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Renormalization Group Study of a Three-Dimensional Lattice Model with Directional Bonding

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We consider a bcc lattice model in which each site is either vacant or occupied by a molecule. The molecules have four symmetrically arranged arms directed towards four of the eight nearest-neighbor sites. Two molecules form a bond if they have bonding arms pointing towards each other and along their line of centers. We introduce bonding energies as well as two-, three-, and four-molecule interactions. The model is studied using a real-space renormalization group method. The form of the pressure–temperature phase diagram is found to be very sensitive to small changes in the relative sizes of the energy parameters. Adjustment of these parameters allows us to obtain a phase diagram which resembles that of the ice–water–steam system. The nature of the transitions between the various ordered phases is examined and the critical exponents are obtained.

KEY WORDS: Water; phase transitions; lattice gas; directional bonding; renormalization group.

1. INTRODUCTION

It has long been recognized that many of the "anomalous" properties of water arise from competition between open and close-packed forms of molecular order which originates in the ability of the water molecule to form tetrahedrally directed hydrogen bonds. A bonded-fluid model on a bcc lattice was introduced by Bell(1) to simulate hydrogen-bonding effects in water. In this model each molecule had four preferential bonding directions, or arms, symmetrically placed and pointing towards four of the

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eight nearest-neighbor sites. The asymmetry of the bond was represented by taking two of the bonding arms of a molecule as positive and two as negative. A bond was formed when a positive arm of one molecule and a negative arm of its neighbor pointed towards each other along their line of centers. Each molecule had 12 possible orientations and a lattice site could be either vacant or occupied by a molecule. A fully bonded arrangement of molecules formed a diamond structure on half the sites of the lattice and if the remaining sites where vacant the structure resembled that of Ice Ic. If, on the other hand, the remaining sites were occupied by an identical fully bonded arrangement of molecules the structure resembled Ice VII. Bell(1) used the first-order mean-field method in which the bonded structures appeared only as a form of short-range order. Long-range order was incorporated in the zeroth-order mean-field calculations of Bell and Salt.(2) Fleming and Gibbs(3) used the model to obtain virial coefficients and also derived results with a different choice of energy parameters from Bell's using a functional integral formulation. The model has also been used by Lavis and Christou(4) to calculate the dielectric constant of water and in a modified form by Wilson and Bell(5) to consider aqueous solutions of nonelectrolytes.

The Bell model described above is essentially a 13 state model which makes it very difficult to treat using other than mean-field methods. In this paper we modify the Bell model by removing the bond asymmetry. A molecule now has four equivalent arms and two orientations. A bond is formed if the arms of two neighboring molecules point towards each other and lie along their line of centers. The lattice is divided into four equivalent fcc sublattices A, B, C, and D and a spin variable S is defined at each lattice site so that $S = 0$ corresponds to a vacant site and $S = +1, -1$ correspond to the two molecular orientations. This is done in such a way that a molecule on a $A/B/C/D$ site has bonding arms towards $D/C/A/B$ sites if it is in state $S = +1$ and towards $C/D/B/A$ sites if it is in state $S = -1$ (see Fig. 1). This model is a generalization of the Blume–Emery–Griffiths(6) model, which is itself a generalization of the spin-1 Ising model to include biquadratic and crystal field terms. Exact results for our model have been derived by Heilmann and Huckaby.(7) With certain pair interactions but no three- or four-molecule interactions they obtained upper and lower bounds on the region of phase transitions in the chemical potential–temperature plane. Their discussion of lower bounds is based on the arguments of Peierls(8) and, as we shall see in Section 3, their results can also be applied to our choice of parameters. Their calculation of upper bounds derives from the results of Ruelle(9) and these are not so easily generalized to cases with interactions involving more than two molecules.

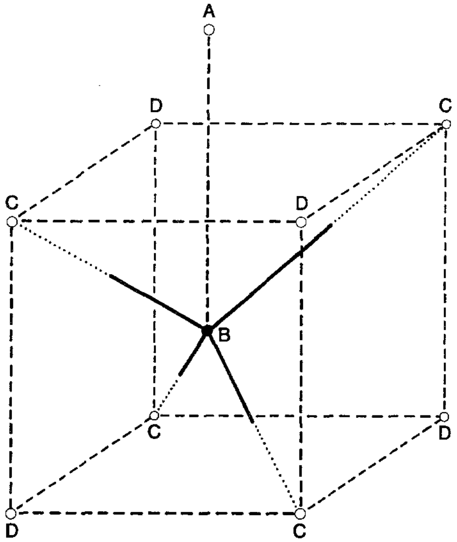


Fig. 1. The molecule with directional bonds on a site of the bcc lattice. The bonding arms for a molecule on a B site point either to the neighboring C sites or to the neighboring D sites.

We shall investigate the model using a block-spin real-space renormalization group (RSRG) method.$^{(10)}$ In order to preserve the sublattice ordering which occurs in the solid phases we use a 16-site cluster (see Fig. 2) with periodic boundary conditions. The renormalization procedure reduces the four sites of each sublattice in the cluster to a single site. The model is a three-dimensional version of the two-dimensional triangular bonded lattice model of Bell and Lavis$^{(11)}$ and our method of treatment is similar to that used by Southern and Lavis$^{(12)}$ for that model. The most important difference between the two- and three-dimensional models is that the bcc lattice allows a dense fully bonded structure whereas the fully occupied two-dimensional model is equivalent to the triangular antiferromagnetic spin-1/2 Ising model for which there is no ordering transition. In three dimensions the fully occupied system, at infinite chemical potential, is equivalent to the simple-cubic sublattice antiferromagnet. The transition in that system, which corresponds to the high-density limit of the ordering transition to the dense fully bonded phase, is in the universality class of the spin-1/2 ferromagnetic Ising transition which is continuous. In our RSRG procedure the fixed point governing this Ising transition controls the whole of the transition curve to the dense bonded phase with finite chemical potential. That transition is therefore continuous. Meijer *et al.*$^{(13)}$ have recently used a cluster variation method for the Bell–Salt model and also

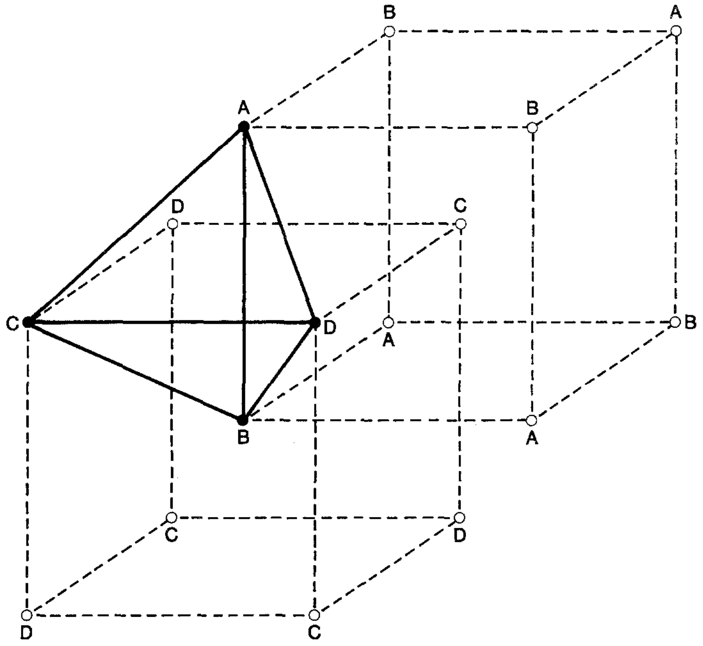


Fig. 2. The 16-site cluster used for the RSRG calculation. The heavy lines connect the sites of one of the 96 basic tetrahedra in the cluster.

find the transition from the fluid to close-packed solid phase to be second order. This contrasts with the transitions in the water system to high-pressure forms of ice which are first order.(14)

The outline of the paper is as follows. In Section 2 we introduce the details of the model and in Section 3 we discuss its ground states and use the method of Heilmann and Huckaby(7) to determine lower bounds on the region of phase transitions. In Section 4 we describe the RSRG method and in Section 5 the phase diagrams, fixed points, and critical exponents are given. Our conclusions are presented in Section 6.

2. THE MODEL

Consider a bcc lattice of N sites with periodic boundary conditions ($N = 16$ in our RSRG calculation). The lattice is divided into four equivalent FCC sublattices A, B, C, and D and decomposed into $6N$ tetrahedra each consisting of one site from each sublattice (see Fig. 2). At each lattice site there is a spin variable S which takes the values 0, $+1$, -1 as described in Section 1. Only those interactions which can be contained within a basic tetrahedron of the lattice are introduced. A molecule on a lattice site has chemical potential μ and a nearest-neighbor pair of molecules has nonbonding interaction energy $-\epsilon_1$. We also include interaction energy $-\epsilon_2$ between second-neighbor molecules, an interaction $-\epsilon_3$ between three molecules occupying sites of a basic tetrahedron, and an interaction $-\epsilon_4$ between four molecules which fill a basic tetrahedron. It is by no means obvious how the hydrogen-bonding energy of a pair of water molecules is to be defined and distinguished from other interaction energies between the molecules. This is made clear by the discussion in Chapter 3 of Ref. 14 where, for Ice I, four different definitions are given for this quantity leading to different estimates for its magnitude. There does however appear to be general agreement that the bonding energy in Ice I is significantly larger than that in liquid water (cf. Ref. 14, Tables 3.18 and 4.2). It must be concluded from this that the environment of a hydrogen bond affects its strength. Whether this is due to the proximity of other hydrogen bonds or a function of local density or both is by no means clear. In any event the scope within our model for incorporating such effects is rather limited given that we are considering a lattice model with at most two hydrogen bonds per basic tetrahedron. We have chosen to include the environmental effect on the strength of a hydrogen bond purely in terms of the local density. In our model each bonded pair belongs to six tetrahedra. If n_2 of these tetrahedra are occupied by just the pair of molecules, n_3 are occupied by the pair and one other, and n_4 are fully occupied, we assign to the pair a bonding energy $-(n_2w_2 + n_3w_3 + n_4w_4)/6$ where $n_2 + n_3 + n_4 = 6$ and w_2, w_3, w_4 are all greater than zero. In a ground state the bonding energy will be $-w_2$, $-w_3$, or $-w_4$ according to whether the system contains $N/2$, $3N/4$, or N molecules. At finite temperatures the energy of any bond will in general be a weighted combination of these.

The Hamiltonian of the system can be expressed in the form

$$H = \sum_i h(S_{Ai}, S_{Bi}, S_{Ci}, S_{Di}) \tag{1}$$

where $S_{\alpha i}$, $\alpha = A, B, C, D$ is the spin state of the α site in the ith tetrahedron, $h(S_{Ai}, S_{Bi}, S_{Ci}, S_{Di})$ is the contribution to the Hamiltonian from the tetrahedron and the sum is over all $6N$ tetrahedra of the lattice.

The RSRG method generates all interactions consistent with the symmetry of the model even if they are not present initially. To determine the most general form for h we consider the symmetry properties of the above model. We define the following operations on the spin states on the lattice sites of a tetrahedron: π_0 is spin inversion at all four sites, π_1 the interchange of S_A with S_B, π_2 the interchange of S_C with S_D, and π_3 the interchange of S_A with S_C and S_B with S_D. The corresponding two element groups are $\mathscr{S}_k = [\mathscr{I}, \pi_k]$ $k = 0, 1, 2, 3$, where $\mathscr{I}$ is the identity element. For the Blume–Emery–Griffiths(6) model the symmetry group of h is the sixteen element group $\mathscr{G}_I = \mathscr{S}_0 \otimes \mathscr{S}_1 \otimes \mathscr{S}_2 \otimes \mathscr{S}_3$ and there are 12 distinct polynomials in $\{S_A, S_B, S_C, S_D\}$ which have this symmetry. Taking into account the vacant state the system has 13 ground states. If h includes bonding terms the symmetry group is reduced to $\mathscr{G}_B = [\mathscr{I}, \pi_0\pi_1, \pi_0\pi_2, \pi_0\pi_3, \pi_1\pi_3, \pi_2\pi_3, \pi_0\pi_1\pi_2\pi_3]$. This reduction in symmetry increases the number of distinct polynomials to 14 and the number of ground states to the 15 listed in Table I.

Table I. Spectrum of h

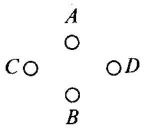
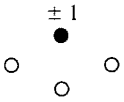
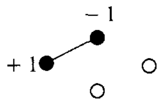
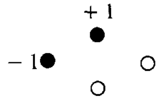
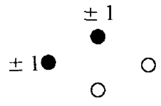
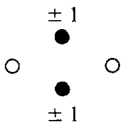
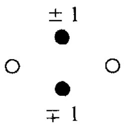
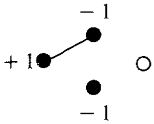
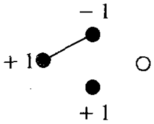
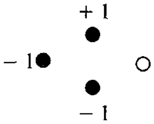
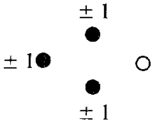
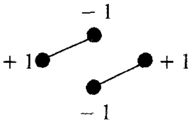
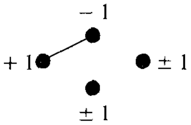
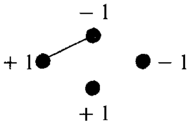
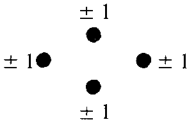
Name C_j	Configuration	Degeneracy ω_j	Energy e_j
C_1 (vapor)		1	0
C_2		8	$-\frac{1}{24}\mu$
C_3 (open solid)		4	$-\frac{1}{12}\mu - \frac{1}{6}\epsilon_1 - \frac{1}{6}w_2$
C_4		4	$-\frac{1}{12}\mu - \frac{1}{6}\epsilon_1$
C_5		8	$-\frac{1}{12}\mu - \frac{1}{6}\epsilon_1$
C_6		4	$-\frac{1}{12}\mu - \frac{1}{4}\epsilon_2$
C_7		4	$-\frac{1}{12}\mu - \frac{1}{4}\epsilon_2$

Table I. (Continued)

Name C_j	Configuration	Degeneracy ω_j	Energy e_j
C_8		8	$-\frac{1}{8}\mu-\frac{1}{3}\epsilon_1-\frac{1}{4}\epsilon_2-\frac{1}{2}\epsilon_3$ $-\frac{1}{6}w_3$
C_9		8	$-\frac{1}{8}\mu-\frac{1}{3}\epsilon_1-\frac{1}{4}\epsilon_2-\frac{1}{2}\epsilon_3$ $-\frac{1}{6}w_3$
C_{10}		8	$-\frac{1}{8}\mu-\frac{1}{3}\epsilon_1-\frac{1}{4}\epsilon_2-\frac{1}{2}\epsilon_3$
C_{11}		8	$-\frac{1}{8}\mu-\frac{1}{3}\epsilon_1-\frac{1}{4}\epsilon_2-\frac{1}{2}\epsilon_3$
C_{12} (dense solid)		2	$-\frac{1}{6}\mu-\frac{2}{3}\epsilon_1-\frac{1}{2}\epsilon_2-2\epsilon_3$ $-\epsilon_4-\frac{1}{3}w_4$
C_{13}		8	$-\frac{1}{6}\mu-\frac{2}{3}\epsilon_1-\frac{1}{2}\epsilon_2-2\epsilon_3$ $-\epsilon_4-\frac{1}{6}w_4$
C_{14}		4	$-\frac{1}{6}\mu-\frac{2}{3}\epsilon_1-\frac{1}{2}\epsilon_2-2\epsilon_3$ $-\epsilon_4-\frac{1}{6}w_4$
C_{15}		2	$-\frac{1}{6}\mu-\frac{2}{3}\epsilon_1-\frac{1}{2}\epsilon_2-2\epsilon_3$ $-\epsilon_4$

The general form for h invariant under the symmetry group $\mathscr{G}_B$ is

$$\begin{aligned}
&h(S_A, S_B, S_C, S_D)\\
&\quad= -\tfrac{1}{24}\Delta\left(S_A^2+S_B^2+S_C^2+S_D^2\right)-\tfrac{1}{6}K_1\left(S_A^2+S_B^2\right)\left(S_C^2+S_D^2\right)\\
&\qquad-\tfrac{1}{4}K_2\left(S_A^2S_B^2+S_C^2S_D^2\right)-\tfrac{1}{6}J_1(S_A+S_B)(S_C+S_D)\\
&\qquad-\tfrac{1}{4}J_2(S_AS_B+S_CS_D)-\tfrac{1}{6}R_1(S_AS_B-S_CS_D)^2(S_A+S_B)(S_C+S_D)\\
&\qquad-\tfrac{1}{4}R_2\left[S_AS_B\left(S_C^2-S_D^2\right)^2+S_CS_D\left(S_A^2-S_B^2\right)^2\right]\\
&\qquad-\tfrac{1}{6}M_1S_AS_BS_CS_D(S_A+S_B)(S_C+S_D)\\
&\qquad-\tfrac{1}{4}M_2S_AS_BS_CS_D(S_AS_B+S_CS_D)\\
&\qquad-\tfrac{1}{2}U\left[S_A^2S_B^2\left(S_C^2+S_D^2\right)+S_C^2S_D^2\left(S_A^2+S_B^2\right)\right]-LS_A^2S_B^2S_C^2S_D^2\\
&\qquad-QS_AS_BS_CS_D+\tfrac{1}{8}\Omega_1(S_A-S_B)(S_C-S_D)(S_A+S_B-S_C-S_D)\\
&\qquad+\tfrac{1}{8}\Omega_2(S_A-S_B)(S_C-S_D)\\
&\qquad\times\left[S_AS_B(S_C+S_D)-S_CS_D(S_A+S_B)\right] \qquad (2)
\end{aligned}$$

The terms with coefficients Ω_1 and Ω_2 are those with the reduced symmetry of $\mathscr{G}_B$. If $\Omega_1=\Omega_2=0$ h has the symmetry group $\mathscr{G}_I$.

In terms of the energies $\mu, w_2, w_3, w_4, \epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ the coefficients of (2) take the form

$$\begin{gathered}
\Delta=\mu, \qquad K_1=\left(\epsilon_1+\tfrac{1}{4}w_2\right), \qquad K_2=\epsilon_2, \qquad J_1=-\tfrac{1}{4}w_2, \qquad J_2=0\\
R_1=-\tfrac{1}{4}(w_3-w_2), \qquad R_2=0, \qquad M_1=-\tfrac{1}{4}(w_4-w_2), \qquad M_2=0\\
U=\left[\epsilon_3+\tfrac{1}{6}(w_3-w_2)\right], \qquad L=\left[\epsilon_4+\tfrac{1}{6}(w_4-w_2)-\tfrac{1}{3}(w_3-w_2)\right]\\
Q=0, \qquad \Omega_1=-\tfrac{1}{3}w_2, \qquad \Omega_2=0
\end{gathered} \qquad (3)$$

Although some of the coefficients above are zero for our model, the RSRG procedure will generate nonzero values for these quantities and they must therefore be taken into account.

3. GROUND STATES AND LOWER BOUNDS

The 15 possible ground states of the system $C_1, C_2, \ldots, C_{15}$ are listed in Table I, together with their energies e_j derived from (2) and (3). For particular values of the energy parameters the stable ground state C_i, if it is unique, will be the one for which $e_i < e_j$, for all $j \neq i$. If there is a degenerate set of states with least energy then these values of the energy parameters correspond to a point on the boundary between the degenerate states. We wish to determine which ground state is stable for a particular choice of the parameters $\mu, w_2, \ldots, w_4, \epsilon_1, \ldots, \epsilon_4$ and to find a lower bound on the temperature range for which the stable ground-state gives rise to an ordered structure. If the bonding energies w_2, w_3, and w_4 are all positive then the only possible stable ground states are C_1, C_2, C_3, C_6, C_7, C_8, C_9, and C_{12}. If we further impose the conditions

$$(w_2 + \epsilon_1) > 0 \tag{4a}$$

$$(w_2 + \epsilon_1) > \epsilon_2 \tag{4b}$$

Then the possible stable ground states are C_1, C_3, C_8, C_9, and C_{12}. Phase C_1 corresponds to the vapor phase (V), phase C_3 to the open solid (Ice Ic type) phase (OS), and phase C_{12} to the dense solid (Ice VII type) phase (DS). The degenerate phases C_8 and C_9 correspond to an intermediate form of ordering not present in the water system. If we impose the conditions

$$4w_2 - 4w_3 + 2w_4 > 3\epsilon_2 - 6\epsilon_4 \tag{4c}$$

and

$$w_2 - 2w_3 + 2w_4 > -\epsilon_1 - 6\epsilon_3 - 6\epsilon_4 \tag{4d}$$

then phases C_8 and C_9 are never stable ground states. For waterlike behavior we also need a region of stability of C_3 between those of C_1 and C_{12}, which are, respectively, the stable phases for large negative and large positive values of the chemical potential. This is achieved if conditions (4a)–(4d) are satisfied together with

$$2\epsilon_1 + 3\epsilon_2 + 12\epsilon_3 + 6\epsilon_4 < 2w_2 - 2w_4 \tag{4e}$$

A sufficient condition for any ground state C_j to give rise to an ordered structure at finite temperature has been obtained for this model by Heilmann and Huckaby.(7) Although they use their results only for pair interactions they apply equally well to the case in which there are three- and four-particle interactions. We now quote their result adapted to our notation in the form of a theorem, the proof being given in their paper.

Theorem. For the ground state C_j, ζ_j is given as the solution of the equation

$$\sum_{n=24}^{\infty} n^{1/2} \zeta_j^n = (\omega_j - 1)/\omega_j \tag{5a}$$

and

$$\gamma_j = -e_j + \min_{k \neq j} \{e_k\} \tag{5b}$$

where the degeneracies ω_j and the expressions for the energies e_j per tetrahedron are listed in Table I. If, for the phase C_j, $\gamma_j > 0$ the ordered phase with the ground state C_j is present in the temperature range $T < T_j^*$

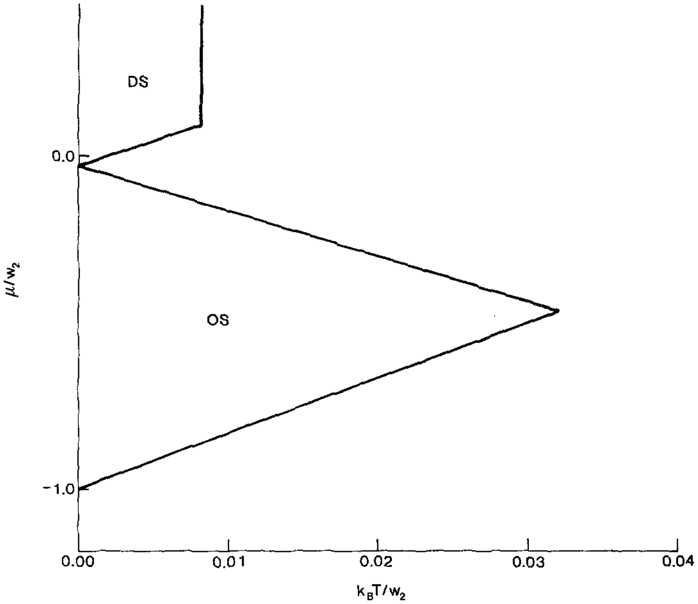


Fig. 3. Lower bound phase diagram in the $\mu/w_2 - k_BT/w_2$ plane for the parameter values used to obtain Fig. 4–6.

where

$$k_BT_j^* = \gamma_j/\ln[3/\zeta_j] \tag{5c}$$

Since the system is disordered at high temperature this means that the transition to the ordered phase with ground state C_j occurs at a temperature greater than or equal to T_j^*. We are interested in the ground states C_1, C_3 and C_{12} for which the respective solutions of (5a) are $\zeta_1 = 0$, $\zeta_3 = 0.8545$, and $\zeta_{12} = 0.8436$. At any point in the space of energy parameters at most one $\gamma_j > 0$ corresponding to the stable ground state. (The other possibility, which will not concern us here, is when the most stable ground states are members of a degenerate set for each of which $\gamma_j = 0$.) Using this theorem and the information contained in Table I a lower bound phase diagram in the $k_BT/w_2 - \mu/w_2$ plane is shown in Fig. 3 for the values of the energy parameters $w_2, \ldots, w_4, \epsilon_1, \ldots, \epsilon_4$ used in our RSRG calculations (see Section 5).

4. RSRG CALCULATIONS

Beginning with a cluster of 16 sites, four from each sublattice (see Fig. 2), the renormalization procedure reduces the cluster to four sites with periodic boundary conditions. If $\mathbf{S}_\alpha = (S_{\alpha 1}, S_{\alpha 2}, S_{\alpha 3}, S_{\alpha 4})$ is the spin state of the four α sites on the initial cluster and S'_α is the spin state of the renormalized α site ($\alpha = A, B, C, D$), the renormalization equation takes the form

$$\exp\left[-\frac{H'(\{S'_\alpha\})}{k_B T}\right] = g(\{\mathbf{S}_\alpha\}) \sum_{\{\mathbf{S}_\alpha\}} \left[\prod_\alpha \Pr(S'_\alpha \mid \mathbf{S}_\alpha)\right] \exp\left[-\frac{H(\{\mathbf{S}_\alpha\})}{k_B T}\right] \tag{6}$$

where

$$H(\{\mathbf{S}_\alpha\}) = \sum_i h(S_{Ai}, S_{Bi}, S_{Ci}, S_{Di}) \tag{7a}$$

the sum being over all 96 tetrahedra of the initial cluster and

$$H'(\{S'_\alpha\}) = 24 h(S'_A, S'_B, S'_C, S'_D) \tag{7b}$$

where h is given by (2) and the factor 24 in (7b) arises from the periodic boundary conditions given that each site belongs to 24 tetrahedra. The function $g(\{\mathbf{S}_\alpha\})$ is determined by the condition that

$$h(0,0,0,0) = 0 \tag{8}$$

and $\Pr(S'_\alpha \mid \mathbf{S}_\alpha)$ is a conditional probability function. As in all calculations of this type its choice is to some extent arbitrary as long at it obeys the rules of probability theory. In our calculations we used a form of double-majority rule[15] given by

$$\Pr(S'_\alpha \mid \mathbf{S}_\alpha) = \begin{cases} \delta_k(S'_\alpha), & \mathbf{S}_\alpha^2 < 2 \\ \delta_k\left\{S'_\alpha - \sum(\mathbf{S}_\alpha)\right\}, & \mathbf{S}_\alpha^2 = 2 \\ \delta_k\left\{S'_\alpha - \sum(\mathbf{S}_\alpha)\right\} + \frac{1}{2}\delta_k\left(\sum(\mathbf{S}_\alpha)\right)\{1 - 3\delta_k(S'_\alpha)\}, & \mathbf{S}_\alpha^2 > 2 \end{cases} \tag{9}$$

where δ_k is the Kronecker δ function and $\sum(\mathbf{S}_\alpha) = 1, 0, -1$ according as $(S_{\alpha 1} + S_{\alpha 2} + S_{\alpha 3} + S_{\alpha 4}) > 0$, $= 0$, < 0, respectively.

If the set $\{S'_\alpha\}$ in Eq. (6) is varied over its possible values we obtain the equations

$$x_j^{(k+1)} = x_0^{(k)} Z_j^{1/24}(\{x_i^{(k)}\}) \qquad j = 1, \ldots, 15; \quad k = 0, 1, 2, \ldots \tag{10}$$

where $x_j = \exp(-e_j/k_B T)$, e_j being the value of h given by (2) in ground state C_j as listed in Table I. The quantity $x_0 = g^{1/24}$, the Z_j are homogeneous polynomials of degree 96 and k is the iteration index of the RSRG transformation. The recurrence relations (10) determine trajectories in the space of couplings or equivalently in the space of the variables $\{x_j\}$ where x_0 is given at each stage of the iteration process by (8), which now takes the form

$$x_1^{(k)} = 1, \qquad k = 0, 1, \ldots \tag{11}$$

We are interested in trajectories which begin at points in the space $\{x_j\}$ for which the couplings are given in terms of the energy parameters by equations (3) although these conditions will in general no longer hold as the trajectory progresses and the additional couplings, which were zero at the initial point, are generated. A trajectory which starts at a point $\{x_j\}$ where the behavior of the system is not critical will iterate to a sink which characterizes that phase. These regions are separated by critical regions which form domains of attraction for critical fixed points. Once the fixed points have been located the recurrence relations can be linearized about them and the eigenvalues λ_i of the linear equations calculated. The critical exponents y_i are related to the eigenvalues by $y_i = \ln(\lambda_i)/\ln(b)$ where b is the scale factor which is $4^{1/3}$ in the present calculation. For a sink all the critical exponents are negative (irrelevant). A fixed point controlling a critical surface separating two phases will have one positive (relevant) exponent. An exponent $y_i = d = 3$ is a necessary condition for the first-order phase transition.(16)

The partition function Z associated with the initial cluster of 16 sites is given by

$$Z = \sum_j \omega_j Z_j \tag{12}$$

where the degeneracies ω_j are listed in Table I. After the renormalization transformation the partition function Z' associated with the cluster of four sites is

$$Z' = \sum_j \omega_j (x_j')^{24} \tag{13}$$

Using (10) we find that the free energies per site are related by

$$f = \tfrac{3}{2}\ln(x_0) + \tfrac{1}{4}f' \tag{14}$$

where

$$f = -\tfrac{1}{16}\ln Z, \qquad f' = -\tfrac{1}{4}\ln Z' \tag{15}$$

Iterating (14) we find that the free energy per site (in units of $k_B T$) can be written

$$f^{(0)} = \tfrac{3}{2}\sum_{s=0}^{\infty} (1/4)^s \ln(x_0^{(s)}) \tag{16}$$

In practice the infinite series usually converges very quickly and the free energy for an initial point $\{x_j^{(0)}\}$ can be obtained after only a few iterations. The pressure P of the system is given by

$$PV_0 = -k_B T f^{(0)} \tag{17}$$

and the molecular number density ρ is given by

$$\rho = (\partial P/\partial \mu)_T V_0 \tag{18}$$

where V_0 is the volume per lattice site. The latter is used to determine whether a critical surface controlled by a fixed point with one relevant exponent $y_i = 3$ is in fact a surface of first-order phase transitions.

5. PHASE DIAGRAMS AND CRITICAL BEHAVIOR

In investigating the model described in this paper we aimed to determine the extent to which it is capable of simulating waterlike behavior. The liquid phase (L) is characterized as the dense disordered phase. The RSRG method employed preserves the ground state of the system and a necessary but not sufficient condition for waterlike behavior is that the energy parameters satisfy conditions (4) with the bonding energies w_2, w_3, w_4 all positive. In order for the model to be a realistic description of the water system the V–OS and OS–DS transitions should be first order and the OS–DS transition should change to a first-order OS–L transition beyond the meeting point of the three phases (OS), (DS), and (L). Ideally this meeting point would be a triple point but, as indicated in Section 1, our method gives a continuous DS–L transition in the same universality class as the ferromagnetic spin-1/2 Ising model and so the meeting of the three phases will at best be a critical end-line point. It is necessary for the OS–L and OS–V transitions to meet at a point which is a triple-point from which a first-order L–V transition proceeds to higher temperatures and terminates at a critical end point. With our final choice of values for the energy parameters we were able to obtain a phase diagram with all these characteristics (Fig. 4) but since, beyond ground state considerations there is no *a priori* method of arriving at these results without trying a number of sets of values it is perhaps of interest to describe some of the initial results which ultimately led us to the values used here.

The mean-field calculations of Bell and Salt,(2) for the similar model with asymmetric bonds, used choices of energy parameters with $w_2 = w_3 = w_4 > 0$, $\epsilon_1 > 0$, $\epsilon_2 < 0$, $\epsilon_3 = \epsilon_4 = 0$. We investigated a number of cases in this category. In no example were we able to obtain a first-order L–V transition. We also found regions of stability of the partially bounded dense phases which correspond to ground states C_{13} and C_{14}. At high temperatures the process of phase change between the (OS) and (DS) phases seems

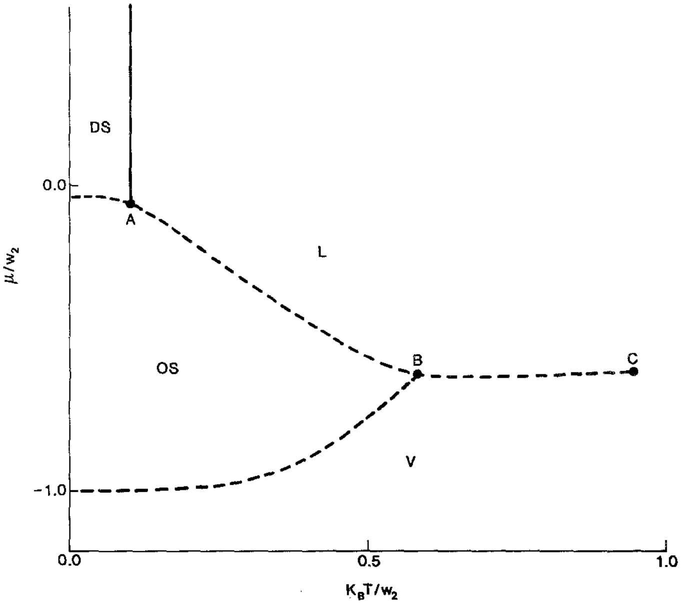


Fig. 4. Phase diagram in the $\mu/w_2 - k_BT/w_2$ plane. First-order transitions are indicated by broken lines.

to occur in two stages, a continuous transition in which the vacant sites become occupied by nonbonded molecules followed by a second continuous transition in which the molecules bond. The zeroth-order mean-field method of Bell and Salt$^{(2)}$ includes only three independent long-range order parameters. Within this method such continuous transitions if they exist would be difficult to detect. The work of Bell,$^{(1)}$ again for the model with asymmetric bonds, used choices of energy parameters with $w_2 = w_3 = w_4 > 0$, $\epsilon_1 > 0$, $\epsilon_2 = 0$, $\epsilon_3 < 0$, $\epsilon_4 = 0$. We also investigated cases of this type and our results were similar to those obtained for the parameters of Bell and Salt,$^{(2)}$ namely, the absence of a first-order (L)–(V) transition and regions of stability of partially bonded dense phases.

The reason for both these effects appears to be the fact that the (OS) phase persisted to rather high temperatures swamping the first-order (L)–(V) transition which would be present in the absence of bonding ($w_2 = w_3 = w_4 = 0$) and resulting in entropic advantage for the partially bonded dense phases. In order to reduce the temperature range of the (OS) phase we set $\epsilon_1 < 0$ and $\epsilon_4 > 0$. At the same time we introduce small negative values for ϵ_2 and ϵ_3 although neither of these appear to have significant effect upon our results. This choice of parameters had the desired effect in suppressing the partially bonded dense phases and producing a first-order (L)–(V) transition. We, however, found that with $w_2 = w_3 = w_4$, the (DS)–(L) phase transition occurred at too high a temperature relative to the range of the phase (OS) and a first-order (DS)–(V) transition occurred with a critical end-line point at the meeting of the phases (DS), (L), and (V). As indicated in Section 1 experimental evidence suggests that bonding energy decreases with density in water. By choosing $w_2 > w_3 > w_4 > 0$ we were able to reduce the temperature at which the (DS)–(L) transition occurred and to obtain phase diagrams with the topological characteristics of the phase diagram of the water system. Our final choice for the energy parameters was $\epsilon_1 = -0.5w_2$, $\epsilon_2 = -0.0625w_2$, $\epsilon_3 = -0.055w_2$, $\epsilon_4 = 0.54w_2$, $w_3 = 0.9375w_2$, and $w_4 = 0.0625w_2$. Figure 4 is the phase diagram for these values. The lower-bound phase diagram, Fig. 3, is consistent with the results in Fig. 4 although comparison of the temperature scales in these two diagrams shows that the lower bounds are very low excluding, in the interests of clarity, their presentation on the same figure. Pressure–temperature and molecular density–temperature phase diagrams were obtained using the procedure described in Section 4. They are shown, respectively, as Figs. 5 and 6.

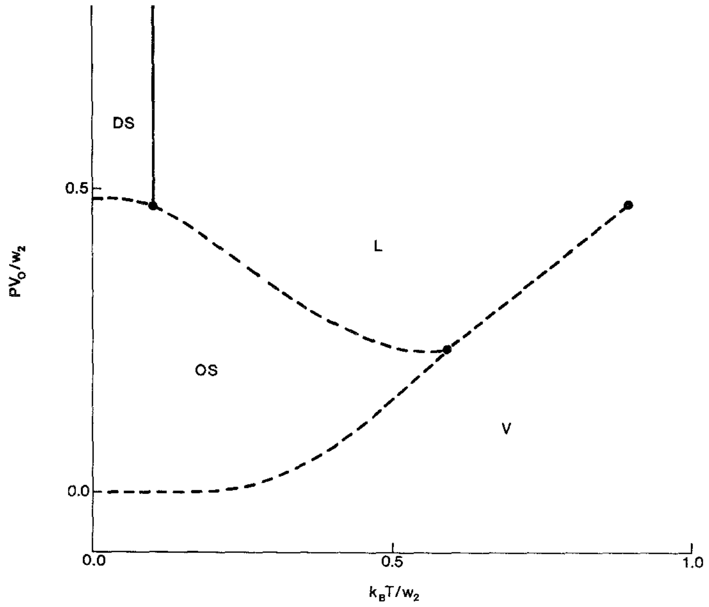


Fig. 5. Phase diagram in the $PV_0/w_2 - k_BT/w_2$ plane for the same parameter values as Fig. 4.

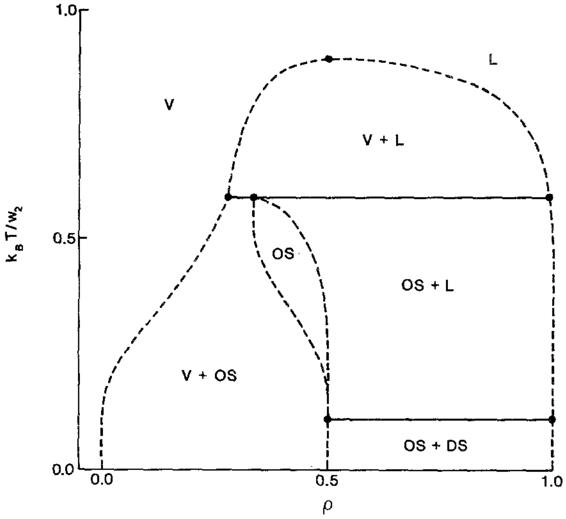


Fig. 6. Phase diagram in the $\rho - k_B T/w_2$ plane for the same parameter values as Fig. 4.

The (DS)–(OS), (L)–(OS), (V)–(OS), and (L)–(V) transitions are all controlled by fixed points with one relevant exponent with characteristic first-order value $d = 3$. That these are indeed first-order transitions is confirmed by our calculation of the molecular density (see Fig. 6). The continuous (DS)–(L) transition is controlled by a fixed point with one relevant exponent 1.238. The critical end-line point labeled A has a fixed point with a relevant exponent, also with value 1.238, and a second exponent with the value 3. The triple point B is controlled by a fixed point which has two relevant first-order exponents. The fixed point which controls the critical end point C lies in the subspace with no bonding (i.e., that of a lattice gas). The transition is in the universality class of the spin-1/2 Ising model. Its relevant exponents $y_1 = 1.238$ and $y_2 = 2.343$ lead to values $\nu = 1/y_1 = 0.807$ and $\gamma = (2y_2 - 3)/y_1 = 1.361$ for correlation length and compressibility exponents. These can be compared with recent estimates of $\nu = 0.631 \pm 0.003$ and $\gamma = 1.239 \pm 0.002$ by Nickel.(17) Our rather poor values for ferromagnetic exponents are characteristic of renormalization procedures designed to preserve sublattice ordering.

6. CONCLUSIONS

All RSRG procedures, such as those used in the present paper, which begin with a cluster of N sites each with q degrees of freedom and renormalize to a smaller cluster, have one factor in common. All the q^N configurations of the original cluster are used to determine the recurrence relations. For any reasonably sized cluster and anything more than a two-state system q^N becomes large and machine computations are necessary in order to distribute these q^N configurations among the monomial terms of the recurrence relations. In our system with $N = 16$, $q = 3$ the large number of configurations led to some storage and computing-time difficulties and placed the problem near to the limits of present computer technology. This fact shows rather clearly the current intractibility of attempting the same cluster method for the Bell(1) model with asymmetric bonds ($N = 16$, $q = 13$). We are therefore not in a position to determine the extent to which the "waterlike" phase diagrams of Bell and Salt,(2) and our failure to obtain a comparable phase diagram for their parameter values, are due to their use of asymmetric bonds or an artifact of mean-field methods. The fact that Meijer et al.,(13) using a cluster variation method for symmetric bonds, were able to obtain waterlike behavior with a similar choice of parameters to Bell and Salt,(2) seems to indicate that the results are dependent on the use of mean-field methods. Recent Monte Carlo calculations of Whitehouse *et al.*(18) for the asymmetric bond model and the same energy parameters as Bell(1) indicate the presence of a first-order (DS)–(OS) transition at lower temperatures. Our calculations for Bell's parameter values are consistent with these results. The absence of the first-order (L)–(V) transition and the presence of regions for which partially bonded dense structures are stable is not evident until rather higher temperatures.

Using this conceptually simple lattice model we have been able to obtain phase diagrams with the general topological characteristics of the water system. The form of these phase diagrams is crucially dependent on the presence of directional bonding. This lends support to the contention that the special character of water is a consequence of hydrogen bonding. The necessity for the bonding energies to be combined with a particular arrangement of nonbonding interactions is probably an artifact of the lattice structure of the model, although the need to vary the bonding energy in proportion to the degree of occupation of neighboring sites is likely to be of more general validity.

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