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A two-dimensional bonded lattice model for water

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Abstract. A lattice fluid model on a two-dimensional quadratic lattice is considered in which molecules are capable of preferential bonding between second neighbours. A Hamiltonian is introduced which has interactions which differentiate between parallel and antiparallel spins and parallel and orthogonal spins. A number of interesting special cases are considered including a four-state dilute Potts model and a five-state Potts model. The phase transitions are investigated using Landau symmetry theory. The fluid transition is studied using a mean-field approximation. Within the limitations of this method the system is predicted to have water-like properties.

1. Introduction

It is now widely recognised that many of the 'anomalous' properties of water arise from the strongly directional nature of hydrogen bonding, which leads to the existence of regions of open structure with a lower density than other molecular arrangements (see e.g. Eisenberg and Kauzmann 1969, Fletcher 1970, Perram and Levine 1974). This point of view has motivated the introduction of two-dimensional (Bell and Lavis 1970) and three-dimensional (Bell 1972) lattice fluid models. In these models each molecule has a number of bonding arms pointing to a subset of the neighbouring sites. If one of these neighbouring sites is also occupied by a molecule with a bonding arm in the direction of the first molecule then a low-energy bond may be formed. In the case of the model of Bell and Lavis (1970), which is based on a triangular lattice, the bonding arms are all equivalent and a bond is always formed by the molecules in the configuration described. In the three-dimensional body-centred cubic model of Bell (1972) the arms are directional (positive and negative) and a bond is formed if and only if there is a conjunction of a positive and a negative arm.

The work of Bell and Lavis (1970) and subsequent papers by Lavis (1973, 1975) for the triangular lattice model employ a mean-field approximation method. Within the limitations inherent in such a method the model is shown to have some of the anomalous properties of water. The form of the pressure-temperature phase diagram follows quite closely that derived from a transfer matrix calculation (Lavis 1976). It is clear that the complexity of this model excludes at present an exact solution. In this context it is interesting to note that if this triangular lattice model is expressed in spin-1 form then it becomes a generalisation of the well known model of Blume *et al* (1971). This, on the one hand, emphasises the difficulty involved in the search for an exact solution, but on

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the other hand suggests that real-space renormalisation methods are feasible (see e.g. Berker and Wortis 1976). These calculations have now been completed (Young and Lavis 1979, Southern and Lavis 1979) using the block-spin method employed by Schick *et al* (1977) for the spin- $\frac{1}{2}$ Ising model and by Schick and Griffiths (1977) for the three-state Potts model. In the work of Southern and Lavis the phase diagram is obtained. It follows quite closely that derived from previous calculations. The one significant difference is that the solid-liquid transition, which was predicted to be first order by mean-field methods, now becomes second order. This result is probably due to the two-dimensionality of the system rather than the directional bonding character of the molecules. In this respect these results do of course add a cautionary note to any conclusions which may be drawn from the present calculations. The discrepancy between mean-field calculations and real-space renormalisation methods may not be evident in a three-dimensional model such as that of Bell (1972).

In this paper we wish to discuss an alternative two-dimensional model with molecules with directional bonds. The model is based on a square lattice and the bonding is between second rather than first neighbours. In § 2 we propose a rather general Hamiltonian which has a number of interesting special cases. One of these is a five-state analogue of the Blume-Emery-Griffiths model, and another is a five-state Potts model. In § 3 we consider the possible phase transitions of the model predicted by Landau symmetry theory (Landau and Lifshitz 1958, Lyubarskii 1960). In subsequent sections we consider the vapour-liquid transition using the mean-field approximation of Guggenheim and McGlashan (1951). Again within the limitations of the method, the model is predicted to have water-like properties.

2. The detailed model

We consider a quadratic lattice of N sites with periodic boundary conditions. Beginning at an arbitrary site with position vector r_0 the lattice sites are given by the vectors

$$r = r_0 + l(n_1 \hat{i} + n_2 \hat{j}) \quad (n_1 = 0, 1, \dots, N_1 - 1, \quad n_2 = 0, 1, \dots, N_2 - 1)$$

where l is the nearest-neighbour lattice distance, $\hat{i} = (1, 0)$ and $\hat{j} = (0, 1)$ are orthogonal unit vectors in the directions of the sides of the basic lattice square, and $N_1 N_2 = N$. The lattice is divided into two equivalent interpenetrating sublattices α and β so that, taking r_0 to be an α site, the vector r represents either an α or a β site according to whether $n_1 + n_2$ is respectively even or odd.

Each lattice site is either occupied by a molecule or it is vacant. The 'spin' s of a molecule is aligned along one of the sides of the lattice square. We therefore represent the state at a lattice site by the vector $s = \pm \hat{i}, \pm \hat{j}, \mathbf{0}$, where $s = \mathbf{0}$ represents a vacant site. The four molecular states are shown in figure 1, where we have represented the bonding arms by plus and minus signs. It will be seen that the bonding arms of a molecule point towards the four second-neighbour sites. A bond will be formed between a pair of molecules on second-neighbour sites if and only if there is conjunction between a positive and a negative bonding arm. In order to deal with molecular bonding which distinguishes between sublattices we must divide the lattice into two types of basic square (see figure 1). A square of type A has an α site at the bottom left and top right and a β site at the bottom right and top left; a square of type B has the converse arrangement.

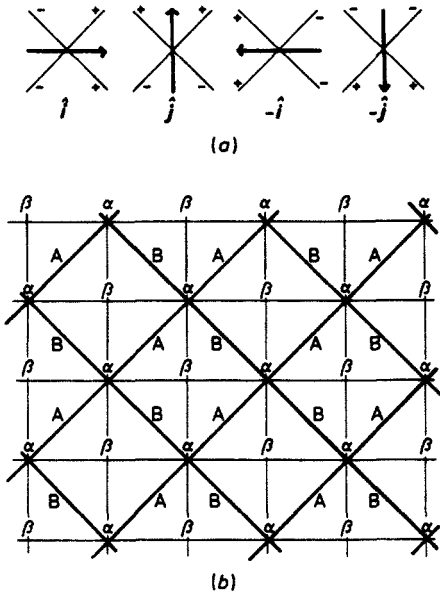


Figure 1. (a) The four orientational states of a molecule. The bonding arms are labelled with plus and minus signs. (b) The fully bonded open state [2, 1] on sublattice α , all sites of sublattice β being vacant. Squares of sites of types A and B are labelled.

The number M of molecules on the lattice is given by

$$M(\{s\}) = \sum_{\langle r \rangle} s^2(r) \tag{2.1}$$

where the sum is over all sites r of the lattice. If we use the grand canonical distribution then the exponent factor which appears in the distribution is

$$-\mathcal{H}(\{s\})/kT = [\mu M(\{s\}) - H(\{s\})]/kT \tag{2.2}$$

where μ is the chemical potential per molecule, H is the Hamiltonian, k is Boltzmann's constant and T is the absolute temperature. Our proposed form of \mathcal{H} is given by

$$\mathcal{H}(\{s\}) = \sum_{\square} \mathcal{H}_{\square}(s_{\alpha 1}, s_{\alpha 2}, s_{\beta 1}, s_{\beta 2}) \tag{2.3a}$$

where the summation is over every nearest-neighbour square of the lattice and

$$\begin{aligned} \mathcal{H}_{\square}(s_{\alpha 1}, s_{\alpha 2}, s_{\beta 1}, s_{\beta 2}) &= -\frac{1}{4}\mu(s_{\alpha 1}^2 + s_{\alpha 2}^2 + s_{\beta 1}^2 + s_{\beta 2}^2) + \frac{1}{2}\epsilon_1(s_{\alpha 1}^2 + s_{\alpha 2}^2)(s_{\beta 1}^2 + s_{\beta 2}^2) \\ &+ \frac{1}{2}J_1(s_{\alpha 1} + s_{\alpha 2}) \cdot (s_{\beta 1} + s_{\beta 2}) + \frac{1}{2}z_1[(s_{\alpha 1} \cdot s_{\beta 1})^2 + (s_{\alpha 1} \cdot s_{\beta 2})^2 \\ &+ (s_{\alpha 2} \cdot s_{\beta 1})^2 + (s_{\alpha 2} \cdot s_{\beta 2})^2] + (\epsilon_2 + \frac{1}{2}w)(s_{\alpha 1}^2 s_{\alpha 2}^2 + s_{\beta 1}^2 s_{\beta 2}^2) \\ &+ (J_2 + \frac{1}{2}w)(s_{\alpha 1} \cdot s_{\alpha 2} + s_{\beta 1} \cdot s_{\beta 2}) + z_2[(s_{\alpha 1} \cdot s_{\alpha 2})^2 + (s_{\beta 1} \cdot s_{\beta 2})^2] \\ &+ us_{\alpha 1}^2 s_{\alpha 2}^2 s_{\beta 1}^2 s_{\beta 2}^2 \pm \frac{1}{2}w(s_{\alpha 1} \mathbf{K} s_{\alpha 2}^{(i)} - s_{\beta 1} \mathbf{K} s_{\beta 2}^{(i)}). \end{aligned} \tag{2.3b}$$

In equation (2.3b) the plus or minus sign before the final term applies respectively to a square of type A or type B, and

$$\mathbf{K} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{2.4}$$

We see that a pair of first- or second-neighbour molecules will interact with energy ϵ_1 or ϵ_2 respectively, irrespective of their orientations. The energies J_1 and J_2 distinguish energetically between parallel and antiparallel orientations, between and within sublattices respectively. The energies z_1 and z_2 distinguish energetically between aligned and orthogonal orientations, between and within sublattices respectively. The second-neighbour bonding energy is w and the interaction energy u occurs only for a fully occupied square of molecules.

For the case $w = 0$ the 'effective Hamiltonian' \mathcal{H} is similar to that of the Blume–Emery–Griffiths model, except that now we have five rather than three states. The other main differences are that we have included both first- and second-neighbour interactions and, since in this case $(s_1 \cdot s_2)^2 \neq s_1^2 s_2^2$, terms of both types are included.

We now consider the group operations under which \mathcal{H} is invariant. We define the following groups:

- (a) $\tilde{\mathcal{F}}_2 = \{\tilde{I}, \tilde{\sigma}\}$ operating on sublattice labels, where \tilde{I} is the identity element and $\tilde{\sigma}$ permutes sublattice labels;
- (b) $\mathcal{C}_{4v} = \{I, C_2, C_4, C_4^3, \sigma_x, \sigma_y, \sigma_a, \sigma_b\}$, the eight-order group operating on the four molecular states as shown in figure 2;
- (c) \mathcal{S}_4 , the 24-order symmetric group operating on the four molecular states;
- (d) \mathcal{S}_5 , the 120-order symmetric group operating on the five states at a lattice site including the vacant state.

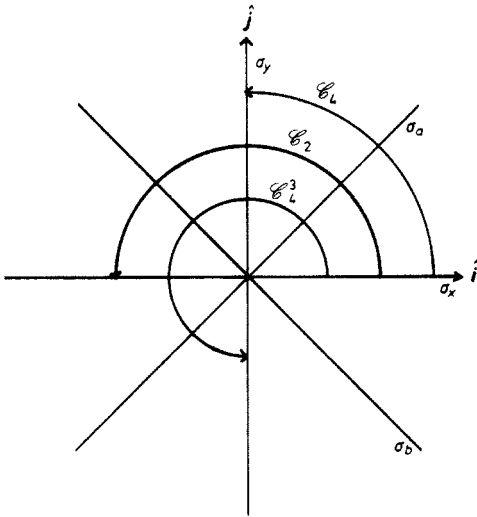


Figure 2. The operators of group \mathcal{C}_{4v} on molecular states. The rotations \mathcal{C}_4 , \mathcal{C}_2 and \mathcal{C}_4^3 are denoted by directed arcs of a circle. Reflections σ_x , σ_y , σ_a and σ_b about axes are indicated by labels attached to the axes.

In terms of these groups we have the following special cases:

- (i) $w = u = 0$, $J_1 = z_1 = \epsilon_1/2$, $J_2 = z_2 = \epsilon_2/2$, $\mu = 8(J_1 + J_2)$. \mathcal{H} is invariant under $\tilde{\mathcal{F}}_2 \otimes \mathcal{S}_5$ and we have a five-state Potts model.
- (ii) $w = 0$, $J_1 = z_1$, $J_2 = z_2$. \mathcal{H} is invariant under $\tilde{\mathcal{F}}_2 \otimes \mathcal{S}_4$ and we have a four-state Potts model with respect to the molecular states. This could be called a 'dilute four-state Potts model'.
- (iii) $w = 0$. \mathcal{H} is invariant under $\tilde{\mathcal{F}}_2 \otimes \mathcal{C}_{4v}$ and we have, as indicated above, a five-state analogue of the Blume–Emery–Griffiths model.

In the general case the symmetry group is further reduced to the eight-order subgroup G of $\tilde{\mathcal{S}}_2 \otimes \mathcal{C}_{4v}$ given by $G = \{(\tilde{\text{I}}), (\tilde{\text{I}}C_2), (\tilde{\sigma}C_4), (\tilde{\sigma}C_4^3), (\tilde{\sigma}\sigma_x), (\tilde{\sigma}\sigma_y), (\tilde{\text{I}}\sigma_a), (\tilde{\text{I}}\sigma_b)\}$. This group is isomorphic to \mathcal{C}_{4v} .

3. Landau theory

Let $p(\mathbf{r}; s)$ be the probability that the lattice site located at vector position \mathbf{r} has a molecule (or vacancy) specified by the state vector s . Clearly for each \mathbf{r}

$$p(\mathbf{r}; \hat{i}) + p(\mathbf{r}; -\hat{i}) + p(\mathbf{r}; \mathbf{0}) + p(\mathbf{r}; \hat{j}) + p(\mathbf{r}; -\hat{j}) = 1 \tag{3.1}$$

and a general state of the system needs $4N$ probabilities for complete specification. In the spirit of Landau theory we impose homogeneity within sublattices so that $p(\mathbf{r}; s) = p_\alpha(s)$ for every α site and $p(\mathbf{r}; s) = p_\beta(s)$ for every β site. We now have eight independent probabilities, in terms of which we define the independent order parameters

$$\rho = \frac{1}{2}\{p_\alpha(\hat{i}) + p_\alpha(-\hat{i}) + p_\alpha(\hat{j}) + p_\alpha(-\hat{j}) + p_\beta(\hat{i}) + p_\beta(-\hat{i}) + p_\beta(\hat{j}) + p_\beta(-\hat{j})\} \tag{3.2a}$$

$$\theta = \frac{1}{2}\{p_\alpha(\hat{i}) + p_\alpha(-\hat{i}) + p_\beta(\hat{i}) + p_\beta(-\hat{i}) - p_\alpha(\hat{j}) - p_\alpha(-\hat{j}) - p_\beta(\hat{j}) - p_\beta(-\hat{j})\} \tag{3.2b}$$

$$\xi_1 = \frac{1}{2}\{p_\alpha(\hat{i}) + p_\beta(\hat{i}) - p_\alpha(-\hat{i}) - p_\beta(-\hat{i})\} \tag{3.2c}$$

$$\xi_2 = \frac{1}{2}\{p_\alpha(\hat{j}) + p_\beta(\hat{j}) - p_\alpha(-\hat{j}) - p_\beta(-\hat{j})\} \tag{3.2d}$$

$$\psi = \frac{1}{2}\{p_\alpha(\hat{i}) + p_\alpha(-\hat{i}) + p_\alpha(\hat{j}) + p_\alpha(-\hat{j}) - p_\beta(\hat{i}) - p_\beta(-\hat{i}) - p_\beta(\hat{j}) - p_\beta(-\hat{j})\} \tag{3.3a}$$

$$\phi = \frac{1}{2}\{p_\alpha(\hat{i}) + p_\alpha(-\hat{i}) + p_\beta(\hat{j}) + p_\beta(-\hat{j}) - p_\alpha(\hat{j}) - p_\alpha(-\hat{j}) - p_\beta(\hat{i}) - p_\beta(-\hat{i})\} \tag{3.3b}$$

$$\gamma_1 = \frac{1}{2}\{p_\alpha(\hat{i}) + p_\beta(-\hat{i}) - p_\beta(\hat{i}) - p_\alpha(-\hat{i})\} \tag{3.3c}$$

$$\gamma_2 = \frac{1}{2}\{p_\alpha(\hat{j}) + p_\beta(-\hat{j}) - p_\beta(\hat{j}) - p_\alpha(-\hat{j})\}. \tag{3.3d}$$

It is not difficult to show that, in terms of these order parameters, the probability weight function $p(\mathbf{r}; s)$ is given by

$$\begin{aligned} p(\mathbf{r}, s) = & \frac{1}{3} \left\{ 1 + 2 \cos\left(\frac{2\pi\hat{i} \cdot s}{3}\right) \cos\left(\frac{2\pi\hat{j} \cdot s}{3}\right) \right\} \\ & - \left(\frac{\rho}{6}\right) \left\{ 1 + 5 \cos\left(\frac{2\pi\hat{i} \cdot s}{3}\right) \cos\left(\frac{2\pi\hat{j} \cdot s}{3}\right) \right\} - \left(\frac{\theta}{6}\right) \left\{ \cos\left(\frac{2\pi\hat{i} \cdot s}{3}\right) - \cos\left(\frac{2\pi\hat{j} \cdot s}{3}\right) \right\} \\ & + \left(\frac{\xi_1}{\sqrt{3}}\right) \sin\left(\frac{2\pi\hat{i} \cdot s}{3}\right) + \left(\frac{\xi_2}{\sqrt{3}}\right) \sin\left(\frac{2\pi\hat{j} \cdot s}{3}\right) - \cos\left(\frac{\pi[\hat{i} + \hat{j}] \cdot \mathbf{r}}{l}\right) \\ & \times \left[\frac{\psi}{6} \left\{ 1 + 5 \cos\left(\frac{2\pi\hat{i} \cdot s}{3}\right) \cos\left(\frac{2\pi\hat{j} \cdot s}{3}\right) \right\} + \left(\frac{\phi}{6}\right) \left\{ \cos\left(\frac{2\pi\hat{i} \cdot s}{3}\right) - \cos\left(\frac{2\pi\hat{j} \cdot s}{3}\right) \right\} \right. \\ & \left. - \left(\frac{\gamma_1}{\sqrt{3}}\right) \sin\left(\frac{2\pi\hat{i} \cdot s}{3}\right) - \left(\frac{\gamma_2}{\sqrt{3}}\right) \sin\left(\frac{2\pi\hat{j} \cdot s}{3}\right) \right]. \tag{34} \end{aligned}$$

We are concerned with the transformations of the order parameters under the elements of the groups G , $\tilde{\mathcal{S}}_2 \otimes \mathcal{C}_{4v}$, $\tilde{\mathcal{S}}_2 \otimes \mathcal{S}_4$ and $\tilde{\mathcal{S}}_2 \otimes \mathcal{S}_5$. The generators of these groups are as

follows:

$$G: \{(\tilde{I}\sigma_a), (\tilde{\sigma}\sigma_x)\}$$

$$\tilde{\mathcal{S}}_2 \otimes \mathcal{C}_{4v}: \{(\tilde{I}\sigma_a), (\tilde{\sigma}\sigma_x), (\tilde{I}\sigma_x)\}$$

$$\tilde{\mathcal{S}}_2 \otimes \mathcal{S}_4: \{(\tilde{I}\sigma_a), (\tilde{\sigma}\sigma_x), (\tilde{I}\sigma_x), (\tilde{I}\tau)\}$$

$$\tilde{\mathcal{S}}_2 \otimes \mathcal{S}_5: \{(\tilde{I}\sigma_a), (\tilde{\sigma}\sigma_x), (\tilde{I}\sigma_x), (\tilde{I}\tau), (\tilde{I}, \nu)\}$$

where τ interchanges the states \hat{i} and \hat{j} leaving $\mathbf{0}$, $-\hat{i}$ and $-\hat{j}$ unchanged and ν interchanges $-\hat{j}$ and $\mathbf{0}$ leaving \hat{i} , $-\hat{i}$ and \hat{j} unchanged. The effect of these generators on the order parameters is given in table 1. We denote the irreducible representations of

Table 1. The transformations of the order parameters by the generators of the symmetry groups.

	$(\tilde{I}\sigma_a)$	$(\tilde{\sigma}\sigma_x)$	$(\tilde{\sigma}I)$	$(\tilde{I}\tau)$	$(\tilde{I}\nu)$
$\rho^{-\frac{4}{5}}$	$\rho^{-\frac{4}{5}}$	$\rho^{-\frac{4}{5}}$	$\rho^{-\frac{4}{5}}$	$\rho^{-\frac{4}{5}}$	$-\frac{1}{4}(\rho^{-\frac{4}{5}}) + \frac{1}{4}\theta + \frac{1}{2}\xi_2$
θ	$-\theta$	θ	θ	$\xi_2 - \xi_1$	$\frac{5}{4}(\rho^{-\frac{4}{5}}) + \frac{3}{4}\theta - \frac{1}{2}\xi_2$
ξ_1	ξ_2	ξ_1	ξ_1	$\frac{1}{2}(\xi_1 + \xi_2 - \theta)$	ξ_1
ξ_2	ξ_1	$-\xi_2$	ξ_2	$\frac{1}{2}(\xi_1 + \xi_2 + \theta)$	$\frac{5}{4}(\rho^{-\frac{4}{5}}) - \frac{1}{4}\theta + \frac{1}{2}\xi_2$
ψ	ψ	$-\psi$	$-\psi$	ψ	$-\frac{1}{4}\psi + \frac{1}{4}\phi + \frac{1}{2}\gamma_2$
ϕ	$-\phi$	$-\phi$	$-\phi$	$\gamma_2 - \gamma_1$	$\frac{5}{4}\psi + \frac{3}{4}\phi - \frac{1}{2}\gamma_2$
γ_1	γ_2	$-\gamma_1$	$-\gamma_1$	$\frac{1}{2}(\gamma_1 + \gamma_2 - \phi)$	γ_1
γ_2	γ_1	γ_2	$-\gamma_2$	$\frac{1}{2}(\gamma_1 + \gamma_2 + \phi)$	$\frac{5}{4}\psi - \frac{1}{4}\phi + \frac{1}{2}\gamma_2$

\mathcal{C}_{4v} (and G) by the standard notation $\{A_1, A_2, B_1, B_2, E\}$ (see e.g. Kilpatrick 1948) and the irreducible representations of $\tilde{\mathcal{S}}_2$ by $\{\tilde{A}, \tilde{B}\}$. The one-dimensional symmetric representation of \mathcal{S}_4 is denoted by A' and the three-dimensional irreducible representation whose characters are given by the number of one-cycles minus one is denoted by F. Similarly we denote the four-dimensional irreducible representation of \mathcal{S}_5 whose characters are given by the number of one-cycles minus one by D. The way in which the order parameters give irreducible representations of the symmetry groups is shown in table 2. It will be seen that the parameter ρ , given by equation (3.2a), is the molecular number density M/N . Except in the special case (i) of § 2, where the symmetry group is

Table 2. The irreducible representations of the symmetry groups given by the order parameters.

	G	$\tilde{\mathcal{S}}_2 \otimes \mathcal{C}_{4v}$	$\tilde{\mathcal{S}}_2 \otimes \mathcal{S}_4$	$\tilde{\mathcal{S}}_2 \otimes \mathcal{S}_5$
$\rho^{-\frac{4}{5}}$	A_1	$\tilde{A} \otimes A_1$	$\tilde{A} \otimes A'$	$\tilde{A} \otimes D$
θ	B_1	$\tilde{A} \otimes B_1$	$\tilde{A} \otimes F$	
ξ_1	E	$\tilde{A} \otimes E$		
ξ_2				
ψ	B_2	$\tilde{B} \otimes A_1$	$\tilde{B} \otimes A'$	$\tilde{B} \otimes D$
ϕ	A_2	$\tilde{B} \otimes B_1$	$\tilde{B} \otimes F$	
γ_1	E	$\tilde{B} \otimes E$		
γ_2				

$\mathcal{P}_2 \otimes \mathcal{P}_5$ this parameter corresponds to the one-dimensional symmetric representation. As in most fluid systems ρ is not an order parameter in the Landau sense; there does not exist a critical density ρ_c such that $(\rho - \rho_c) = 0$ for all temperatures above a critical temperature T_c . The exception to this comment concerning fluid systems is, of course, the simple lattice gas, which in the grand canonical distribution has the hole-particle symmetry arising from the equivalent Ising model. In that case if the chemical potential μ is fixed at the critical value μ_c then the parameter $(\rho - \frac{1}{2})$ remains equal to zero down to the critical temperature at which a second-order phase separation into vapour and liquid phases occurs. We show in § 5 that, within the first-order mean-field approximation of Guggenheim and McGlashan (1951), this system exhibits similar symmetry properties, except that here the curve of approach to the critical point in the $\mu - T$ plane is of the form $\mu = \mu^*(T)$, where $\mu^*(T)$ is not a constant. This symmetry is a product of a particular classical approximation method and is not evident from Landau theory.

The order parameters θ , ξ_1 and ξ_2 , given by equations (3.2b)–(3.2d), are all zero in the high-temperature disordered phase. They are related to orientational ordering of the molecules; θ distinguishes between molecules aligned in the $\pm \hat{i}$ direction and those aligned in the $\pm \hat{j}$ direction and ξ_1 and ξ_2 correspond to the occurrence of ‘spin moments’ in the \hat{i} and \hat{j} directions respectively. It is clear from table 1 that, in the general case and in the special case (iii) ($w = 0$), the irreducible representations $\{\theta\}$ and $\{\xi_1, \xi_2\}$ yield no third-order invariants. The transitions to the orientationally ordered states, if they occur, are predicted by Landau theory to be second order. In the special case (ii) ($J_1 = z_1, J_2 = z_2, w = 0$) the irreducible representation $\{\theta, \xi_1, \xi_2\}$ yields the third-order invariant $\theta(\xi_1^2 - \xi_2^2)$ and here the prediction for a possible phase transition is that it would be first order. In the special case (i) the symmetry group is $\mathcal{P}_2 \otimes \mathcal{P}_5$. The parameter $(\rho - \frac{4}{3})$ is now zero in the high-temperature disordered phase and the irreducible representation $\{(\rho - \frac{4}{3}), \theta, \xi_1, \xi_2\}$ yields the third-order invariant $2\theta(\xi_1^2 - \xi_2^2) + (\rho - \frac{4}{3})(\theta^2 + 2\xi_1^2 + 2\xi_2^2) - 5(\rho - \frac{4}{3})^3$. Again a possible phase transition is predicted to be first order by Landau theory. The order parameters ψ , ϕ , γ_1 and γ_2 given by equations (3.3) are all zero in the high-temperature disordered phase. They are related to sublattice ordering of the molecules; ψ measures the difference of molecular number density on the two sublattices and ϕ , γ_1 and γ_2 are related to differences of occupations of particular molecular orientations on the sublattices. It is clear that every possible phase transition to a sublattice-ordered state is predicted to be second order.

It is necessary at this point to emphasise the limitation of Landau theory in two respects. (i) It gives guidance only in relation to *possible* phase transitions. It does not predict that such phase transitions will *necessarily* occur. (ii) It is not infallible in its predictions, which are always those of mean-field theory. An example of this latter weakness is provided by the q -state Potts model. Here mean-field theory predicts a first-order phase transition for $q > 2$ (Mittag and Stephen 1974) in the case of only nearest-neighbour coupling. Baxter (1973) has, however, shown rigorously that the transition in such a model on a two-dimensional quadratic lattice is first-order only for $q > 4$, it being of higher order for $q \leq 4$.

The value of Landau symmetry theory is also twofold. (a) It provides an elegant way of deriving the predictions of mean-field theory without detailed calculations using a particular approximation method. (ii) It gives good guidance with respect to the symmetry properties of the Hamiltonian. This can be particularly useful in the initial stages of group renormalisation calculations (see e.g. Schick and Griffiths 1977, Young and Lavis 1979).

4: The vapour–liquid phase transition

To eliminate the complications arising from orientational ordering we set $z_1 = z_2 = 0$ (ensuring that θ remains equal to zero) and $J_1 = J_2 = 0$ (ensuring that ξ_1 and ξ_2 remain equal to zero). We are left with four energy parameters: w the bonding energy, ϵ_1 and ϵ_2 the first- and second-neighbour energies and u the four-molecule energy. With these energies the spectrum of the single-square effective Hamiltonian \mathcal{H}_\square has ten levels. These we denote by $[n, i]$, where n is the number of occupied sites ($n = 0, 1, 2, 3, 4$) and i distinguishes between the different non-equivalent occupations corresponding to a particular value of n . Let $\epsilon[n, i]$ be the value of \mathcal{H}_\square when the square is in level $[n, i]$ and let $\omega[n, i]$ be the degeneracy of the level. In table 3 we list the possible configurations $[n, i]$ together with their values of $\epsilon[n, i]$ and $\omega[n, i]$. It is clear that it is possible to occupy every square of the lattice by identical configurations corresponding to any one of the levels $[n, i]$. These ten configurations therefore represent possible groundstates of the system. The most stable groundstate will be that which corresponds to the lowest value of $\epsilon[n, i]$ and the pressure of the system in configuration $[n, i]$ at $T = 0$ is given by $P = -\epsilon[n, i]/l^2$.

Since this model is intended to simulate the behaviour of the water system, we impose conditions on the energy parameters in order to ensure that the stable groundstates reflect our intentions. Clearly, for large negative chemical potentials, state $[0, 1]$ is the stable groundstate and we identify this with the vapour phase. At the other extreme for large positive chemical potentials a fully occupied state ($n = 4$) will be most stable. In order to ensure that this is state $[4, 1]$, the fully bonded structure analogous to close packed ice, we need simply to impose the condition

$$w < 0. \quad (4.1)$$

This automatically ensures not only that $[4, 1]$ is more stable than $[4, 2]$ and $[4, 3]$ but that $[2, 1]$ is more stable than $[2, 2]$ and $[3, 1]$ is more stable than $[3, 2]$. Configuration $[2, 1]$ is our analogue for the ordinary low density ice structure. For it to be more stable than configuration $[2, 3]$ we must have

$$2(w + \epsilon_2) < \epsilon_1. \quad (4.2)$$

In order for there to be a range of chemical potentials, corresponding to positive pressures, for which configuration $[2, 1]$ is more stable than either $[0, 1]$ or $[4, 1]$ we must have

$$0 < 2\epsilon_1 + u. \quad (4.3)$$

In addition we wish to exclude the possibility of stability ranges for configurations $[1, 1]$ and $[3, 1]$. This is achieved if

$$w + \epsilon_2 < 0 \quad (4.4)$$











and

$$w + \epsilon_2 + u < 0 \quad (4.5)$$

respectively. Finally, to complete the analogy with water, we impose the condition that there is a range of pressures such that along an isobar in this range in the ρ - T plane the density has a maximum. A sufficient condition for this to be the case can be derived by considering small perturbations on the open ground state $[2, 1]$. We find that

$$0 < \epsilon_1 + u. \quad (4.6)$$

Table 3. Molecules are denoted by full circles and vacant sites by open circles. A bond is represented by a double line.

Configuration	$\epsilon[n, i]$	$\omega[n, i]$	
[0, 1]		0	1
[1, 1]		$-\frac{1}{4}\mu$	16
[2, 1]		$w + \epsilon_2 - \mu/2$	16
[2, 2]		$\epsilon_2 - \mu/2$	16
[2, 3]		$\frac{1}{2}\epsilon_1 - \mu/2$	64
[3, 1]		$w + \epsilon_1 + \epsilon_2 - 3\mu/4$	128
[3, 2]		$\epsilon_1 + \epsilon_2 - 3\mu/4$	128
[4, 1]		$2w + 2\epsilon_1 + 2\epsilon_2 + u - \mu$	64
[4, 2]		$w + 2\epsilon_1 + 2\epsilon_2 + u - \mu$	128
[4, 3]		$2\epsilon_1 + 2\epsilon_2 + u - \mu$	64

When all these conditions are satisfied we have:

Configuration [0, 1] is stable if $\mu < \mu_0$, $P = 0$;

Configuration [2, 1] is stable if $\mu_0 < \mu < \mu_1$, $0 < P < P_1$, with a density maximum along isobars in the range $P_2 < P < P_1$;

Configuration [4, 1] is stable if $\mu_1 < \mu$, $P_1 < P$, where

$$\mu_0 = 2(w + \epsilon_2) \quad (4.7a)$$

$$\mu_1 = 2(w + \epsilon_2 + 2\epsilon_1 + u) \quad (4.7b)$$

$$P_1 = (2\epsilon_1 + u)/l^3 \quad (4.7c)$$

$$P_2 = \epsilon_1/l^2. \quad (4.7d)$$

We now investigate the possibility of a vapour-liquid phase transition using the approximation method of Guggenheim and McGlashan (1951), based on a square of sites. We divide the lattice into $N/2$ squares of sites, with sites but not nearest-neighbour pairs in common. This means that, in terms of the formulation given for the Hamiltonian in § 2, we are considering a distribution of molecules only with respect to either squares of type A or type B. This effectively removes the distinction between α and β sublattices and eliminates the possibility of sublattice ordering; the parameters ψ , ϕ , γ_1 and γ_2 remain equal to zero. This means that the molecular ordering configurations of the types described above for the ground states can occur only as forms of short-range ordering. In the case for example of configuration [2, 1], where the perfect ground state would entail A squares bonded from the top right to the bottom left with B squares bonded from the top left to the bottom right or conversely, our method is equivalent to averaging over the two arrangements. Since we are considering only vapour and liquid phases, where for the latter we expect uncorrelated regions of ordering of the types exhibited by the ground states, the method is satisfactory.

The details of the derivation of the thermodynamic equations are given in the Appendix. We find that a state of the system at fixed μ and T can be expressed in terms of a parameter Λ , which is related to the probability p_n that the basic square of sites is occupied by exactly n molecules, for $n = 0, 1, 2, 3, 4$, by the equations

$$p_1/p_0 = 4\Lambda c(T) \quad (4.8a)$$

$$p_2/p_0 = 6\Lambda^2 b(T) \quad (4.8b)$$

$$p_3/p_0 = 4\Lambda^3 c(T) \quad (4.8c)$$

$$p_4/p_0 = \Lambda^4 \{1 + v(T)\}. \quad (4.8d)$$

Where

$$v(T) = \exp(-2u/kT) - 1 \quad (4.9a)$$

$$c(T) = \sqrt{2} \exp[(\epsilon_1 + \epsilon_2)/kT] [1 + \exp(-2w/kT)]^{-1/2} \quad (4.9b)$$

$$b(T) = \frac{2}{3}c^2(T) \exp(-\epsilon_1/kT) + \frac{1}{3} \exp(2\epsilon_1/kT). \quad (4.9c)$$

The molecular number density ρ , the chemical potential μ and the pressure P are related to the parameter Λ by the equations

$$\rho = \frac{1}{4} \sum_n n p_n = \frac{f(T; \Lambda^{-1}) + \Lambda^2 v(T)}{f(T; \Lambda^{-1}) + f(T; \Lambda) + \Lambda^2 v(T)} \quad (4.10)$$

$$\mu = g(T; \Lambda) \quad (4.11)$$

$$Pl^2 = h(T; \Lambda) \quad (4.12)$$

where

$$f(T; \Lambda) = c(T)\Lambda + 3b(T) + 3c(T)\Lambda^{-1} + \Lambda^{-2} \quad (4.13)$$

$$g(T; \Lambda) = kT \ln \left[\frac{c^2(T)f(T; \Lambda)\Lambda^2}{4f(T; \Lambda^{-1}) + \Lambda^2v(T)} \right] \quad (4.14)$$

and

$$h(T; \Lambda) = \frac{1}{2}kT \ln \left[\frac{f^2(T; \Lambda)\Lambda^2}{f(T; \Lambda) + f(T; \Lambda^{-1}) + \Lambda^2v(T)} \right]. \quad (4.15)$$

The thermodynamic potential Φ per site associated with the grand canonical distribution is given by

$$\Phi(\mu, T; \Lambda) = \rho\{g(T; \Lambda) - \mu\} - h(T; \Lambda). \quad (4.16)$$

Equation (4.10) can be regarded as the definition of ρ in terms of Λ and, since

$$\rho \partial g / \partial \Lambda = \partial h / \partial \Lambda \quad (4.17)$$

equation (4.11) is the equilibrium condition for Λ at constant μ and T obtained by minimising Φ . Equation (4.12) is then given by

$$\Phi_{\min}(\mu, T) = -Pl^2. \quad (4.18)$$

We now investigate the possibility of the existence of pairs of solutions $\{\Lambda, 1/\Lambda\}$ of equation (4.11). At the outset we prove that if such a pair exists then the members of the pair represent minima of the potential Φ of equal depth. This follows from the equation

$$\begin{aligned} Pl^2 = & \frac{1}{2}kT \ln[v(T) + \Lambda^2f(T; \Lambda) + \Lambda^{-2}f(T; \Lambda^{-1})] \\ & + \mu - \frac{1}{2}kT \ln\{\{\exp(\mu/kT) + c^2(T)\Lambda^2/4\} \\ & \times [\exp(\mu/kT) + c^2(T)/(4\Lambda^2)]\} \end{aligned} \quad (4.19)$$

which has been derived from equations (4.11) and (4.12). The right-hand side of equation (4.19) is symmetric under the mapping $\Lambda \leftrightarrow 1/\Lambda$, and it follows that if Λ and $1/\Lambda$ satisfy equation (4.11) then the equilibrium situation is one of phase coexistence. The condition for the existence of this pair of solutions can now be derived from equation (4.11). Following the procedure of Lavis (1975) we define the new variable χ by the equation

$$\Lambda = (1 + \sin \chi) / \cos \chi \quad (-\pi/2 \leq \chi \leq \pi/2) \quad (4.20)$$

and we look for a pair of solutions $\pm\chi$ where, from equation (4.11), χ must be a solution of

$$\Psi(T; \cos \chi) = 0 \quad (4.21)$$

where

$$\Psi(T; y) = B_0(T) + B_1(T)y + B_2(T)y^2 + B_3(T)y^3 \quad (4.22)$$

$$B_0(T) = 4c^2(T) \quad (4.23a)$$

$$B_1(T) = 12b(T)c(T) \quad (4.23b)$$

$$B_2(T) = 4c^2(T) + 9b^2(T) - 1 - v(T) \quad (4.23c)$$

$$B_3(T) = c(T)[6b(T) - 2 - v(T)]. \quad (4.23d)$$

On physical grounds our requirements are that: (i) $\Psi(T; y)$ should have no root in the range $[0, 1]$ at high temperatures; (ii) $\Psi(T; y)$ should have at most one root in the range $[0, 1]$; (iii) if a root of $\Psi(T; y)$ appears in the range $[0, 1]$ at a temperature T_c then it should make its appearance at $y = 1$; (iv) $\Psi(T; y)$ should have a root in the range $[0, 1]$ at low temperatures. It is clear that condition (i) is satisfied since as T tends to infinity $b(T) \sim c(T) \sim 1$, $v(T) \sim 0$ and $\Psi(T; y) \sim 4(1+y)^3$. Now $B_0(T) > 0$ and $B_1(T) > 0$ for all $T > 0$. Since $9b^2(T)$ contains the term $\exp(4\epsilon_1/kT)$ (see equation (4.9c)) and we have imposed the condition (4.3), it is also the case that $B_2(T) > 0$ for $T > 0$. Thus we see that $\Psi(T; y)$ has at most one positive root, and this if and only if $B_3(T) < 0$. At high temperatures $B_3(T) > 0$ and if T_1 is the temperature at which $B_3(T) = 0$ then $\Psi(T_1; 1) > 0$. Conditions (ii) and (iii) are satisfied. To satisfy condition (iv) we must ensure that $B_3(T)$ is negative at low temperatures and that it dominates $B_2(T)$, $B_1(T)$ and $B_0(T)$ so that $\Psi(T; 1)$ is negative. Now if $c(T)$ tends to infinity as T tends to zero then we must have $u < 0$, otherwise the negative part of $B_3(T)$ is dominated by $B_0(T)$. In this case for $B_3(T)$ to be negative as T tends to zero we must have $-2u > 2\epsilon_1$, which violates condition (4.6). It is equally clear that, if $c(T)$ remains finite as T tends to zero, then the negative part of $B_3(T)$ is dominated by $B_2(T)$. We are left with the condition that $c(T)$ tends to zero as T tends to zero. Now we have

$$u > 0 \quad (4.24)$$

$$\epsilon_1 < 0. \quad (4.25)$$

The function $c(T)$ will tend to zero in such a way that the negative part of $B_3(T)$ dominates $B_2(T)$, $B_1(T)$ and $B_0(T)$ if

$$-\epsilon_1 > 3(w + \epsilon_2) \quad (4.26)$$

$$w + \epsilon_2 > 3\epsilon_1. \quad (4.27)$$

We now have two sets of conditions on our energy parameters (4.1)–(4.6) and (4.24)–(4.27). Of these conditions, (4.2), (4.4), (4.6) and (4.26) are automatically implied by the remaining six.

In our numerical calculations we consider three cases: (i) $\epsilon_2/w = 0.5$, $u/w = -1.1$, (ii) $\epsilon_2/w = 0.6$, $u/w = -1.38$, (iii) $\epsilon_2/w = 0.8$, $u/w = -1.8$. It will be observed that case (iii) corresponds to condition (4.5) becoming an equality. This means that at the pressure P_1 or the chemical potential μ_1 the configurations $[2, 1]$, $[3, 1]$ and $[4, 1]$ are all equally stable at $T = 0$. This has a negligible effect on the behaviour of the system, since in any case the ground state at this special value of the pressure or chemical potential would be a mixture of configurations $[2, 1]$ and $[4, 1]$. In figure 3 we show curves of the reduced critical temperature $kT_c/|w|$ as a function of ϵ_1/w for cases (i)–(iii). The lower endpoint of the curves corresponds to the violation of condition (4.27) and the upper endpoint to the violation of condition (4.3). To satisfy both conditions we need to choose values of ϵ_1/w with the ranges of these curves. This we do for cases (ii) and (iii) by choosing respectively the values $\epsilon_1/w = 0.65$ and $\epsilon_1/w = 0.85$. To emphasise the fact that condition (4.27) is a sufficient, but not necessary, condition for the existence of a critical temperature we choose for case (i) the value $\epsilon_1/w = 0.5$, which corresponds to the lower endpoint of the curve in figure 3, when condition (4.27) becomes an equality.

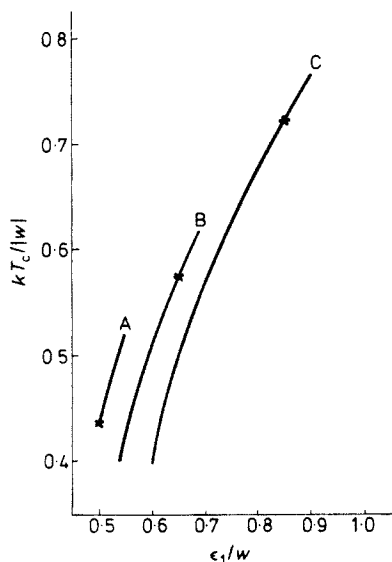


Figure 3. The reduced critical temperature $kT_c/|w|$ plotted against ϵ_1/w for: A $\epsilon_2/w = 0.5$, $u/w = -1.1$; B $\epsilon_2/w = 0.6$, $u/w = -1.38$; C $\epsilon_2/w = 0.8$, $u/w = -1.8$. The values of ϵ_1/w chosen for computation are indicated by crosses.

A non-zero solution χ_σ to equation (4.21) exists in the temperature range $0 \leq T < T_c$, where T_c is the critical temperature, given as the unique solution of

$$\Psi(T; 1) = 0. \quad (4.28)$$

In the μ - T plane we now have the coexistence curve

$$\mu = \mu_\sigma(T) \equiv g(T; \Lambda_\sigma)$$

where

$$\Lambda_\sigma = (1 + \sin \chi_\sigma) / \cos \chi_\sigma.$$

Along the coexistence curve the pressure is given by

$$P = P_\sigma(T) \equiv h(T; \Lambda_\sigma) / l^2.$$

The densities of the coexistent phases are given by substituting Λ_σ and $1/\Lambda_\sigma$ in equation (4.10). We identify the denser of these phases as the liquid phase with $\rho = \rho_L(T)$ and the less dense as the vapour phase with $\rho = \rho_V(T)$. The critical constants are $\mu_c = \mu_\sigma(T_c)$, $P_c = P_\sigma(T_c)$ and $\rho_c = \rho_L(T_c) = \rho_V(T_c)$. In the μ - T plane the coexistence curve begins at the origin and terminates at the critical point (μ_c, T_c) . We also have, in this plane, the line of symmetry $\mu = \mu_s(T) \equiv g(T; 1)$. Along this curve the pressure is given by $P = P_s(T) \equiv h(T; 1) / l^2$ and the density $\rho = \rho_s(T)$ is given by substituting $\Lambda = 1$ in equation (4.10). In figure 4 we show the coexistence curves for cases (i)–(iii), defined above, in the ρ - T plane. We also show the line of symmetry for case (iii).

5. Asymptotic forms in a neighbourhood of the critical point

For the simple lattice fluid and for a number of other models (Widom and Rowlinson 1970, Widom and Stillinger 1973), a line of symmetry can be defined either (i) as the set of invariant states of a symmetry transformation or (ii) as the line of states for which the

chemical potential in the one-phase region is the analytic continuation of the chemical potential along the transition curve. Not only is there no conflict between these two possible definitions; it can also be shown that, in the density–temperature plane, the line of symmetry is the analytic continuation of the diameter of the two-phase region. It has however been shown by Mulholland (1973) that if, for a general classical model for which no particular symmetry is assumed, the line of symmetry is defined by (iii), then the line of symmetry in the density–temperature plane is no longer the analytical continuation of the two-phase diameter.

Lavis (1975) has shown that for the model of Bell and Lavis (1970), treated by the mean-field method of Guggenheim and McGlashan (1951), there is a line of symmetry defined by (i) above. This coincides neither with a possible line of symmetry defined by (ii) nor, in the density–temperature plane, with the analytic continuation of the two-phase diameter.

For the present model in a neighbourhood of the critical point

$$\Psi(T; 1) \sim \nu(T/T_c - 1) \quad (5.1)$$

where ν is a positive constant, and on the coexistence curve it follows from equation (4.21) that

$$\chi_\sigma^2 \sim -2\nu(T/T_c - 1)d(T_c)/c(T_c) \quad T \leq T_c \quad (5.2)$$

where

$$d(T) = [8c(T) + 6b(T) + v(T) + 2]^{-1}. \quad (5.3)$$

By expanding $\mu_\sigma(T)$ in powers of χ_σ and substituting from (5.2), it may be shown that in a neighbourhood of the critical point

$$\mu_\sigma(T) - \mu_s(T) \sim kT_c\tau(T/T_c - 1)^2 \quad T < T_c \quad (5.4)$$

where

$$\tau = \frac{2}{3}\nu^2 v(T_c)d^3(T_c)/\{c(T_c)[c(T_c) + b(T_c)]\}. \quad (5.5)$$

Similarly from equation (4.10) it may be shown that, for the two-phase diameter $\rho_d(T) = [\rho_L(T) + \rho_V(T)]/2$

$$\rho_d(T) - \rho_s(T) \sim \zeta(T/T_c - 1) \quad T < T_c \quad (5.6)$$

where

$$\zeta = 12\nu v(T_c)d^2(T_c)[c(T_c) + b(T_c)]/c(T_c). \quad (5.7)$$

Again we have a situation where the line of symmetry coincides neither with the analytic continuation of the coexistence curve in the μ – T plane nor with the analytic continuation of the two-phase diameter in the ρ – T plane.

Consider now the curve

$$\mu = \mu^*(T) \equiv \begin{cases} \mu_s(T) & T \geq T_c \\ \mu_\sigma(T) & T \leq T_c \end{cases} \quad (5.8)$$

in the μ – T plane. It is clear from equation (5.4) that this curve is continuous with a continuous gradient at $T = T_c$. Now let us suppose that the system has independent variables μ and T and we fix the chemical potential according to equation (5.8) and lower the temperature through the critical point. In a neighbourhood of the critical

point the thermodynamic potential Φ is given, from equation (4.16), by

$$\Phi(\mu^*(T), T; \chi) \sim \alpha_0(T) + \alpha_1(T)\chi + \alpha_2(T)\chi^2 + \alpha_3(T)\chi^3 + \alpha_4(T)\chi^4 \quad (5.9)$$

where

$$\alpha_0(T) = \rho_s(T)\{\mu_s(T) - \mu^*(T)\} - P_s(T)l^2 \quad (5.10a)$$

and

$$\alpha_1(T) = 2\rho_s(T)\{1 - \rho_s(T)\}\{\mu_s(T) - \mu^*(T)\}. \quad (5.10b)$$

The remaining coefficients can be expanded in power series with respect to $(T/T_c - 1)$ and retaining only the leading terms we have

$$\alpha_2(T) \sim 2kT_c\nu d^2(T_c)(T/T_c - 1) \quad (5.10c)$$

$$\alpha_3(T) \sim -\frac{4}{3}kT_c\nu v(T_c)d^3(T_c)(T/T_c - 1) \quad (5.10d)$$

and

$$\alpha_4(T) \sim \frac{1}{2}kT_c c(T_c)d(T_c). \quad (5.10e)$$

Above the critical point $\alpha_1(T) = 0$, $\alpha_2(T) > 0$ and the potential Φ has a minimum at $\chi = 0$. Below the critical point $\alpha_1(T)$ is of the order of $(T/T_c - 1)^2$, $\alpha_2(T) < 0$ and $\alpha_4(T) > 0$. The potential Φ has a minimum at

$$\chi^2 \sim -\alpha_2(T)/\{2\alpha_4(T)\}$$

which is equivalent to equation (5.2). The system separates by a second-order phase transition into coexistent liquid and vapour phases as it passes through the critical point. This is a classical Landau situation, but it differs in a number of interesting respects from the case of a simple lattice fluid. There we have

$$\mu^* = \mu_\sigma = \mu_s = \mu_c$$

and using the zeroth-order approximation we obtain a potential of the form (5.9) with

$$\chi = (\rho/\rho_c - 1) \quad (5.11a)$$

$$\alpha_0(T) = \frac{1}{2}\{\mu_c - \mu - 2P_s l^2\} \quad (5.11b)$$

$$\alpha_1(T) = \frac{1}{2}(\mu_c - \mu) \quad (5.11c)$$

$$\alpha_2(T) = kT_c(T/T_c - 1) \quad (5.11d)$$

$$\alpha_4(T) = \frac{1}{3}kT_c \quad (5.11e)$$

$$\alpha_{2i+1}(T) = 0 \quad i > 0. \quad (5.11f)$$

The differences between the two cases are therefore:

(i) For the simple lattice fluid the order parameter is the scaled number density. This is true even in higher-order approximations in virtue of the intrinsic hole-particle symmetry of the system. The order parameter in our system is related to the basic lattice group probabilities of our approximation method by equations (4.8) and (4.20). In this sense the symmetry which we have used is less fundamental than that of the simple lattice fluid.

(ii) For the simple lattice fluid, along the curve $\mu = \mu^*$, the potential Φ is an even function of χ , the minimum at $\chi = 0$, for $T > T_c$, becoming a maximum for $T < T_c$. For

our system, since $\alpha_1(T) \neq 0$ for $T < T_c$, $\chi = 0$ is not a stationary point of Φ for $T < T_c$ and the potential is an even function of χ only when $\chi = \chi_\sigma$.

(iii) The critical point in the simple lattice fluid is an isolated point with a second-order transition because μ does not appear in $\alpha_i(T)$ for $i > 0$ and $\alpha_1(T) = 0$ and $\alpha_2(T) = 0$ are lines parallel to the axes in the μ - T plane intersecting at (μ_c, T_c) . In our system μ appears in $\alpha_i(T)$ for $i > 1$, but by choosing $\mu = \mu^*(T)$ we have ensured that $\alpha_1(T) = 0$ passes through the critical point together with $\alpha_2(T) = 0$ and $\alpha_3(T) = 0$, which are tangential to the line $T = T_c$. This is sufficient to make the critical point an isolated second-order transition.

6. Discussion of water-like properties

Part of the purpose of this work has been to investigate the extent to which this lattice model, which incorporates a simple form of directional bonding, is capable of exhibiting some of the anomalous properties associated with the water system. We shall be concerned with five of these properties.

For a range of subcritical pressures the water system has, along an isobar in the liquid state: (i) a maximum in density; (ii) a minimum in the isothermal compressibility κ_T (Eisenberg and Kauzmann 1969, pp 183 and 184 respectively). On the liquid branch of the coexistence curve: (iii) there is a minimum in the isothermal compressibility; (iv) the coefficient of isobaric thermal expansion α_P changes from its normal positive value to a negative value as the temperature is lowered (Rowlinson 1969, p 55); (v) the discontinuous change Δc_P in the constant pressure heat capacity c_P , as the system changes from liquid to vapour, is positive near the liquid-vapour critical temperature but negative at lower temperatures (Eisenberg and Kauzmann 1969, p 69 and 99).

Of course the extent to which our model appears to exhibit water-like properties may well be influenced not only by the form of approximation used but also by the fact that within this approximation we have eliminated the possibility of the occurrence of a

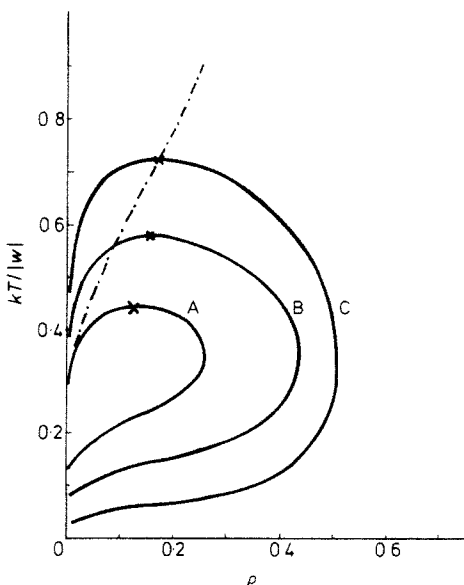


Figure 4. The liquid-vapour coexistence curves in the density-temperature plane for: A $\epsilon_1/w = 0.5$, $\epsilon_2/w = 0.5$, $u/w = -1.1$; B $\epsilon_1/w = 0.65$, $\epsilon_2/w = 0.6$, $u/w = -1.38$; C $\epsilon_1/w = 0.85$, $\epsilon_2/w = 0.8$, $u/w = -1.8$. Critical points are denoted by crosses and the line of symmetry for case C is represented by a chain curve

long-range ordered solid phase. The effect of the latter can clearly be seen in figure 4, where at $T = 0$ vapour-liquid coexistence occurs at zero density. If long-range order were included we should expect from ground state considerations to have two phase transitions; a liquid-solid transition and a solid-vapour transition, both associated with nonzero discontinuities in density. The transition represented in figure 4 would then be metastable. Having recorded these reservations which must necessarily be attached to our calculations, we now discuss our results.

We found, in each of the three cases investigated numerically, that there were clear maxima in the density along isobars at temperatures below the liquid-vapour transition temperature and pressures less than the critical pressure. Isobars in the $\rho-T$ plane are shown in figure 5 for the case $\epsilon_2/w = 0.8$, $u/w = -1.8$, $\epsilon_1/w = 0.85$.³ The liquid-vapour transition temperature was calculated by comparing the values of the chemical potential along the isobars.

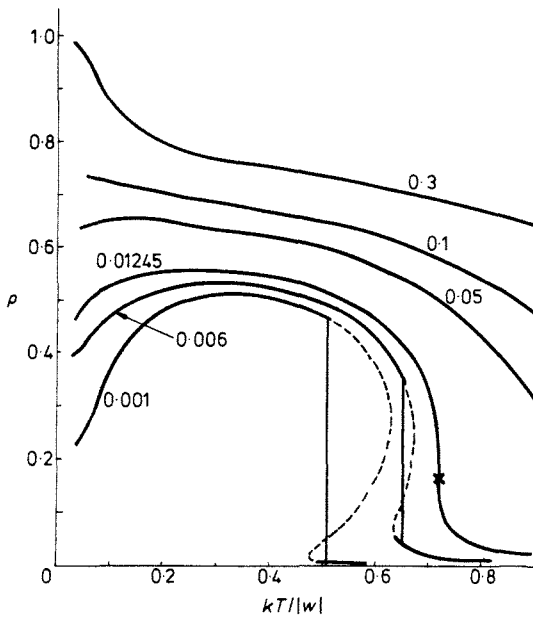


Figure 5. Isobars in the density temperature plane for $\epsilon_1/w = 0.85$, $\epsilon_2/w = 0.8$, $u/w = -1.8$. The isobars are labelled with their values of the reduced pressure $P l^2 / |w| (P_1 l^2 / |w| = 0.1, P_c l^2 / |w| = 0.01245)$. Phase transitions are represented by vertical tie lines and metastable or unstable parts of the curves by broken lines.

The isothermal compressibility κ_T is given by

$$\kappa_T = [\rho(\partial P / \partial \rho)_T]^{-1}. \tag{6.1}$$

We found, again in all three cases, minima in the compressibility along isobars in the liquid state. Examples of this, for the same case as figure 5, are shown in figure 6.

In figure 7 the isothermal compressibility $(\kappa_T)_L$ along the liquid branch of the coexistence curve is shown for all three numerical cases. Minima are exhibited and $(\kappa_T)_L$ diverges to order $(T_c - T)^{-1}$ as T approaches T_c .

The coefficient of isobaric thermal expansion $(\alpha_P)_L$ along the liquid branch of the coexistence curve is given by

$$(\alpha_P)_L = (\kappa_T)_L \frac{dP_\sigma}{dT} - \left(\frac{1}{\rho_L}\right) \frac{d\rho_L}{dT}. \tag{6.2}$$

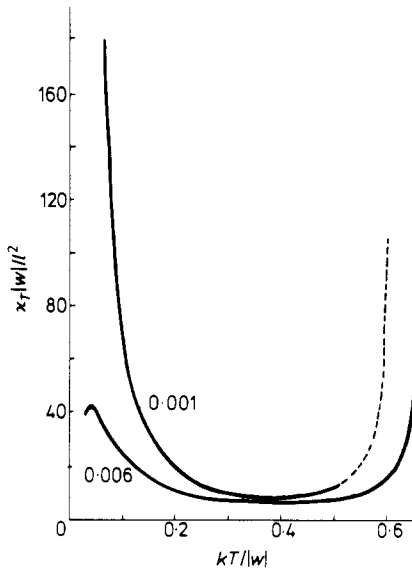


Figure 6. The reduced isothermal compressibility $\kappa_T|w|/l^2$ plotted against reduced temperature along isobars for $\epsilon_1/w = 0.85$, $\epsilon_2/w = 0.8$, $u/w = -1.8$. Curves are labelled with their values of the reduced pressure. Metastable parts of the curves (see figure 5) are represented by broken lines.

This function is shown for all three numerical cases in figure 8. It will be observed that at low temperatures $(\alpha_P)_L$ is negative. As T approaches T_c it diverges to order $(T_c - T)^{-1}$. It has been shown by Lavis (1975) that the discontinuous change Δc_P in the constant pressure heat capacity c_P , as the system changes from liquid to vapour, can be expressed

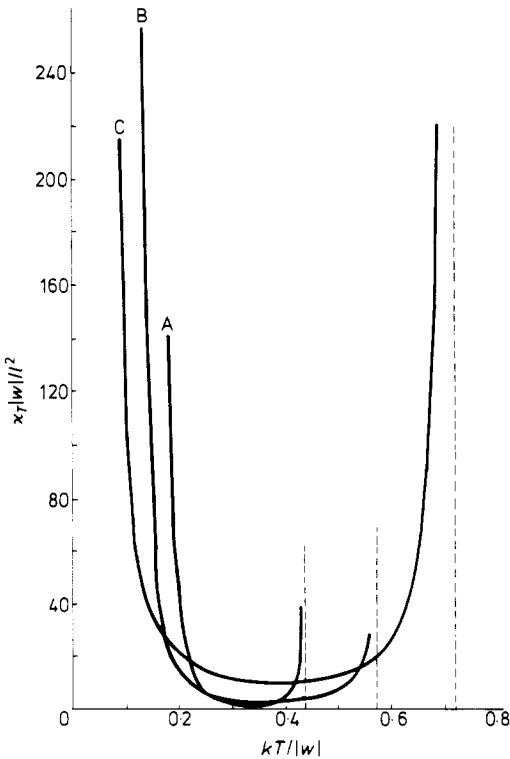


Figure 7. The reduced isothermal compressibility along the liquid branch of the coexistence curve. For case A ($\epsilon_1/w = 0.5$, $\epsilon_2/w = 0.5$, $u/w = -1.1$) the vertical axis is $\kappa_T|w|/(100l^2)$; for case B ($\epsilon_1/w = 0.65$, $\epsilon_2/w = 0.6$, $u/w = -1.38$) the vertical axis is $\kappa_T|w|/(10l^2)$ and for case C ($\epsilon_1/w = 0.85$, $\epsilon_2/w = 0.8$, $u/w = -1.8$) the vertical axis is $\kappa_T|w|/l^2$. The curves tend to infinity as the critical point is approached.

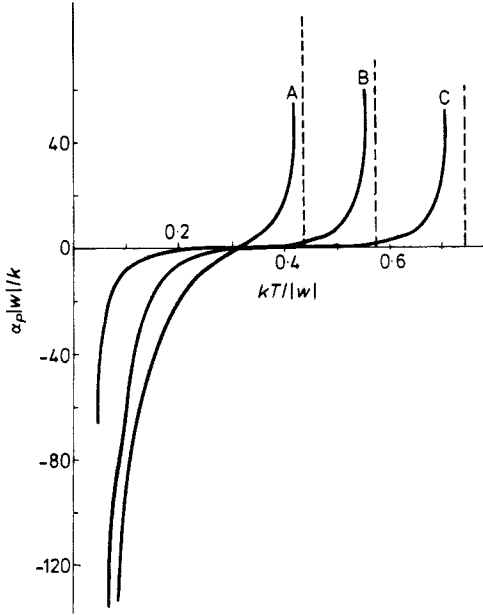


Figure 8. The reduced coefficient of isobaric thermal expansion $\alpha_p|w|/k$ along the liquid branch of the coexistence curve for A $\epsilon_1/w = 0.5$, $\epsilon_2/w = 0.5$, $u/w = -1.1$; B $\epsilon_1/w = 0.65$, $\epsilon_2/w = 0.6$, $u/w = -1.38$; C $\epsilon_1/w = 0.85$, $\epsilon_2/w = 0.8$; $u/w = -1.8$. The curves tend to infinity as the critical point is approached.

in the form

$$\Delta c_P = (c_P)_V - (c_P)_L = \frac{Tl^2}{\rho_L \rho_V} \left[\left(\frac{dP_\sigma}{dT} \right)^2 \{ \rho_L(\kappa_T)_V - \rho_V(\kappa_T)_L \} + 2 \frac{dP_\sigma}{dT} \left\{ \rho_V \frac{d\rho_L}{dT} - \frac{\rho_L}{\rho_V} \frac{d\rho_V}{dT} \right\} + \frac{d^2 P_\sigma}{dT^2} \{ \rho_L - \rho_V \} \right]. \tag{6.3}$$

This function is shown for all three numerical cases in figure 9. It can be shown (Lavis 1975) that Δc_P diverges to infinity as T tends to zero and also as T tends to T_c : in the latter case to the order of $(T_c - T)^{-1/2}$. It follows that negative values of Δc_P can be achieved only by means of a negative minimum. In numerical cases (i) and (ii) there is no evidence for such a minimum, although the possibility does exist, since computation at low temperatures is very uncertain due to machine errors, even with the large computer we employed. In numerical case (ii) there does seem to be some evidence for a negative minimum although there is still a large element of computational uncertainty.

7. Conclusions

We have introduced a lattice model with directional bonding capable of spin and sublattice ordering. We have analysed the behaviour of the fluid phases using a mean-field approximation and shown that, within this approximation, the model exhibits some water-like properties. Landau theory predicts that the transition to sublattice ordering if it occurs will be second order. Since such ordering could correspond to the fluid–solid transition in this model this would be unfortunate for the relationship between the model and the water system. There must however always be serious reservations about the results of classical approximation methods especially in

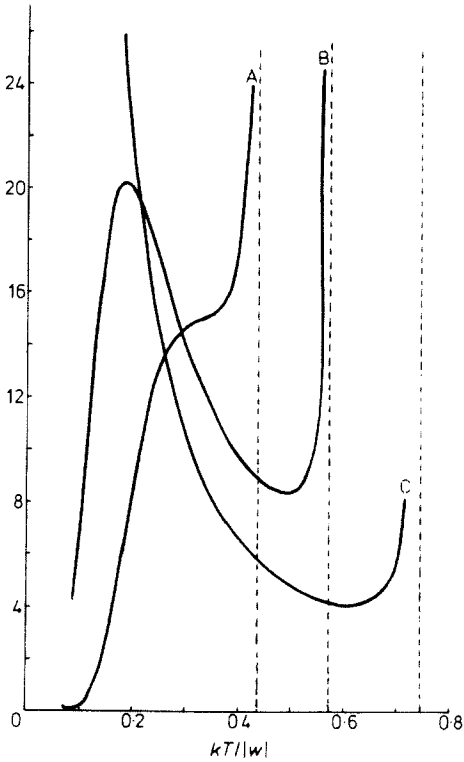


Figure 9. The discontinuous change in the constant pressure heat capacity as the system changes from liquid to vapour. For case A ($\epsilon_1/w = 0.5$, $\epsilon_2/w = 0.5$, $u/w = -1.1$) the vertical axis is $\Delta c_p/k$; for case B ($\epsilon_1/w = 0.65$, $\epsilon_2/w = 0.6$, $u/w = -1.38$) the vertical axis is $\Delta c_p/(2k)$ and for case C ($\epsilon_1/w = 0.85$, $\epsilon_2/w = 0.8$, $u/w = -1.8$) the vertical axis is $\Delta c_p/(4k)$. The curves tend to infinity as the critical point is approached.

two dimensions. A clearer appreciation of the properties of this model should be achieved by means of real space renormalisation calculations on the lines applied to the corresponding triangular lattice model by Young and Lavis (1979) and Southern and Lavis (1979). The present work, especially the Landau analysis, should be regarded as a preliminary to such calculations.

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Appendix: the derivation of equations (4.8)–(4.15)

We consider $N/2$ squares of sites sharing sites but not nearest-neighbour pairs. Let $p[n, i]$ be the probability of a square being occupied by one of the equivalent configurations $[n, i]$ of table 3. Then

$$1 = \sum_{[n,i]} p[n, i] \omega[n, i] \tag{A.1a}$$

$$4\rho = \sum_{[n,i]} np[n, i] \omega[n, i]. \tag{A.1b}$$

In order to compensate for the elimination of half the lattice squares appearing in the Hamiltonian (2.3a), we double the energies $\epsilon[n, i]$ which appear in table 3. We thereby obtain the total energy E for the system, given by

$$E = N \sum_{[n,i]} \epsilon[n, i] p[n, i] \omega[n, i]. \quad (\text{A.2})$$

The thermodynamic potential Φ per site can now be expressed as a function of the set of parameters $\{p[n, i]\}$ and ρ by the equation

$$N\Phi(\mu, T; \{p[n, i]\}, \rho) = -kT \ln \Omega(\{p[n, i]\}, \rho) + E(\{p[n, i]\}). \quad (\text{A.3})$$

The function Ω in the entropy term of equation (A.3) is evaluated using the approximation method of Guggenheim and McGlashan (1951). The calculation is quite standard and follows the same pattern as that for the triangular lattice model of Bell and Lavis (1970) and the body-centred cubic lattice model of Bell (1972). We have

$\ln \Omega(\{p[n, i]\}, \rho)$

$$= N[(1-\rho) \ln(1-\rho) + \rho \ln(\rho/4) - \frac{1}{2} \sum_{[n,i]} \omega[n, i] p[n, i] \ln p[n, i]]. \quad (\text{A.4})$$

Φ is now minimised with respect to $\{p[n, i]\}$ and ρ subject to the constraints imposed by equations (A.1). We obtain the equilibrium conditions

$$p[n, i] = \frac{x^n \exp\{-2\epsilon'[n, i]/kT\}}{\sum_{[n,i]} x^n \omega[n, i] \exp\{-2\epsilon'[n, i]/kT\}} \quad (\text{A.5})$$

and

$$\mu = kT[2 \ln x - \ln\{\rho/4(1-\rho)\}] \quad (\text{A.6})$$

where x is a variable which arises from the use of undetermined multipliers and

$$\epsilon'[n, i] = \epsilon[n, i] + \frac{1}{4} n \mu. \quad (\text{A.7})$$

We defined the probability

$$p_n = \sum_{i(n)} p[n, i] \omega[n, i] \quad (\text{A.8})$$

that a square of sites is occupied by n molecules for $n = 0, 1, 2, 3, 4$ and the variable

$$\Lambda = 4x/c(T) \quad (\text{A.9})$$

where $c(T)$ is given by equation (4.9b). Equations (4.8) now follow from table 3 and equations (A.5) and (A.8). Substituting into equations (A.1) we obtain equation (4.10). From equations (A.6), (A.9) and (4.10) we obtain equation (4.11). Equation (4.12) is finally obtained by substituting into (A.3), giving the minimum value for Φ which, according to equation (4.18), is equal to $-Pl^2$.

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