

Two-dimensional bonded lattice fluids

II. Orientable molecule model

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Abstract. A bonded fluid model on a plane triangular lattice is studied. 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 then a bond is formed and the pair has interaction energy $-(\epsilon + w)$, while a unbonded nearest-neighbour pair has interaction energy $-\epsilon$ ($\epsilon > 0, w > 0$). For $\epsilon/w < \frac{1}{3}$ regions of open structure short-range order became important at low temperatures and pressures, with each molecule in such a region bonded to three others and one third of the sites vacant. At higher pressures the predominant low-temperature configuration is close-packed with all sites occupied.

Calculations are performed, using a first-order approximation based on a triangle of sites, for $\epsilon/w = 0$ and $\epsilon/w = \frac{1}{4}$. Critical points are deduced for separation into liquid and vapour phases, both without long-range order. The behaviour of the density as a function of pressure and temperature in the model resembles that found in fluid water, especially for $\epsilon/w = \frac{1}{4}$. There is a supercritical region where curves of density against temperature at constant pressure show turning points, though at very high pressures the density decreases monotonically. For $\epsilon/w = \frac{1}{4}$ these turning points are also found below the critical pressure in the liquid phase.

It is shown that if there are no vacant sites (i.e. at infinite pressure) the configurational states of the model are equivalent to those of an Ising antiferromagnet on the triangular lattice. When vacancies are present, however, the two models cease to be equivalent.

1. Introduction

In the present series of papers we consider lattice models of fluids in which the molecules form bonds in such a way that an open structure is necessary for the achievement of maximum total bonding energy in the assembly. Pressure and thermal motion tend to promote closer packing and thus break down the open structure, creating a situation resembling that in water (see, for instance, Eisenberg and Kauzmann 1969—pp. 185–9). Although our model is two-dimensional and not complicated enough to be a realistic one for water, we are able to reproduce some of the main features of the anomalous behaviour of water density as a function of temperature and pressure, indicating that this behaviour derives from simple structural considerations.

In a paper on one-dimensional models one of the authors (Bell 1969) gave an accurate treatment of continuous as well as lattice models and found that, with appropriate assumptions, similar anomalous behaviour of the density occurred in both cases though phase separation was, of course, absent at all temperatures above absolute zero. In the previous paper (Bell and Lavis 1970—to be referred to as I) on a two-dimensional bonded fluid on a triangular lattice the authors introduced a bonded structure of the honeycomb type with the remaining sites of the triangular

lattice regarded as interstitial. No bonding was allowed between interstitial molecules and those on the honeycomb sublattice. In the present model this restriction is removed and all sites of the triangular lattice are treated as equivalent. The bonded open structure now appears as a form of short-range order which is, of course, more satisfactory in a fluid model. There proves to be a critical temperature and pressure below which the fluid separates into two phases, both disordered from the long-range point of view, which we term 'liquid' and 'vapour'. At lower temperatures long-range sublattice order might appear giving rise to a transition between the long-range disordered liquid phase and a 'solid' or 'ice' phase but we shall not investigate this in the present paper, apart from showing that such a transition does not occur at infinite pressure. We find a pressure p_0 , considerably greater than the critical pressure, such that for pressures greater than p_0 curves of density against temperature display the normal monotonic decrease while between p_0 and the critical pressure such curves have maxima. Below the critical pressure these density maxima occur in the liquid phase provided the energy of interaction between non-bonded nearest neighbours is a sufficient fraction of the bonding energy.

The basic postulates of our model of an assembly of M molecules on a plane triangular lattice of N sites will now be introduced. Each molecule occupies one site so that $N-M$ sites are vacant. We regard each molecule as possessing three bonding directions at angles of 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's bonding directions point towards three of the six nearest-neighbour sites. If the sites of the triangular lattice are divided into three sublattices labelled α , β and γ then it can be seen from figure 1 that a molecule on, for instance, an α site points its bonding

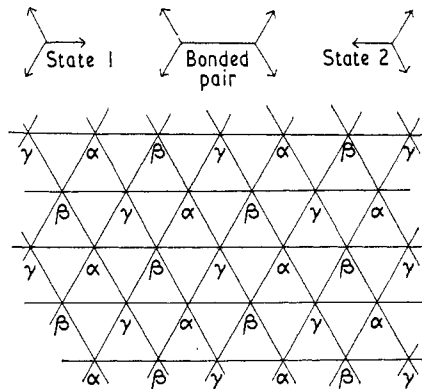


Figure 1. Sublattices of the plane triangular lattice (labelled α , β and γ) and orientational states of the molecules.

directions towards the neighbouring β -sites in state 1 and the neighbouring γ -sites in state 2. If bonding directions from each of a nearest-neighbour pair of molecules point towards each other then a bond is formed. It can be seen from figure 1 that, for bonds between molecules on $\alpha\beta$, $\beta\gamma$ and $\gamma\alpha$ site pairs, the first site of each pair must be occupied by a molecule in state 1 and the second by one in state 2. 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 where ϵ and w are positive constants. The cooperative property of bonding is built

into this model since a molecule on, for instance, an α -site and bonded to three molecules on the neighbouring β -sites cannot break one bond by reorientation without also breaking the other two. Again the molecule on the α -site cannot be bonded to a molecule on one of the neighbouring γ -sites if it is bonded to a molecule on a β -site and vice versa.

As usual in theories of lattice fluids it will be assumed that the internal degrees of freedom of each molecule contribute to the partition function a factor $\psi(T)$, which is independent of the lattice configuration of the molecules, including in the present model the distribution of the molecules between the orientational states. It was shown in I, following Levine and Perram (1968), that by changing w from a constant to a function of temperature it is possible to include the postulate that each bond formed by a molecule changes its internal partition function by a certain factor. However, as in I, we shall put this factor equal to unity and continue to regard w as temperature independent.

It should be noted that the bonds in the present model are symmetrical and differ in this respect from hydrogen bonds which have a 'hydrogen end' and an 'oxygen end'. The water molecule has two hydrogen 'bonding directions' and two oxygen 'bonding directions', a property which accounts for the zero-point entropy of ice. A two-dimensional analogue has been treated accurately by Lieb (1967). Obviously a model incorporating both the unsymmetrical nature of the bonding as well as the possibility of 'holes' and the formation of open and closed structures is desirable, but would be considerably more complicated than the one studied here.

2. The open and close-packed structures

In a state of lowest bonding energy of the assembly each molecule is bonded to exactly three nearest neighbours. If it is then supposed that a molecule on a certain α -site is in orientation state 1 then from figure 1 it follows that the neighbouring β -sites must be occupied by molecules in state 2. The neighbouring γ -sites must then be empty while the remaining α -neighbours of these β -sites must also be occupied by molecules in state 1, and so on. Continuing over the whole lattice we find a type of long-range order with all α - and β -sites occupied by molecules in states 1 and 2 respectively and all γ -sites vacant. The occupied sites form a honeycomb sublattice (see figure 2). This type of configuration, with one third of the sites empty, will be termed

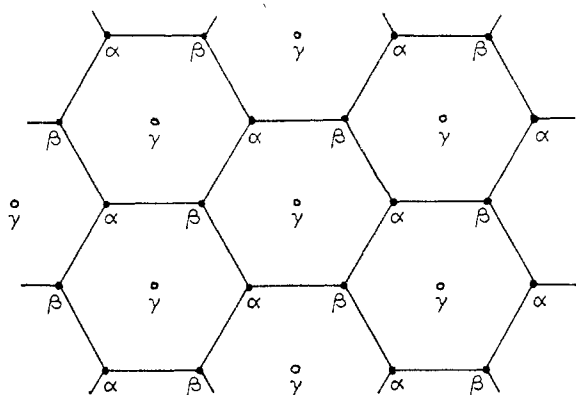


Figure 2. Open structure: honeycomb bond arrangement with γ -sites vacant.

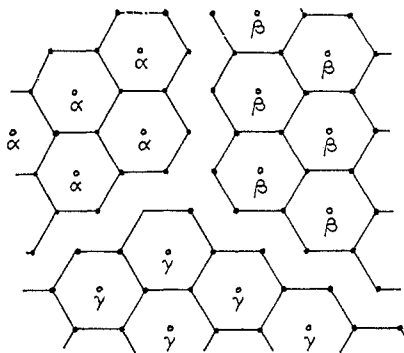


Figure 3. Short-range ordered open structures (vacant sites labelled). Note: scale is smaller than in figure 2.

an 'open structure' and its existence is dependent on the directional and saturation properties of the bonding. As well as the configuration of figure 2 there are also by symmetry open structures of the honeycomb type with α - and β -sites respectively empty. The configurational energy per molecule in the open structure is $-\frac{3}{2}(\epsilon + w)$, when we recall that the energy of each bond is shared between two molecules.

If the assembly has no long-range order but the thermodynamic variables favour the existence of open structures there will be regions of short-range order corresponding to the three types of honeycomb structure with α -, β - and γ -sites respectively vacant. This is illustrated in figure 3 which shows three such regions of short-range order separated by 'zig-zag' dislocations. The energy per molecule will now differ from $-\frac{3}{2}(\epsilon + w)$ since all molecules on dislocation sites have unbonded first neighbours and half of them have only two bonded neighbours. Also at temperatures above absolute zero there will be imperfections not shown in figure 3 in the short-range order since some honeycomb sites will be unoccupied or occupied by a 'wrongly' oriented molecule and some other sites will be occupied. If the temperature tends to zero with the pressure less than a certain value p_0 (given below) then the regions of short-range order will tend to become larger and more nearly perfect and the configuration energy per molecule will tend to $-\frac{3}{2}(\epsilon + w)$ as a limiting value.

If each pair of nearest-neighbour sites on the triangular lattice of N sites is regarded as connected by an 'edge' then the edges can be grouped into N equilateral triangles. From the bonding postulates there cannot be more than one bond to each triangle so that the bonding energy for a lattice of N sites must be greater than or equal to $-Nw$. The configurations of figures 2 and 3 both correspond to exactly one bond per triangle of edges (disregarding the boundary of the triangular lattice) and thus to a bonding energy $-Nw$. The difference between the energy *per molecule* in the two configurations occurs because, in that of figure 2, the number of molecules $M = \frac{2}{3}N$ while, in that of figure 3, $M > \frac{2}{3}N$ owing to the denser packing along the dislocations.

At low temperatures and high pressures the configuration will tend to what we term a 'close-packed structure' with all lattice sites occupied by molecules. The non-bonding configurational energy per molecule will now be -3ϵ and from the considerations of the last paragraph the minimum bonding energy per molecule will be $-w$ since now $M = N$. This minimum or ground-state bonding energy will be realized in, for example, configurations where the bonds are distributed as in figure 2 but the γ - as well as the α - and β -sites are all occupied. Since the orientations of the γ -site molecules are arbitrary there are 2^{3N} such configurations. However, this does not exhaust the degeneracy of the close-packed ground state since the same bonding energy would be obtained if in any of these configurations the orientational states of all α - and β -site molecules were changed. Each γ -site molecule would now be linked by three bonds to either its neighbouring α -site or β -site molecules. Again with all sites occupied any configuration with the bond distribution of figure 3 is a ground state configuration as is also that of figure 4 where the entire lattice is occupied by 'zig-zag' chains of molecules, each bonded to two neighbours. In the appendix we show that there is one-to-one correspondence between the configurational energy states in the close-packed structure of the bonded fluid and those of a triangular lattice Ising antiferromagnet, though this correspondence disappears if the fluid structure ceases to be close-packed. It follows that the degeneracy of the close-packed ground state is equal to that of the ground state of the antiferromagnet and is thus equal to $\exp(0.32306N)$ (Wannier 1950, Domb 1960). At temperatures above absolute zero the close-packed fluid structure will only occur at infinite pressure and

these considerations thus show that no long-range sublattice ordering transition will occur at infinite pressure.

Since the regions of short-range order will become large as the absolute temperature T tends to zero, the enthalpies of the open and close-packed structures at $T = 0$ will be the same as in the interstitial model of I. Although in the model of I the

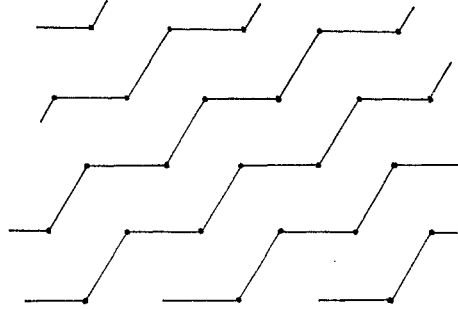


Figure 4. Type of close-packed structure: zig-zag bond arrangement.

zero-point entropy of the close-packed structure is zero this has no effect on the comparative stability of the two structures at $T = 0$. Hence the stability conditions at absolute zero are the same for the present model as for that of I, a point which is confirmed by the behaviour of the triangle approximation solutions near $T = 0$ (see below). Hence the open structure is stable at $T = 0$ for $p < p_0$ and the close-packed structure for $p > p_0$ where

$$p_0 = \frac{w - 3\epsilon}{a_0} = \frac{\Delta w}{a_0}. \quad (2.1)$$

Here a_0 is the area per lattice site which we regard as determined by the distance of closest approach of two molecules and hence as a constant, and the last relation defines Δw .

3. First-order approximation and equilibrium conditions

It is assumed that there is no long-range order so that the distributions of molecules on the three sublattices are equivalent and the open structure appears as a type of short-range order. In these circumstances the use of a zeroth-order approximation would reduce the model to a standard 'lattice gas' with none of the interesting properties associated with the competition between open and close-packed structures. A method taking account of short-range order is necessary and we choose a generalized first-order approximation (Guggenheim and McGlashan 1951) based on a triangular group of three sites, one from each sublattice. The various ways in which such a triangle can be occupied are shown in figure 5 where a bond is represented by a full line. The probabilities of the various configurations are denoted by ψ_i ($i = 1, \dots, 7$) and the weight or number of configurations with the same probability ψ_i is denoted by ω_i . Denoting the number density of the lattice fluid by ρ , these variables are related by

$$1 = \sum_{i=1}^7 \omega_i \psi_i = \psi_1 + 6\psi_2 + 3\psi_3 + 3\psi_4 + 6\psi_5 + 6\psi_6 + 2\psi_7 \quad (3.1)$$

$$\rho = M/N = 2\psi_2 + 2\psi_3 + 2\psi_4 + 4\psi_5 + 6\psi_6 + 2\psi_7 \quad (3.2)$$

so that any five out of the seven ψ_i can be chosen as independent order variables.

Taking ψ_3 and ψ_6 as dependent variables we have from (3.1) and (3.2)

$$\psi_3 = 1 - \rho - \psi_1 - 4\psi_2 - \psi_4 - 2\psi_5 \tag{3.3}$$

$$\psi_6 = \frac{1}{8}(3\rho - 2 + 2\psi_1 + 6\psi_2 - 2\psi_7). \tag{3.4}$$

By considering the interaction energy corresponding to each of the seven types of

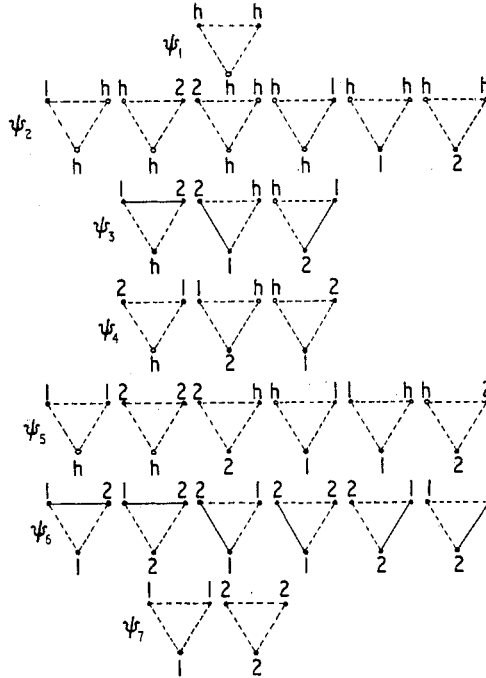


Figure 5. Occupational probabilities for a triangle of sites. (Molecules in their two orientational states and vacant sites or 'holes' are labelled 1, 2 and h respectively. Full lines indicate bonds.)

configuration shown in figure 5 we obtain the configurational energy E_c in the form

$$E_c = -N\{\Delta w(1 - \psi_1 - 6\psi_2 - 3\psi_4 - 6\psi_5 - 2\psi_7) + 3\epsilon(2\rho - 4\psi_2 - 3\psi_4 - 6\psi_5 - 2\psi_7)\}. \tag{3.5}$$

Using N triangles of sites to give the correct total number of $3N$ nearest-neighbour site pairs, the basic assumption of the first-order method is to write, for the number of configurations corresponding to a given set of ψ_i , the relation

$$\ln\Omega = \ln\Omega_0 - N \sum_{i=1}^7 \omega_i \psi_i \ln\psi_i. \tag{3.6}$$

The factor Ω_0 is a function of ρ chosen to give Ω its correct value when the distribution on the lattice is completely random (i.e. at $T = \infty$) and it is easy to show that

$$\ln\Omega_0 = 2N\{\rho \ln(\frac{1}{2}\rho) + (1 - \rho) \ln(1 - \rho)\}. \tag{3.7}$$

From (3.5), (3.6) and (3.7) we can express the Helmholtz free energy f_c per site as a

function of ρ and the independent order variables by the relation

$$f_c(\rho, \psi_1, \psi_2, \psi_4, \psi_5, \psi_7) = \frac{E_c - kT \ln \Omega}{N}. \quad (3.8)$$

For the equilibrium state we equate the derivatives of f_c with respect to the five independent order variables $\psi_1, \psi_2, \psi_4, \psi_5$ and ψ_7 to zero, making use of (3.3) and (3.4), to obtain

$$\begin{aligned} \psi_1/\psi_3 &= tr^{-2}, & \psi_2/\psi_3 &= y^2tr^{-1}, & \psi_4/\psi_3 &= y^3t, & \psi_5/\psi_3 &= y^3t, \\ & & \psi_7/\psi_3 &= y^3tr \end{aligned} \quad (3.9)$$

where

$$y = \exp(-\epsilon/kT), \quad t = \exp(-\Delta w/kT), \quad r = \psi_6/\psi_3. \quad (3.10)$$

From paper I equation (3.14) we have, again using (3.3) and (3.4),

$$pa_0 = \rho \frac{\partial f_c}{\partial \rho} - f_c = 6\epsilon\rho - 2kT\rho \ln\left(\frac{\frac{1}{2}\rho}{1-\rho}\right) + 3kT\rho \ln(r) - f_c. \quad (3.11)$$

It is now easy to derive relations between the thermodynamic variables and the parameter r . Substituting (3.9) into (3.1) and (3.2) we have

$$\begin{aligned} \rho &= \psi_3 r^{-2} \phi(r) \\ 1 - \rho &= \psi_3 r^{-2} \theta(r) \end{aligned} \quad (3.12)$$

where $\phi(r)$ and $\theta(r)$ are polynomials in r , with temperature-dependent coefficients, given by

$$\begin{aligned} \phi(r) &= 2r\{(3 + y^3t)r^2 + (1 + 3y^3t)r + y^2t\} \\ \theta(r) &= (1 + 3y^3t)r^2 + 4y^2tr + t. \end{aligned} \quad (3.13)$$

By dividing the first relation of (3.12) by the second one we obtain

$$\frac{\rho}{1-\rho} = \frac{\phi(r)}{\theta(r)} \quad (3.14)$$

which, for a given temperature expresses ρ as a rational function of r . Again substituting (3.9) into (3.8) we have

$$f_c = -(6\epsilon\rho + \Delta w) - kT\{(1-2\rho) \ln(1-\rho) + 2\rho \ln(\frac{1}{2}\rho) - 3\rho \ln r + \ln\theta(r)\} \quad (3.15)$$

which in conjunction with (3.14) expresses f_c in terms of r . Substitution of (3.15) into (3.11) then gives the simple relation

$$pa_0 = kT \ln\{\theta(r)(1-\rho)\} + \Delta w = kT \ln\{\theta(r)(1-\rho)t^{-1}\}. \quad (3.16)$$

Finally, using equation (3.15) of paper I, rearrangement of (3.11) yields for the configurational chemical potential g_c the relation

$$g_c = \frac{f_c + pa_0}{\rho} = -6\epsilon - kT\left\{2 \ln\left(\frac{\frac{1}{2}\rho}{1-\rho}\right) - 3 \ln r\right\}. \quad (3.17)$$

It is easy to see that the fluid obeys the perfect gas law where ρ becomes very small. From (3.14), r approaches zero with ρ and thus, by (3.13), $\theta(r)$ approaches t . Hence,

for very small ρ ,

$$\theta(r) \sim t, \quad \phi(r) \sim 2y^2tr, \quad \rho \sim 2y^2r.$$

Also

$$\ln\left(\frac{\theta(r)}{t}\right) \sim \ln\left(\frac{4y^2tr+t}{t}\right) \sim 4y^2r \sim 2\rho$$

so that, finally,

$$pa_0 \sim \rho kT, \quad pA \sim MkT.$$

The parameter r may be eliminated numerically between (3.14) and (3.16) to give points on the (ρ, p, T) state surface. This has been done for $\epsilon/w = 0$ and $\epsilon/w = \frac{1}{4}$

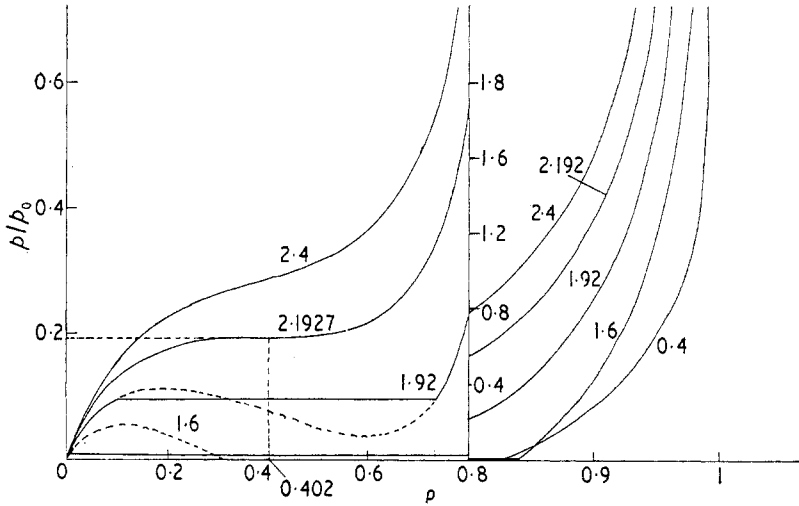


Figure 6. Pressure-density curves at constant temperature for $\epsilon/w = \frac{1}{4}$. Each curve is labelled with the value of $kT/\Delta w$. Note that the scale of the diagram is changed for $\rho > 0.8$ to display isotherms in the intersection region.

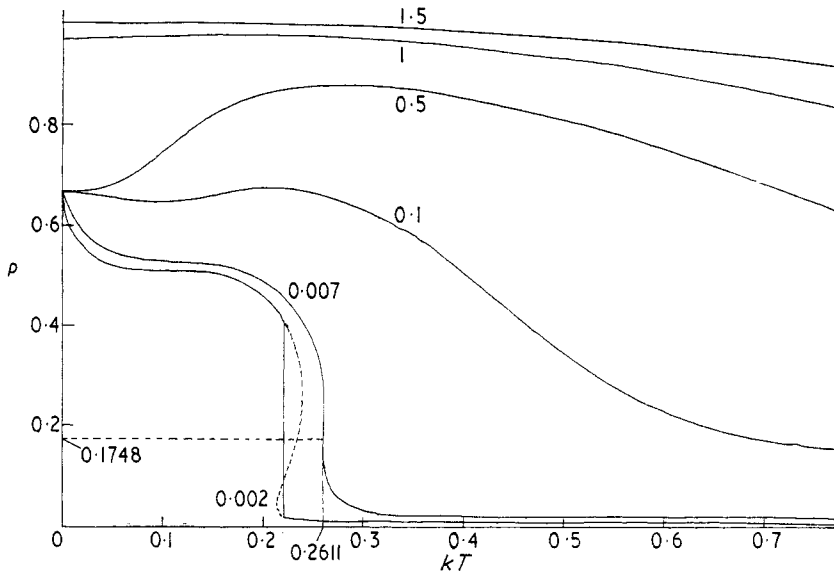


Figure 7. Density-temperature curves at constant pressure for $\epsilon/w = 0$. Each curve is labelled with the value of $pa_0/\Delta w = p/p_0$.

where it should be noted that when ϵ/w is greater than $\frac{1}{3}$ the open structure does not appear at low temperatures and the water-like properties of the model are lost. Figure 6 shows curves of p against ρ at constant temperature for $\epsilon/w = \frac{1}{4}$ and the characteristic properties of the state surface are indicated by the intersecting isotherms on the right-hand part of the diagram, which show that points with the same pressure

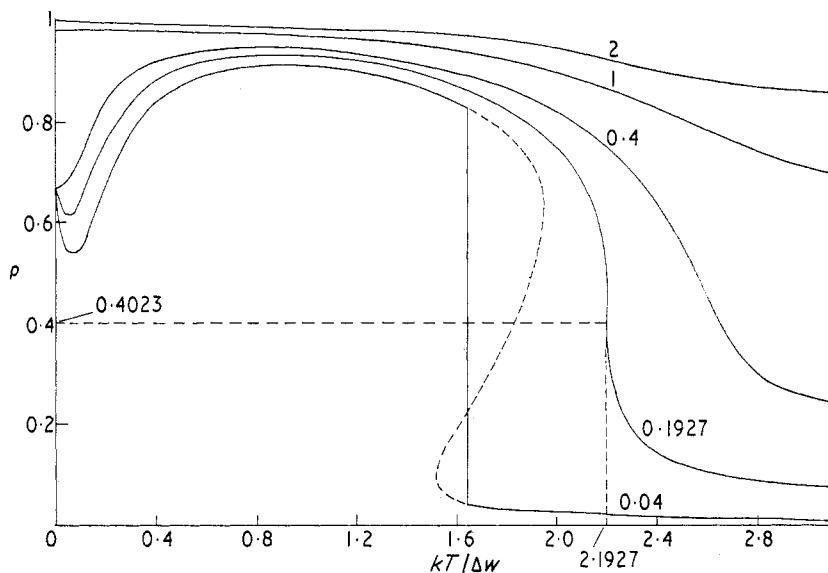


Figure 8. Density-temperature curves at constant pressure for $\epsilon/w = \frac{1}{4}$. Each curve is labelled with the value of $p a_0 / \Delta w = p / p_0$.

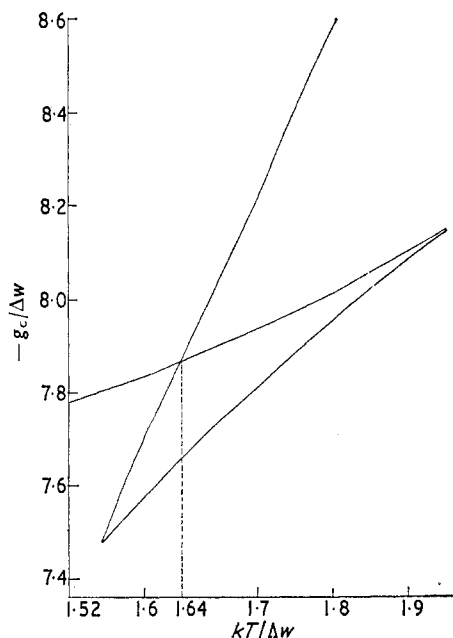


Figure 9. Magnitude of chemical potential against temperature for $\epsilon/w = \frac{1}{4}$ and $p/p_0 = 0.04$.

and density can occur at different temperatures. These characteristic properties can be seen more clearly in the maxima which occur on the isobars shown on figures 7 and 8 where ρ is plotted against T at constant p for $\epsilon/w = 0$ and $\epsilon/w = \frac{1}{4}$ respectively. The broken parts of the curves in figures 6, 7 and 8 correspond to thermodynamically unstable or metastable regions while the straight tie-lines connect liquid and vapour phases in equilibrium at the same temperature and pressure. For a given pressure the temperature at which conjugate phases coexist was found by plotting the chemical potential against temperature. A typical curve is shown in figure 9 where the loop corresponds to unstable regions and the double-point to the conjugate phases.

Comparison of figures 7 and 8 shows that the behaviour of the model is closer to that of fluid water when $\epsilon/w = \frac{1}{4}$ than when $\epsilon/w = 0$. This is physically reasonable since there are a number of sources of interaction energy between water molecules apart from hydrogen bonding. For $\epsilon/w = 0$ there is no apparent density maximum in the liquid phase on the subcritical isobar shown but a liquid phase maximum is well marked for $\epsilon/w = \frac{1}{4}$. Again, for $\epsilon/w = 0$ the temperature of the density maximum on the isobar increases with pressure while for $\epsilon/w = \frac{1}{4}$ it appears to decrease very slightly as it does in fluid water (Eisenberg and Kauzmann 1969, Bridgman 1949).

4. Critical point for liquid-vapour equilibrium

We now give a method of deriving the critical temperature, pressure and density for equilibrium of high-density (liquid) and low-density (vapour) phases. From equations (3.16) and (3.14) the pressure is given in terms of the parameter r by the relation

$$\exp\left(\frac{pa_0 - \Delta w}{kT}\right) = f(r), \quad f(r) = \frac{\theta^2(r)}{\theta(r) + \phi(r)}. \quad (4.1)$$

Hence, at a given temperature, we may write, using a prime to denote differentiation with respect to r ,

$$\begin{aligned} \frac{a_0}{kT} \frac{dp}{d\rho} &= \frac{f'(r)}{f(r)} \frac{dr}{d\rho} \\ \frac{a_0}{kT} \frac{d^2p}{d\rho^2} &= \left[\frac{f''(r)}{f(r)} - \frac{\{f'(r)\}^2}{\{f(r)\}^2} \right] \left(\frac{dr}{d\rho} \right)^2 + \frac{f'(r)}{f(r)} \frac{d^2r}{d\rho^2}. \end{aligned}$$

Now it is not difficult to show from (3.14) that $dr/d\rho$ is always positive so that a necessary and sufficient condition for $dp/d\rho$ and $d^2p/d^2\rho$ to be simultaneously zero is that

$$f'(r) = f''(r) = 0. \quad (4.2)$$

An equivalent condition to (4.2) is

$$q_4 r^4 + q_3 r^3 + q_2 r^2 + q_1 r + q_0 = 0, \quad 4q_4 r^3 + 3q_3 r^2 + 2q_2 r + q_1 = 0 \quad (4.3)$$

where the polynomials are respectively equal to a factor of $f'(r)$ and its derivative. The coefficients in (4.3) are given by

$$\begin{aligned} q_0 &= y^2 t^2, & q_1 &= (12y^4 t - b)t, & q_2 &= 3(3by^2 - a)t, \\ q_3 &= 3b^2 - 4ay^2 t, & q_4 &= ab, & a &= 3 + y^3 t, & b &= 1 + 3y^3 t. \end{aligned} \quad (4.4)$$

Elimination of r between the two relations of (4.3) yields an equation in T , whose solution gives the critical temperature T_c . The elimination was performed by using the condition that the two relations of (4.3) have a common root if the Sylvester

determinant

$$\begin{vmatrix} q_3 & 2q_2 & 3q_1 & 4q_0 & 0 & 0 \\ 0 & q_3 & 2q_2 & 3q_1 & 4q_0 & 0 \\ 0 & 0 & q_3 & 2q_2 & 3q_1 & 4q_0 \\ 4q_4 & 3q_3 & 2q_2 & q_1 & 0 & 0 \\ 0 & 4q_4 & 3q_3 & 2q_2 & q_1 & 0 \\ 0 & 0 & 4q_4 & 3q_3 & 2q_2 & q_1 \end{vmatrix} = 0. \quad (4.5)$$

All the elements of the determinant in (4.5) are functions of the temperature, given by (4.4), and we solved (4.5) numerically to give the critical temperature. The critical value of r and hence the critical pressure and density were then obtained without difficulty. Critical values of T , p and ρ are given in table 1 for $\epsilon/w = 0$ and $\epsilon/w = \frac{1}{4}$.

Table 1. Critical values for the liquid-vapour transition

ϵ/w	$kT_c/\Delta w$	$p_c a_0/\Delta w = p_c/p_0$	ρ_c
0	0.2611	0.0070	0.1748
$\frac{1}{4}$	2.1927	0.1927	0.4023

If we regard p_0 for fluid water as the pressure above which density decreases monotonically with temperature over the whole range then p_0 is between 1500 and 2000 atmospheres (Eisenberg and Kauzmann 1969, Bridgman 1949) so that p_0/p_c is between about 7 and 9. For the orientable model it can be seen from table 1 that the calculated value of p_0/p_c is about 140 for $\epsilon/w = 0$ but about 5 for $\epsilon/w = \frac{1}{4}$. These values are derived from the first-order triangle approximation and the accurate values may be rather higher if the trend is in the same direction as that found for the interstitial model of paper I, with $\epsilon/w = 0$. However, it is clear that as regards this property as well as those discussed in § 3 above, the ratio $\epsilon/w = \frac{1}{4}$ gives results closer to those found for water than $\epsilon/w = 0$.

5. The equilibrium state near absolute zero

It is convenient to define a reduced pressure κ by

$$\kappa = \frac{p a_0}{\Delta w} = \frac{p}{p_0}. \quad (5.1)$$

At very low temperatures $y^3 t \ll 1$ and hence equation (4.1) may be replaced by

$$t^{1-\kappa} \sim \frac{(r^2 + 4y^2 t r + t)^2}{6r^3 + 3r^2 + 6y^2 t r + t}. \quad (5.2)$$

In considering the behaviour of the model as absolute zero is approached we shall consider the three possibilities that the parameter r (i) tends to infinity (ii) tends to a finite non-zero value and (iii) tends to zero.

(i) Suppose $r \rightarrow \infty$ as $T \rightarrow 0$. Then, by (5.2),

$$r \sim 6t^{1-\kappa} \quad (5.3)$$

so that, since $t \rightarrow 0$, a necessary condition is $\kappa > 1$ or $p > p_0$. It can be seen from (3.14) that if $r \rightarrow \infty$ then the density $\rho \rightarrow 1$. Thus the result just obtained agrees with the condition for the stability of the close-packed structure derived by thermodynamic reasoning in § 2.

(ii) Suppose $r \rightarrow r_0$ as $T \rightarrow 0$, where $r_0 \neq 0$ and $r_0 \neq \infty$. Then since $t \rightarrow 0$ and $y^2t \rightarrow 0$ we have, from (5.2),

$$t^{1-\kappa} \sim \frac{r_0^4}{6r_0^3 + 3r_0^2}.$$

This result is self-consistent only if $\kappa = 1$ or $p = p_0$ exactly. Then we have

$$r_0^2 = 6r_0 + 3$$

an equation whose only positive root is $r_0 = 3 + 2\sqrt{3}$. From (3.14) this gives the result

$$\rho \rightarrow 0.9763 \quad \text{as } T \rightarrow 0. \tag{5.4}$$

(iii) Suppose $r \rightarrow 0$ as $T \rightarrow 0$. Then, near $T = 0$, $y^2tr \ll t$ and $r^3 \ll r^2$. Hence (5.2) reduces to

$$t^{1-\kappa} \sim \frac{(r^2 + t)^2}{3r^2 + t}.$$

If r^2/t does not tend to infinity then the right-hand side of this relation becomes proportional to t , which is clearly inconsistent when $\kappa \neq 0$. Hence we must assume $r^2/t \rightarrow \infty$ as $T \rightarrow 0$ and then

$$r^2 \sim 3t^{1-\kappa}. \tag{5.5}$$

Thus, a necessary condition for $r \rightarrow 0$ as $T \rightarrow 0$ is $\kappa < 1$ or $p < p_0$. Using (3.14) and retaining the terms which may be next in magnitude to the leading ones in both numerator and denominator, we have

$$\rho = \frac{\theta(r)}{\theta(r) + \phi(r)} \sim 2r \frac{r + 3r^2}{3r^2 + 6r^3 + t} = \frac{2}{3} \frac{(1 + 3r)}{(1 + 2r + \frac{1}{3}tr^{-2})} \sim \frac{2}{3} \frac{(1 + 3r)}{(1 + 2r + \frac{1}{3}t^\kappa)}. \tag{5.6}$$

It can be seen at once that ρ tends to $\frac{2}{3}$ as $T \rightarrow 0$ which is consistent with the condition for the stability of the open structure derived by thermodynamic reasoning in § 2.

From (5.6), ρ is greater or less than $\frac{2}{3}$ just above $T = 0$ according to whether r is greater or less than $t^\kappa/9$. Using (5.5), we have

$$\frac{9r}{t^\kappa} \sim 9\sqrt{3}t^{-3(\kappa - 1/3)/2}$$

which approaches zero with T if $\kappa < \frac{1}{3}$ but becomes infinite if $\kappa > \frac{1}{3}$. Hence in the range $1 > \kappa > \frac{1}{3}$ (or $p_0 > p > \frac{1}{3}p_0$) ρ takes the value $\frac{2}{3}$ at $T = 0$ and is an increasing function of T just above $T = 0$. Hence ρ must pass through a maximum. On the other hand, in the range $\frac{1}{3} > \kappa$ (or $\frac{1}{3}p_0 > p$) ρ takes the value $\frac{2}{3}$ at $T = 0$ but is a decreasing function of T just above $T = 0$. Thus ρ must pass through a minimum before attaining a maximum. This phenomenon is illustrated by the curves of figures 7 and 8. There is an interesting difference here between the behaviour of the model and that of fluid water. The density of the latter passes a minimum before attaining a maximum in the higher part of the pressure range zero to p_0 (Eisenberg and Kauzmann 1969, Bridgman 1949) while we have just seen that in the model this occurs in the

lower part of the range. However, it is possible that at low temperatures the fluid phase in the model may be metastable since transitions may take place at finite pressures to long-range ordered 'ice' or 'solid' phases. We hope to carry out further work on this point.

Appendix. The orientable bonded fluid and the Ising antiferromagnet

There is an obvious resemblance between the bonded fluid model treated here and an Ising antiferromagnet since in both cases the lowest energy state of a nearest-neighbour pair is attained with the two molecules in different orientational states. However, in the antiferromagnet the latter is a sufficient condition, while in the present model each site of the pair must be occupied by a molecule in a particular orientational state. For instance, an $\alpha\beta$ bond occurs only if the molecule on the α -site is in state 1 and that on the β -site in state 2. Interchange of the molecules' states breaks the bond whereas in an antiferromagnet it leaves the pair energy unchanged. Again, the bonding interaction, unlike the antiferromagnetic interaction, has the property of saturation in that even if a molecule's six nearest-neighbour sites are all occupied it can only form bonds with the molecules on three of them.

In spite of these differences there is a one-to-one correspondence between the configurational energy states of the present model and those of an Ising antiferromagnet on the triangular lattice with suitable energy parameters, provided that no sites are vacant. (In the present model this close-packed state corresponds either to infinite pressure or to zero absolute temperature with pressure greater than p_0 .) If, in the triangular lattice of N sites, the $3N$ edges are grouped into N equilateral triangles of three edges each then the vertices of each triangle can be occupied either by three molecules in the same state or by two in one state and one in the other. In the bonded fluid there are no bonds along the edges if the first case giving an energy -3ϵ for the triangle. In the second case it can be seen from figure 5 that there is one, and only one, bond giving an energy $-(3\epsilon + w)$ for the triangle. In the antiferromagnet suppose that a like pair of nearest neighbours has energy $-\epsilon$ while an unlike pair has energy $-(\epsilon + \frac{1}{2}w)$. Then if the triangle is occupied by three molecules in the same state the energy is -3ϵ while otherwise there is one like pair and two unlike pairs giving an energy $-(3\epsilon + w)$. Thus similar distributions of the two states give equal energies in the two models. In particular the entropy of the configurational ground state is the same and for the antiferromagnet this has been shown by Wannier (1950) to have the value $0.32306 Nk$ (see also Domb 1960). Since no transition to a state of long-range sublattice order occurs in the antiferromagnet on the triangular lattice none can occur in the close-packed structure of the orientable bonded fluid. This means that no such transition occurs in the bonded fluid if we vary the temperature at infinite pressure.

The equivalence between the two models disappears if some sites are vacant. Consider, for example, the bond distribution of figure 2 where each α -site is occupied by a molecule in state 1 and each β -site by one in state 2, giving a honeycomb structure of bonds. If the orientational state of each α -site molecule is changed to 2 and that of each β -site molecule to 1, all $\alpha\beta$ bonds are broken. In the close-packed structure with all γ -sites occupied a bond to a γ -site replaces each broken $\alpha\beta$ bond. However, with the γ -sites vacant no new bonds are formed and the energy of the assembly increases by $\frac{2}{3}Mw$. For an Ising antiferromagnet, on the other hand, the configurational energy is unaltered by reversal of the orientations of all α - and β -site

molecules, even with the γ -sites vacant. Hence, with vacancies present, similar distributions of states can give rise to different energies in the two models.

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