LETTER TO THE EDITOR

Bond-correlated percolation model and the unusual behaviour of supercooled water

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Abstract. It is shown that the partition function of an interaction Hamiltonian for the hydrogen bonding in water molecules may be expressed as the generating function of a bond-correlated percolation model with a bond probability p depending on the hydrogen-bond strength and the temperature T. Assuming that the molecules with larger number of active bonds have a larger volume per molecule, we may show that, for temperatures near but higher than the temperature of maximum bond fluctuations, the isothermal compressibility K_T and the constant pressure specific heat C_p increase, while the thermal expansivity α_p becomes more negative, as T decreases. Other unusual behaviour of supercooled water can also be explained by this model.

The interactions between water molecules include van der Waals attractions and hydrogen-bond couplings. It is clear that the latter play an important role in the properties of water, e.g. the unusual behaviour of supercooled water (see e.g. the recent review of Angell (1982)). However, the way that the hydrogen-bond interactions influence the properties of water is not well understood. Recently Stanley and coworkers (Stanley 1979, Stanley and Teixeira 1981, Stanley et al 1981) made an important step in understanding the unusual behaviour of supercooled water. They used a polychromatic site-correlated percolation model (PSCPM) to explain the anomalous behaviour of (a) the isothermal compressibility $K_T(T, P_0)$, (b) the constant pressure specific heat $C_p(T, P_0)$, and (c) thermal expansivity $\alpha_p(T, P_0)$ for H_2O or D_2O at a supercooled temperature T and atmospheric pressure P_0. Their theory is based on the following assumptions. (A1) The water molecules are located on a lattice G. (A2) For each pair of molecules located on nearest-neighbour sites there is a bond with active probability p and inactive probability $1-p$. The active bonds connect the water molecules to form a percolating network. (A3) The molecules with a larger number of active bonds have larger volume per molecule and (A4) smaller value of entropy per molecule. Based on (A1)–(A4), they were able to predict the behaviour of supercooled H_2O and D_2O listed in table 1. All the qualitative predictions of table 1 are consistent with experiments (Angell (1982), see also reference 3 in Stanley et al (1981)).

Although the PSCPM of Stanley et al is capable of explaining the unusual behaviour of supercooled water, it has some unsatisfactory features. For example, the bond probability p of (A2) is not given unambiguously from the microscopic hydrogen-bond potential between molecules but is introduced as a phenomenological parameter. Stanley et al (1981) have also pointed out that 'among the important (sic) is the

Table 1. Summary of the qualitative predictions of the correlated percolation model for the behaviour of three static response functions: the isothermal compressibility K_T, the constant pressure specific heat C_p, and the thermal expansivity α_p.

	K_T	C_p	α_p
Sign of anomaly	+	+	−
Lower T	↑	↑	↓
Increase P_0	↓	↓	↑
Dilute with D_2O	↑	↑	↓
Dilute with a 'patch-breaking' impurity	↓	↓	↑

creation of an appropriate Hamiltonian that describes simultaneously (i) the interactions and (ii) the connectivity between water molecules'. In this paper, we propose a bond-correlated percolation model of water which satisfies the criterion of a desirable theory emphasised by Stanley *et al* (1981) and in which the bond probability is related unambiguously to the assumed hydrogen-bond coupling strength between molecules. The connection between the bond-correlated percolation model for hydrogen-bond coupling (BCPM-HBC) in water and the interaction Hamiltonian for water molecules is a natural extension of our recent work (Hu 1982, 1983a, b, c), which relates many spin models to correlated percolation models. In the BCPM-HBC, it is also assumed that molecules with larger number of active bonds have larger volume per molecule (i.e. (A3) above). However, the assumption A4 in the model of Stanley *et al* (1981) follows directly from our theory. Our theory can also predict the unusual behaviour of supercooled water listed in table 1.

For the sake of simplicity, we first establish the connection between a simple interaction Hamiltonian for water molecules and a bond-correlated percolation model. The more complicated cases will be discussed at the end of the paper. Suppose we have water molecules located on a lattice G with N sites (vertices) and E bonds (edges), in which each site connects its four nearest neighbours (NN) (i.e. the coordination number of G is four) with four bonds. Each lattice site, say i, $i = 1, 2, \ldots, N$, is occupied by one and only one oxygen of an H_2O and the two hydrogen atoms covalently bonded with this oxygen can point in any two directions of the four bonds emanating from the ith site. Thus at the ith site, there are six possible molecular configurations which can be represented by a spin s_i with six spin components $s_i = 1$, $2, \ldots, 6$. The correspondence between the molecular configurations at a lattice site of a square lattice and the spin components is shown in figure 1. In this example, the angles between two covalent bonds in states $s_i = 5$ and 6 are different from the angles in states $s_i = 1$–4. In the three-dimensional diamond lattice, the angles between any two covalent bonds in all molecular configurations are always the same.
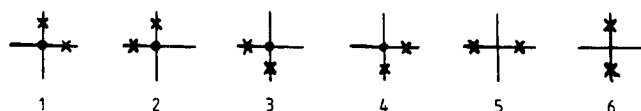

Figure 1. The six water molecular configurations on a vertex of a square lattice. The oxygen is represented by '●' and the hydrogen by '×'. The number below each configuration represents the spin component corresponding to this configuration.

Now we consider the hydrogen-bond interactions between molecules which are nearest neighbour to each other. We assign an interaction energy $-J$ for each bond which satisfies the following hydrogen-bonding condition (HBC): There is one and only one hydrogen atom on each bond.

The interaction Hamiltonian of the hydrogen-bonding can thus be written as

$$H = -J \sum_{\langle ij \rangle} g_{ij}(s_i, s_j), \tag{1}$$

where the summation extends over all NN bonds $\langle ij \rangle$, $1 \le i, j \le N$, $g_{ij}(s_i, s_j) = 1$ when the bond $\langle ij \rangle$ satisfies the condition HBC and $g_{ij}(s_i, s_j) = 0$ when the bond does not satisfy the condition HBC, i.e. there are two or no hydrogen atoms on the bond $\langle ij \rangle$. The system of (1) reduces to the ice problem discussed by Lieb and Wu (1972) in the limit $J/kT \to \infty$, where the molecular configurations which do not satisfy the condition HBC are suppressed.

The partition function for H of (1) is

$$Z(G, K) = \sum_{s_1=1}^{6} \ldots \sum_{s_N=1}^{6} \exp(-H/kT) \tag{2a}$$

which can be rewritten as

$$Z(G, K) = \sum_{s_1=1}^{6} \ldots \sum_{s_N=1}^{6} \prod_{\langle ij \rangle} [1 + (e^K - 1)g_{ij}(s_i, s_j)], \tag{2b}$$

where $K = J/kT$. Now we expand the product in the last expression of (2b) and use the subgraphs $G' \subseteq G$ to represent the terms in the expansion. In each G', there are $e(G')$ bonds (edges) which are attached by the factor $(e^K - 1)g_{ij}(s_i, s_j)$ in the expansion, where $0 \le e(G') \le e(G) = E$. If a particular bond $\langle ij \rangle$ is attached, the sites i and j are said to be in the same cluster. In general, if two sites can be connected through a series of attached bonds, they are said to be in the same cluster. A given G' usually contains a large number of independent clusters including isolated sites which do not connect with any other sites via attached bonds. For a given G', we can carry out the configuration summation of all molecular states, and in such a summation only the terms where each attached bond satisfies the condition HBC have non-zero contributions. Thus (2b) can be written as

$$Z(G, K) = \sum_{G' \subseteq G} p^{e(G')}(1-p)^{E-e(G')} \prod_c D_c \exp(KE) \tag{3}$$

where

$$p = 1 - e^{-K}. \tag{4}$$

The product in (3) extends over all clusters c in G'. D_c is the total number of configurations of the molecules in cluster c in which each bond satisfies the condition HBC. For isolated clusters, i.e. sites without any attached bonds, $D_c = 6$; for two-site clusters $D_c = 6 \times 3 = 18$. In principle, such calculations of D_c can be extended to more and more complicated clusters. We expect that on the average the clusters with a larger number of bonds per site have a smaller value of $\ln(D_c)$ per site. Thus the model defined by (3) has the property (A4) mentioned above for the PSCPM of Stanley *et al* (1981).

Following an assumption of the PSCPM (Stanley and Teixeira 1981, Stanley *et al* 1981), we consider a local quantity, the volume per oxygen atom, v_j, $j = 0, 1, \ldots, 4$,

and assume that v_j depends on the number of bonds emanating from that atom, with[†]

$$v_0 \leqslant v_1 \leqslant v_2 \leqslant v_3 \leqslant v_4. \tag{5}$$

The total volume of the subgraph G' is given by

$$V(G') = \sum_{j=0}^{4} v_j N_j \tag{6}$$

where N_i is the number of sites in G' with i attached bonds and $N_0 + N_1 + N_2 + N_3 + N_4 = N$. Now suppose there is an external pressure of magnitude P_0 applied to the system; the partition function of (3) must be replaced by

$$Z_a(G, K, P_0) = \sum_{G' \subseteq G} p^{e(G')}(1-p)^{E-e(G')} \prod_c D_c \exp[-P_0 V(G')] e^{KE}. \tag{7}$$

It is clear that $Z_a(G, K, P_0)$ of (7) is the generating function of the following bond-correlated percolation model for the hydrogen-bond coupling (BCPM-HBC) defined on G.

(P1) All sites of G are occupied and each bond of G is attached with a bond probability p of (4).

(P2) The overall probability for a subgraph G' is enhanced by a factor D_c for each cluster c in G' and suppressed by a factor $\exp(-P_0 v_j)$, $0 \leqslant j \leqslant 4$, for each site with j bonds emanating from that site. Because of the extra factors of (P2), the average number of attached bonds on each bond of G, $\bar{p}$, is not equal to p of (4), but is given by

$$\bar{p} = \lim_{N \to \infty} \frac{1}{N} \frac{\sum_{G' \subseteq G} p^{e(G')}(1-p)^{E-e(G')} \prod_c D_c \exp[-P_0 V(G')](e(G')N/E)}{\sum_{G' \subseteq G} p^{e(G')}(1-p)^{E-e(G')} \prod_c D_c \exp[-P_0 V(G')]}$$

$$= \langle e(G')N/E \rangle_0. \tag{8}$$

In the following, we will still use $\langle Q(G') \rangle_0$ to denote the mean value of a subgraph-dependent quantity $Q(G')$ per site in the thermodynamic limit $N \to \infty$ and use $\overline{Q(G')}$ to denote the mean value of $Q(G')$ for the whole system.

Using (7), we can calculate various physical quantities of interest. For example, the constant pressure internal energy $U_p(T, P_0)$, the constant pressure specific heat $C_p(T, P_0)$, the mean volume per molecule, $\bar{v}(T, P_0)(=\bar{\rho}^{-1}, \bar{\rho} = $ the mean global mass density), the isothermal compressibility $K_T(T, P_0)$, and the thermal expansivity $\alpha_p(T, P_0)$ are given by:

$$U_p(T, P_0) = -\lim_{N \to \infty} \frac{1}{N} \frac{\partial}{\partial \beta} \ln Z_a(G, K, P_0) = -zJ\bar{p}/(2p), \tag{9}$$

$$C_p(T, P_0) = (\partial/\partial T)U_p(T, P_0) = kK^2 p^{-2}(\langle (e(G') - \overline{e(G')})^2 \rangle_0 - (1-p)\langle e(G') \rangle_0)$$

$$= kK^2 p^{-2}(\langle (\delta e(G'))^2 \rangle_0 - (1-p)\langle e(G') \rangle_0), \tag{10}$$

$$\bar{v}(T, P_0) = -\lim_{N \to \infty} \frac{1}{N} \frac{\partial}{\partial P_0} \ln Z_a(G, K, P_0) = \langle V(G') \rangle_0, \tag{11}$$

$$K_T(T, P_0) = -\bar{v}^{-1}(\partial \bar{v}/\partial P_0)_T = \bar{v}^{-1}\langle (V(G') - \overline{V(G')})^2 \rangle_0 = \bar{v}^{-1}\langle (\delta V(G'))^2 \rangle_0, \tag{12}$$

$$\alpha_p(T, P_0) = \bar{v}^{-1}(\partial \bar{v}/\partial T)_{P_0} = -\bar{v}^{-1}(K/T^2 P)\langle (V(G') - \overline{V(G')})(e(G') - \overline{e(G')}) \rangle_0$$

$$= -\bar{v}^{-1}(K/TP)\langle \delta V(G') \delta e(G') \rangle_0. \tag{13}$$

[†] Some of the signs '$\leqslant$' in (5) are actually '$<$'.

Because of the relations of (5), the sign of $\delta V(G')$ is expected to be the same as $\delta e(G')$ and $\alpha_p(T, P_0)$ of (13) is zero or negative. On the other hand, (12) reveals that K_T is always non-negative. For $P_0 = 0$, $Z_a(G, K, P_0)$ of (9) is the same as $Z(G, K)$ of (2a) and it is easy to show that C_p of (10) is always non-negative. For $P_0 > 0$, it is not obvious whether or not C_p of (10) is always non-negative. But in the region of large bond fluctuations, the first term of (10) dominates and it is expected that $C_p > 0$. Thus in the region of large bond fluctuations, the effect of the hydrogen bonds is predicted to 'correct' the response functions K_T, C_p and α_p in the way summarised in the first line of table 1.

At high temperatures, $p \to 0$, there is no significant number of bonds and the bond fluctuations $\langle(\delta e(G'))^2\rangle_0$ are approximately zero. At very low temperatures, $p \to 1$, most bonds of G are attached and the bond fluctuations are also expected to be very small. As the temperature is lowered from high temperatures to very low temperatures, we expect that the bond fluctuations will first increase to reach a maximum at a temperature T_p. From (5), we expect that the volume fluctuations $\langle(\delta V(G'))^2\rangle_0$ have similar behaviour. The expected behaviour of bond fluctuations and volume fluctuations should appear in the systems without percolation transitions for $T > 0$ (e.g. one-dimensional model) as well as the systems with percolation transitions. In the latter case, T_p is just the percolation transition temperature and bond fluctuations and volume fluctuations bec_me infinite at T_p. Unless specified otherwise, in the following we will always consider systems at temperatures near but higher than T_p. From (12), (10) and (13), we expect the 'unusual behaviour' of K_T, C_p and α_p listed in the second line of table 1, as T is lowered. At a fixed T, if we increase P_0, the system favours subgraphs with smaller numbers of attached bonds because of (5), and T_p becomes smaller; thus we expect the behaviour of K_T, C_p and α_p listed in the third line of table 1. If the system of H_2O is diluted with D_2O or a bond-breaking impurity, we can still write down an interaction Hamiltonian for the new system and show that the partition function for such an interaction Hamiltonian is the generating function of a site–bond correlated percolation model (cf Hu 1983c), in which the sites with D_2O have a larger bond probability to connect with their NN sites and the sites with a bond-breaking impurity have a smaller or zero bond probability to connect with their NN sites. Thus we expect the behaviour of K_T, C_p and α_p listed in the fourth and fifth lines of table 1.

In the BCPM-HBC, the percolation transition temperature T_p is below temperatures of supercooled water, where K_T, C_p and α_p have unusual behaviour. It is reasonable to identify T_p with the singular point T_s ($T_s = 228 \pm 3$ °K for $P_0 = 1$ atm) used to characterise the rapid increases of the magnitude of unusual physical quantities (e g. K_T) for supercooled water (Angell 1982). For a given P_0, T_s was found to be slightly lower than the homogeneous nucleation temperature T_H (Angell 1982). However, according to the theory of supercooled water proposed by Stanley *et al* (1981), the temperatures for supercooled water are below the percolation transition temperature of their percolation model (Stanley 1981), because they judged from results of the molecular dynamics simulation (MDS) that the bond probability p_B for NN molecules is well above the bond percolation threshold. One of the reasons for this difference is that our definition of attached bonds for NN pairs of molecules is different from that used in the MDS. In the MDS (Geiger *et al* 1979), an arbitrary cut-off parameter V_{HB} of arbitrary magnitude is introduced. When the mutual energy of interaction between two molecules is stronger than V_{HB}, the two molecules, by definition, have a bond between them; otherwise no bond is said to exist. In our approach the bond

probability p depends on the interaction energy $-J$ and the temperature T in the equation $p = 1 - \exp(-J/kT)$. Thus p becomes 1 only when $J \to \infty$ or $T \to 0$. As T is lowered from high temperatures to approach T_s, the behaviour of many physical quantities (e.g. K_T) for supercooled water is found to be similar to the behaviour of some physical quantities (e.g. magnetic susceptibility) for systems with a second-order phase transition as T is lowered to approach the critical temperature T_c (Angell 1982). Thus the identification of T_p in our percolation model with T_s of supercooled water seems to be better than the alternative approach of Stanley and Teixeira (1981) and Stanley *et al* (1981).

In the above, we have used a simple model to illustrate the mechanism underlying the unusual behaviour of supercooled water. This result may be extended to the more realistic and complicated model in which the molecules may move in a continuous space and have mutual van der Waals and hydrogen-bond interactions depending on the separations between molecules and the orientations of molecules. The partition function for such a complicated interaction Hamiltonian may still be related to the generating function of a correlated percolation model with the bond probability between two molecules depending on the molecular separation. In defining the bond probability for two molecules, we need not impose a discrete symmetry on the continuous interaction potential as in the MDS (Geiger *et al* 1979) and the model of Stanley *et al* (1981). Instead of using the assumption of (5), we can simply choose an appropriate intermolecular potential so that, on the average, the subgraphs G' with a larger number of attached bonds have a larger value of total volume. Thus many artificial or phenomenological features of the model of Stanley and Teixeira (1981) and Stanley *et al* (1981) need not present in our more realistic model mentioned above. This model may also be used to explain the unusual behaviour of supercooled water and properties of different phases of water. The details of this model will be presented later in another paper.

References

Angell C A 1982 in *Water: A Comprehensive Treatise* vol 7, ed F Franks (New York: Plenum)
Geiger A, Stillinger E H and Rahman A 1979 *J. Chem. Phys.* **70** 4185–93
Hu C K 1982 *Physica* **116A** 265–71
—— 1983a *Physica* in press
—— 1983b *University of Toronto preprint*
—— 1983c *University of Toronto preprint*
Lieb E H and Wu F Y 1972 in *Phase Transitions and Critical Phenomena* ed C Domb and M S Green (New York: Academic)
Stanley H E 1979 *J. Phys. A: Math. Gen.* **12** L329–37
Stanley H E and Teixeira J 1981 *J. Chem. Phys.* **73** 3404–22
Stanley H E, Teixeira J, Geiger A and Blumberg R L 1981 *Physica* **106A** 260–77