LETTER TO THE EDITOR

Continuum model of water and percolation theory

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Abstract. We discuss how one can combine a bichromatic formulation of the percolation problem with the 'pure' continuum model of water without broken H bonds. We also propose a method for comparing the computer energy distribution with spectroscopic contours and demonstrate them to be inconsistent.

When applied to the problem of water structure (Stanley 1979, Stanley and Teixeira 1980, Geiger *et al* 1979, Naberukhin 1984) percolation theory struck the so-called mixture models of water an unexpectedly strong blow. Indeed, they propose, on the one hand, the existence of small isolated associates and, on the other hand, quite a large fraction of intact hydrogen bonds, x_H, which, as a rule, exceeds 40% (Geiger *et al* 1979). Such a situation is impossible geometrically according to percolation theory, since x_H turns out to be above the percolation threshold $x_H^c = 0.33$–0.39 for the four-coordinated networks. Hence, a single continuous network of hydrogen bonds filling all space must be considered as the main image of the water structure. Thus, percolation theory supports rather the continuum models of water (Stanley and Teixeira 1980, Naberukhin 1984). However, the relations between both concepts have some interesting points which have not been discussed in the literature and to which we should like to call attention.

Concrete calculations of water properties in terms of percolation theory (numbers and properties of clusters of different sizes, critical exponents, etc) are performed on the basis of structural information obtained by computer simulation methods (molecular dynamics or Monte Carlo). A characteristic feature of these methods in their present state is that they are based on the analytical models of the *total* interaction energies of molecules. Hydrogen bonding is not separated among other interaction types and requires an additional definition by means of artificial recipes. The energetic definition of the hydrogen bond is used most extensively. A given pair of water molecules are considered to be hydrogen bonded if their total interaction energy E is stronger than a certain chosen H-bonding threshold V_H ($E < V_H < 0$). For each threshold value V_H one can find, in molecular configurations generated by a computer, an average number of hydrogen bonds per water molecule n_H and a fraction of intact bonds $x_H = \frac{1}{4}n_H$ (relative to their highest possible number $n_H = 4$ when each water molecule is engaged in four H bonds). Changing V_H one can vary the x_N value from zero to one and verify the predictions of percolation theory throughout this range (Blumberg *et al* 1984, Geiger *et al* 1984).

Though it is used in most water models and satisfies the needs of percolation theory, the separation of all the H bonds in water into intact and broken ones contradicts the

physics of the situation. H bonding, as well as any interaction, is a continuous function of parameters (distances, angles) and one cannot point out such an energy value, low as it may be, which could be ascribed to the H bond. Moreover, experimental data on the stretching vibration contour do not show any trace of broken H bonds in water under ordinary conditions (Gorbunov and Naberukhin 1975) which is the basis of the 'pure' continuum models of water comprising no broken H bonds (Naberukhin 1984, Zhukovskii 1976, 1981, Efimov and Naberukhin 1978, 1980, 1981, 1982, Pople 1951, Rice and Sceats 1981).

How can one combine a traditional (black-white) formulation of the percolation problem with the 'pure' continuum model? This can be done very simply if we treat the threshold V_H as a conditional boundary between strong and weak H bonds rather than as the H-bond definition. In other words, we consider each water molecule to be involved in four hydrogen bonds exactly, with their energies fluctuating and distributed at random among four bonds. The function $n_H(V_H)$ is interpreted in this case as the number of hydrogen bonds per molecule with the energy equal to, or smaller than, a given value V_H. Dividing all the variety of H bonds into two species—strong $(E \leq V_H)$ and weak $(E > V_H)$ ones—we can formulate a conventional bichromatic problem of percolation through strong H bonds and then investigate its dependence on V_H. Hence, the function $n_H(V_H)$ is intended for energy classification of H bonds, but not for counting the number of intact H bonds (they are all intact).

Such an interpretation of the function $n_H(V_H)$ means that it is nothing else but a distribution function of a random variable—the H-bond energy—in the sense of probability theory: $n_H(V_H) = P\{E \leq V_H\}$ (see, for example, Feller 1968). This function is connected with another important characteristic—the probability frequency of the random variable or, more physically, the H-bond energy distribution $p(E)$—by the relations

$$n_H(V_H) = 4 \int_{-\infty}^{V_H} p(E)\, dE$$

or

$$p(V_H) = \frac{1}{4} \frac{d n_H(V_H)}{d V_H}. \tag{1}$$

This allows us to write the mean H-bond energy $\bar{E} = \int_{-\infty}^{0} E p(E)\, dE$ in the form $\bar{E} = -\frac{1}{4} \int_{-\infty}^{0} n_H(V_H)\, d V_H$.

Figure 1 shows the functions $n_H(V_H)$ and $p(V_H)$ obtained by molecular dynamics computations of water (Geiger *et al* 1984) at two temperatures. A significant feature of the function $n_H(V_H)$, as follows from computer experiment, is its sharp increase up to n_H values much greater than $n_H = 4$ when $V_H \to 0$. This is a consequence of the fact that the interaction energy model does not distinguish the hydrogen bond from the van der Waals interaction. The latter prevails at small energy values, $E \gtrsim -4\,\text{kJ mol}^{-1}$, and corresponds to the interaction of a given particle with many distant molecules, which results in $n_H \gg 4$. To distinguish H bonds, at least formally, Blumberg *et al* (1984) declare the four strongest interactions to be these and here we extrapolate the $n_H(V_H)$ curves so that $n_H(V_H) \to 4$ at $V_H \to 0$ (see figure 1).

Separation of the H-bond energy distribution $p(E)$ from computer calculations is of importance since $p(E)$ can be compared with the experimental distribution obtained from the band contours of water vibrational spectra. In spectroscopy, an empirical
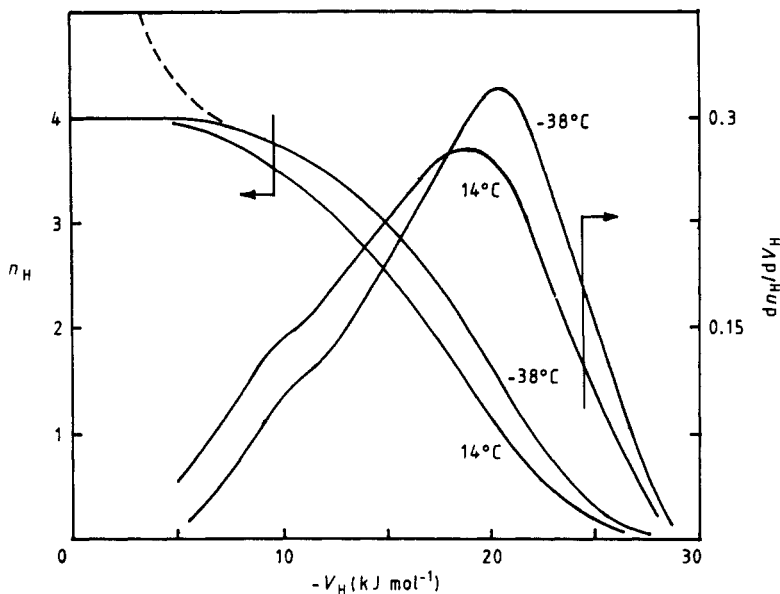
Figure 1. Distribution function of the hydrogen bond energy, $n_H(V_H)$, and corresponding probability frequency function, $p(V_H)$. $p(V_H)$ is calculated by equation (1) from the $n_H(V_H)$ data of Geiger *et al* (1984). The broken curve shows the real behaviour of $n_H(V_H)$ at small V_H.

correlation between the H-bond energy and the OH stretching vibration frequency has been established (Efimov and Naberukhin 1980):

$$E = -b(\omega_u - \omega) \tag{2}$$

where $\omega_u = 3707 \text{ cm}^{-1}$ is the OH oscillator frequency in the vapour, $b \sim 51.5 \text{ J (mol cm}^{-1})^{-1}$. Therefore the stretching band contour $I(\omega)$ will duplicate the H-bond energy distribution $p(E)$. This holds only for the isotropic Raman scattering contour where the transition intensity does not depend on the H-bond strength, and for the HOD molecules dissolved in D_2O to prevent inter- and intramolecular coupling of the OH oscillators. It is very important that a simple law exists describing the temperature transformation of the contour. According to Zhukovskii (1976, 1981) the function $p(E)$ is given by Boltzmann's distribution:

$$p(E) = Q^{-1}(T) W(E) \exp(-E/kT) \tag{3}$$

where $W(E)$ is the statistical weight of the state with an energy E and $Q(T) = \int_{-\infty}^{0} W(E) \exp(-E/kT) \, dE$. This gives the relation between the distributions at some temperatures T_1 and T_2:

$$\frac{p(E, T_1)}{p(E, T_2)} = \frac{Q(T_2)}{Q(T_1)} \exp\left[-\frac{E}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \right]. \tag{4}$$

By virtue of correlation (2) we obtain an analogous formula for the relation of spectral contours (the Zhukovskii formula):

$$\frac{I(\omega, T_1)}{I(\omega, T_2)} = \frac{Q(T_2)}{Q(T_1)} \exp\left[\frac{b}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)(\omega_u - \omega) \right]. \tag{5}$$

Figure 2 shows that formula (5) is an excellent fit to the spectral experiments. Such a comparison has been made in more detail by Zhukovskii (1976, 1981) and Efimov and Naberukhin (1980, 1981, 1982). Quite a different situation occurs for the computer distribution $p(E)$. We see (in figure 3) that Boltzmann's distribution (3) does not hold here. Moreover, the computer simulated $p(E)$ transformed into the vibrational spectrum contour, by means of equation (2), is far from the experimental contour (figure 4). All this demonstrates the imperfection of modern water computer simulation methods. It is probably not sufficient to improve the existing water–water interaction models of the ST2 type to achieve agreement with spectral experiment. It may be necessary to construct a model for the hydrogen bonding alone, rather than for the total interaction, since the vibrational contour reflects the perturbation of the OH oscillator by the H bond only.

So in the present letter we should like to emphasise two points. Firstly, percolation theory is an adequate method for investigating the continuum model of water. The interpretation given here removes the nuance of approximation or artificiality from the concept of a cutoff parameter V_H, which is regarded as imposing a discrete symmetry on a continuous function, the interparticle potential (see Stanley and Teixeira 1980). We attach a formal, rather than a physical, meaning to the threshold V_H which allows one to strictly formulate a bichromatic and, if desired, polychromatic percolation problem in the pure continuum system.

Secondly, we emphasise that spectroscopic data on the stretching contours are helpful for testing the computer calculations of the water H-bond distributions, which have not yet been used. Comparison with spectroscopic experiment can favour the improvement of interaction potential models for water.
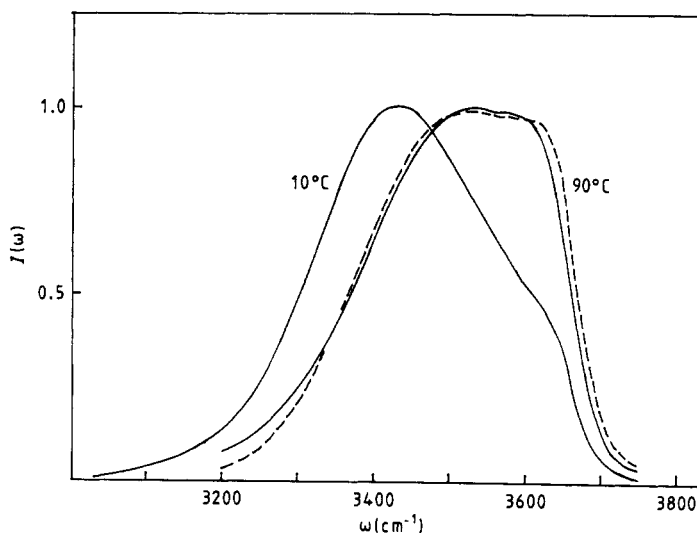
Figure 2. Temperature transformation of the stretching vibration contour of the OH oscillator of HOD molecules in isotropic Raman scattering. Full curves are experimental data according to Scherer *et al* (1974). The broken curve is the calculation by the Zhukovskii formula (5) from $T_1 = 10\,°C$ to $T_2 = 90\,°C$.
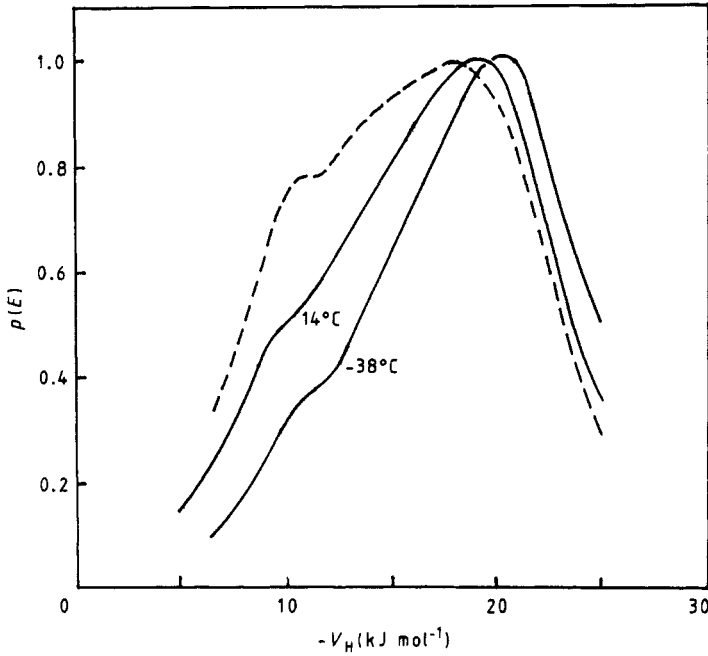
Figure 3. Temperature transformation of the H-bond energy distribution. Full curves: computer experiment according to Geiger *et al* (1984) (see figure 1). Broken curve: calculation by formula (4) from $T_1 = -38\,°C$ to $T_2 = 14\,°C$.
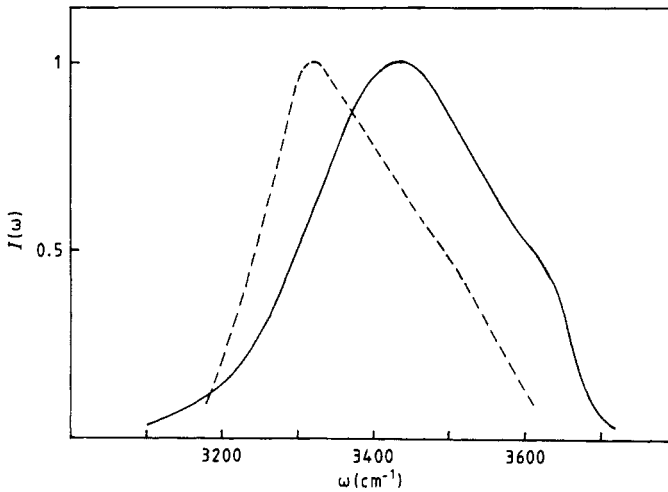
Figure 4. Comparison of the OH stretching vibration contours of HOD molecules from the experiment of Scherer *et al* (1974) (10 °C, full curve) and the computer distribution $p(E)$ transformed into $I(\omega)$ by means of equation (2) (9 °C, broken curve).

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