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## A grand ensemble Monte Carlo investigation of the Bell lattice model for water

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**Abstract.** The lattice model for water, previously investigated by Bell using a Guggenheim-McGlashan first-order type of approximation (FOA), has been examined at three reduced temperatures  $T^* = (kT/w) = 0.2, 0.5$  and  $0.9$  using grand ensemble Monte Carlo simulations. The parameters of the model are  $\epsilon, w, u$  associated with first-neighbour energies, a hydrogen bond increment to this, and a 'penalty' incurred by molecules in triad sets on the two intertwined cubic ice lattices of the model. These parameters were given values suggested to be optimum by Bell ( $\epsilon/w = 2.0, u/w = 1.25$ ).

Our results indicate that the cooperativity of the model is significantly underestimated by the FOA, although the general behaviour of the model is correctly represented.

We have also made a preliminary examination of the possibility of introducing values of  $\epsilon, w$  and  $u$  into the model which are directly related to  $H_2O$  dimer potentials, rather than being estimated *a posteriori* from thermodynamic criteria. It is shown that this approach is feasible and that the advantage of extremely rapid calculation offered by the lattice model would not be lost.

### 1. Introduction

Of the possible statistical mechanical models for water, lattice models have attracted considerable attention. Their appeal lies in their ability to represent the properties of the fluid in a relatively simple way, based on the idea of a predominantly hydrogen-bonded network as the essential feature of aqueous phases, in which cubic ice,  $I(c)$ , is used as a framework for the representation of this structure. This type of model has been used as a starting point by various authors (Bell 1972, Weres and Rice 1972, Fleming and Gibbs 1974, O'Reilly 1973) who developed it along different lines. For example, Weres and Rice and O'Reilly concentrated attention mainly on vibrational properties, using in the one case a cell model, and in the other a scaled particle approach. Weres and Rice argued for the superiority of the lattice type of model over those postulating micro structures of different densities, and of any model requiring an appreciable proportion of non-hydrogen-bonded molecules.

Bell, following the suggestion made by Bernal and Fowler (1933), emphasised the potential inherent in such a model to explain the well known density maximum and compressibility minimum of liquid water near the melting temperature. In the model which he proposed, the molecules can occupy sites on two intertwined cubic ice

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(diamond) sublattices. In the open structure only one of these sublattices is occupied, but increased thermal motion above the melting temperature causes breakdown of the  $I(c)$  lattice and higher-density packing becomes possible in which sites on both sublattices can be occupied.

Originally Bell and Lavis (1970) demonstrated, using a two-dimensional model of this type, that a density anomaly could be found. Subsequently Bell developed a three-dimensional model, and used the first-order or Guggenheim-McGlashan treatment to calculate thermodynamic properties. The success of the model against qualitative criteria has led to its subsequent developments in other directions by Bell and co-workers (Bell and Salt 1976, Wilson and Bell 1978, Lavis and Christou 1977, 1979). The model was characterised by three parameters:  $-\epsilon$ , the interaction between non-hydrogen-bonded molecules,  $-w$ , the increment in energy when hydrogen bonding occurs, and  $u$  which is described by Bell as a 'penalty' for molecules in triads with two adjacent occupied sites on one sublattice and the third molecule occupying a neighbouring site on the other sublattice. Every group of three molecules having this close-packed arrangement increases the energy of the system by  $u/3$ , the triad energy. Bell showed that, subject to certain constraints on these three quantities, the observed density maximum and compressibility minimum are found; corresponding, at least qualitatively, to the behaviour of the real fluid. The optimum values for the pair of quantities ( $\epsilon/w$ ,  $u/w$ ) were found to be  $(2, \frac{5}{4})$  by comparison with experiment. Weres and Rice, in their critical appraisal of the Bell model, express reservations about the use of the parameter  $u$  which they believed contributed an unrealistically large positive term to the free energies of less dense structures. On the other hand their cell theory, in which the modified BNS potential was used, did not give density compressibility anomalies, a fact which they concede to be worrying.

The lattice model has other weaknesses in the form developed by Bell and co-workers; it does not for example take into account vibration of the bonds and makes no allowance for interaction beyond the next-nearest neighbours. The first deficiency means that distribution functions can only be obtained as a set of delta functions, while the importance of the second deficiency is not easy to judge unless calculations which include larger-range interaction are carried out. In addition to these limitations there is uncertainty surrounding the validity of low-order approximations, whilst approximations of higher order are very difficult to obtain, especially in the more complex type of lattice model under discussion. In particular, as we show here, the cooperative nature of the transition may be incorrectly represented at the level of approximation used by Bell.

It is possible to remove this last-mentioned limitation by resorting to computer simulation which, in principle, gives an exact treatment of the statistical mechanics. Although simulations of aqueous systems have mostly been of the continuous (i.e. non-lattice) type, an advantage to be considered in using the lattice approach, other than the one so far discussed, of gaining an estimate of the validity of low-order approximations, is the speed with which calculations can be carried out compared with continuous models. Thus our own work has shown a 600-fold reduction in computing costs, using the kind of algorithm described below, making it feasible, for example, to cover wide areas of a phase diagram. Again, given this advantage, it is of considerable interest to discover just which features of the properties of real systems can be reproduced with model calculations of this type.

In this paper we compare simulations of the model with calculations using the FOA and with the properties of real water. The FOA model is outlined in § 2 and the

simulation method in § 3. The results are discussed in § 4 where it is suggested that a significant improvement could be effected by introducing new interaction parameters.

## 2. Calculations using the first-order approximation

### 2.1. The model

The methods developed by Bell and co-workers have been discussed in detail in the papers cited above. Here we give a brief resumé of the model and method of calculation, and describe some new results which are of relevance to the present work.

In the Bell model, the water molecules are distributed over the sites of a BCC lattice. Each molecule has four bonding arms which point to the vertices of a regular tetrahedron; two of these arms lie along the OH direction and the other two are associated with lone pairs. For each molecule, there are 12 possible orientations as illustrated in figure 1. The numbering of these orientations, although significant in later sections, is arbitrary. First-neighbour sites for any molecule lie at the corners of the surrounding cube, and first neighbours interact with an energy  $-\epsilon$  if non hydrogen bonded, and  $-(\epsilon + w)$  if hydrogen bonded.

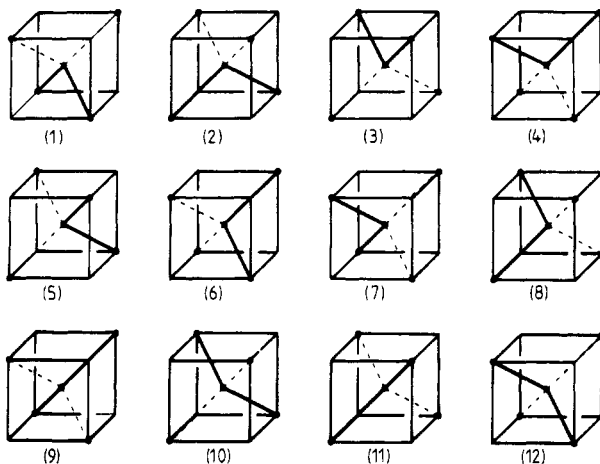


Figure 1.

Each site is surrounded by six second-neighbour sites lying at the centres of surrounding cubes. Any triad of molecules involving a second-neighbour pair with a common first-neighbour contributes a repulsive energy term  $u/3$ . A pair of second-neighbour sites share four common first-neighbour sites, and it follows that if all these six sites are occupied the total repulsive term will be  $4u/3$ . It can be shown (Bell 1972) that these triad contributions ensure that the  $I(c)$  or open structure will have the lowest free energy provided that

$$\epsilon < 2u < w + \epsilon. \quad (2.1)$$

Bell decomposed the lattice into ten tetrahedra containing two second neighbours and two shared first neighbours. It is to be noted that this decomposition omits all the

second neighbours which lie in pairs along one axis and consequently underestimates the number of triads by a factor of three which has to be compensated for in the FOA calculations.

## 2.2. The first-order approximation

The configurational free energy,  $f_c$ , is calculated as a function of the temperature  $T$ , the probability  $\Psi_i$  of the  $i$ th tetrahedral site grouping, its degeneracy  $\omega_i$ , and the fractional occupation (or density)  $\rho$  ( $\rho = \frac{1}{2}$  for the  $I(c)$ , open structure). The last three quantities satisfy the equations

$$\sum_{i=1}^{10} \omega_i \Psi_i = 1, \quad (2.2)$$

$$\frac{1}{4} \sum_{i=1}^{10} n_i \omega_i \Psi_i = \rho, \quad (2.3)$$

where  $n_i$  is the number of molecules in the  $i$ th tetrahedral group. The lattice degeneracy  $g$  is obtained by the Guggenheim–McGlashan method, to give a random distribution at  $T = \infty$ , and after eliminating two  $\Psi_i$  terms between the above equations, the remainder can be determined by minimising  $f_c$  with respect to each in turn and solving the resulting equations. In the original calculations the equations were solved at constant pressure. Here we have preferred to work with constant temperature and to vary the density  $\rho$ . This has the advantage of avoiding difficulties with multiple roots, and leads more easily to results which can be compared with simulation data, for which pressure cannot be obtained, since the variation of potential energy with position has no meaning in a lattice calculation.

The starting point was Bell's equation (3.16),

$$\rho/(1-\rho) = \theta(r)/\phi(r) \quad (2.4)$$

in which  $\theta$ ,  $\phi$  are 3rd- and 4th-order polynomials of the parameter  $r = (\Psi_8/\Psi_4)^{1/2}$  and the coefficients can be expressed in terms of  $\exp(-\varepsilon/2kT)$ ,  $\exp(-w/2kT)$  and  $\exp(-u/kT)$ .  $\theta(r)/\phi(r)$  increases monotonically with  $r$ , and (2.4) gives solutions for  $r$  at given values of  $\rho$ ,  $T$ . From  $r$ , the individual  $\Psi_i$  terms for the tetrahedral groupings can be found using the equation (cf Bell 1972, equations (3.14) and (3.12))

$$\Psi_i = r^{n_i} \exp[-(u + 2\varepsilon + \varepsilon_i + \varepsilon_8 - 2\varepsilon_4 + \frac{1}{2}n_i(\varepsilon_4 - \varepsilon_8))/kT]/\theta(r) \quad (2.5)$$

in which  $\varepsilon_i$  is the energy of the  $i$ th tetrahedral grouping as given in table 1 of Bell's paper.

The pressure  $p$  is given by

$$pv_0 = kT \ln \{ [1 - \rho]^3 \theta(r) / \rho \} + 5u \quad (2.6)$$

where  $v_0$  is the volume per site. The configurational energy per molecule is

$$\langle u \rangle = \sum_{i=1}^{10} \omega_i \Psi_i \varepsilon_i / \rho \quad (2.7)$$

and the compressibility  $\kappa$  is given by

$$kT\kappa/wv_0 = \phi(\phi\theta' - \theta\phi')/\theta(3\theta\phi' + \phi\phi' - 2\phi\theta') \quad (2.8)$$

where the primes denote differentiation with respect to  $r$ .

Finally the chemical potential is

$$\mu = 3 kT \ln[12 r^{4/3}(1-\rho)/\rho] + 8u - 2w - 6\varepsilon + kT \ln(\Lambda^3/v_i) \quad (2.9)$$

in which the first two terms comprise the configurational chemical potential  $\mu_c$ , and the final term is the kinetic part of  $\mu$ , with  $\Lambda = h/(2\pi mkT)^{1/2}$  and  $v_i$  the volume available to the centres of the molecules. Since a great deal of uncertainty attaches to  $v_i$ , the properties of the system are discussed as functions of  $\mu_c$  in what follows.

The mean number  $\langle n_j \rangle$  of first neighbours ( $j=1$ ), second neighbours ( $j=2$ ) and hydrogen bonds ( $j=B$ ) is given by

$$\langle n_j \rangle = k_j \sum \omega_i \Psi_i n_i^{(j)} / \rho$$

where  $n_i^{(j)}$  is the number with property  $j$  in the  $i$ th tetrahedral group, and  $k_j = (2, 3, 2)$  for  $j = (1, 2, B)$ .

### 3. Computer simulation of the Bell model

In the model, water molecules can occupy sites on a BCC lattice, while in the computer program these are represented by positions on two intertwined simple cubic lattices  $A$  and  $B$ , displaced one from the other by the vector  $(a/2, a/2, a/2)$  so that one corner of each cube lies at the body centred site of the other, as shown in figure 2 with the sites on each sublattice labelled as indicated.

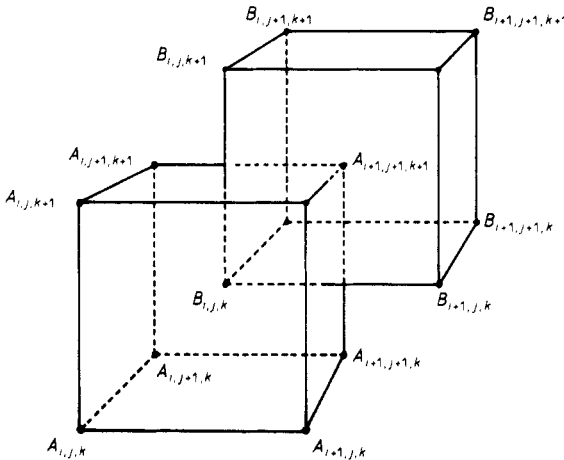


Figure 2.

In the program the possible orientations of a molecule shown in figure 1 are stored as the integers 1 to 12 with 0 representing an unoccupied site. First-neighbour sites lie at opposite ends of the four diagonals of a cube. These diagonals we number anticlockwise, 1 to 4 on the top face of the cube, beginning at the front right-hand vertex (they will also of course be similarly numbered on the bottom face, beginning with the back left-hand vertex). We assign an integer  $k_3$  to each diagonal and consider the combination of this with the integers  $k_1, k_2$  which are already assigned to the

molecules at either end of the diagonal, according to their orientations. With the conventions described, hydrogen bonding exists if and only if the conditions given in table 1 are fulfilled for  $k_1$ ,  $k_2$ ,  $k_3$ .

**Table 1.**

$k_3 =$	$k_2 \in$	$k_1 \in$
1	{3, 5, 11}	{4, 6, 12}
2	{3, 5, 10}	{4, 6, 9}
3	{3, 8, 10}	{4, 7, 9}
4	{3, 8, 11}	{4, 7, 12}

or

$k_3 =$	$k_2 \in$	$k_1 \in$
1	{2, 8, 10}	{1, 7, 9}
2	{2, 8, 11}	{1, 7, 12}
3	{2, 5, 11}	{1, 6, 12}
4	{2, 5, 10}	{1, 6, 9}

The simulation box contained  $6 \times 6 \times 6 = 216$  sites for the open  $I(c)$  lattice, equivalent to a total of 432 for the fully occupied dense lattice, and the usual periodic boundary conditions were imposed. The  $I(c)$  structure can only exist if the number of sites in a given direction is even. New configurations were generated in four different ways by calling the subroutines MOVE, ROTATE, CREATE, or DESTROY in a random sequence but with equal frequency (although in fact this constraint is only essential for CREATE and DESTROY). MOVE attempts to move a molecule to a vacant first-neighbour position without change of orientation; in ROTATE only the orientation was changed. CREATE and DESTROY attempt to place or remove molecules in randomly chosen vacant or occupied sites respectively. In canonical ensemble simulations, only the first two of the above subroutines are used. All molecules in the ice  $I(c)$  structure on the same  $A$  or  $B$  sublattice of figure 2 will have the same parity (odd or even) for  $i+j+k$ . By monitoring this parity during the simulation, it is possible to gain an indication of the presence of the  $I(c)$  structure. Thus, if we define the ordered quadruplet of fractional occupations within the four odd and even sublattices as  $(A/o, A/e, B/o, B/e)$ , then a perfect  $I(c)$  structure would be  $(1, 0, 1, 0)$ ,  $(1, 0, 0, 1)$ ,  $(0, 1, 1, 0)$  or  $(0, 1, 0, 1)$ , a uniform phase (such as ice VIII where  $\rho = 1$ ) would have  $(\rho, \rho, \rho, \rho)$ , and a cage structure would be indicated by  $(a, b, a, b)$  or  $(a, b, b, a)$  where either  $a$  is close to 1.00 and  $b$  is small or *vice versa*.

In a typical run a total of  $8.5 \times 10^5$  trials were sampled after initially discarding  $2 \times 10^5$  trials. In addition to the sublattice quantities already mentioned, specific heats and mean dipoles were also collected and averaged. In most cases convergence was good to excellent, as judged by the variation of quantities averaged over every  $2 \times 10^4$  trials.

In most runs the initial configuration, expressed as occupation of the four sublattices specified above, was  $(108, 11, 11, 108)$ . A few runs were initiated from completely full or nearly empty lattices, especially in the vicinity of a transition. It was observed

that nearly empty lattices often failed to fill up to the final densities found from the more dense initial configurations. This apparent hysteresis can be explained in terms of the importance of cluster formation in these water-like systems. This was demonstrated in the following way: a nearly empty initial configuration was run for a few thousand steps without allowing creation or destruction, then run for the same number of creation/destruction steps, and subsequently in the normal way with all four trials sampled at random. The same final density was found as that reached from the standard initial configuration. Clearly the initial stage of moves and rotations had permitted a stable nucleus to form from which a hydrogen-bonded network could grow. By judicious use of alternative starting configurations, we believe therefore that a true representation of the equilibrium properties of the model has been obtained.

In order to compare simulation data with the first-order approximation (FOA) the parameters  $(\epsilon/w, u/w)$  were chosen as  $(2, 5/4)$ , which were found by Bell (1972) to give good qualitative agreement between the FOA and experimental behaviour. Simulations were carried out at  $T^*(=kT/w)=0.2, 0.5$  and  $0.9$  for a range of chemical potentials.

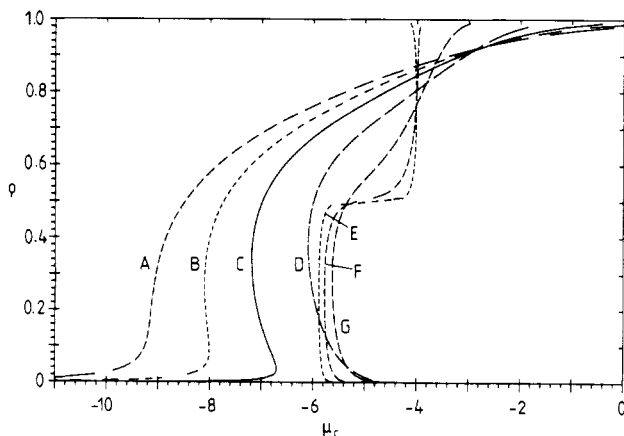
It was not possible to obtain reliable data at much lower temperature. This is because there is no adjustable quantity in a lattice simulation which corresponds to step length in the continuous case. At low temperatures therefore, the acceptance probability term, proportional to  $\exp(-\Delta E/kT)$ , becomes very small.

## 4. Results

### 4.1. The first-order approximation

For comparison with simulation data it was necessary to obtain graphs of  $\rho$  against  $\mu_c$  rather than  $\rho$  against  $T^*$  as previously calculated by Bell.

A set of curves covering a wide temperature range ( $T^*=0.05$  to  $1.5$ ) is shown in figure 3. In this and subsequent figures, the chemical potential is expressed in units of  $kT$ . It can be seen that, in general, there are two transition regions; one from low density to  $\rho=0.5$  ( $I(c)$ ), and the second from densities rather above this value to



**Figure 3.** Graph of  $\rho$  against  $\mu_c$ , for a range of temperatures  $T^*$ . Curve A:  $T^* = 1.50$ ; B:  $T^* = 1.20$ ; C:  $T^* = 0.90$ ; D:  $T^* = 0.50$ ; E:  $T^* = 0.05$ ; F:  $T^* = 0.10$ ; G:  $T^* = 0.20$ .



$\rho \approx 1.0$ . The first stage is clearly discernible at all temperatures, but the second stage only at the lowest temperature. Information about the nature of the transition was found by plotting  $p v_0$  against  $\mu_c$  (Hill 1960). When the transition is of low order this gives two curves of different slope, linked by a non-physical region of negative compressibility. The point of intersection of these lines gives the exact  $\rho$  and  $\mu_c$  values for the transition. These curves showed a continuous change of slope associated with the low-density transition for  $T^* > 1.20$  and a sharp intersection at temperatures below  $T^* = 1.20$ . This is consistent with Bell's estimate for the critical temperature of  $T^* = 1.35$  in the FOA. The high-density transition was found to be a continuous one down to  $T^* \approx 0.05$ .

It should be noted that the temperature dependence of the transition would be changed by the inclusion of the  $kT (\ln \Lambda^3 / v_i)$  term appearing in (2.9). Since both  $v_i$  and its dependence on  $T$  are unknown there are considerable uncertainties in attempting to include this term, which would in any case obscure our main objectives of comparing the Monte Carlo (MC) calculations with the FOA, and examining trends in various ensemble averages. Suffice it to say that when reasonable assumptions are applied to  $v_i$ , the expected trend, in which the chemical potential for transition increases with  $T$ , is obtained.

#### 4.2. Monte Carlo calculations

The transitions occurring in the grand ensemble MC calculations are exhibited by the specific heat curves (figure 4), each of which has two sharp maxima corresponding to a high-density transition (HDT) and low-density transition (LDT). These transition points are summarised in table 2.

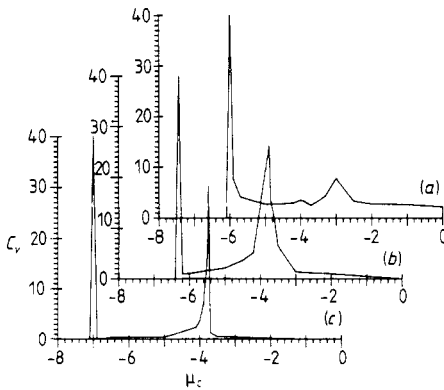
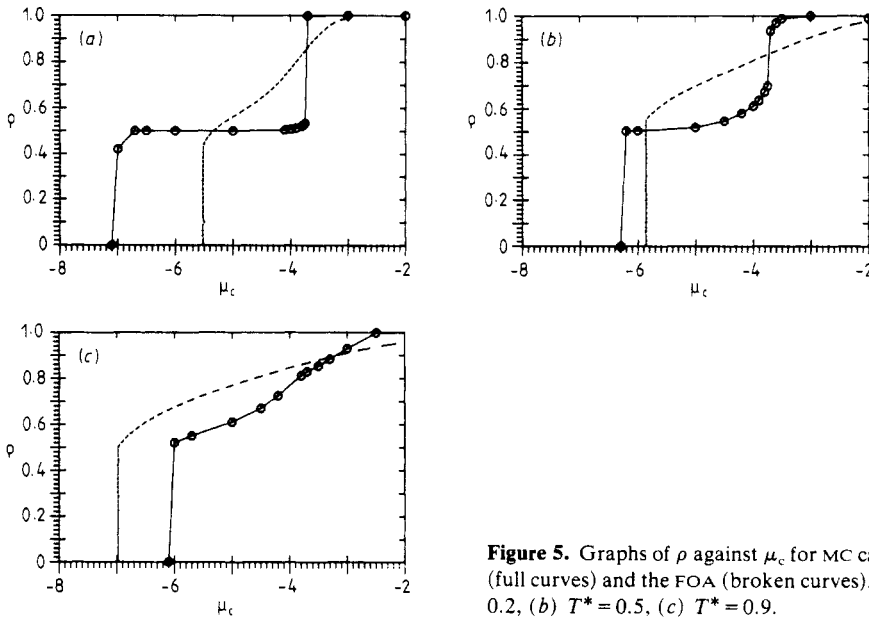


Figure 4. Specific heat curves, for (a)  $T^* = 0.9$ , (b)  $T^* = 0.5$ , (c)  $T^* = 0.2$ .

Table 2.

$T$	$\mu_c(\text{MC})$		$\mu_c(\text{FOA})$
	HDT	LDT	LDT
0.2	-3.75	-7.0	-5.49
0.5	-5.75	-6.3	-5.86
0.9	-3.0	-6.0	-6.98

The curves of density against  $\mu_c$  are shown in figure 5 where they are compared with  $\rho-\mu_c$  curves for the FOA. It is clear that at the two lowest temperatures, these points represent low-order transitions from the dense phase to the  $I(c)$  phase, and from the  $I(c)$  phase to a rarefied one. At  $T^*=0.9$  the  $\lambda$  feature in the specific heat curve is noticeably displaced to higher chemical potential and there is no sharp change in density which corresponds to this. There are some indications that the  $\lambda$  feature at  $\mu_c = -3.75$  occurs as a function of temperature at around  $T^*=0.4$ , but this cannot be confirmed without further calculations.



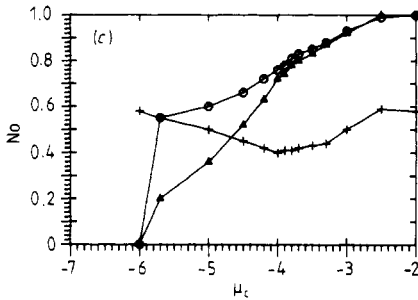
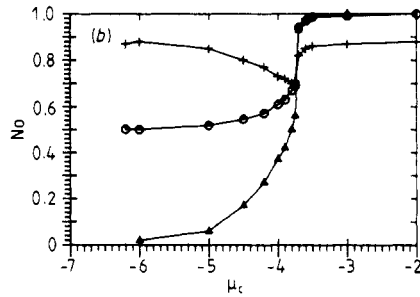
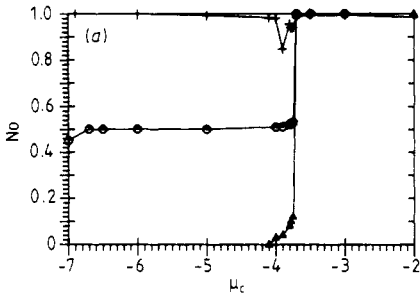
**Figure 5.** Graphs of  $\rho$  against  $\mu_c$  for MC calculations (full curves) and the FOA (broken curves). (a)  $T^* = 0.2$ , (b)  $T^* = 0.5$ , (c)  $T^* = 0.9$ .

The transitions in the corresponding FOA density curves are decidedly less distinct at these temperatures. However, figure 3 shows that very similar behaviour to that exhibited at  $T^*=0.2$  is found in the FOA, at around  $T^*=0.05$ , and that the more gradual changes at the two higher temperatures are quite similar to those found in the FOA at  $T^*=0.10$  and  $T^*=0.15/0.2$ . Furthermore the same trend can be seen in the values of  $\mu_c$  for the LDT, which increases with increasing temperature from  $-5.9$  to  $-5.5$  over this range, as do the values given in table 2 for the MC calculations. Similarly the HDT transition from the FOA appears to be first order for  $T^* \leq 0.1$  and occurs at  $\mu_c \approx -4.0$ .

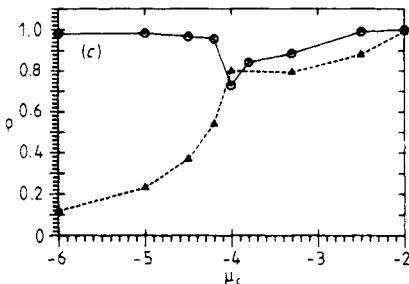
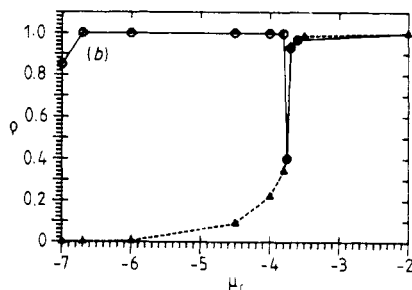
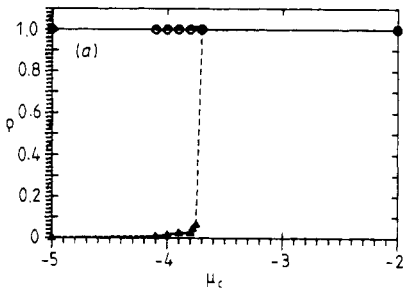
Thus it appears that reasonable qualitative agreement between the FOA and MC calculations could be obtained if temperatures for the former were to be scaled up, but quantitative agreement could not then be achieved by a similar adjustment of chemical potential. Corresponding qualitative similarities have been noted for the other properties calculated here (Whitehouse 1983).

This observation can be readily understood in terms of the increased cooperativity of the present calculations in comparison with the FOA which acts in favour of the intermediate structure, as compared with the adjacent states in which the first and second lattices respectively are only partly occupied.

In figure 6 the trends in numbers of first neighbours,  $N_1^*$ , second neighbours,  $N_2^*$ , and hydrogen bonds,  $N_B^*$ , are shown normalised with respect to their maximum values of 8, 6 and 4 respectively. These curves are best discussed in conjunction with those showing fractional occupation of the sublattices in figure 7. Only very small differences were found in the occupation of the pairs ( $A/o$ ,  $B/e$ ) and ( $A/e$ ,  $B/o$ ) and these are therefore shown as single curves in the latter figure.



**Figure 6.** Numbers of first neighbours  $N_1^*$  (circles), second neighbours  $N_2^*$  (triangles) and hydrogen bonds  $N_B^*$  (crosses) plotted against  $\mu_c$ . (a)  $T^* = 0.2$ , (b)  $T^* = 0.5$ , (c)  $T^* = 0.9$ .



**Figure 7.** Density in the first sublattice (circles) and second sublattice (triangles) (a)  $T^* = 0.2$ , (b)  $T^* = 0.5$ , (c)  $T^* = 0.9$ .

At the lowest temperature studied,  $T^* = 0.2$ , the behaviour of  $N_1^*$  and  $N_2^*$  is very clear cut, with sharp transitions in  $N_1^*$  at  $\mu_{\text{LDT}}$  and  $\mu_{\text{HDT}}$  and a sharp transition in  $N_2^*$  at  $\mu_{\text{HDT}}$ . Sublattice occupations are mainly  $\{0, 0\}$ ,  $\{1, 0\}$  and  $\{1, 1\}$  indicating uniform gas,  $I(c)$  and ice-VII phases respectively. The slight deviation of  $N_B^*$  from unity around the transitions is due to the build up of interstitial concentrations within the cage of the  $I(c)$  lattice.

At  $T^* = 0.5$ , this feature becomes much more clearly marked. It can be seen most distinctly in the curve for  $N_B^*$  where it is notable that the full complement of hydrogen bonds is never achieved. But it is also indicated by the gradual increase in  $N_2^*$  from  $\mu = -6$  onwards, and in the switch from sublattice occupancies of  $\{1, 0\}$ , characterising a uniform  $I(c)$  phase, through a non-uniform intermediate region to uniform  $\{1, 1\}$  occupancy above  $\mu_c = -2$ .

At the highest temperature,  $T^* = 0.9$ , where there is no clear transition in density, some features which nevertheless correspond to a change of phase are still to be found. Thus, although  $N_1^*$  and  $N_2^*$  both change continuously above  $\mu_{\text{LDT}}$ , there is a strong minimum in  $N_B^*$ . The switch to an interstitial/cage structure is even more clearly signalled, and it is apparent that the interstitials are not strongly hydrogen-bonded in this region. It is reasonable to interpret this behaviour as that of a dense fluid rather than attribute it to solid phases.

#### 4.3. Comparison with real water

In order to compare the  $\rho-\mu_c$  curves with those for real water (see e.g. Cooper and LeFevre 1969) it is necessary to account for the term  $\ln(\Lambda^3/v_i)$  in (2.9). Alternatively we may assume that the low to medium density transition occurs at the same value of  $\mu$  in the MC calculations as it does in real water, and estimate  $v_i$ . It was found that the 'vibration length' ( $= (v_i)^{1/3}$ ) available to the centre of a molecule is of the order of  $0.03 \text{ \AA}$ , which although small is not unreasonable. However, the rise in density with  $\mu$  above the transition appeared to be more rapid in real water than in the model, suggesting that the model may be too cooperative.

One obvious shortcoming in the approach followed here is the difficulty in relating the energy parameters  $\epsilon$ ,  $w$  and  $u$  to what is known about the interaction potential between water molecules. In particular, it is hard to justify the introduction of a positive triad energy ( $u$ ) on this basis, even though this stabilises the  $I(c)$  open structure which is clearly an important requirement. Both FOA and MC calculations carried out with  $u = 0$  but retaining  $\epsilon/w = 2$  at  $T^* = 0.2$  and  $0.5$  respectively resulted in direct transitions from zero density to unity, confirming this expectation.

However, if we examine the interaction potential energy which would be expected in the lattice model from a typical  $\text{H}_2\text{O}$  interaction potential, a new possibility emerges. Calculations based on the density of ice show that a typical nearest-neighbour separation would be in the region of  $2.8 \text{ \AA}$ , similar to that for liquid water (see e.g. Impey *et al* 1981 and references therein). At this separation, nearest neighbours are well within the repulsive region of the dispersion part of the interaction. In the present model this corresponds to a positive value for  $\epsilon$  and a larger negative value for  $w$ . The polarised electropole model of Barnes *et al* (1979) for example leads to  $\epsilon/w = -0.155$ .

MC calculations carried out using the pair  $(-0.155, 0)$  do in fact lead to stable  $I(c)$  structures and to rather better agreement with experiment (Whitehouse 1983). In the FOA, on the other hand, the model is not improved by this choice of parameters, suggesting that the full cooperation of the present calculations plays a vital role. It is

to be noted that this new choice of parameters is of course consistent with the criterion of equation (2.1).

Preliminary calculations of interaction energies in this model, using the ST2 potential (see e.g. Impey *et al* 1981), show that the attractive second-neighbour energy can be as high as  $\frac{1}{3}$  of the hydrogen-bond energy for first neighbours. Such interactions would be expected to greatly reduce the emphasis which the original model places on the  $I(c)$  structure.

## 5. Conclusion

Comparison of the MC simulation with the FOA makes it clear that the latter seriously underestimates the importance of cooperative effects within the model. When these are fully accounted for, the  $I(c)$  ( $\rho = \frac{1}{2}$ ) phase tends to be stabilised at the expense of the adjacent low- and high-density phases, and consequently melting to a fluid-like phase occurs at a higher temperature. A change from a uniform-density phase to a cage plus interstitial structure, in the vicinity of the transition from open structure to ice VII (the HDT), is clearly shown by many of the quantities examined in the simulations. It is this aspect of the model which enables it to account for the density and compressibility anomalies shown by real water. It is encouraging that the increased cooperativity which can be achieved in the computer simulations does not lead to the disappearance of this property.

It seems probable from the preliminary work described in § 4.3 of this paper that a model which is more consistent with H<sub>2</sub>O dimer potentials could be constructed and investigated using MC lattice methods. Furthermore it appears feasible to improve the model along these lines without sacrificing the advantages of extremely rapid calculation. We hope to report further explorations of this kind in the future.

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## References

- Barnes P, Finney J L, Nicholas J D and Quinn J E 1979 *Nature* **282** 459  
 Bell G M 1972 *J. Phys. C: Solid State Phys.* **5** 889  
 Bell G M and Lavis D A 1970 *J. Phys. A: Gen. Phys.* **3** 427  
 Bell G M and Salt D W 1976 *J. Chem. Soc. Faraday II* **72** 76  
 Bernal J D and Fowler R H 1933 *J. Chem. Phys.* **1** 515  
 Cooper J R and LeFevre E J 1969 *Thermophysical properties of water substance* (London: Edward Arnold)  
 Fleming P D and Gibbs J N 1974 *J. Stat. Phys.* **101** 57, 351  
 Hill T L 1960 *Introduction to Statistical Thermodynamics* (London: Addison-Wesley)  
 Impey R W, Klein M L and McDonald I R 1981 *J. Chem. Phys.* **74** 647  
 Lavis D A and Christou N I 1977 *J. Phys. A: Math. Gen.* **10** 2153  
 ——— 1979 *J. Phys. A: Math. Gen.* **12** 1869  
 O'Reilly D E 1973 *Phys. Rev. A* **7** 1659  
 Weres O and Rice S A 1972 *J. Am. Chem. Soc.* **94** 8983  
 Whitehouse J S 1983 *Thesis, London University*  
 Wilson G L and Bell G M 1978 *J. Chem. Soc. Faraday II* **74** 1702