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Symmetry properties and the two-phase coexistence curve of a two-dimensional bonded lattice fluid

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Abstract. By examining the symmetry properties of a two-dimensional bonded lattice fluid we are able to obtain in a simple way the two-phase coexistence curve and the line of symmetry. We show that, in the density-temperature plane, the line of symmetry, the analytically continued two-phase diameter and the curve on which the chemical potential is equal to the analytic continuation of its values along the coexistence curve are all distinct. These curves intersect at the critical point in nonzero angles. We examine the behaviour of the thermodynamic response functions on the coexistence curve and show that on the high-density branch of the curve the isothermal compressibility and the coefficient of isobaric thermal expansion exhibit anomalies similar to those shown by the water system. We show also that the discontinuous change in the constant pressure heat capacity as the system changes from the high-density to the low-density phase becomes negative below a certain temperature. This again is a characteristic of the water system.

1. Introduction

The main purpose of this work is to extend the studies of the two-dimensional lattice model of Bell and Lavis (1970b, hereafter referred to as BL(b)) by deriving an explicit form for the two-phase coexistence curve, and by investigating the behaviour of the thermodynamic response functions along the branches of this curve. Derivation of the coexistence curve is shown to be comparatively simple once we have obtained a symmetry transformation for the model. This symmetry transformation is a one-to-one mapping between states of the system at the same temperature. We shall show in §2 that all pairs of states under this transformation for which pressure is invariant will also have chemical potential invariant. There will be one such pair for each temperature less than the critical temperature such that the members of the pair are distinct. These two states will represent points on the two branches of the coexistence curve. The line of symmetry of the system is defined to be the set of invariant states under the transformation. Here we show that it coincides neither with the analytically continued two-phase diameter nor with the curve on which the chemical potential is equal to the analytic continuation of its values along the coexistence curve.

In order to obtain some analytic information about the behaviour of the thermodynamic functions along the coexistence curve, we consider their asymptotic forms in the limit as the temperature tends towards absolute zero and in the limit as the temperature tends towards its critical value. In the latter case we obtain the rectilinear diameter law and some of the critical exponents of the model. Since the model is classical, in the sense that there exists in the one-phase region a Taylor expansion in temperature and density

for the Helmholtz free energy about the critical point, these exponents will all take their classical values (Fisher 1964).

The model of BL(b) consists of a two-dimensional triangular lattice system in which the molecules form bonds in such a way that an open honeycomb structure with vacant sites is necessary for the achievement of minimum configurational energy in the assembly. Close packing occurs when the open structure breaks down under the influence of pressure and thermal motion. This situation resembles that occurring in water (see eg Eisenberg and Kauzmann 1969 pp 185–9, Fletcher 1970 pp 73–85). The approximation method used by BL(b) is an extension of the quasi-chemical approximation, using as a basic unit a triangle of nearest-neighbour sites. This was the approximation used by Guggenheim and McGlashan (1951) for a binary mixture. This method allows the molecules to attain only a form of short-range ordering measurable in terms of the different occupational probabilities for the basic triangle of sites. The analogy with the water system can therefore be drawn only with respect to the liquid and vapour states. Isobars were obtained in the density–temperature plane which exhibited one phase transition to a denser state as temperature decreased and which showed a density maximum below the transition temperature. These characteristics parallel those shown by the water system. The work of BL(b) was extended by Lavis (1973) to include a long-range ordered phase realized through a phase transition from a denser short-range ordered phase, the type of phase transition exhibited when water freezes.

The present work is supplementary to that of BL(b) and we shall therefore avoid a complete discussion of the model, referring the reader to the original paper for full details. We consider a triangular lattice of N sites containing ρN molecules, ($0 \leq \rho \leq 1$), there being at most one molecule per site. The (two-dimensional) volume of the lattice is NA_0 , where A_0 is the area per lattice site. We regard each molecule as possessing three bonding directions at 120° to each other. A molecule on a lattice site has two orientational states, referred to as states 1 and 2, in each of which the molecule has bonding directions pointing towards three of the six nearest-neighbour sites. If bonding directions from each of a nearest-neighbour pair of molecules point towards each other, a bond is formed (see figure 1). It is supposed that the interaction energy for pairs of molecules is

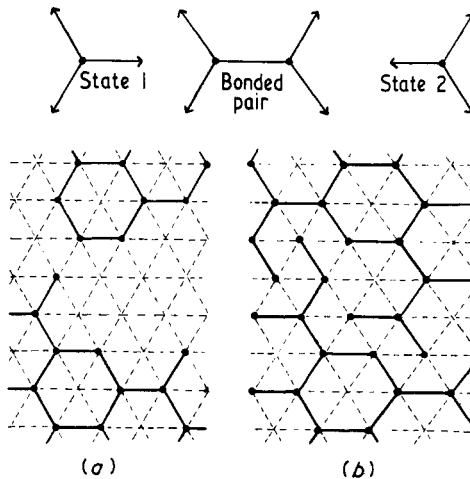


Figure 1. Orientational states of molecules and typical forms of short-range ordering for (a) $\rho \sim \frac{1}{2}$, (b) $\rho \sim \frac{2}{3}$.

confined to nearest-neighbour pairs and is $-\epsilon$ and $-(\epsilon + w)$ for unbonded and bonded pairs respectively, ϵ and w being constant with $\epsilon \geq 0$, $w \geq 0$ and $(\epsilon + w) > 0$.

Let p_i be the probability that a triangle of nearest-neighbour sites is occupied by exactly i molecules for $i = 0, 1, 2, 3$. Then

$$1 = p_0 + p_1 + p_2 + p_3 \quad (1.1a)$$

and

$$\rho = \frac{1}{3}(p_1 + 2p_2 + 3p_3). \quad (1.1b)$$

Now a triangle of nearest-neighbour sites contains at most one bonded pair of molecules. Let p_{iB} be the conditional probability that the triangle of nearest-neighbour sites contains a bonded pair of molecules given that it contains exactly i molecules for $i = 2, 3$. The equilibrium values of the occupational probabilities were calculated in BL(b) by minimization of the Helmholtz free energy. From figure 1, equations (3.9) and (3.10) of BL(b) we have

$$p_{2B} = (1 + 3 e^{-w/kT})^{-1} \quad (1.2a)$$

$$p_{3B} = 3(3 + e^{-w/kT})^{-1} \quad (1.2b)$$

$$p_1 p_3 / p_2^2 = \frac{1}{3} a(T) \quad (1.3a)$$

$$p_0 p_2 / p_1^2 = \frac{1}{3} b(T) \quad (1.3b)$$

where

$$a(T) = 4 e^{(\epsilon - w)/kT} (3 + e^{-w/kT}) / (1 + 3 e^{-w/kT})^2 \quad (1.4a)$$

and

$$b(T) = \frac{1}{4} e^{(\epsilon + w)/kT} (1 + 3 e^{-w/kT}). \quad (1.4b)$$

The degree of short-range molecular ordering is measured in terms of the extent to which molecules will form clusters. We therefore define the short-range order variable z by the equation

$$z = p_2 / p_1. \quad (1.5)$$

Substituting from equations (1.3) and (1.5) into (1.1) we have the equation

$$\rho(b(T) + 2z + z^2) = (1 - \rho)z(1 + 2z + z^2 a(T)) \quad (1.6)$$

which determines the equilibrium value for z at density ρ and temperature T . The variable r of BL(b) is related to the short-range order variable z by the equation

$$r = 2z e^{(\epsilon - w)/kT} / (1 + 3 e^{-w/kT}). \quad (1.7)$$

By substituting from (1.7) into equation (3.15) of BL(b) we see that the Helmholtz free energy f per lattice site is given by

$$f(\rho, T) = -kT[(1 - 2\rho) \ln(1 - \rho) + 2\rho \ln \rho + \rho \ln 2 - 3\rho \ln z - (1 - 3\rho) \ln b(T) + \ln(b(T) + 2z + z^2)]. \quad (1.8)$$

Equations (1.6) and (1.8) determine completely the thermodynamic properties of the model and allow us to obtain the pressure P given by

$$P(\rho, T)A_0 = \rho \left(\frac{\partial f}{\partial \rho} \right)_T - f = kT \ln [(1 - \rho)(b(T) + 2z + z^2) / b(T)] \quad (1.9)$$

and the configurational chemical potential μ given by

$$\begin{aligned}\mu(\rho, T) &= \frac{1}{\rho}(P(\rho, T)A_0 + f(\rho, T)) = \left(\frac{\partial f}{\partial \rho}\right)_T \\ &= -kT \left[2 \ln \left(\frac{\rho}{1-\rho} \right) + 3 \ln \left(\frac{b(T)}{z} \right) + \ln 2 \right].\end{aligned}\quad (1.10)$$

The isobar for $(\epsilon/w) = \frac{1}{4}$ and $PA_0/w = 0.01$ is displayed in figure 3.

2. The line of symmetry and the coexistence curve

We now prove the following theorem: *The one-to-one symmetry transformation $\mathcal{S} : z \rightarrow 1/z$ between states of the system at the same temperature has the property that states which are images under \mathcal{S} will have equal pressures if and only if they have equal chemical potentials.*

Consider the function Y given by

$$Y(z, T) = \frac{\exp(PA_0/kT)}{b^2(T)} \left[\left(\frac{b(T)}{z} \right)^{3/2} + \exp\left(-\frac{\mu}{2kT}\right) \right] \left[(zb(T))^{3/2} + \exp\left(-\frac{\mu}{2kT}\right) \right]. \quad (2.1)$$

Substituting from equations (1.9) and (1.10) into (2.1) we have

$$Y(z, T) = a(T) + b(T) + 2 \left(z + \frac{1}{z} \right) + \left(z^2 + \frac{1}{z^2} \right). \quad (2.2)$$

Equation (2.2) establishes that Y is invariant under \mathcal{S} and the theorem follows.

Consider a curve in the density-temperature plane on which the short-range order variable takes the fixed value z' . On the transform of this curve under \mathcal{S} the short-range order variable has the value $z'' = 1/z'$. Denoting by primes the corresponding values of the occupational probabilities on the two curves, we have, from equations (1.1a), (1.3) and (1.5)

$$\begin{aligned}p'_0 &= b(T)/u(z', T), & p'_1 &= 3z'/u(z', T), & p'_2 &= 3z'^2/u(z', T), \\ p'_3 &= z'^3 a(T)/u(z', T) \\ p''_0 &= z'^3 b(T)/v(z', T), & p''_1 &= 3z'^2/v(z', T), & p''_2 &= 3z'/v(z', T), \\ p''_3 &= a(T)/v(z', T)\end{aligned}\quad (2.3)$$

where

$$\begin{aligned}u(z, T) &= b(T) + 3z + 3z^2 + z^3 a(T) \\ v(z, T) &= a(T) + 3z + 3z^2 + z^3 b(T).\end{aligned}\quad (2.4)$$

In the special case $w = 0$, $a(T) = b(T) = \exp(\epsilon/kT)$, and we have from equations (2.3) and (1.6) the molecule-vacancy symmetry of the simple lattice gas:

$$p'_0 = p''_3, \quad p'_1 = p''_2, \quad \bullet p'_2 = p''_1, \quad p'_3 = p''_0, \quad \rho' = (1 - \rho''). \quad (2.5)$$

We shall, for reasons which are discussed in § 4, be concerned in this work with the case $w > 3\epsilon$. Here the simple molecule-vacancy symmetry is broken, except asymptotically as T tends to infinity when $a(T) \sim b(T) \sim 1$ and equations (2.5) are asymptotically satisfied. The type of symmetry which exists at finite temperatures, being determined by

the sizes of $a(T)$ and $b(T)$, is difficult to describe in simple geometric terms. We can however see from equations (1.4) that at low temperatures $a(T) \sim 12 \exp[(\epsilon - w)/kT]$ is small and $b(T) \sim \frac{1}{4} \exp[(\epsilon + w)/kT]$ is large. It follows from equations (1.6) and (1.9) that, on the curves $z = z'$ and $z = z''$, as the temperature tends to absolute zero the densities and pressures tend to zero. For a fixed number of molecules the number of lattice sites becomes infinitely large. Apart from a set of measure zero these sites will be empty. For these remaining sites, the molecular bonding ensures that it is overwhelmingly probable that a triangle of nearest-neighbour sites is occupied by either one molecule or two bonded molecules, the relationships between the probabilities being given by

$$\frac{p'_1}{p''_2} \sim \frac{p'_2}{p''_1} \sim z'^3. \quad (2.6)$$

The line of symmetry corresponds to the case $z' = 1$ and, denoting by an asterisk the values of the variables on the line of symmetry, we have, from equations (1.6), (1.9) and (1.10)

$$\rho^*(T) = \frac{3 + a(T)}{6 + a(T) + b(T)}, \quad (2.7a)$$

$$P^*(T) = \frac{kT}{A_0} \ln \left(\frac{(3 + b(T))^2}{b(T)(6 + a(T) + b(T))} \right) \quad (2.7b)$$

and

$$\mu^*(T) = -kT \ln \left[2b^3(T) \left(\frac{3 + a(T)}{3 + b(T)} \right)^2 \right]. \quad (2.7c)$$

It is clear from the above discussion and from equation (2.7a) that the line of symmetry in the density-temperature plane tends asymptotically to the line $\rho = \frac{1}{2}$ at high temperatures and that it tends to $\rho = 0$ as the temperature tends towards absolute zero. Lines of constant z in the density-temperature plane are shown, for $(\epsilon/w) = \frac{1}{4}$, in figure 2.

Derivation of the coexistence curve for the system is simplified by defining a new variable ψ in terms of which the short-range order variable z is given by

$$z = (1 + \sin \psi)/\cos \psi \quad -\frac{1}{2}\pi \leq \psi \leq \frac{1}{2}\pi, \quad (2.8)$$

with $\mathcal{S} : \psi \rightarrow -\psi$. According to the theorem at the beginning of this section, we may find a pair of states at the same temperature with equal pressures and chemical potentials by imposing either one of these conditions. We use equations (1.6), (1.9) and (2.8) to construct a condition for two states to have equal pressures. This condition reduces to an equation for ψ satisfied either by $\psi = 0$ (a point on the line of symmetry) or by the roots of the equation

$$\cos^2 \psi (7 - a(T) - b(T) - a(T)b(T)) + 2 \cos \psi (5 - a(T)b(T)) + 4 = 0. \quad (2.9)$$

The function of ψ represented by the left-hand side of equation (2.9) is even and, for sufficiently small temperatures, will be negative for $\psi = 0$ and positive for $\psi = \pm\pi/2$. Equation (2.9) will therefore have roots ψ_σ and $-\psi_\sigma$ in the range $0 < \psi_\sigma \leq \frac{1}{2}\pi$. As T increases to the temperature T_c , given by the equation

$$64 - (1 + 3a(T_c))(1 + 3b(T_c)) = 0, \quad (2.10)$$

ψ_σ decreases to zero. The pair of states with $\psi = \psi_\sigma$, $-\psi_\sigma$ will represent points on the coexistence curve corresponding respectively to the dense and less dense phases. For

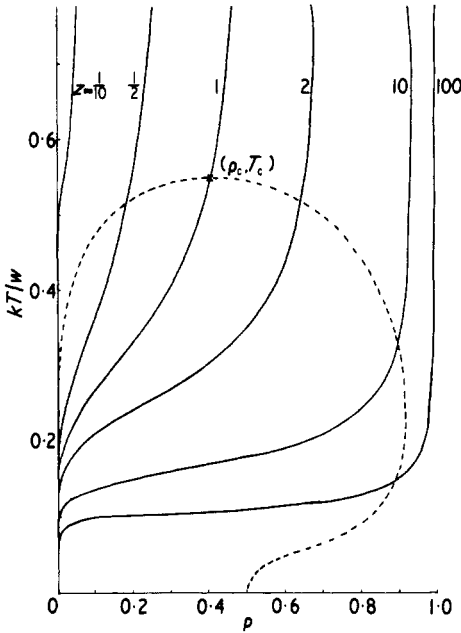


Figure 2. Curves of constant short-range order (full curves) and the coexistence curve (broken curve) in the density-temperature plane for $\epsilon/w = \frac{1}{4}$.

the sake of brevity and by analogy with a real fluid system, we shall refer to the dense and less dense phases as the liquid and vapour phases respectively. The temperature T_c given by equation (2.10) is the liquid-vapour critical temperature†. The critical point lies of course on the line of symmetry, and the critical density, pressure and chemical potential are given by

$$\rho_c = \rho^*(T_c), \quad P_c = P^*(T_c), \quad \mu_c = \mu^*(T_c). \tag{2.11}$$

We denote the short-range order variable and density at points on the vapour and liquid branches of the coexistence curve by $z_n(T)$ and $\rho_n(T)$ with $n = 1, 2$. Thus we have

$$z_n = [1 + (-1)^n \sin \psi_\sigma] / \cos \psi_\sigma, \quad 0 \leq \psi_\sigma \leq \frac{1}{2}\pi, \quad n = 1, 2 \tag{2.12}$$

and from equation (1.6)

$$\rho_n(T) = g(\psi_\sigma, T) + (-1)^n h(\psi_\sigma, T) \quad n = 1, 2 \tag{2.13}$$

where

$$g(\psi_\sigma, T) = \frac{2(1 - \cos \psi_\sigma)(1 + 2 \cos \psi_\sigma) + \cos^2 \psi_\sigma(3 + a(T))}{4(1 - \cos \psi_\sigma)(1 + 2 \cos \psi_\sigma) + \cos^2 \psi_\sigma(6 + a(T) + b(T))} \tag{2.14a}$$

and

$$h(\psi_\sigma, T) = \frac{2 \sin \psi_\sigma(1 + \cos \psi_\sigma)}{4(1 - \cos \psi_\sigma)(1 + 2 \cos \psi_\sigma) + \cos^2 \psi_\sigma(6 + a(T) + b(T))}. \tag{2.14b}$$

† We note that when $w = 0$ equation (2.10) immediately yields the result $kT_c/\epsilon = (\ln \frac{3}{2})^{-1}$ which is the critical temperature obtained by Guggenheim and McGlashan (1951) for the binary mixture on a triangular lattice.

On the two branches of the coexistence curve the pressure and the chemical potential both have common values which we denote by $P_\sigma(T)$ and $\mu_\sigma(T)$ respectively. From equations (1.9), (1.10), (2.12) and (2.13) we obtain expressions for these quantities which can be simplified using equation (2.9) to give

$$P_\sigma(T) = \frac{kT}{A_0} \ln \left(\frac{\cos \psi_\sigma + b(T)(2 + \cos \psi_\sigma)}{b(T)(2 + \cos \psi_\sigma)} \right) \quad (2.15)$$

and

$$\mu_\sigma(T) = -kT \ln \left[2b^3(T) \left(\frac{\cos \psi_\sigma + a(T)(2 + \cos \psi_\sigma)}{\cos \psi_\sigma + b(T)(2 + \cos \psi_\sigma)} \right) \right]. \quad (2.16)$$

From equations (1.4) and (2.7) we see that ρ^* , P^* and μ^* are regular functions of T and, since from equation (2.9) $\cos \psi_\sigma$ is a regular function of T , it follows that P_σ and μ_σ are also regular functions of T . Although ρ_1 and ρ_2 are not regular functions of T the density ρ_d on the diameter of the two-phase region, given by

$$\rho_d(T) = \frac{1}{2}(\rho_1(T) + \rho_2(T)) = g(\psi_\sigma, T) \quad (2.17)$$

is a regular function of T .

Coexistence curves for a number of values of (ϵ/w) are shown in figure 3 together with the line of symmetry, the critical isochore and the diameter of the coexistence region for $(\epsilon/w) = \frac{1}{4}$. The critical constants for $(\epsilon/w) = \frac{1}{4}$ are given in table 1. The general shape of the coexistence curves and the significance for it of the ratio $(\epsilon/w) = \frac{1}{3}$ will be discussed in detail in § 4.

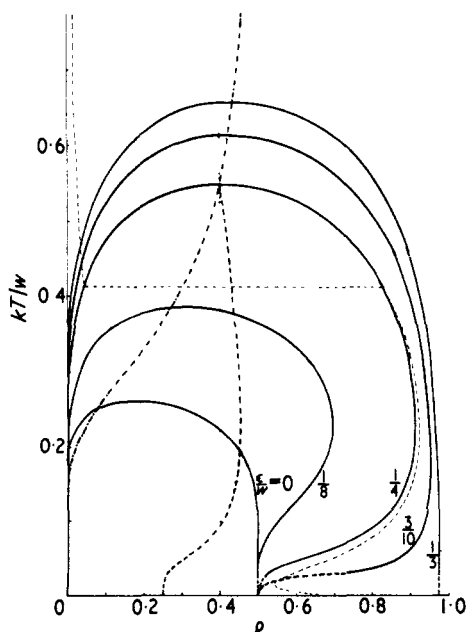


Figure 3. Coexistence curves in the density-temperature plane. The critical isochore (dotted line), the line of symmetry (chain curve), the diameter of the two-phase region (bold broken curve) and the isobar for $PA_0/w = 0.01$ (light broken curve) are shown for $\epsilon/w = \frac{1}{4}$.

Table 1.

	Theoretical values, $\epsilon/w = \frac{1}{4}$	Experimental values
T_c	0.548 w/k	647 K ^a
Molecular number density	0.402/ A_0	$102 \times 10^{20} \text{ cm}^{-3}$ ^a
P_c	0.0482 w/A_0	$221 \times 10^6 \text{ dyne cm}^{-2}$ ^a
$P_c A_0 / k T_c \rho_c$	0.218	0.243 ^a
$(T_c/P_c)(dP_\sigma/dT)_c$	5.06	7.71 ^b
T_1/T_c	0.44	0.49 ^b
T_2/T_c	0.41	0.43 ^b
T_3/T_c	0.13	0.80 ^c
T'_3/T_c	0.07	—
T_4/T_c	0.82 ^d	0.42 ^a

^a Values given by Eisenberg and Kauzmann (1969).

^b Derived from values given by Rowlinson (1969).

^c Derived graphically from saturated liquid values given by Rowlinson (1969) and saturated vapour values given by Keyes (1949).

^d From Lavis (1973).

3. The thermodynamic response functions

The isothermal compressibility κ_T is given by

$$\kappa_T = \left[\rho \left(\frac{\partial P}{\partial \rho} \right)_T \right]^{-1} \quad (3.1)$$

where, from equations (1.6) and (1.9),

$$\left(\frac{\partial P}{\partial \rho} \right)_T = - \frac{kT}{A_0(1-\rho)} \left(\frac{4z(1+z) - 3\rho(b(T) + 2z + z^2)}{2z(1+z) - 3\rho(b(T) + 2z + z^2)} \right). \quad (3.2)$$

We shall be concerned with the response functions at points on the coexistence curve. By substituting from equations (2.12) and (2.13) into (3.2) we have

$$(\kappa_T)_n = \frac{A_0(1 + 2 \cos \psi_\sigma)[\cos \psi_\sigma + b(T)(2 + \cos \psi_\sigma)]}{2kT \tan^2 \psi_\sigma [1 + (-1)^n \sin \psi_\sigma][1 + \cos \psi_\sigma + (-1)^n \sin \psi_\sigma]} \quad n = 1, 2 \quad (3.3)$$

respectively for the isothermal compressibility at points on the vapour and liquid branches of the coexistence curve.

The coefficient of isobaric thermal expansion α_P is given by

$$\alpha_P = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P. \quad (3.4)$$

At points on the coexistence curve we are however considering either a saturated liquid or a saturated vapour. If such a saturated substance is heated, its vapour pressure will increase and the change in density is no longer associated with a constant pressure. We shall therefore define, at points on the vapour and liquid branches of the coexistence curve, the two response functions

$$\alpha_n = -\frac{1}{\rho_n} \frac{d\rho_n}{dT} \quad n = 1, 2 \quad (3.5)$$

respectively. Thus we have, for points on the coexistence curve,

$$(\alpha_p)_n = \alpha_n + (\kappa_T)_n \frac{dP_\sigma}{dT} \quad n = 1, 2. \quad (3.6)$$

Let s be the entropy of the system *per lattice site* and consider the Helmholtz free energy *per molecule* (f/ρ) plotted in a three-dimensional Gibbs space as a function of the variables (s/ρ) and (A_0/ρ). The coexistence region will appear as a 'bridged' section of the surface with the generator at temperature T in the direction

$$(\Delta(f/\rho), \Delta(s/\rho), \Delta(A_0/\rho)) = (-P_\sigma, dP_\sigma/dT, 1) \quad (3.7)$$

(Buckingham 1972). It follows therefore that the entropy per site s_σ at a point in the coexistence region with temperature T and density ρ is given by either of the equations

$$s_\sigma = \frac{\rho}{\rho_n} s_n - \left(\frac{\rho}{\rho_n} - 1 \right) A_0 \frac{dP_\sigma}{dT} \quad n = 1, 2 \quad (3.8)$$

where s_n is the entropy per site at temperature T on the corresponding branch of the coexistence curve. Thus the constant density heat capacities c_σ and $(c_\rho)_n$ *per molecule* are related by the equations

$$c_\sigma = (c_\rho)_n - T\alpha_n \left[\left(\frac{\partial s}{\partial \rho} \right)_T \right]_n + \frac{T}{\rho_n} \alpha_n s_n - \frac{T}{\rho_n} \alpha_n A_0 \frac{dP_\sigma}{dT} - T A_0 \left(\frac{1}{\rho_n} - \frac{1}{\rho} \right) \frac{d^2 P_\sigma}{dT^2} \quad n = 1, 2. \quad (3.9)$$

Since from Maxwell's relationships

$$\left(\frac{\partial s}{\partial \rho} \right)_T = \frac{1}{\rho} \left(s - \frac{A_0 \alpha_p}{\kappa_T} \right), \quad (3.10)$$

equations (3.9) can be transformed using equations (3.5) and (3.6) into

$$c_\sigma = (c_\rho)_n + \frac{T A_0}{\rho_n} \left(\frac{\alpha_n^2}{(\kappa_T)_n} - \frac{1}{\rho} \frac{d^2 P_\sigma}{dT^2} (\rho - \rho_n) \right) \quad n = 1, 2. \quad (3.11)^\dagger$$

The discontinuities of c_ρ across the two branches of the coexistence curve are given from equations (3.11) by

$$(\Delta c_\rho)_n = \lim_{\rho \rightarrow \rho_n} [c_\sigma - (c_\rho)_n] = \frac{T A_0 \alpha_n^2}{\rho_n (\kappa_T)_n} \quad n = 1, 2. \quad (3.12)$$

Since the constant pressure heat capacity per molecule c_p is given by

$$c_p = c_\rho + \frac{T A_0 \alpha_p^2}{\rho \kappa_T} \quad (3.13)$$

† The equation for c_σ of Fisher (1964) is obtained by eliminating $d^2 P_\sigma/dT^2$ between the two equations (3.11).

we can obtain from equations (3.5), (3.11) and (3.13) the discontinuous increase Δc_P in c_P as the system changes from liquid to vapour along an isobar. This is given by

$$\Delta c_P = (c_P)_1 - (c_P)_2 = \frac{TA_0}{\rho_1\rho_2} \left[\left(\frac{dP_\sigma}{dT} \right)^2 [\rho_2(\kappa_T)_1 - \rho_1(\kappa_T)_2] + 2 \frac{dP_\sigma}{dT} (\rho_2\alpha_1 - \rho_1\alpha_2) + \frac{d^2P_\sigma}{dT^2} (\rho_2 - \rho_1) \right]. \quad (3.14)$$

The functions $(\kappa_T)_2$, $(\alpha_T)_2$ and Δc_P are shown in figures 4–6 for a number of values of (ϵ/w) . Curves of Δc_P against density are shown in figure 7.

4. The limit of absolute zero temperature

The effect in this model of the occurrence of molecular bonding can be seen, not only in terms of the conditional probability of a bonded pair occurring on a triangle of nearest-neighbour sites with a particular occupation (equations (1.2)), but also by examining the occupational probabilities themselves (equations (1.3) and (2.3)). In §2 we examined this effect upon curves of constant short-range order in the density–temperature plane. Consider now the situation where the system is subjected to increasing pressure in isothermal conditions with $T < T_c$. For some pressure less than the critical pressure the system will undergo a phase transition from the vapour to the liquid phase. The interesting case for the model will be when the bonding energy w is sufficiently large relative to the non-bonding energy ϵ to prevent the system undergoing the phase transition from collapsing into a very dense short-range ordered liquid phase. This will yield a liquid phase with regions of short-range ordered honeycomb structure. The effect of molecular bonding will therefore be seen most clearly by examining the density and the thermodynamic response functions along the liquid branch of the coexistence curve, particularly in the region of absolute zero temperature where the effect of thermal agitation is small. From equation (1.4*b*), since at least one of the energy parameters ϵ and w is greater than zero, it follows that $b(T)$ tends to infinity as the temperature tends to absolute zero. From equation (2.9) we see that it must be the case that the zero-temperature limit of $\cos \psi_\sigma$ is zero. It follows from equation (2.13) that

$$\rho_2(T) \sim \frac{2(1 + \cos \psi_\sigma)}{4 + \cos \psi_\sigma(7 - a(T)b(T))} \quad (4.1)$$

and from equations (2.9) and (1.4) it is not difficult to show that

$$\rho_2(T) \sim \begin{cases} 1 & w < 3\epsilon \\ (20 - 6\sqrt{10})^{-1} = 0.973 & w = 3\epsilon \\ \frac{1}{2}(1 + 3 \exp[(3\epsilon - w)/2kT]) & w > 3\epsilon > 0 \\ \frac{1}{2}[1 - 12 \exp(-w/kT)] & \epsilon = 0. \end{cases} \quad (4.2)$$

We see therefore that molecular bonding becomes important for $\epsilon/w < \frac{1}{3}$, when the liquid branch of the coexistence curve tends to $\rho = \frac{1}{2}$ as the temperature tends to absolute zero. For $0 < \epsilon/w < \frac{1}{3}$ this limiting behaviour occurs together with a region for $T > 0$ in which $\rho > \frac{1}{2}$, producing the ‘bulge’ in the liquid branch of the coexistence curve which is a characteristic of our model. From equations (2.3), (2.9) and (2.12) it follows that, for

$\epsilon/w < \frac{1}{3}$, $z_2 \sim \frac{1}{2} \exp[(\epsilon + w)/2kT]$ with $p_0 \sim \frac{1}{4}$ and $p_2 \sim \frac{3}{4}$. Apart from a set of measure zero each basic nearest-neighbour triangle of sites is either occupied by a pair of bonded molecules or is unoccupied, the ratio of these occupations being three to one.

The importance of the condition $\epsilon/w = \frac{1}{3}$ can also be seen if, after the manner of Lavis (1973), we consider the limiting behaviour of an isobar in the density-temperature plane as the temperature tends to absolute zero. From equations (1.6) and (1.9) we have

$$\rho \sim \begin{cases} 1 & P > (w - 3\epsilon)/A_0 \\ \frac{4}{3}(\sqrt{3} - 1) = 0.9763 & P = (w - 3\epsilon)/A_0 \\ \frac{2}{3} & P < (w - 3\epsilon)/A_0. \end{cases} \quad (4.3)$$

This result was also achieved by Bell and Lavis (1970a) by considering the stable state at $T = 0$. In the case where $(\epsilon/w) < \frac{1}{3}$ and $P < (w - 3\epsilon)/A_0$ we have

$$z \sim \frac{3}{4} \exp[(\epsilon + w + PA_0)/kT]$$

and $p_2 \sim 1$ on an isobar in a neighbourhood of absolute zero. A perfect arrangement of this type is of course a honeycomb arrangement of molecules with each nearest-neighbour triangle of sites occupied by a bonded pair. This would be a state with long-range order. Short-range ordering will occur when the honeycomb arrangement is broken by lines of imperfections, the number of nearest-neighbour triangles involved being of measure zero. Examples of the types of ordering at low temperatures with $\rho \sim \frac{1}{2}$ and $\rho \sim \frac{2}{3}$ are displayed in figure 1. An isobar of the type which we have just discussed is shown in figure 3.

We shall omit details of the calculations of the asymptotic forms for the response functions along the liquid branch of the coexistence curve, simply quoting the results which, for $\epsilon/w < \frac{1}{3}$, are

$$(\kappa_T)_2 \sim \frac{A_0}{kT} \quad (4.4)$$

$$(\alpha_T)_2 \sim \alpha_2 \sim \begin{cases} -\frac{3(w - 3\epsilon)}{2kT^2} \exp[(3\epsilon - w)/2kT] & \epsilon > 0 \\ \frac{12w}{kT^2} \exp(-w/kT) & \epsilon = 0 \end{cases} \quad (4.5)$$

and

$$(\Delta c_\rho)_2 \sim \begin{cases} \frac{9(w - 3\epsilon)^2}{2kT^2} \exp[(3\epsilon - w)/kT] & \epsilon > 0 \\ \frac{288w^2}{kT^2} \exp(-2w/kT) & \epsilon = 0. \end{cases} \quad (4.6)$$

We can also show that

$$\Delta c_P \sim \begin{cases} \frac{3(\epsilon + w)^2}{kT^2} & \epsilon > 0 \\ \frac{27w^2}{4kT^2} & \epsilon = 0. \end{cases} \quad (4.7)$$

5. Asymptotic forms in a neighbourhood of the critical point

In a neighbourhood of the critical point we have, from equations (1.4),

$$a(T) \sim a(T_c) \left[1 + a_1 \left(1 - \frac{T}{T_c} \right) \right] \quad (5.1a)$$

and

$$b(T) \sim b(T_c) \left[1 + b_1 \left(1 - \frac{T}{T_c} \right) \right] \quad (5.1b)$$

where

$$a_1 = \frac{\epsilon}{kT_c} + \frac{w}{kT_c} \frac{(7e^{-w/kT_c} - 3)}{(1 + 3e^{-w/kT_c})(3 + e^{-w/kT_c})} \quad (5.2a)$$

and

$$b_1 = \frac{\epsilon}{kT_c} + \frac{w}{kT_c} \frac{1}{(1 + 3e^{-w/kT_c})}. \quad (5.2b)$$

From equations (2.10) and (2.11)

$$a(T_c) = \frac{(9\rho_c - 1)}{3(1 - \rho_c)} \quad (5.3a)$$

$$b(T_c) = \frac{(8 - 9\rho_c)}{3\rho_c}. \quad (5.3b)$$

From these equations and equations (2.7), we obtain asymptotic forms for the line of symmetry in a neighbourhood of the critical point given by

$$\frac{\rho^*(T)}{\rho_c} \sim 1 - B^* \left(\frac{T}{T_c} - 1 \right) \quad (5.4a)$$

$$\frac{P^*(T)}{P_c} \sim 1 + \Pi^* \left(\frac{T}{T_c} - 1 \right) \quad (5.4b)$$

and

$$\frac{\mu^*(T)}{\mu_c} \sim 1 + \Lambda^* \left(\frac{T}{T_c} - 1 \right) \quad (5.4c)$$

where

$$B^* = -\frac{1}{8}(1 - \rho_c)[a_1(9\rho_c - 1) - b_1(8 - 9\rho_c)] \quad (5.5a)$$

$$\Pi^* = 1 + \frac{kT_c\rho_c}{8A_0P_c}[a_1(9\rho_c - 1) + b_1(9\rho_c + 1)] \quad (5.5b)$$

and

$$\Lambda^* = 1 + \frac{kT_c}{4\mu_c}[a_1(9\rho_c - 1) + b_1(9\rho_c + 4)]. \quad (5.5c)$$

In order to obtain asymptotic forms for functions on the branches of the coexistence curve

in a neighbourhood of the critical point we need an asymptotic form for ψ_σ . This is given from equations (2.9) and (5.1)–(5.3) by

$$\psi_\sigma^2 \sim v \left(1 - \frac{T}{T_c} \right) \quad (5.6)$$

where

$$v = 3[a_1(1 - \rho_c)(9\rho_c - 1) + b_1\rho_c(8 - 9\rho_c)]. \quad (5.7)$$

From equations (2.17), (5.4a) and (5.6) we have

$$\frac{\rho_d(T)}{\rho_c} \sim 1 - B_2 \left(\frac{T}{T_c} - 1 \right) \quad (5.8)$$

where

$$B_2 = B^* - \frac{9}{8}v(1 - \rho_c)(1 - 2\rho_c). \quad (5.9)$$

Equation (5.8) is the rectilinear diameter law. From equations (2.7), (2.15) and (2.16) we have

$$P_\sigma(T) - P^*(T) \sim \frac{3\rho_c^2 k T_c v^2}{64A_0} \left(\frac{T}{T_c} - 1 \right)^2 \quad (5.10a)$$

and

$$\mu_\sigma(T) - \mu^*(T) \sim \frac{9kT_c v^2}{64} (1 - \rho_c)(1 - 2\rho_c) \left(\frac{T}{T_c} - 1 \right)^2. \quad (5.10b)$$

We have therefore

$$\Pi^* = \frac{T_c}{P_c} \left(\frac{dP_\sigma}{dT} \right)_c = \frac{T_c}{P_c} \left(\frac{dP^*}{dT} \right)_c. \quad (5.11)$$

The value of this dimensionless quantity for $\epsilon/w = \frac{1}{4}$ is given in table 1. Since we are dealing with a closed form approximation with the two-phase region represented by a bridged section of the Helmholtz free energy surface, the line of symmetry, with density, pressure and chemical potential given by ρ^* , P^* and μ^* respectively, represents realizable states of the system only when $T \geq T_c$. In the two-phase region at temperature T , the pressure and chemical potential are given by $P_\sigma(T)$ and $\mu_\sigma(T)$ for all densities. These latter functions together with the two-phase diameter are of course defined only for $T \leq T_c$. Since however they are regular functions of T in their domain of definition, they may be analytically continued into the domain $T > T_c$ by obtaining their Taylor expansions about the critical point. The first term of the series expansion of ρ_d is given by equation (5.8). The first nonzero terms of the differences between the series expansions of P_σ and μ_σ and the corresponding series expansions for the pressure and chemical potential along the line of symmetry are given by equations (5.10). Let $\rho_\sigma^{(P)}$ and $\rho_\sigma^{(\mu)}$ be functions of T which represent the curves in the density–temperature plane, with $T \geq T_c$, on which the pressure and chemical potential, respectively, take the analytic continuations of their values along the coexistence curve. From equations (1.6), (1.9), (1.10) and (5.10)

$$\frac{\rho_\sigma^{(P)}(T)}{\rho_c} \sim 1 + B_3 \left(\frac{T}{T_c} - 1 \right) \quad (5.12a)$$

and

$$\frac{\rho_\sigma^{(\omega)}(T)}{\rho_c} \sim 1 + B_4 \left(\frac{T}{T_c} - 1 \right) \tag{5.12b}$$

where

$$B_3 = B^* + \frac{9}{16} v \rho_c (1 - \rho_c) \tag{5.13a}$$

and

$$B_4 = B^* + \frac{27}{16} v (1 - \rho_c)^2 (1 - 2\rho_c). \tag{5.13b}$$

These equations are important for the discussion, in § 6, of the symmetry properties of the model.

It is also of some interest to obtain asymptotic expressions for the shape of the coexistence curve in a neighbourhood of the critical point and for the thermodynamic response functions. Derivation of these formulae is straightforward and we omit all details, simply stating our results. From equations (2.13) and (2.14)

$$\frac{\rho_2(T) - \rho_1(T)}{2\rho_c} = \frac{h(\psi_\sigma, T)}{\rho_c} \sim B_1 \left(1 - \frac{T}{T_c} \right)^\beta \tag{5.14}$$

where

$$B_1 = \frac{3}{2} (1 - \rho_c) v^{1/2} \tag{5.15}$$

and $\beta = \frac{1}{2}$. From equation (3.3)

$$(\kappa_T)_n P_c \sim \left(1 - \frac{T}{T_c} \right)^{-\gamma'} \left[C_1 - (-1)^n C_2 \left(1 - \frac{T}{T_c} \right)^{1/2} \right] \quad n = 1, 2 \tag{5.16}$$

where

$$C_1 = \frac{6P_c A_0 (1 - \rho_c)}{k T_c \rho_c v} \tag{5.17a}$$

$$C_2 = \frac{9P_c A_0 (1 - \rho_c)}{k T_c \rho_c v^{1/2}} \tag{5.17b}$$

and $\gamma' = 1$. From (3.6)

$$(\alpha_P)_n T_c \sim \mathcal{A} \left(1 - \frac{T}{T_c} \right)^{-1} \quad n = 1, 2 \tag{5.18}$$

where

$$\mathcal{A} = \Pi^* C_1. \tag{5.19}$$

From (3.12)

$$(\Delta c_\rho)_n \sim (\Delta c_\rho)_c = \frac{3}{32} k (1 - \rho_c) \quad n = 1, 2 \tag{5.20}$$

and from (3.14)

$$\Delta c_P \sim \mathcal{E} \left(1 - \frac{T}{T_c} \right)^{-1/2} \tag{5.21}$$

where

$$\mathcal{E} = \frac{P_c A_0}{T_c \rho_c} \Pi^* [\Pi^*(C_1 B_1 + C_2) - B_1]. \quad (5.22)$$

The values given for the critical exponents β and γ' and the finite discontinuity in the constant density heat capacity along the critical isochore are consequences of the classical nature of the model.

6. Conclusions

For the simple lattice fluid and for a number of other models (Widom and Rowlinson 1970, Widom and Stillinger 1973), the line of symmetry can be defined either (i) as the invariant states of a symmetry transformation between states of the system 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 but it can be shown that, in the density-temperature plane, the line of symmetry is the analytic continuation of the diameter of the two-phase region. But Mulholland (1973) has shown that if, for a general classical model for which no particular structure is assumed, the line of symmetry is defined by (ii) then the line of symmetry in the density-temperature plane is no longer the analytic continuation of the two-phase diameter.

We have seen in §2 that for $w = 0$, our model has the vacancy-molecule symmetry of the simple lattice fluid with $a(T) = b(T)$. In this case from equations (2.7), (2.11), (2.14a), (2.17) and (2.16)

$$\rho^*(T) = \rho_d(T) = \rho_c = \frac{1}{2} \quad (6.1)$$

and

$$\mu^*(T) = \mu_c(T) = -(3\epsilon + kT \ln 2). \quad (6.2)$$

The curve $\rho = \rho_\sigma^{(\mu)}(T)$, on which the chemical potential is the analytic continuation of the chemical potential on the coexistence curve, coincides with the line of symmetry. However the curve $\rho = \rho_\sigma^{(P)}(T)$, on which the pressure is the analytic continuation of the pressure on the coexistence curve, does not coincide with the line of symmetry. The coefficient B_3 in equation (5.12a) has the value $\frac{189}{256} \ln \frac{7}{3}$.

For the general case of our model with bonding ($w \neq 0$) ρ^* is a regular function of T which coincides neither with the critical isochore nor with the two-phase diameter in the two-phase region (see figure 3). In the one-phase region we have obtained the first terms of the analytic continuations of ρ_d and $\rho_\sigma^{(\mu)}$ (equations (5.8) and (5.12b)). We see by comparing these equations with (5.4a) that the curves $\rho = \rho^*(T)$, $\rho = \rho_d(T)$ and $\rho = \rho_\sigma^{(\mu)}(T)$ are all distinct and meet at the critical point in nonzero angles. (For $\epsilon/w = \frac{1}{4}$, $B^* = 0.604$, $B_2 = -0.398$ and $B_4 = 1.503$.)

As we indicated in the introduction, the model investigated by BL(b), by Lavis (1973) and in the present work was designed to be analogous in a simple way to the water system. Detailed examinations of the thermodynamic response functions along the vapour-liquid transition curve have been made for a number of common substances including water (see eg Rowlinson 1969, chapter 2). These investigations exemplify in a particularly clear manner the anomalous behaviour of water in that:

(a) On the liquid branch of the coexistence curve

(i) there is a minimum of the isothermal compressibility κ_T ,

(ii) 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, table 2.10).

(b) The discontinuous change Δc_p in the constant pressure heat capacity c_p as the substance changes from liquid to vapour is positive at temperatures near to the liquid-vapour critical temperature but is negative for lower temperatures (Eisenberg and Kauzmann 1969, figures 2.11, 3.12). It is of interest to consider the extent to which these properties are reflected by our model.

For thermodynamic stability it must be the case that $(\kappa_T)_2 > 0$ for $0 \leq T \leq T_c$ and from equations (4.4) and (5.16) it is clear that for all ϵ/w in the range $[0, \frac{1}{3})$ this function tends to infinity when $T \rightarrow 0$ and $T \rightarrow T_c$. It follows that $(\kappa_T)_2$ must have a minimum for some temperature T_1 with $0 < T_1 < T_c$. Computer calculations have shown that this is also the case when $3\epsilon = w$, (figure 4). Thus the existence of a minimum in the isothermal compressibility on the liquid branch of the coexistence curve is a characteristic which is fairly insensitive to the value of the ratio ϵ/w .

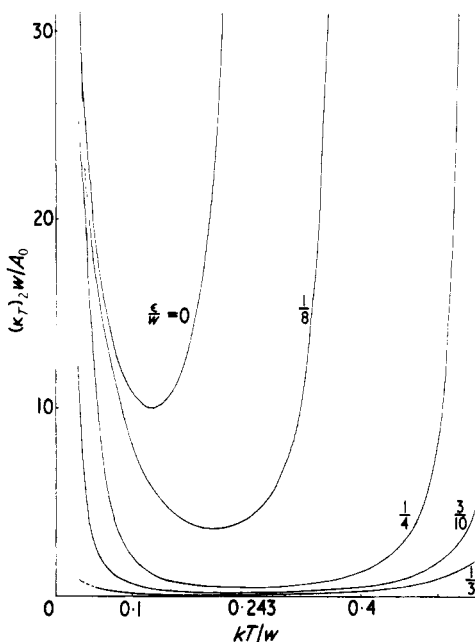


Figure 4. The isothermal compressibility plotted against temperature along the liquid branch of the coexistence curve.

We have shown in § 4 that the case $3\epsilon = w$ does not produce the local (short-range ordered) honeycomb arrangement of molecules as the temperature is reduced to absolute zero along an isobar, and numerical calculations have shown also that in this case $(\alpha_p)_2$ is positive for all $0 \leq T \leq T_c$. From equations (4.5) and (5.18) we see that, for $\epsilon = 0$, $(\alpha_p)_2$ is positive when $T \rightarrow 0$ and when $T \rightarrow T_c$. This is not conclusive evidence that this function remains positive throughout the length of the liquid branch of the coexistence curve, but numerical calculations confirm that this is the case (figure 5). On the other hand we see

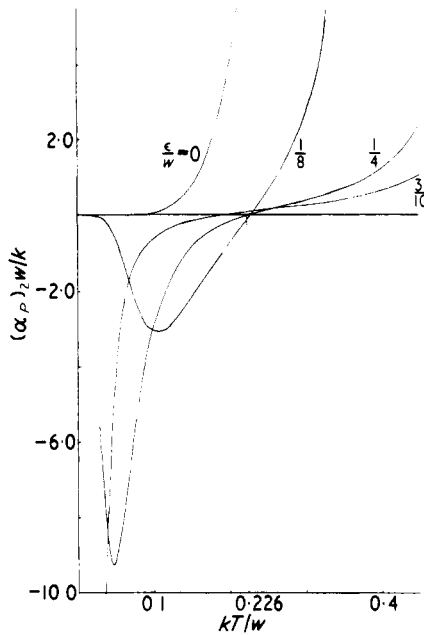


Figure 5. The coefficient of isobaric thermal expansion plotted against temperature along the liquid branch of the coexistence curve.

from these same equations that for ϵ/w in the range $(0, \frac{1}{3})$ there must be a temperature T_2 at which $(\alpha_p)_2$ becomes negative (see figure 5). This property is therefore somewhat more sensitive to the value of ϵ/w than is the occurrence of a minimum in the isothermal compressibility. A rather simpler quantity with which to deal, both mathematically and experimentally, is α_2 (Rowlinson 1969, § 2.3). This quantity also exhibits the anomalous behaviour of water in that it becomes negative at low temperatures. Since however from equation (3.6) $(\alpha_p)_2 > \alpha_2$ it follows that if $(\alpha_p)_2 < 0$ then $\alpha_2 < 0$ and we do not need to devote a separate figure to a display of this function.

Of the properties which interest us, that which is most sensitive to the value of ϵ/w is the occurrence of a temperature T_3 at which Δc_p is zero. From equation (4.7) we see that Δc_p tends to infinity as $T \rightarrow 0$. If a temperature T_3 exists there must be a lower temperature T'_3 at which Δc_p again becomes positive. The existence of these temperatures has been definitely established by numerical calculation for the case $\epsilon/w = \frac{1}{4}$ (see figure 6). They probably exist for the case $\epsilon/w = \frac{3}{10}$, but even using double precision variables for a large computer, the existence of rounding errors yielded numerical values which were unreliable at sufficiently low temperatures.

From table 1 we see that the ratio $(P_c A_0/kT_c \rho_c)$ for $\epsilon/w = \frac{1}{4}$ corresponds quite closely to that derived from the experimental data for water as do also the ratios T_1/T_c and T_2/T_c . The deficiencies of the model are revealed by the value of T_3/T_c which is much too low. This is probably due to the fact that c_p is more sensitive than the other properties to the entropy of the system which is always rather inaccurate for lattice fluid models. For the sake of comparison we have included the vapour-liquid-solid triple point T_t of Lavis (1973). Ideally of course we should have liked to have $T'_3 < T_t < T_3$ so that the temperature T'_3 corresponded to a sign change for Δc_p in the supercooled region. However, in addition to the low value for T_3/T_c , the value of T_t/T_c is much too high and we have

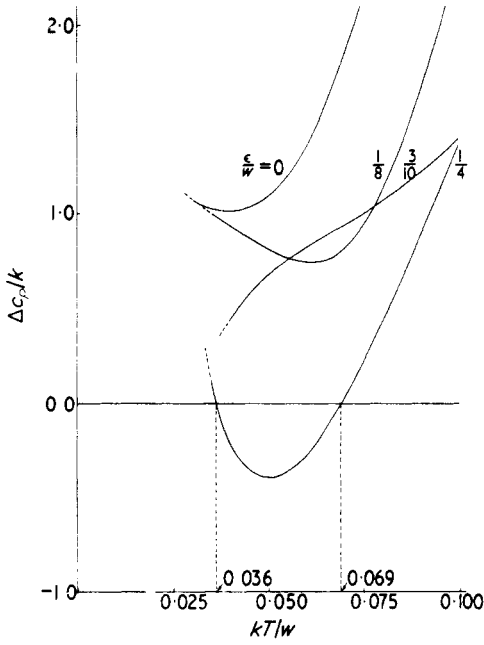


Figure 6. The discontinuous change in the constant pressure heat capacity as the system changes from liquid to vapour, plotted against temperature.

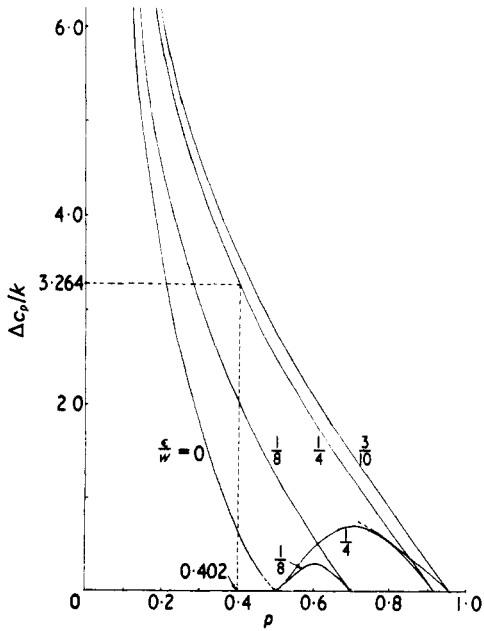


Figure 7. The discontinuous change in the constant density heat capacity across the coexistence curve plotted against density.

in this respect been unsuccessful. We may nevertheless claim qualitative success in that the anomalous properties of water, listed above, do all occur in our model. We have modified a simple lattice fluid model only with respect to the introduction of preferential bonding directions designed to represent in a simple way the hydrogen bonding properties of the water molecule. It may therefore be suggested that, contrary to the comments of Eisenberg and Kauzmann (1969, p 105) on the negative coefficient of expansion, the anomalous properties of water discussed in this work are due mainly to the role played by hydrogen bonding in the structure of water.

The behaviour of the system in the immediate neighbourhood of the critical point is of course determined by the classical nature of the model which results from the use of a first-order approximation of the mean-field type. Critical exponents and amplitudes for the vapour-liquid transition of water are known (see eg Levelt Sengers and Greer 1972), but no real purpose would be served by comparing them with values computed from our model. Recent work of Bell and Sallouta (1975) on the comparison of accurate and approximation methods for interstitial models of the water system shows however that, in contrast to the zeroth-order method, the first-order method gives good approximation to the accurate calculations for the shape of the coexistence curve and for the behaviour of the isothermal compressibility. It is possible therefore that the deficiencies of our model with respect to experimental data away from the critical point are due not so much to the use of an approximation method as to the use of a simplified lattice model.

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