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The steam–water–ice system: a two-dimensional bonded lattice model. The first-order approximation

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Abstract. The model studied consists of a two-dimensional triangular lattice of which some sites are occupied by the centres of molecules, the remainder being unoccupied. Each molecule has three bonding directions at angles of 120° to each other and two possible orientations, in each of which its bonding directions point to three of the six nearest-neighbour sites. If the molecules of a nearest-neighbour pair have bonding directions pointing towards each other a bond is formed; bonded and unbonded pairs have different interaction energies.

The calculations of Bell and Lavis, using a first order approximation based on a triangle of sites, are extended to include both short- and long-range order. Two transitions are obtained, one of a vapour–liquid type and another of a liquid–solid type, the solid being less dense than the liquid. It is thus possible to obtain a complete phase diagram for vapour, liquid and one solid phase. The close-packed state is shown to be the low temperature form of the liquid phase.

1. Introduction

The present paper is an extension of the work of Bell and Lavis (1970b), (hereafter referred to as BL(b)), to include an ice phase. We shall consider a two-dimensional triangular lattice model in which the molecules form bonds in such a way that an open honeycomb structure with vacant sites is necessary for the achievement of maximum bonding energy in the assembly, (see figure 1). Close packing occurs when the open structure is broken down under the influence of pressure and thermal motion. This situation resembles that occurring in water, (see eg Eisenberg and Kauzmann 1969 pp 185–9, Fletcher 1970 pp 73–85), although, because of the simplifications made, the model cannot be regarded as entirely realistic.

In the liquid state there is some form of molecular order which is short-range in character. This may, for example, consist of separate groups of molecules bonded within themselves to form parts of a honeycomb structure, (see BL(b), figure 3). BL(b) introduced into the lattice model short-range ordering using a first-order approximation based on a triangle of sites. One phase transition of the steam–water type was obtained together with the characteristic density maximum found in liquid water. This suggests that these features can be accounted for by simple structural characteristics like those of

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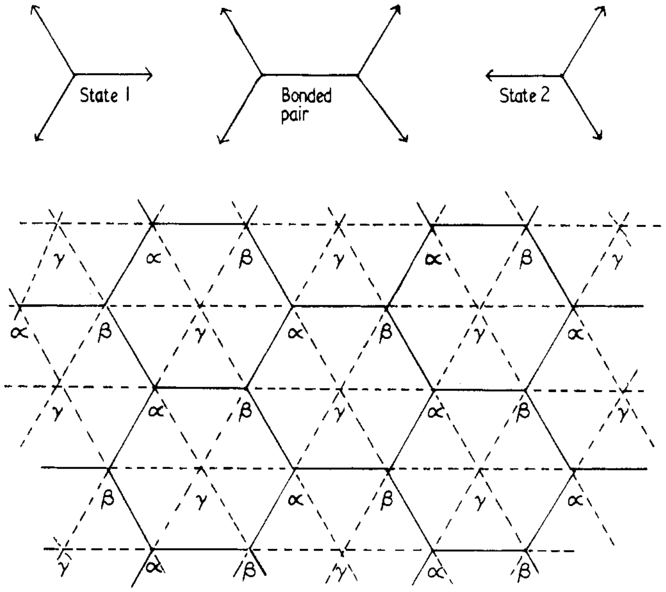

Figure 1. The arrays α, β and γ of the plane triangular lattice and the orientational states of the molecules. The γ sites are regarded as interstitial for the long-range order. The low temperature honeycomb arrangement corresponds to a fully bonded configuration of molecules occupying the α and β sites, (indicated by unbroken lines), with the γ sites unoccupied.

this two-dimensional model. Solid phases correspond to forms of long-range order. To include an ice phase in this two-dimensional model we shall therefore introduce, in the present work, a form of long-range ordering.

Bell and Lavis (1970a), (hereafter referred to as BL(a)), considered an 'interstitial' model designed to include liquid and gaseous states. The low-temperature open honeycomb configuration was ensured by an initial choice of a honeycomb array. Bonding was allowed to occur only between nearest-neighbour sites of this array; the remaining sites were regarded as interstitial. Long-range ordering was introduced between the sites of the honeycomb array and the interstitial sites. This long-range ordering is seen to be distinct in purpose and nature from that of the present paper. The approximation method used by BL(a) was first-order. Such a model could also have been investigated using a zeroth-order approximation; it has been shown by Perram (1971) that this would yield results equivalent to those for a three-dimensional 'cage' model.

A three-dimensional model based on a body-centred cubic lattice was investigated by Bell (1972). Short-range ordering was introduced in a manner similar to that of BL(b) and phase diagrams were obtained which were not unlike those of the two-dimensional model. The natural extension of the work of both BL(b) and Bell (1972) is to include both short- and long-range ordering. There are two reasons for dealing initially with the two-dimensional model:

(i) Since in the three-dimensional model there is the possibility of both a high- and low-density long-range ordered phase, the calculations for this model will be more difficult than that for the two-dimensional model where there is only a low-density long-range ordered state. However, as has been mentioned above, the phase diagrams for short-range ordering only are similar and it is interesting to be able to compare them with long-range ordering included.

(ii) A wider variety of alternative approximation methods exist for two-dimensional models. It is possible, for example, to make useful comparisons with semi-infinite matrix models as has been done by Bellemans and Nigam (1967) for a lattice gas of hard square molecules. The basic premises of the model will now be introduced.

We consider M molecules on the N lattice sites, ($N \geqslant M$), of a two-dimensional triangular lattice consisting of three equivalent interpenetrating triangular arrays labelled α, β and γ, (see figure 1). The (two-dimensional) volume of the lattice is NA_0, where A_0 is the area of the lattice per lattice site. We regard each molecule as possessing three bonding directions at 120° to each other. A molecule on a lattice site has two orientational states, termed states 1 and 2, in each of which the molecule has bonding directions pointing towards three of the six nearest-neighbour sites, (see figure 1). If bonding directions from each of a nearest-neighbour pair of molecules point towards each other then a bond is formed. It is supposed that the interaction energy for pairs of molecules is confined to nearest-neighbours and is $-\epsilon$ and $-(\epsilon + w)$ for unbonded and bonded pairs respectively, ϵ and w being constants with $\epsilon \geqslant 0$, $w > 0$.

It was shown in BL(a) §2 that there exists a separation pressure P_0 given by

$$P_0 = \frac{w - 3\epsilon}{A_0} \tag{1.1}$$

such that for $0 < P < P_0$ the stable equilibrium state at absolute zero temperature is a fully bonded arrangement of molecules on a honeycomb array, the remaining sites being vacant. For $P_0 < P$ the stable equilibrium state at absolute zero temperature has all sites occupied by molecules. These calculations apply equally well to the present model and it is therefore convenient to choose as energy parameters $\Delta w = w - 3\epsilon$ and ϵ rather than w and ϵ, imposing the condition that $\Delta w > 0$.

As in the two previous papers we assume that the internal degrees of freedom of the molecules contribute to the partition function a multiplicative factor $\{\Psi,(T)\}^M$ which is independent of the lattice configurations and of the orientations of the molecules.

2. First-order approximation and equilibrium conditions

We shall consider a closed isothermal–isobaric system, M the number of molecules, T the absolute temperature and P the pressure being constants, with μ, the chemical potential of the molecules, and N, the number of lattice sites, being variables. We define the density ρ of the system by

$$\rho = \frac{M}{N}. \tag{2.1}$$

The purpose of this section is to obtain equations relating the equilibrium values of ρ and μ to the equilibrium values of long- and short-range order variables for fixed value of T and P.

Let E_c be the configuration energy corresponding to a particular arrangement of M molecules on N lattice sites and Ω be the degeneracy associated with this arrangement.

The canonical partition function is given by

$$Z(N, M, T) = \{\Psi_1(T)\}^M \sum \Omega \exp\left(-\frac{E_c}{kT}\right). \tag{2.2}$$

The summation in (2.2) is over all possible configurations of the molecules. The constant pressure partitition function is given by

$$\Lambda(M, T, P) = \sum_{N=M}^{\infty} \exp\left(-\frac{PNA_0}{kT}\right) Z(N, M, T) \tag{2.3}$$

and the equilibrium value of the chemical potential by

$$\mu = -\frac{kT}{M} \ln \Lambda(M, T, P). \tag{2.4}$$

The equilibrium value of N, and hence of ρ, corresponds to the maximum term in the summation in (2.3) and the equilibrium values of the internal ordering variables correspond to the maximum term in the summation in (2.2). From (2.2), (2.3) and (2.4) we have, therefore,

$$\mu = \frac{1}{\rho} \{PA_0 + f_c\} \tag{2.5}$$

where f_c is the Helmholtz free energy per site given by

$$f_c = \frac{1}{N} \{E_c - kT \ln \Omega\}. \tag{2.6}$$

The problem now is to obtain explicit expressions for E_c and Ω and to minimize μ with respect to the internal order variables and with respect to ρ.

We shall adopt a formulation and notation which reduces in the absence of long-range order to that of BL(b). The degeneracy among the occupations of a triangle of sites which arises in BL(b), because the arrays are regarded as equivalent, (see BL(b), figure 5), is partly removed by introducing some long-range order parameters. These serve to distinguish between array γ and the other two arrays but still leave α and β equivalent. This introduces into the situation a certain degree of artificiality since a thoroughgoing analysis would leave the possibility of which array arises as the set of interstitial sites open; but we shall see that this model is sufficient for our purpose, (ie for the occurrence of a solid phase). As in BL(b) we shall use the first-order triangle approximation of Guggenheim and McGlashan (1951), and assign the probabilities of occupation of triangles of sites ψ_i, $i = 1, \ldots, 7$, as shown in figure 2. These variables measure the degree of clustering of the molecules on the lattice, and thus indicate the degree of short-range order. At high temperatures we should expect the arrangement of molecules to be completely random with

$$\psi_1 = (1-\rho)^3 \qquad 6\psi_2 = \rho(1-\rho)^2$$
$$3\psi_3 = 3\psi_4 = 6\psi_5 = \rho^2(1-\rho) \qquad 6\psi_6 = 2\psi_7 = \rho^3.$$

In addition we define the probabilities η_i, $i = 1, \ldots, 8$ to distinguish between occupations in terms of their relationship to the arrays α, β and γ, (see figure 2). Thus, for example, the probability that, on a triangle of sites, there is a bonded pair of molecules on the α and β sites, the γ site being unoccupied, is $\psi_3(3 - 2\eta_3)$. On the other hand the probablities that the bonded pair occupies either the α and γ or β and γ pair of sites are both $\psi_3\eta_3$. The variable η_3, therefore, measures the tendency for ordering to occur between α, β and γ. The same applies to all the other η. In the absence of long-range order $\eta_i = 1$, $i = 1, \ldots, 8$, (and, for example, $\psi_3(3 - 2\eta_3) = \psi_3\eta_3$). An essential feature of the method of Guggenheim and McGlashan is that compatibility is ensured between the occupations

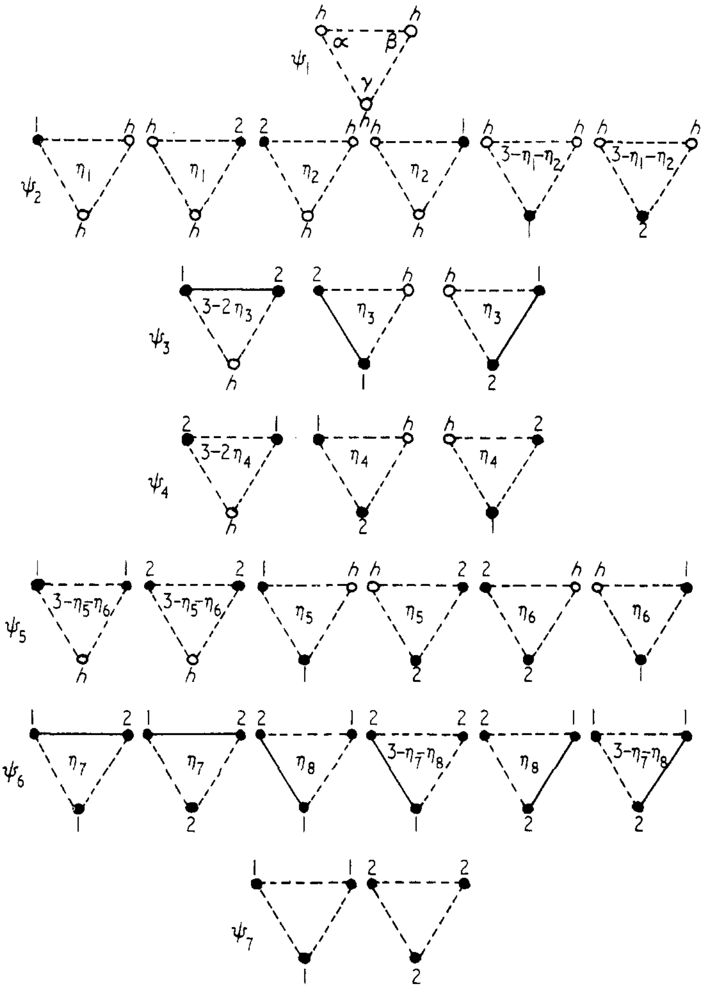

Figure 2. Occupational probability for a triangle of sites with short- and long-range ordering. Molecules in their two orientational states and vacant sites are labelled 1, 2 and h respectively. Full lines indicate bonds. The sites are situated with respect to α, β and γ as shown in the top diagram.

of triangles of sites and the occupations of single sites. We shall need, therefore, to introduce single-site probabilities. Let $p_\delta(k)$ be the probability of a δ-site, where $\delta = \alpha, \beta, \gamma$, being occupied in a way specified by k, where $k = 1,2$, for different molecular orientations and $k = h$, for a vacant site. The single site variables x_i, $i = 1, \ldots, 5$, are defined by

$$x_1 = p_\alpha(1) = p_\beta(2) \tag{2.7a}$$

$$x_2 = p_\alpha(2) = p_\beta(1) \tag{2.7b}$$

$$x_3 = p_\alpha(h) = p_\beta(h) = 1 - x_1 - x_2 \tag{2.7c}$$

$$x_4 = p_\gamma(1) = p_\gamma(2) = (3\rho/2) - x_1 - x_2 \tag{2.7d}$$

$$x_5 = p_\gamma(h) = 1 - 3\rho + 2x_1 + 2x_2. \tag{2.7e}$$

In the absence of long-range ordering $x_1 = x_2 = x_4 = \rho/2$, $x_3 = x_5 = 1 - \rho$; these variables, therefore, also measure the degree of long-range ordering.

We have introduced in all twenty internal variables, related by the conditions

$$x_1 = \psi_2\eta_1 + \psi_3(3-2\eta_3) + \psi_4\eta_4 + \psi_5(3-\eta_6) + \psi_6(3+\eta_7-\eta_8) + \psi_7 \tag{2.8a}$$

$$x_2 = \psi_2\eta_2 + \psi_3\eta_3 + \psi_4(3-2\eta_4) + \psi_5(3-\eta_5) + \psi_6(3-\eta_7+\eta_8) + \psi_7 \tag{2.8b}$$

$$x_3 = \psi_1 + \psi_2(6-\eta_1-\eta_2) + \psi_3\eta_3 + \psi_4\eta_4 + \psi_5(\eta_5+\eta_6) \tag{2.8c}$$

$$x_4 = \psi_2(3-\eta_1-\eta_2) + \psi_3\eta_3 + \psi_4\eta_4 + \psi_5(\eta_5+\eta_6) + 3\psi_6 + \psi_7 \tag{2.8d}$$

$$x_5 = \psi_1 + 2\psi_2(\eta_1+\eta_2) + \eta_3(3-2\eta_3) + \psi_4(3-2\eta_4) + 2\psi_5(3-\eta_5-\eta_6) \tag{2.8e}$$

$$1 = \psi_1 + 6\psi_2 + 3\psi_3 + 3\psi_4 + 6\psi_5 + 6\psi_6 + 2\psi_7 \tag{2.8f}$$

$$\rho = 2\psi_2 + 2\psi_3 + 2\psi_4 + 4\psi_5 + 6\psi_6 + 2\psi_7. \tag{2.8g}$$

In terms of these variables the configuration energy is given by

$$E_c = -3N\{\Delta w(\psi_3 + 2\psi_6) + \epsilon(4\psi_3 + \psi_4 + 2\psi_5 + 12\psi_6 + 2\psi_7)\}. \tag{2.9}$$

Using N triangles of sites to give the correct total number, $3N$, of nearest-neighbour pairs of sites, the basic assumption of the first order approximation is that

$$\ln \Omega = \ln \Omega_1 + \ln \Omega_0 \tag{2.10}$$

where Ω_1 would be the number of ways of arranging the occupations of the triangles of sites if each triangle could be occupied by molecules independently of the occupation of neighbouring triangles and Ω_0 is a factor which ensures that Ω gives the correct value when the arrangement is random apart from the constraints imposed by fixed values of x_i, $i = 1, \ldots, 5$.

Using Stirling's approximation we have

$$\begin{aligned}\ln \Omega_1 = -N\{&\psi_1 \ln \psi_1 + 6\psi_2 \ln \psi_2 + 3\psi_3 \ln \psi_3 + 3\psi_4 \ln \psi_4 + 6\psi_5 \ln \psi_5 \\ &+ 6\psi_6 \ln \psi_6 + 2\psi_7 \ln \psi_7 + 2\psi_2 L(\eta_1, \eta_2) + \psi_3 L(\eta_3, \eta_3) \\ &+ \psi_4 L(\eta_4, \eta_4) + 2\psi_5 L(\eta_5, \eta_6) + 2\psi_6 L(\eta_7, \eta_8)\}\end{aligned} \tag{2.11}$$

where

$$L(a, b) = a \ln a + b \ln b + (3 - a - b) \ln (3 - a - b) \tag{2.12}$$

and

$$\ln \Omega_0 = \tfrac{2}{3} N\left(2 \sum_{i=1}^{4} x_i \ln x_i + x_5 \ln x_5\right). \tag{2.13}$$

The chemical potential given by (2.5) is now minimized with respect to the twenty internal variables and ρ subject to the constraints imposed by equations (2.8). These constraints are most easily dealt with by using Lagrange's undetermined multipliers. The detailed manipulation will not be given but is available on request as unpublished appendix A. The results may most conveniently be given by defining

$$\lambda = \exp\left(\frac{\mu}{kT}\right) \tag{2.14a}$$

the absolute activity,

$$\lambda = \exp\left(\frac{PA_0}{kT}\right) \tag{2.14b}$$

$$t = \exp\left(-\frac{\Delta w}{kT}\right) \tag{2.14c}$$

$$y = \exp\left(-\frac{\epsilon}{kT}\right) \tag{2.14d}$$

and in terms of these the variables

$$z = \left[\frac{\lambda x_4^2}{y^6 x_5^2}\right]^{1/3} \tag{2.15a}$$

$$r = \left[\frac{\lambda x_1^2}{y^6 x_3^2}\right]^{1/3} \tag{2.15b}$$

$$q = (x_3^2 x_5)^{2/3} \frac{r^2}{t\lambda} \tag{2.15c}$$

with

$$s = \left(\frac{x_2}{x_1}\right)^{1/3}. \tag{2.15d}$$

The equilibrium values of the variables ψ_i, $i = 1, \ldots, 7$, η_i, $i = 1, \ldots, 8$ are given by

$$\psi_1 = \frac{tq}{r^2} \tag{2.16a}$$

$$\psi_2(3 - \eta_1 - \eta_2) = \frac{ty^2zq}{r^2} \tag{2.16b}$$

$$\psi_3(3 - 2\eta_3) = q \tag{2.16c}$$

$$\psi_4(3 - 2\eta_4) = ty^3s^4q \tag{2.16d}$$

$$\psi_5(3 - \eta_5 - \eta_6) = ty^3s^2q \tag{2.16e}$$

$$\psi_6(3 - \eta_7 - \eta_8) = s^2zq \tag{2.16f}$$

$$\psi_7 = ty^3s^2zq \tag{2.16g}$$

$$\frac{\eta_1}{3 - \eta_1 - \eta_2} = \frac{r}{z} \tag{2.17a}$$

$$\frac{\eta_2}{3 - \eta_1 - \eta_2} = \frac{s^2r}{z} \tag{2.17b}$$

$$\frac{\eta_3}{3 - 2\eta_3} = \frac{s^2z}{r} \tag{2.17c}$$

$$\frac{\eta_4}{3 - 2\eta_4} = \frac{z}{rs^4} \tag{2.17d}$$

$$\frac{\eta_5}{3-\eta_5-\eta_6}=\frac{z}{rs^2} \tag{2.17e}$$

$$\frac{\eta_6}{3-\eta_5-\eta_6}=\frac{z}{r} \tag{2.17f}$$

$$\frac{\eta_7}{3-\eta_7-\eta_8}=\frac{1}{s^2} \tag{2.17g}$$

$$\frac{\eta_8}{3-\eta_7-\eta_8}=s^2. \tag{2.17h}$$

From (2.15*a*), (2.15*b*) and (2.7)

$$\left(\frac{r}{z}\right)^{3/2}=\frac{p_\alpha(1)p_\gamma(h)}{p_\alpha(h)p_\gamma(1)}$$

or

$$\left(\frac{r}{z}\right)^{3/2}=\frac{p_\beta(2)p_\gamma(h)}{p_\beta(h)p_\gamma(2)}.$$

The variable (r/z) is, therefore, a measure of the extent to which molecules congregate on the α or β arrays compared to the extent to which they congregate on the γ array. From equations (2.15*d*), (2.7*a*) and (2.7*b*)

$$s^3=\frac{p_\alpha(2)+p_\beta(1)}{p_\alpha(1)+p_\beta(2)}.$$

With respect to the formation of a perfectly bonded honeycomb structure of molecules on the α and β arrays, a molecule with orientation 1 on the α array or a molecule with orientation 2 on the β array is 'correctly' oriented; but a molecule with orientation 2 on the α array or a molecule with orientation 1 on the β array is 'incorrectly' oriented. Thus the variable s measures the ratio of incorrectly to correctly oriented molecules on the α and β arrays. The variables (r/z) and s are, therefore, both long-range order variables the former measuring the degree of segregation between the honeycomb array formed by α and β and the interstitial sites of γ and the latter the degree of molecular orientation on this honeycomb array. We have already seen that the variables η_i, $i = 1, \dots, 8$ are long-range order variables with $\eta_i = 1$, $i = 1, \dots, 8$ in the absence of long-range order. It follows from equations (2.17) that in the absence of long-range order $s = 1$ and $r = z$. In this case from (2.16*c*) and (2.16*f*) $z = r = \psi_6/\psi_3$ and by dividing the remaining equations of (2.16) by (2.16*c*) we obtain the equations of BL(b), (3.9). The variables r and z are, therefore, in the absence of long-range order, both equal to the short-range order variable r of BL(b), which measures the extent to which molecules form bonded clusters with the remaining sites occupied, (close-packing), compared to the extent to which they form groups bonded to form parts of an open honeycomb arrangement. When short- and long-range ordering are present the temperature dependence of r and z is affected by the long-range order, but, since they occur in the relationships involving the short-range order variables ψ_i, $i = 1, \dots, 6$, they can still be regarded as short-range order variables. This applies also to the variable q, which has been introduced mainly to simplify the presentation.

Substitution from (2.16) and (2.17) into (2.18) gives seven equations relating the variables x_i, $i = 1, \dots, 5$, z, r, q, s, ρ and λ at constant pressure and temperature. These together with the four equations of (2.15) give eleven equations in eleven variables. The procedure henceforth consists of the elimination of x_i, $i = 1, \ldots, 5$, z and q to give four equations in the four variables r, s, ρ and λ. The details of these calculations are contained in appendix A and the results are given as follows:

Defining

$$a_0(s) = \{1 + ty^3(1 - 2s)\}/(1 - ty^3) \tag{2.18a}$$

$$a_1(s) = \{2s(s - 1) + (1 - s^3)(1 + ty^3)\}/(1 - ty^3) \tag{2.18b}$$

$$a_2(s) = ty^2(s - 1)/(1 - ty^3) \tag{2.18c}$$

$$a_3(s) = \{s - ty^3(1 + s^2 - s^3)\}/(1 - ty^3\} \tag{2.18d}$$

$$b_1(s) = 1 + ty^2(s^2 - 1) + 2ty^3 + ty^3s^2 \tag{2.19a}$$

$$b_2(s) = 1 + 2s^2 + ty^3s^4 \tag{2.19b}$$

$$c_0(s) = ta_0(s) + 2ty^2a_2(s) \tag{2.20a}$$

$$c_1(s) = ty^2(1 + s^2)a_0(s) + ta_1(s) + \{s^2 + ty^3(2 + s^2)\}a_2(s) + 2ty^2a_3(s) \tag{2.20b}$$

$$c_2(s) = ty^2(1 + s^2)a_1(s) + \{s^2 + ty^3(2 + s^2)\}a_3(s) \tag{2.20c}$$

$$d_1(s) = s^2 + ty^3(2 + s^2) \tag{2.21a}$$

$$d_2(s) = 1 + s^2 + s^4 + ty^3s^2 \tag{2.21b}$$

$$e_1(s) = 2ty^2(1 + s^2) \tag{2.22a}$$

$$e_2(s) = 1 + 2ty^3s^2 + ty^3s^4 \tag{2.22b}$$

with

$$h_1(s, r) = \left(\frac{a_2 + ra_3}{a_0 + ra_1}\right)^{1/2}\left(\frac{t + e_1r + e_2r^2}{ty^2 + d_1r + d_2r^2}\right) \tag{2.23a}$$

$$h_2(s, r) = r^{1/2}\left(\frac{c_0 + c_1r + c_2r^2}{ty^2 + b_1r + b_2r^2}\right). \tag{2.23b}$$

r and s are related at constant pressure and temperature by the equations

$$h_1(s, r) = h_2(s, r) \tag{2.24}$$

and

$$\begin{aligned}(c_0 + c_1r + c_2r^2)^4 (t + e_1r + e_2r^2)^2 - \chi^3t^3(a_0 + a_1r)[c_0 \\ + \{c_1 + ty^2(1 + s^3)\}r + \{c_2 + b_1(1 + s^3)\}r^2 + b_2(1 + s^3)r^3]^3 = 0.\end{aligned} \tag{2.25}$$

The absolute activity is given by

$$\lambda = y^6h_1^2(s, r) \tag{2.26a}$$

or

$$\lambda = y^6h_2^2(s, r) \tag{2.26b}$$

and the density by

$$\rho = \frac{2}{3}\left(\frac{(a_2 + ra_3)(ty^2 + d_1r + d_2r^2) + r(1 + s^3)(ty^2 + b_1r + b_2r^2)}{c_0 + [c_1 + ty^2(1 + s^3)]r + [c_2 + b_1(1 + s^3)]r^2 + b_2(1 + s^3)r^3}\right). \tag{2.27}$$

3. The stable equilibrium state at absolute zero temperature

In the limit as the temperature T tends to absolute zero, t and y, given by (2.14*c*) and (2.14*d*) respectively, also tend to zero. In this case we may obtain simplified asymptotic forms for equations (2.23), (2.25) and (2.27). There are five possible limiting behaviours for the variable r:

(i) $r \to 0$, $r^2/t \to 0$
(ii) $r \to 0$, $r^2/t \to c$, c finite and nonzero
(iii) $r \to 0$, $r^2/t \to \infty$
(iv) $r \to r_0$, r_0 finite and nonzero
(v) $r \to \infty$.

From the asymptotic form of (2.24) we may obtain the limits for s in these cases and from (2.25) the ranges of pressures to which these limits apply. Finally from (2.26) and (2.27) asymptotic forms for chemical potential μ and density ρ may be obtained. The details of these calculations are given in unpublished appendix B available on request. The results are summarized in table 1.

Table 1. The limiting values for absolute zero temperature of s, r and ρ and the asymptotic form for μ.

	r	s	ρ	μ
$P = 0$	0	1	0	$-\infty$
	0	1	0	$-kT\ln(9/2) - (w + \epsilon)$
	0	1	$\frac{1}{2}$	$kT\ln(4) - \frac{3}{2}(w + \epsilon)$
	0	0·3498	0	$-kT\ln(5{\cdot}207) - (w + \epsilon)$
	∞	0	$\frac{2}{3}$	$-\frac{3}{2}(w + \epsilon)$
$0 < P < P_0$	∞	0	$\frac{2}{3}$	$-\frac{3}{2}(w + \epsilon) + \frac{3}{2}PA_0$
	0	1	$\frac{2}{3}$	$\frac{3}{2}kT\ln(3) - \frac{3}{2}(w + \epsilon) + \frac{3}{2}PA_0$
$P = P_0$	231	0·4138	0·8963	$2\,kT\ln(0{\cdot}7997) - 6\epsilon$
	6·464	1	0·9763	$2\,kT\ln(0{\cdot}8059) - 6\epsilon$
$P > P_0$	∞	1	1	$kT\ln 6 - (w + 3\epsilon) + PA_0$

4. Numerical calculations and results

For particular values of P and T, (2.25) is a polynomial equation in r with coefficients which are functions of the long-range order variable s. The equilibrium values of s for a particular value of P and T are, from (2.24), the roots of the equation

$$0 = h_1(s, r(s)) - h_2(s, r(s)) \tag{4.1}$$

in the range $0 \leqslant s \leqslant 1^+$, where $r(s)$ is a positive root of (2.25). (Computation of the equilibrium value of s was programmed so that, at each stage of the iteration, if (2.25) had more than one positive root, $r(s)$ was chosen to be that one for which $|h_1 - h_2|$ had the smallest value).

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† It is clear from (2.15*d*) that $s \geqslant 0$ and from (2.7*a*) and (2.7*b*) we see that $s > 1$ corresponds to a form of ordering with either the α or the β array forming the interstitial sites. Since, however, we have imposed a random arrangement of states on the γ array, (see (2.7*d*)), this ordering cannot be perfect throughout the lattice even at absolute zero temperature.

4.1. The liquid and vapour phases

Clearly $s = 1$ is a root of (4.1) for all temperatures since $h_1(1, r)$ and $h_2(1, r)$ are, from (2.23), identical functions. This is the solution with no long-range order obtained in BL(b). In this case, if more than one positive solution of (2.25) occurs, each will represent an equilibrium solution. In BL(b) numerical calculations were performed for $\epsilon/w = 0{\cdot}25$ and $\epsilon/w = 0{\cdot}0$ and in each case it was found that there was a critical pressure P_c such that, on isobars in the density–temperature plane with $P \leqslant P_c$, a transition occurred. This transition was marked by the occurrence of a region of temperature within which there were three equilibrium values for r and ρ. The actual transition temperature was obtained by plotting against temperature the chemical potential along the isobar. The transition occurs at the temperature where this curve intersects itself forming a loop, (see BL(b), figures 7, 8 and 9). When such a transition occurs the phase above the transition is referred to as 'the vapour phase' and the phase below the transition 'the liquid phase'. The transition is first order except for $P = P_c$ where it becomes second order. We have

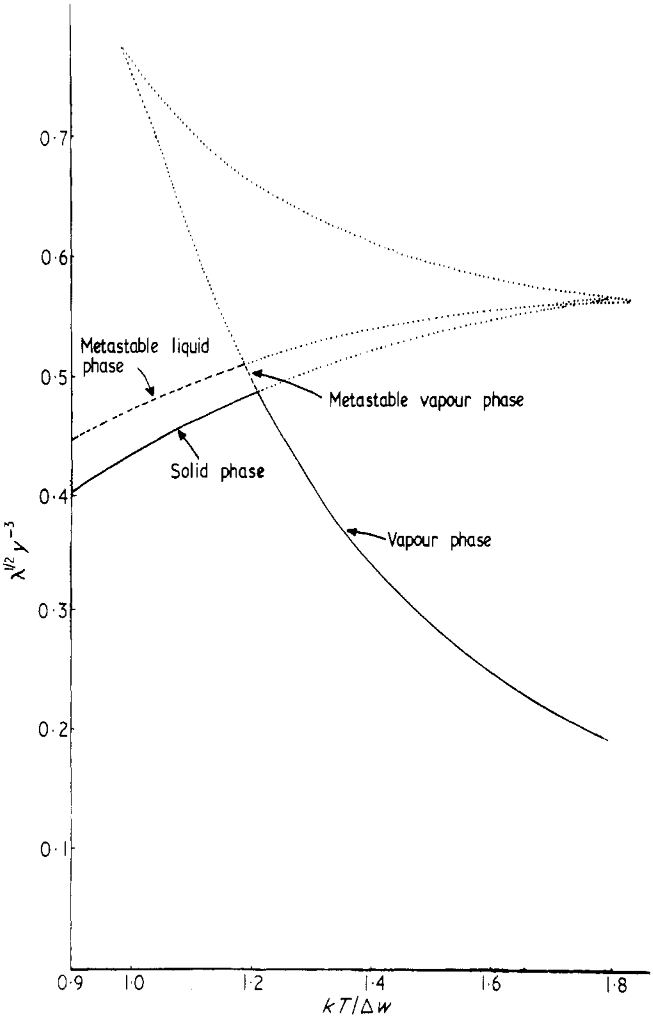

Figure 3. $\lambda^{\frac{1}{2}}y^{-3}$ plotted against temperature for $\epsilon/w = 0{\cdot}25$ at $P/P_0 = 0{\cdot}005$.

shown that as the temperature is reduced along an isobar a density maximum occurs, (see figure 4 and also figures 7 and 8 of BL(b)). This is a characteristic of liquid water occurring for atmospheric pressure at 4 °C.

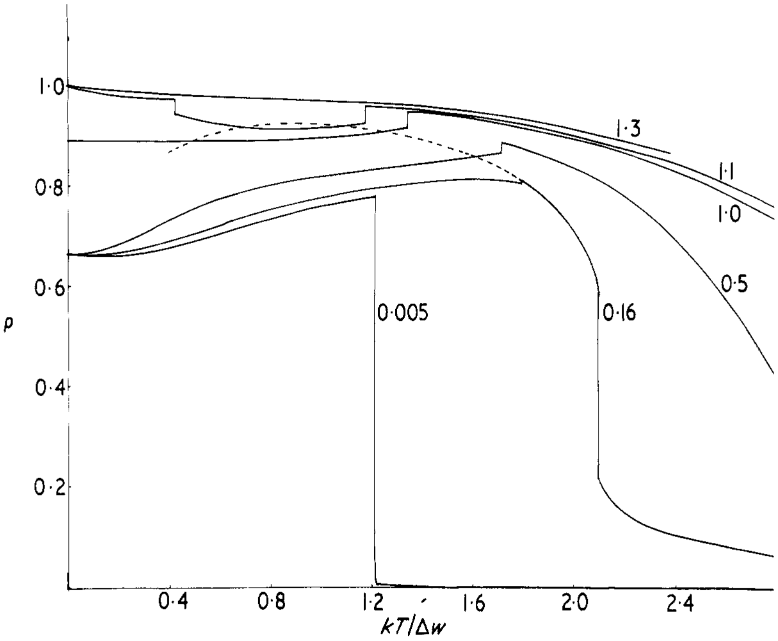

Figure 4. Isobars in the density–temperature plane for $\epsilon/w = 0{\cdot}25$. Each curve is labelled with the value of P/P_0.

In table 1 it may be seen that in the range $0 < P < P_0$ and in the absence of long-range order, $r = \psi_6/\psi_3 \to 0$ and $\rho \to \frac{2}{3}$ as $T \to 0$. We therefore have a form of short-range ordering consisting of clusters of molecules bonded in a honeycomb structure. This is a limiting form of the liquid state; it occurs by a first order transition from the vapour state for $0 < P < P_c$ and by a continuous change in the variable r for $P_c \leqslant P < P_0$. (We considered only cases for which $P_c < P_0$). For $P > P_0$, $r = \psi_6/\psi_3 \to \infty$ and $\rho \to 1$ as $T \to 0$ and a high density liquid state is achieved at low temperatures. This state occurs by a continuous change of the variable r.

4.2. *The solid phase*

The extension of the results of BL(b) to include solutions for $s \neq 1$ is, as we have said, the task of the present paper. Such a long-range ordered state will be referred to as 'the solid phase'. The computation was again performed for $\epsilon/w = 0{\cdot}25$ and $\epsilon/w = 0{\cdot}0$. In each case the transition to the solid phase was first order and was accompanied by a decrease in density, (see figure 4). Again the actual transition temperature is obtained by considering the chemical potential of the states, (see figure 3, (it was more convenient to consider $\lambda^{1/2}y^{-3}$ rather than μ but this makes no material difference)). In the case $\epsilon/w = 0{\cdot}25$ it was found (see figure 5), that at high pressures no transition of any kind

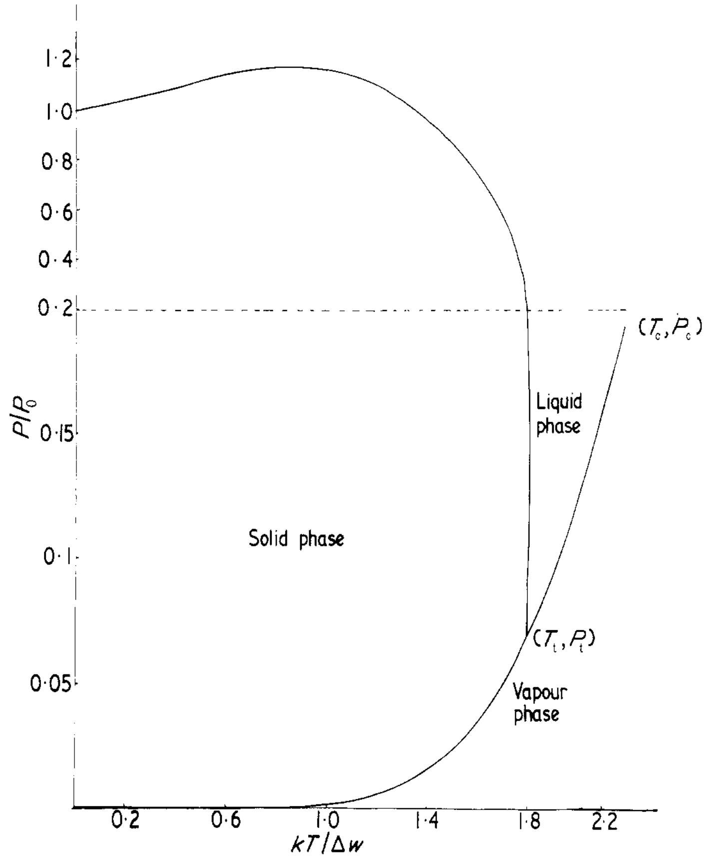

Figure 5. The phase diagram for $\epsilon/w = 0{\cdot}25$.

occurs. For pressures between $P \doteqdot 1{\cdot}16\,P_0$ and $P = P_0$ two transitions occur as the temperature is lowered, first into the solid phase and then back to the dense liquid phase, (see figure 4). Below $P = P_0$ and above $P = P_c$ $(= 0{\cdot}1927\,P_0)$ one transition to the solid phase occurs. Between $P = P_c$ and $P = P_t$ $(\doteqdot 0{\cdot}0693\,P_0)$ two transitions occur. As the temperature is lowered the transition to the liquid phase, detected in BL(b), is the first to occur followed by a second transition to the solid phase. For pressures below the triple point the transition to the solid phase occurs at temperatures above that at which the transition to the liquid phase would occur, (see figure 3). Similar results were obtained for $\epsilon/w = 0{\cdot}0$ except that there is no range of pressures for which the transition to the liquid phase occurs at temperatures above that to the solid phase, $(P_t > P_c)$.

It may be seen from table 1 that, apart from the particular pressures $P = 0$ and $P = P_0$, there is only one long-range ordered state at low temperatures. This is the state for which $s \to 0$, $r \to \infty$ and $\rho \to \frac{2}{3}$ as $T \to 0$. It occurs for $P < P_0$ and at $T = 0$ corresponds to the fully bonded honeycomb arrangement of molecules on the α and β arrays (see figure 1). It is reasonable to regard this state as corresponding to the ice I phase in the water system. That this solid phase is more stable at low temperatures than the low density liquid state can be seen from the presence of the additional term $\frac{2}{3}kT\ln(3)$ in the asymptotic form of the chemical potential for the liquid, (see table 1).

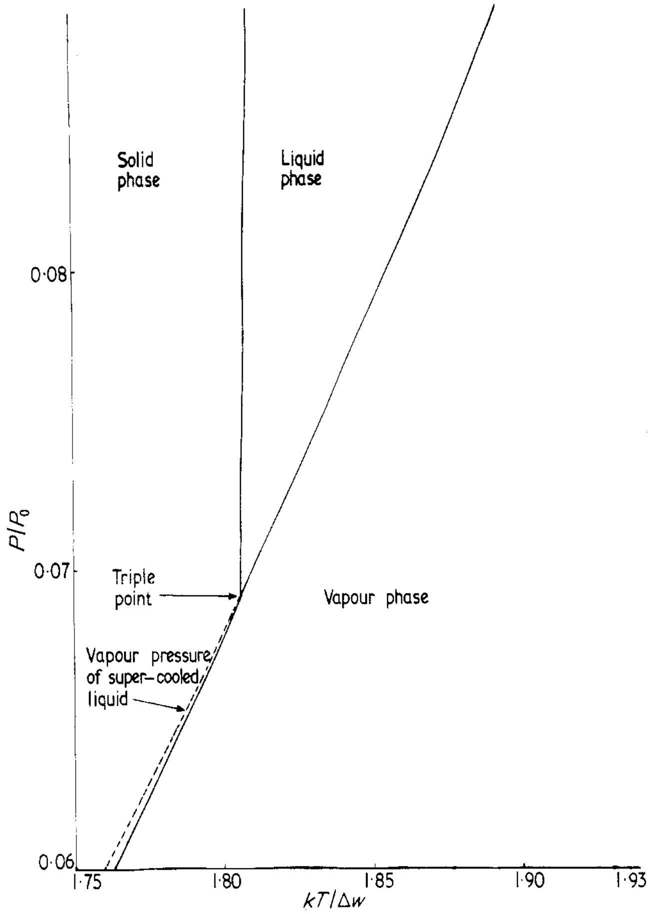

Figure 6. Magnified section of figure 5.

5. Conclusions

Four unsatisfactory aspects of the model are evident:

(i) The density maximum in the liquid state occurs, (for $\epsilon/w = 0{\cdot}25$), in the metastable region below the liquid–solid transition. In the liquid state the density increases monotonically along an isobar for decreasing temperature. It does not appear to be possible to ameliorate this deficiency by varying the parameter (ϵ/w).

(ii) At temperatures above and near to the triple-point the liquid–solid transition curve has a positive gradient in the phase diagram. Thus we may deduce from the Clapyron equation that the transition as temperature is decreased is accompanied by an increase in entropy. This conflicts with experimental results, (see Eisenberg and Kauzmann (1969) table (3.7)). This appears to be a limitation of lattice models resulting from their inability to provide sufficient entropy in states with no long-range order.

(iii) Within the limitations of the two-dimensional model it is not possible to provide for a high density long-range ordered state. (It will be seen from table 1 that, at the density $\rho = 1$ for $T = 0$, $s = 1$. Although groups of molecules are able to achieve the maximum bonding for $\rho = 1$, with an average of two bonds per molecule, no preferential arrangement with respect to α, β and γ is exhibited.) This deficiency is related to the large number of possible arrangements of the molecules for $\rho = 1$ and $T = 0$ compatible with the maximum configurational energy. In BL(b) it was shown that the residual entropy of this state is the same as that of an Ising antiferromagnet.

(iv) Using a two-dimensional triangular lattice, it is not possible to introduce, in any satisfactory way, the nonsymmetric character of the hydrogen bonds between molecules, (see eg Eisenberg and Kauzmann 1969 p 143). As a consequence of this our open honeycomb arrangement of molecules at $T = 0$, with $\rho = 2/3$ and $s = 0$, has no residual entropy. This particular deficiency was overcome by Lieb (1967) who employed a square lattice. He, however, made no attempt to introduce vacant sites into his model. Such vacant sites are, of course, necessary for any model which attempts to account for liquid and gaseous phases.

It is likely that an extension of the three-dimensional model of Bell (1972) to include long-range ordering would represent an improvement. At the very least it would provide for a close-packed solid phase, since on the body-centred cubic lattice it is possible to form an arrangement of molecules which occupies all the sites of the lattice and which allows each molecule to be fully bonded. This phase is similar to that of ice VII.

Because of the limitations of our model we are able to make only qualitative comparison with experiment. Nevertheless it is clear that many of the characteristics of the water system have been simulated by the introduction of a simple form of bonding into a two-dimensional lattice model. In particular, we have obtained two transitions, the vapour–liquid transition achieving a phase of greater density and the liquid–solid transition achieving a phase of lower density. We have found also that in the solid phase there are intervals of temperature on each isobar for which the coefficient of expansion is negative. The results of Dantl (1962) indicate that this is the case for ice cooled below 63 K. The work of Collins and White (1964), for other tetrahedral structures, (eg silicon and germanium), produces similar results. It is suggested by Eisenberg and Kauzmann (1969) p 105, that this negative coefficient of expansion is associated with the excitation of hindered translational vibrations. Our results tend to contradict this suggestion since we have made no provision for such vibrations and yet we achieve similar behaviour.

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