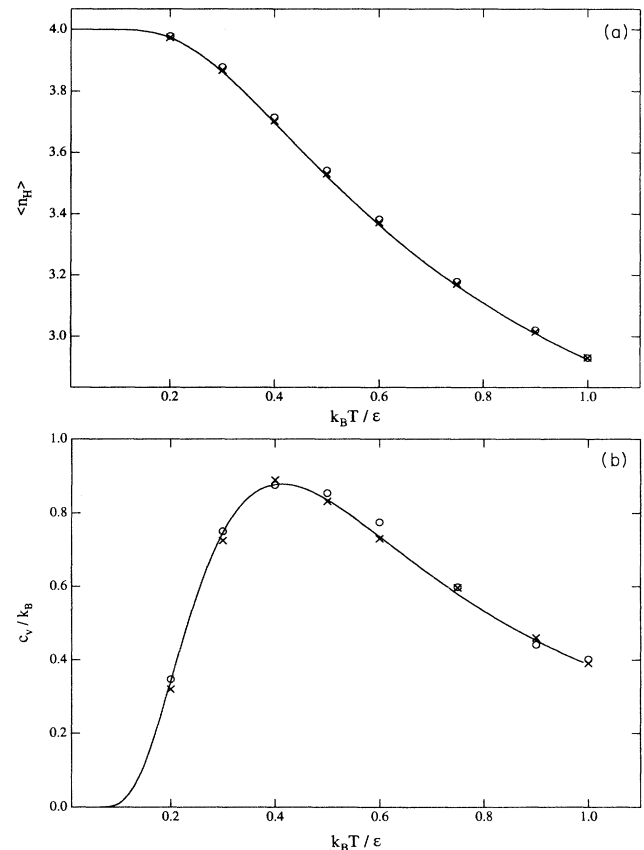
FIG. 2. (a) Average number of hydrogen bonds per molecule, $\langle n_H \rangle$, and (b) specific heat c_v vs temperature for the models discussed in the text; (——) independent-bond results, Eqs. (2) and (3), respectively; (O) results from MC simulations of SW on a 50×50 lattice with periodic boundary conditions [7]; (×) results from MC simulations of BW on a 12×12×12 lattice with periodic boundary conditions [7]; the error bars for the MC results are in (a) less than and in (b) about the size of the symbols.
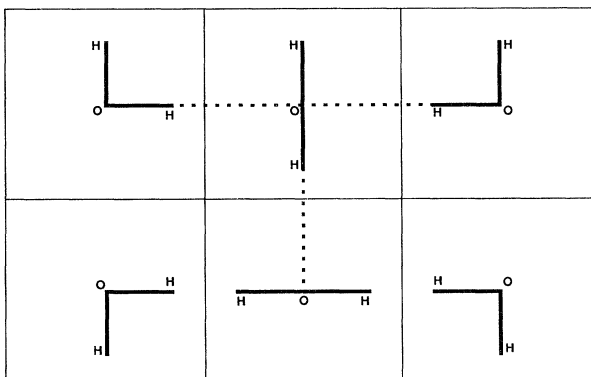

FIG. 1. Allowed conformations of water molecules on the square lattice in the SW model; closed hydrogen bonds are indicated as dotted lines.

temperature T and Boltzmann's constant k_B). We have also investigated a three-dimensional extension of SW by putting the water molecules with their tetrahedral hydrogen-bond structure on a diamond lattice (which has a coordination number of four like the square lattice). Due to the peculiar connectivity that arises when a diamond lattice is, for computational reasons, represented as a simple-cubic lattice, we termed this model *brick water* (BW). This model was analyzed again by MC simulations [7], and the results are also shown in Fig. 2.

The behavior of both models, BW and SW, is very similar and it can readily be described by an independent-bond approach due to Angell [10]. We give here a derivation slightly different from Angell's original paper. In this approach, the partition function of a hydrogen-bond network factorizes into the contribution from the N possible independent bonds in such a network. Since each of these bonds can only be open or closed, the resulting independent-bond partition function Z_{IB} is

$$Z_{IB} = Z_{SB}^N = (1 + e^{\beta\varepsilon})^N , \qquad (1)$$

where Z_{SB} denotes the single-bond contribution. In dense systems, like ice and liquid water, one can assume that, in principle, every possible hydrogen bond of a water molecule may be closed. Since water molecules can participate in up to four hydrogen bonds, regardless of the actual topology of the hydrogen-bond network, the maximum number of possible hydrogen bonds in ice and water is $N = 2M$, where M is the number of water molecules in the network. From the partition function, Eq. (1), the pertinent observables like the average number of hydrogen bonds per molecule, $\langle n_H \rangle$, and the specific heat c_v can be deduced easily:

$$\langle n_H \rangle = \frac{1}{M\varepsilon} \frac{d}{d\beta} \ln Z_{IB} = \frac{2N}{M} \frac{e^{\beta\varepsilon}}{1 + e^{\beta\varepsilon}} , \qquad (2)$$

$$c_v/k_B = \tfrac{1}{4}(\beta\varepsilon)^2 \langle \delta n_N^2 \rangle = \frac{(\beta\varepsilon)^2}{M} \frac{d^2}{d\beta^2} \ln Z_{IB}$$

$$= \frac{N}{M} \frac{(\beta\varepsilon)^2 e^{\beta\varepsilon}}{(1 + e^{\beta\varepsilon})^2} . \qquad (3)$$

$\langle n_H \rangle$ and c_v in Eqs. (2) and (3) show the same behavior as the mean energy and the specific heat, respectively, in the one-dimensional Ising model [11], which can be regarded as a particular realization of an independent-bond system. Figure 2 demonstrates that the simulation results from SW and BW follow closely the analytical results of Eqs. (2) and (3).

Another lattice model which we termed *simplified square water* (SSW) is arrived at by omitting the stretched configurations of Fig. 1 in SW (i.e., reducing the number of allowed conformations), and can be solved exactly [7]. It leads—asymptotically in the thermodynamic limit—to a partition function identical to Eq. (1).

These similar results for various lattice models, together with their description by the independent-bond model, lead us to the hypothesis that there exists a (possibly large) class of hydrogen-bond network models whose thermodynamic behavior is governed by the independent-bond theory given in Eqs. (1)–(3). Because the models in this universality class exhibit a similar thermodynamic behavior over the whole temperature range, in the thermodynamic limit the partition function Z of a particular hydrogen-bond network model should have the asymptotic form

$$Z = Z_{IB} \exp(M S^0/k_B) , \qquad (4)$$

where M is the number of molecules, and S^0 is the zero-temperature entropy of the model in question. For example, for SW this is the entropy of the square-ice model [8], $S_{SW}^0/k_B = \tfrac{1}{2} \ln \tfrac{4}{3}$, and for SSW it is zero [7].

The above considerations were limited to hydrogen-bond networks in which the translational degree of freedom is frozen. Therefore, the results are applicable, for example, to hydrogen bonds in ice. However, we believe that those results are not limited to ice, but the considerations leading to the above results are also relevant for hydrogen-bond networks in the liquid state, particularly in liquid water. From the point of view of statistical mechanics, the liquid state can be viewed as a collection of different spatial arrangements of molecules. For each of these configurations the above independent-bond approach for the evaluation of the partition function can be employed. In liquid water we can assume that for most of the relevant configurations $N \approx 2M$ holds, the resulting thermodynamic behavior being the same as above. The partition function will simply be renormalized by the appropriate entropy, as in Eq. (4).

For a comparison with real water the temperature scale has to be adjusted by viewing the single free parameter in the independent-bond theory, the hydrogen-bond energy ε, as an *effective free energy:*

$$\varepsilon = \varepsilon' - T\sigma' . \qquad (5)$$

This generalization is necessary in order to account for entropy differences between open and closed hydrogen bonds due to other degrees of freedom (which show up, e.g., in different vibrational spectra) as already noted by Angell [10]. He obtained the parameters $\varepsilon' = 1.3 \times 10^{-20}$ J and $\sigma' = 3.3 \times 10^{-23}$ J/K from a comparison with data [12] on the configurational contribution to the specific heat of water. ε' is well within the range of energies discussed for hydrogen bonds (from 9×10^{-21} to 3×10^{-20} J, see Ref. [12]). In Fig. 3 we compare the independent-bond results for $\langle n_H \rangle$ using these parameters with experimental results on water [13] and MD results on ST2 water [4], data that were not available at the time of Angell's work. As can be seen, the MD results follow the behavior of the independent-bond results very closely. We note, however, that, due to the choice of the cutoff distance for assigning hydrogen bonds, there is also a free parameter involved in the results of MD simulations [4,14], which allows for a possible shift of those results along the vertical axis. Unfortunately, no MD results on the part of c_v that originate from hydrogen-bond fluctuations are available. The experimental results on $\langle n_H \rangle$ for water are reliable only at $T = 0\,°C$. At higher temperatures those data of Ref. [13] give just lower limits to the actual values. Both the MD results and the independent-bond results are compatible with those data.
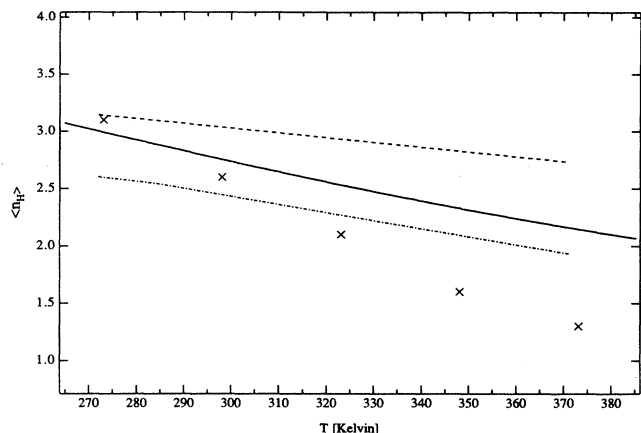
The success of the independent-bond approach in

FIG. 3. Average number of hydrogen bonds per molecule, $\langle n_H \rangle$, vs temperature; (——): independent-bond results with $\varepsilon' = 1.3 \times 10^{-20}$ J and $\sigma' = 3.3 \times 10^{-23}$ J/K from Ref. [10]; (---) and (-·-·): results from MD simulations [4] for two different values of the energy cutoff for a hydrogen-bond assignment ($V_{HB} = 2.1 \times 10^{-20}$ J and $V_{HB} = 2.5 \times 10^{-20}$ J, respectively); and (×): experimental results from liquid water [13]; we note that the experimental results for $T > 0\,°C$ are extrapolations and give only lower limits to the actual values [13].

describing the thermodynamic properties of more microscopic models for hydrogen-bond networks and of real water provides also a justification for an alternative description of water in terms of bond percolation models. Such models for water have already been analyzed extensively [5,15]. The pertinent parameter in those models, the probability p_H of a particular hydrogen bond to be closed, is related to the average number of hydrogen bonds per molecule by $p_H = \langle n_H \rangle / 4$ in the case of water. Using Eqs. (2) and (5) and the above parameters it can be seen that

$p_H > \frac{1}{2}$ holds for temperatures up to about 400 K and is, therefore, well above the percolation threshold of most lattices [16], particularly in three dimensions. This result corroborates the existence of a percolating cluster of hydrogen-bonded water molecules in liquid water [1,4,5]. Due to the independence of the bonds from one another, the distribution f_j of water molecules with j bonds follows a binomial distribution [5],

$$f_j = \binom{4}{j} p_H^j (1 - p_H)^{4-j}. \tag{6}$$

This distribution is a general feature of most water models [15], in particular, it is observed in MD simulations [14]. The results of the independent-bond approach go beyond the results of percolation models in that the temperature dependence of p_H and, consequently, of f_j is predicted.

Despite its simplicity, the independent-bond model is a surprisingly good description of the hydrogen-bonding behavior of water [10]. Although its quality was recognized early on [17,18], in recent publications on this topic it is hardly mentioned anymore [2,15,19], undeservedly as we believe. The simple lattice models we introduced in this contribution belong to the universality class of the independent-bond model and provide, therefore, an equally good description of the hydrogen-bonding behavior of water. Moreover, this equivalence supports the use of such models for studying, at least qualitatively [20], solvent-solute interactions in situations still too complex to be analyzed by detailed MD simulations. A foremost candidate is the solvent-protein interaction. Hydrogen bonds probably are the main contribution to this interaction. For example, the reduction of accessible volume for the protein, due to hydrophobic interactions, is discussed to be the main driving force of protein folding [21]. We note that in the SSW model hydrophobicity and hydrophilicity of a solute molecule, as measured by the free-energy change, can be evaluated analytically, with qualitatively correct results [22].

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