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Two-dimensional bonded lattice fluids
I. Interstitial model

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Abstract. The density, pressure and temperature state surface is studied for a 'bonded' fluid on a plane triangular lattice. Bonds are formed between nearest-neighbour molecules on a honeycomb sublattice comprising $\frac{2}{3}$ of the total number of sites, while molecules on the remaining sites, which are regarded as interstitial, do not participate in bonding. There is competition between a low-energy 'open structure' with all interstitial sites empty and each molecule participating in three bonds, and a 'close-packed structure' with all sites occupied. Calculations were made using a first-order statistical approximation based on a triangular group of sites. Separation between liquid and vapour phases occurs below a critical pressure p_c. Another significant value of the pressure in this model is termed p_0 which is greater than p_c and such that curves of density against temperature at constant pressure between p_c and p_0 display maxima. For a suitable ratio of the non-bonding energy of a nearest-neighbour pair to the energy of bond formation there are density maxima in the liquid as well as the supercritical state, as in fluid water. If the interaction energy of an unbonded nearest-neighbour pair of molecules is zero the properties of the model can be related to those of an Ising ferromagnet on a honeycomb sublattice and accurate values deduced for the critical density, pressure and temperature.

1. Introduction

The accepted explanation for the anomalous behaviour of water density at normal pressures is that the usual decrease in density due to the increase in amplitude of thermal vibrations with temperature is counteracted by closer packing due to breakdown of tetrahedral coordination (see, for instance, Eisenberg and Kauzmann 1969). However, the construction and treatment of an adequate model for water, in which this behaviour together with other properties could be deduced from first principles by the methods of statistical mechanics, presents a formidable task. The aim of the present series of papers is to examine simple models of fluids with bonding properties which imply that open configurations are in competition with closer-packed configurations of higher energy. The models are tractable enough for the behaviour of the density as a function of temperature and pressure to be deduced to a reasonable approximation from their basic postulates.

The preceding paper (Bell 1969) treated one-dimensional models in which the breaking of a bond allowed neighbouring molecules to approach more closely. The present paper deals with a two-dimensional bonded lattice fluid on a plane triangular (hexagonal) lattice. One third of the sites are 'interstitial' and molecules on these sites cannot participate in the framework of bonds. The extension to two dimensions permits the abandonment of the one-dimensional postulate that a molecule's bonded neighbours must remain further away from it than its unbonded neighbours. The existence of the open structure is now dependent on rules restricting the angles between the directions from a molecule to its bonded neighbours. Furthermore, the two-dimensional lattice fluid displays a separation into 'liquid' and 'vapour' phases so that it is possible to study the interaction between phase separation and anomalous density behaviour. A (two-dimensional) pressure p_0 is found above which the density decreases monotonically with temperature but below which anomalous behaviour occurs. As with real water, p_0 is considerably greater than the critical pressure p_c for liquid–vapour phase separation. Thus, above p_c there is a range of pressures in which the density passes through a maximum as the temperature increases. For a suitable value of ratio of the non-bonding nearest-neighbour energy to the energy of formation of a bond, the density maximum is also found in the liquid phase below p_c.

The present treatment is confined to lattice fluids although in one dimension it was shown that the anomalous behaviour of a continuous fluid with a parabolic potential well was similar to that of a lattice model. In one dimension an exact treatment was possible but in the present paper we make use of a first-order statistical approximation based on triangular groups of sites on the lattice. Exact values for the critical pressure, density and temperature are given in one case.

We conclude this section with some remarks on the relation of this work to existing theories of fluid water. Those developed up to 1967 have been classified by Eisenberg and Kauzmann (1969) into mixture models where the water molecules are distinguished by their state of association, interstitial models where molecules are displaced from a hydrogen-bonded framework, and models where the hydrogen bonds may be bent or distorted. From this point of view the model of the present paper is a very simple interstitial one. Levine and Perram (1968) have recently used methods from the theory of cooperative phenomena to examine the states of association of molecules on a lattice and have criticized the statistical basis of earlier theories. They give a brief sketch of a lattice liquid theory with some vacant lattice sites but do not introduce the restrictions on bonding direction which give rise to the 'open structure' of our present model and lead to its most interesting properties.

2. The interstitial bonded fluid model and states at absolute zero

We assume that each molecule in the two-dimensional assembly on the triangular lattice can participate in at most three bonds, which are at angles of 120° to each other. The energy of formation of each bond is $-w (w > 0)$ so that, while an unbonded nearest-neighbour pair of molecules has an energy $-\epsilon (\epsilon > 0)$, a bonded pair has an energy of $-(\epsilon + w)$. The triangular lattice is divided into a honeycomb sublattice (sublattice a) and interstitial sites (sublattice b) as shown in figure 1 where aa and ab

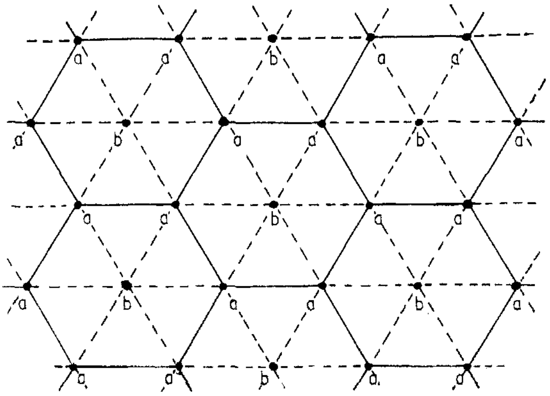

Figure 1. The honeycomb (a) and interstitial (b) sublattices.

nearest-neighbour site links are respectively represented by full and by broken segments. It can be seen that each a-site has three a- and three b-sites as nearest neighbours, while each b-site has six nearest-neighbour a-sites. It is supposed that the molecules on the a-sites are oriented in such a way that any aa nearest-neighbour pair of molecules is bonded but no ab pair is bonded. With the pair energies stated above, the configurational energy E_c of the assembly is then given by

$$E_c = -N_{mm}\epsilon - N_{mm}^{(a)}w \tag{2.1}$$

where N_{mm} is the total number of nearest-neighbour pairs on the triangular lattice and $N_{mm}^{(a)}$ is the number on the honeycomb sublattice a. With these postulates no molecule can be bonded except on an a-site and then only to molecules on the neighbouring a-sites so that the maximum number of bonds from any one molecule is three at angles of 120° to each other. The rule stated at the beginning of the section is thus satisfied.

Sites of both sublattices can be either vacant or occupied by molecules. With the postulates made above, the configuration in which each molecule participates in the maximum number of bonds is one with all a-sites occupied and all b-sites vacant. Thus M molecules will occupy the M sites of a honeycomb sublattice of a triangular lattice of $\frac{3}{2}M$ sites with the remaining $\frac{1}{2}M$ sites vacant. This will be termed the open structure and the pattern of bonds is that made by the solid segments in figure 1.

The open structure can break down locally owing to movement of molecules from a-sites to b-(interstitial) sites but our postulates exclude the possibility of cooperative reorientation of molecules to form bonds between ab site pairs. (A model in which this is not excluded will be considered in the next paper of this series). The total number of triangular lattice sites will be denoted by N so that there are $\frac{2}{3}N$ a-sites and $\frac{1}{3}N$ b-sites. If there are M molecules of which M_a and M_b are on a- and b-sites respectively then we can define an overall number density ρ and densities ρ_a and ρ_b on the a- and b-sublattices respectively by

$$\rho = \frac{M}{N}, \qquad \rho_a = \frac{M_a}{\frac{2}{3}N}, \qquad \rho_b = \frac{M_b}{\frac{1}{3}N}. \tag{2.2}$$

In the perfect open structure $\rho = \frac{2}{3}$, $\rho_a = 1$ and $\rho_b = 0$. In general the three densities are connected by the relation

$$3\rho = \frac{3M}{N} = \frac{M_a + M_b}{\frac{1}{3}N} = 2\rho_a + \rho_b. \tag{2.3}$$

As is usual for a lattice fluid it will be assumed that the Hamiltonian is separable into terms corresponding to the internal degrees of freedom of the molecules and a configurational term depending on the arrangement of the M molecules on the N sites and that these terms are independent. Each term in the assembly partition function thus contains a factor $\{\psi(T)\}^M$ where $\psi(T)$ is the partition function over the internal degrees of freedom of one molecule. It would be possible, without increasing the difficulty of the analysis, to assume that, for each bond formed by a given molecule, $\psi(T)$ is modified by a factor which we could call $\exp\{-\delta(T)\}$, following Levine and Perram (1968). Then a term $\exp\{-2N_{mm}^{(a)}\,\delta(T)\}$ would appear in the assembly partition function having the effect of replacing the constant w by the function of temperature $\{w+2\delta(T)\}$. Any equilibrium relation would remain valid provided this substitution was made. However, as we lack criteria to determine $\delta(T)$ for the present model and as we wish to keep the number of parameters as small as possible, we shall put $\delta(T) = 0$.

At low temperatures the alternative equilibrium state to the open structure discussed above is the 'close-packed' structure where all sites of the triangular lattice are occupied so that $\frac{2}{3}M$ molecules lie on a-sites and participate in bonding while $\frac{1}{3}M$ lie on b-sites and are unbonded. If the configurational energies of the open and close-packed structures are respectively denoted by $E_{c,o}$ and $E_{c,c}$ then for an assembly of M molecules

$$\begin{aligned} E_{c,o} &= -\tfrac{3}{2}M(\epsilon+w) \\ E_{c,c} &= -M(\epsilon+w)-2M\epsilon = -M(3\epsilon+w). \end{aligned} \tag{2.4}$$

However, if the pressure is specified, the most stable state at absolute zero is that of least configurational enthalpy (E_c+pA) where A is the area occupied by the assembly and p the two-dimensional pressure. We shall assume that the area per lattice site is determined only the forces between two molecules and is independent of temperature and pressure so that $A = Na_0$ where a_0 is constant. Then since in the open and close-packed structures we have $N = \frac{3}{2}M$ and $N = M$ respectively, we find that for an assembly of M molecules the corresponding configurational enthalpies are

$$\begin{aligned} H_{c,o} &= -\tfrac{3}{2}M(\epsilon+w)+\tfrac{3}{2}Mpa_0 \\ H_{c,c} &= -M(3\epsilon+w)+Mpa_0. \end{aligned} \tag{2.5}$$

If we define an energy difference Δw and a pressure p_0 by

$$\Delta w = w-3\epsilon, \qquad p_0 = \Delta w/a_0 \tag{2.6}$$

then the difference between the enthalpies of the two structures is given by

$$H_{c,c}-H_{c,o} = \tfrac{1}{2}M(\Delta w-pa_0) = \tfrac{1}{2}Ma_0(p_c-p). \tag{2.7}$$

It is clear that the condition for the open structure to be stable relative to the close-packed structures at absolute zero is $p < p_0$. If the energy of bond formation is not large enough relative to the interaction energy of unbounded neighbours then $p_0 < 0$ and the close-packed structure is stable for all pressures at absolute zero.

3. The first-order triangle approximation

In the generalized first-order (quasi-chemical or Bethe) approximation a basic group of sites is chosen and the system is regarded as an assembly of such groups occupied in various ways (Guggenheim and McGlashan 1951). In the best-known form of the approximation the group is simply a nearest-neighbour pair of sites but we shall choose a triangle of two a-sites and one b-site, giving the correct ratio of 'honeycomb' to 'interstitial' sites. Where there are second-neighbour interaction energies it is important that the ratio of first- to second-neighbour site pairs in the group should be equal to that in the whole lattice (Bell 1953). In the present work only first-neighbour interaction energies are considered but these are different for aa and ab pairs so that it is desirable that the ratio of aa to ab site pairs in the group should be equal to that in the lattice. This criterion is satisfied in the triangle group of sites with one aa pair and two ab pairs. Using N triangles to give the correct total number of $3N$ nearest-neighbour site pairs, the first-order approximation, in the Guggenheim and McGlashan (1951) formulation, consists of writing for the configuration number Ω the relation

$$\ln \Omega = \ln \Omega_0 - N \sum_k \theta_k \ln \theta_k \tag{3.1}$$

where each θ_k is the probability of one of the types of occupation of the triangle. There are eight of the latter but two pairs obviously have equal probability so that six distinct θ_k are listed in table 1. The correlation between the triangles is to some extent allowed for by the factor Ω_0 which is such as to give Ω its correct value when the distribution in each sublattice is random. Hence

Table 1. The probabilities of the configurations on the triangular group of sites

(The two lower sites are a-sites and the upper one a b-site. A bond is denoted by a horizontal bar)

Probability	Configurations
θ_1	m m or m h h m
θ_2	h h or m h h m
θ_3	m m - m
θ_4	h m - m
θ_5	m h h
θ_6	h h h

$$\ln \Omega_0 = 2N[\tfrac{2}{3}\{\rho_a \ln \rho_a + (1-\rho_a)\ln(1-\rho_a)\} + \tfrac{1}{3}\{\rho_b \ln \rho_b + (1-\rho_b)\ln(1-\rho_b)\}]. \tag{3.2}$$

The probabilities $\theta_1, \ldots, \theta_6$ are not independent. Since the probabilities for all types of occupation of the triangle must add up to unity,

$$2\theta_1 + 2\theta_2 + \theta_3 + \theta_4 + \theta_5 + \theta_6 = 1. \tag{3.3}$$

From table 1 we can write an expression for the overall number density ρ in terms of the θ_k:

$$4\theta_1 + 2\theta_2 + 3\theta_3 + 2\theta_4 + \theta_5 = 3\rho \tag{3.4}$$

and, since we regard ρ as a thermodynamic variable, (3.4) constitutes a second relation between the θ_k. We choose θ_1, θ_2, θ_3 and θ_4 as independent order variables and then from (3.3) and (3.4) the dependent variables θ_5 and θ_6 are given by

$$\theta_5 = 3\rho-4\theta_1-2\theta_2-3\theta_3-2\theta_4 \tag{3.5}$$

$$\theta_6 = 1-3\rho+2\theta_1+2\theta_3+\theta_4. \tag{3.6}$$

In deriving the equilibrium conditions the sublattice number densities ρ_a and ρ_b appearing in $\ln \Omega_0$ will be regarded as dependent variables. From table 1 and equation (2.3) they are given by

$$\rho_a = \theta_1+\theta_2+\theta_3+\theta_4, \qquad \rho_b = 3\rho-2\rho_a. \tag{3.7}$$

Again from table 1, the configurational energy E_c, given by equation (2.1) may be expressed as

$$E_c = -N\{w(\theta_3+\theta_4)+\epsilon(2\theta_1+3\theta_3+\theta_4)\}. \tag{3.8}$$

We define a configurational Helmholtz free energy F_c for the assembly and a configurational free energy f_c per lattice site by

$$F_c = Nf_c(T, \rho, \theta_1, \theta_2, \theta_3, \theta_4) = E_c-kT\ln\Omega. \tag{3.9}$$

A procedure equivalent to finding the maximum term in the assembly partition function is to minimize F_c with respect to the independent order variables θ_1, θ_2, θ_3 and θ_4 at fixed values of the temperature T, area A and number of molecules M. The two latter thermodynamic variables are specified by N and ρ since the area a_0 per lattice site is a constant. For brevity we introduce the notation

$$s = \left\{\frac{\rho_a(1-\rho_b)}{\rho_b(1-\rho_a)}\right\}^{2/3} = \left\{\frac{\rho_a(1-3\rho+2\rho_a)}{(1-\rho_a)(3\rho-2\rho_a)}\right\}^{2/3} \tag{3.10}$$

and it is also convenient to define

$$y = \exp\left(\frac{-\epsilon}{kT}\right), \qquad z = \exp\left(\frac{-w}{kT}\right), \qquad \phi = \frac{\theta_6}{\theta_5}. \tag{3.11}$$

The four equilibrium relations obtained by equating to zero the derivatives of f_c with respect to θ_1, θ_2, θ_3 and θ_4 at constant T and ρ can then be expressed in the form

$$\begin{aligned} \frac{\theta_1}{\theta_5} &= \frac{s}{y\phi}, & \frac{\theta_2}{\theta_5} &= s \\ \frac{\theta_3}{\theta_5} &= \frac{s^2}{(y^3z\phi^2)}, & \frac{\theta_4}{\theta_5} &= \frac{s^2}{(yz\phi)}. \end{aligned} \tag{3.12}$$

We now require expressions for certain thermodynamic functions. The configurational chemical potential g_c is given, using the first relation of (2.3), by

$$g_c = \left(\frac{\partial F_c}{\partial M}\right)_{T,A} = \left(\frac{\partial f_c}{\partial \rho}\right)_T \tag{3.13}$$

and the two-dimensional pressure p by

$$p = -\left(\frac{\partial F_c}{\partial A}\right)_{M,T} = -a_0^{-1}\left\{\frac{\partial(Nf_c)}{\partial N}\right\}_{M,T}$$

which yields

$$pa_{\mathrm{o}} = \rho\left(\frac{\partial f_{\mathrm{c}}}{\partial \rho}\right)_{T} - f_{\mathrm{c}}. \tag{3.14}$$

From (3.13) and (3.14)

$$g_{\mathrm{c}} = \frac{f_{\mathrm{c}}+pa_{\mathrm{o}}}{\rho} = \frac{F_{\mathrm{c}}+pA}{M} \tag{3.15}$$

verifying that the present formulation satisfies the thermodynamic relation that chemical potential in a one-component system is equal to Gibbs free energy per molecule. Since we equate to zero the derivatives of f_{c} with respect to the four independent order variables θ_1, θ_2, θ_3 and θ_4 the latter can be held constant when the differentiation in (3.13) is performed so that

$$g_{\mathrm{c}} = -kT\left(2\ln\frac{\rho_{\mathrm{b}}}{1-\rho_{\mathrm{b}}} + 3\ln\phi\right). \tag{3.16}$$

After simplifying f_{c} with the help of the equilibrium relations (3.12) we have, from (3.14),

$$pa_{\mathrm{o}} = kT\{\tfrac{4}{3}\ln(1-\rho_{\mathrm{a}}) + \tfrac{2}{3}\ln(1-\rho_{\mathrm{b}}) - \ln\theta_5 - \ln\phi\}. \tag{3.17}$$

With the aid of (3.3), the last definition of (3.11) and the equilibrium relations (3.12) we obtain θ_5 as a function of ϕ and s, and then from (3.4) we can also express ρ in terms of these variables. Since s is given in terms of ρ_{a} and ρ by the definition (3.10) we now have, at any temperature, the pressure p and the density ρ expressed implicitly in terms of the two parameters ρ_{a} and ϕ. Another relation between these parameters is necessary and it proves convenient to use (3.3), (3.4) and (3.7) together with the equilibrium relations (3.12) to write

$$\frac{\phi\rho_{\mathrm{b}}-(1-\rho_{\mathrm{b}})}{1-\rho_{\mathrm{a}}} = \frac{s(1-y)\{2y^2\phi + s(1+y)z^{-1}\}}{y^2\{(1+\phi)y\phi + s(1+y\phi)\}}. \tag{3.18}$$

This shows at once that for $y = 1$ (i.e. $\epsilon = 0$ or $T = \infty$) $\phi = (1-\rho_{\mathrm{b}})/\rho_{\mathrm{b}}$. Otherwise, $y < 1$ and the right-hand side of (3.18) is a positive monotonically decreasing function of ϕ so that (3.18) yields a unique positive value of ϕ at a given temperature and given values of ρ and ρ_{a}. Points on the (ρ, p, T) state surface may now be obtained numerically by adjusting ρ_{a} until the equation for ρ is satisfied and then using equation (3.17) for the pressure. Results are discussed in § 6 below.

4. Low-temperature behaviour

Important properties of the model can be derived from the equilibrium relations at small T (i.e. when y, z and $\exp(-pa_{\mathrm{o}}/kT)$ are all much less than unity). If the configuration tends towards the open structure then, from table 1, $\theta_4 \to 1$ as $T \to 0$ and, if towards the close-packed structure, then $\theta_3 \to 1$. We now consider the behaviour of the interstitial sublattice number density ρ_{b} which, from (3.4), (3.7), (3.11) and (3.12) can be expressed as

$$\rho_{\mathrm{b}} = 2\theta_1 + \theta_3 + \theta_5 = 2\frac{\theta_1+\theta_2}{1+y\phi} + \frac{\theta_3+\theta_4}{1+y^2\phi} + \frac{\theta_5+\theta_6}{1+\phi}. \tag{4.1}$$

We now suppose that the triangle configuration obtainable from the dominant one without breaking a bond is the next most probable. Hence if θ_4 is nearly 1 the occupation probability next in order of magnitude is θ_3 and vice-versa. This is physically reasonable and may be verified by treating the open and close-packed structures separately. It may then be deduced from (4.1) that, near $T = 0$,

$$\rho_b \sim (1+y^2\phi)^{-1}, \qquad y^2\phi \sim (1-\rho_b)/\rho_b. \tag{4.2}$$

Also, using two of the equilibrium relations (3.12),

$$1 \sim \theta_3+\theta_4 \sim \frac{\theta_5 s^2(1+y^2\phi)}{y^3 z\phi^2}. \tag{4.3}$$

Substitution of (4.2) and (4.3) into the pressure relation (3.17) yields

$$\exp\left\{\frac{3(pa_o+3\epsilon-w)}{kT}\right\} = \exp\left\{\frac{3(p-p_o)a_o}{kT}\right\} \sim \frac{\rho_b{}^2}{(1-\rho_b)^3}. \tag{4.4}$$

It follows that, for $p > p_o$, $\rho_b \to 1$ as $T \to 0$ (close-packed structure) while, for $p < p_o$, $\rho_b \to 0$ as $T \to 0$ (open structure) in accordance with the conclusions of § 2 above. If $p = p_o$, exactly, then from (4.4) the limiting value of ρ_b at absolute zero is given by the cubic

$$(1-\rho_b)^3-\rho_b{}^2 = 0$$

which has only one real root, $\rho_b = 0{\cdot}43$. Since $\rho_a = 1$ in both the open and close-packed structures it follows from (2.3) that the overall number density $\rho \to 0{\cdot}81$ as $T \to 0$ when $p = p_o$.

We now consider the open structure separately. When $p < p_o$ it follows from (4.1), (4.2) and (4.4) that $y^2\phi \to \infty$ as $T \to 0$ and we may write the asymptotic relation

$$\theta_3 \sim \rho_b \sim \exp\left(\frac{\frac{3}{2}pa_o}{kT}\right) z^{3/2}y^{-9/2} = \exp\left\{\frac{-\frac{3}{2}(p_o-p)a_o}{kT}\right\}. \tag{4.5}$$

The limiting behaviour of $(1-\rho_a)$ (or s) can be obtained from the relation

$$1-\rho_a = \theta_1+\theta_2+\theta_5+\theta_6. \tag{4.6}$$

It is found that θ_2 is next in order of magnitude after θ_4 and θ_3 and that

$$\theta_2 \sim 1-\rho_a \sim \exp\left(\frac{-\frac{3}{2}pa_o}{kT}\right) z^{3/2}y^{3/2}. \tag{4.7}$$

Equation (2.3) can be written in the form

$$\rho = \tfrac{2}{3}+\tfrac{1}{3}\rho_b-\tfrac{2}{3}(1-\rho_a) \tag{4.8}$$

and, from (4.5) and (4.7), ρ_b is of higher order of magnitude than $(1-\rho_a)$. Hence ρ increases with temperature near $T = 0$ and thus, if $p_c < p < p_o$ (p_c being the critical pressure), there must be at least one maximum in the curve of density against temperature at this value of p. If $p < p_c$ the question of whether such a maximum occurs before separation into conjugate phases must be resolved by calculation.

For $p > p_o$, the configuration tends to the close-packed structure, $y^2\phi \to 0$ with T and we have the asymptotic relation

$$\theta_4 \sim 1-\rho_b \sim \exp\left(\frac{-pa_o}{kT}\right) z^{-1}y^3 = \exp\left\{\frac{(p_o-p)a_o}{kT}\right\}. \tag{4.9}$$

For $(p-p_{\mathrm{o}})a_{\mathrm{o}} > \epsilon$ it is found that θ_1 is next in order of magnitude after θ_3 and θ_4 and that

$$\theta_1 \sim 1-\rho_{\mathrm{a}} \sim \exp\left(\frac{-pa_{\mathrm{o}}}{kT}\right) z^2y^3. \tag{4.10}$$

For positive $(p-p_{\mathrm{o}})a_{\mathrm{o}} < \epsilon$, on the other hand, it is found that θ_2 is next in order of magnitude after θ_3 and θ_4 and that

$$\theta_2 \sim 1-\rho_{\mathrm{a}} \sim \exp\left(\frac{-2pa_{\mathrm{o}}}{kT}\right) zy^3. \tag{4.11}$$

These relations mean that, while for $p < p_{\mathrm{o}}$ and $(p-p_{\mathrm{o}})a_{\mathrm{o}} > \epsilon$ defects in the a- and b-sublattices are uncorrelated at low T, in the case $0 < (p-p_{\mathrm{o}})a_{\mathrm{o}} < \epsilon$ a defect (vacancy) on sublattice a is likely to occur next to a defect (vacancy) on sublattice b.

5. Model with zero interaction energy between unbonded neighbours

If $\epsilon = 0$ the states of the interstitial bonded fluid can be related to those of the Ising ferromagnet on the honeycomb lattice. Although it will be seen in § 6 that a non-zero value of ϵ gives results which are physically of more significance, it is of interest to compare critical values derived from the triangle approximation for $\epsilon = 0$ with accurate values obtained by comparison with the Ising model.

With $\epsilon = 0$ there is no energy of interaction between interstitial and honeycomb molecules so that the distribution on sublattice a is random and uncorrelated with that on sublattice b. Hence we may write for the configurational Helmholtz free energy per site

$$f_{\mathrm{c}} = \tfrac{1}{3}kT\{\rho_{\mathrm{b}}\ln\rho_{\mathrm{b}}+(1-\rho_{\mathrm{b}})\ln(1-\rho_{\mathrm{b}})\}+\tfrac{2}{3}f_{\mathrm{c}}^{(\mathrm{a})}(\rho_{\mathrm{a}}) \tag{5.1}$$

where $f_{\mathrm{c}}^{(\mathrm{a})}$ is the free energy per site for the assembly on sublattice a, regarded as a function of the number density ρ_{a}. We show in the Appendix that

$$f_{\mathrm{c}}^{(\mathrm{a})}(\rho_{\mathrm{a}}) = \tfrac{3}{8}w-\tfrac{3}{2}w\rho_{\mathrm{a}}+f_{\mathrm{c}}^*(\rho_{\mathrm{a}}) \tag{5.2}$$

where $f_{\mathrm{c}}^*(\rho_{\mathrm{a}})$ is the free energy per lattice site for a zero-field Ising ferromagnet on the honeycomb lattice with a fraction ρ_{a} of the spins pointing in one direction and the Ising interaction constant J equal to $\tfrac{1}{4}w$. Substituting (5.2) into (5.1) we have

$$f_{\mathrm{c}} = \tfrac{1}{3}kT\{\rho_{\mathrm{b}}\ln\rho_{\mathrm{b}}+(1-\rho_{\mathrm{b}})\ln(1-\rho_{\mathrm{b}})\}+\tfrac{1}{4}w-w\rho_{\mathrm{a}}+\tfrac{2}{3}f_{\mathrm{c}}^*(\rho_{\mathrm{a}}). \tag{5.3}$$

Applying equation (2.3) it follows from (5.3) that the equilibrium relation for transfer of molecules between the sublattices is

$$\left(\frac{\partial f_{\mathrm{c}}}{\partial\rho_{\mathrm{a}}}\right)_{\rho} = -\tfrac{2}{3}kT\ln\left(\frac{\rho_{\mathrm{b}}}{1-\rho_{\mathrm{b}}}\right)-w+\frac{\tfrac{2}{3}\partial f_{\mathrm{c}}^*(\rho_{\mathrm{a}})}{\partial\rho_{\mathrm{a}}} = 0. \tag{5.4}$$

Applying equation (3.13) to the form of f_{c} given by (5.3), where the only dependence on the overall density ρ is through ρ_{b} in the first term on the right-hand side, we find that the chemical potential is

$$g_{\mathrm{c}} = \frac{\partial f_{\mathrm{c}}}{\partial\rho} = kT\ln\frac{\rho_{\mathrm{b}}}{1-\rho_{\mathrm{b}}}. \tag{5.5}$$

Substituting (5.3), (5.5) and (5.4) into equation (3.14) for the pressure we derive

$$pa_{\mathrm{o}} = \rho\frac{\partial f_{\mathrm{c}}}{\partial\rho}-f_{\mathrm{c}} = -\tfrac{1}{3}kT\ln(1-\rho_{\mathrm{b}})-\tfrac{1}{4}w+\tfrac{2}{3}\left(\rho_{\mathrm{a}}\frac{\partial f_{\mathrm{c}}^*}{\partial\rho_{\mathrm{a}}}-f_{\mathrm{c}}^*\right). \tag{5.6}$$

The zero-field Ising model satisfies an equilibrium condition for reversal of dipole direction which can be written

$$\frac{\partial f_c^*}{\partial \rho_a} = 0. \tag{5.7}$$

Comparing this relation with (5.4) and noting that ρ_b is given in terms of ρ_a by (2.3) we see that (5.4) corresponds to an equilibrium condition for an Ising model in an applied field depending on ρ_a. Although exact closed-form solutions exist for the honeycomb lattice zero-field Ising model they are not available when the applied field differs from zero and we must still resort to approximation methods. However, we shall now show that critical properties in the interstitial bonded fluid model can be related to the zero-field Ising model. The Ising free energy f_c^* satisfies the symmetry relation

$$f_c^*(\rho_a) = f_c^*(1-\rho_a). \tag{5.8}$$

Hence, below the Curie temperature T_c, the Ising model equilibrium condition (5.7) is satisfied at $\rho_a = \frac{1}{2}$ and a pair of points $\rho_a = \frac{1}{2}(1 \pm |m|)$, m being the relative magnetization. Where (5.7) is satisfied the bonded fluid equilibrium relation (5.4) is also satisfied if

$$\rho_b = \left\{1+\exp\left(\frac{\frac{3}{2}w}{kT}\right)\right\}^{-1} \tag{5.9}$$

irrespective of the value of ρ_a given by (5.7). Hence from (5.6) pa_0 has the same value for the bonded fluid phases where $\rho_a = \frac{1}{2}(1 \pm |m|)$ and ρ_b is given by (5.9). Again from (5.5) and (5.9) the chemical potential g_c has the same value $-\frac{3}{2}w$ in the two phases, which are thus in equilibrium. The two conjugate bonded fluid phases become identical when $m = 0$ ($\rho_a = \frac{1}{2}$) so the Curie temperature T_c of the honeycomb lattice Ising model is also the critical temperature for the bonded fluid on the triangular lattice with $\epsilon = 0$. From (2.3) and (5.9) the critical density ρ_c is given by

$$\rho_c = \tfrac{1}{3}\left\{1+\exp\left(\frac{\frac{2}{3}w}{kT_c}\right)\right\}^{-1} + \tfrac{1}{3} \tag{5.10}$$

while from (5.6), (5.7) and (5.9) the critical pressure p_c is given by

$$p_c a_0 = \tfrac{1}{3}kT_c \ln\left\{1+\exp\left(\frac{-\frac{3}{2}w}{kT_c}\right)\right\} - \tfrac{1}{4}w - \tfrac{2}{3}f_c^* \quad (\rho_a = \tfrac{1}{2},\ T = T_c). \tag{5.11}$$

Accurate values for $kT_c/w = kT_c/4J$ and $p_c a_0/w$ were derived from honeycomb Ising model critical values given by Domb (1960—appendix II, § 3) identifying the critical value of f_c^* with Domb's $-kT_c \ln \lambda_c$. The accurate critical values are compared with those derived from the zeroth and first-order approximations in table 2.

Table 2. Accurate and approximate critical values for $\epsilon = 0$

	Zeroth order	First order	Accurate
kT_c/w	0·750	0·455	0·380
ρ_c	0·373	0·345	0·340
$p_c a_0/w$	0·1282	0·0313	0·0119

It should be noted that the value of pressure p_0 (separating the regions of open and closed-packed structure at $T = 0$) derived in § 2 is also accurate so that the last entry in the last column of table 2 gives the accurate value of p_c/p_0 for the case $\epsilon = 0$. The properties of the bonded fluid differ from those of the 'lattice gas' on the honeycomb lattice alone. For instance, the conjugate phase densities of the latter are $\frac{1}{2}(1 \pm |m|)$ and the critical density is $\frac{1}{2}$ as opposed to the bonded fluid value given by (5.10). Even for the case $\epsilon = 0$ considered here, the bonded fluid density displays anomalous properties not shown by standard lattice gases, as can be seen both from the considerations of § 2 and § 4 above and from the first-order results in figures 2 and 5 below.

6. Numerical results and discussion

Calculations have been performed using the first-order triangle approximation discussed in § 3. With the bonding energy w absorbed into a reduced temperature kT/w the only arbitrary parameter is the ratio ϵ/w which must lie in the range 0 to $\frac{1}{3}$ for the open structure to exist at low temperatures and pressures. For calculation we have chosen the two values 0 and $\frac{1}{4}$ for ϵ/w. Isobars (curves of T against ρ at constant p) are plotted on figure 2 for $\epsilon/w = 0$ and on figure 3 for $\epsilon/w = \frac{1}{4}$. For subcritical pressures ($p < p_c$) the thermodynamically unstable portions of the curves are shown as broken while the straight 'tie-lines' connect conjugate liquid (high density) and vapour (low density) phases. For a given subcritical pressure the temperature at which

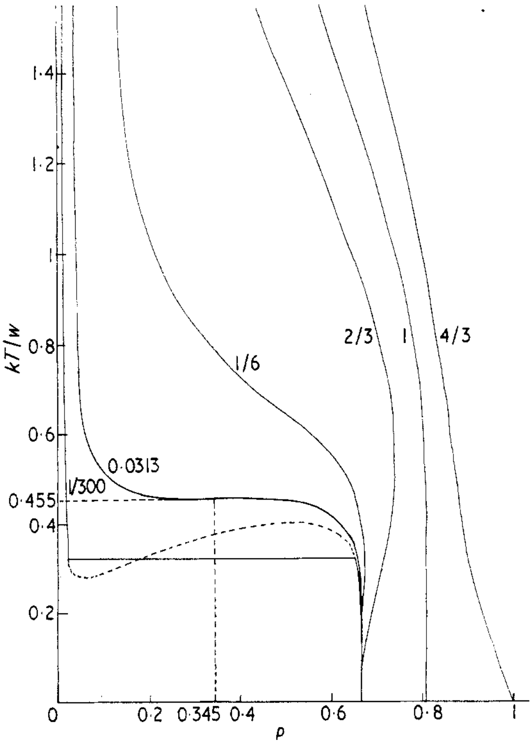

Figure 2. Temperature–density curves at constant pressure for $\epsilon/w = 0$, first-order triangle approximation. Each curve is labelled with the value of pa_0/w. ($p_0a_0/w = 1$ where $\epsilon/w = 0$).

liquid and vapour phases are in equilibrium can be obtained by plotting the chemical potential g_0 against temperature and a curve of this type is shown in figure 4. The closed loop corresponds to thermodynamically unstable states while the double point gives the temperature of phase equilibrium at the given pressure. The phenomenon of density increase with temperature at constant pressure and the appearance of a density maximum is easily seen on each isobar in the range $p_c < p < p_0$ on both figure 2 ($\epsilon/w = 0$) and figure 3 ($\epsilon/w = \frac{1}{4}$). However, at subcritical pressures $p < p_c$ a density maximum appears (in the liquid state) only for $\epsilon/w = \frac{1}{4}$. Isobars were also calculated for the zeroth-order approximation and are qualitatively similar to those shown in figures 2 and 3.

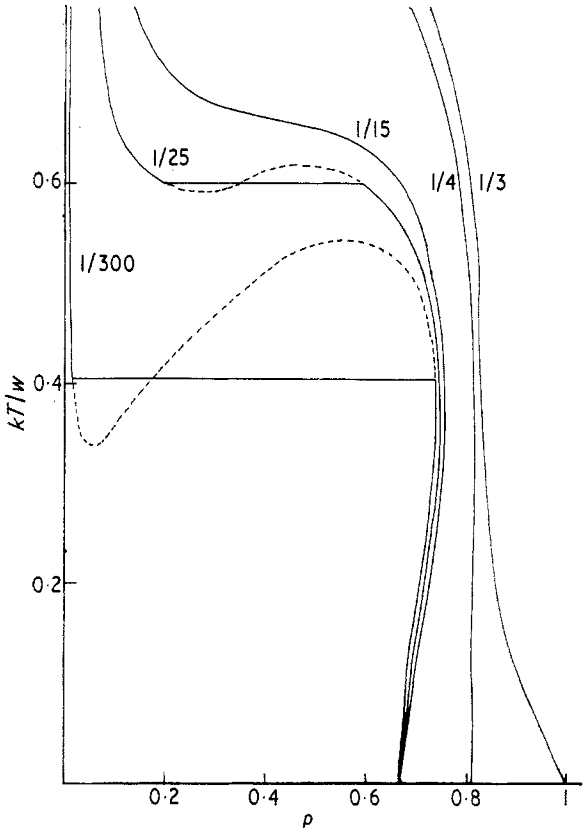

Figure 3. Temperature–density curves at constant pressure for $\epsilon/w = \frac{1}{4}$, first-order triangle approximation. Each curve is labelled with the value of pa_0/w. ($p_0a_0/w = \frac{1}{4}$ where $\epsilon/w = \frac{1}{4}$).

The fluid state surface is more often represented by isotherms than by isobars. For the present model, in the case $\epsilon/w = 0$, isotherms (curves of pressure against density at constant temperature) are plotted in figure 5. The form of the curves in the phase-separation region, with thermodynamically unstable parts represented by broken curves, is familiar for approximate theories of fluids. The characteristic properties of the state surface of the present model are shown by the appearance of density maxima on the isobars. This implies that pairs of points exist corresponding to the same density and pressure but different temperatures so that isotherms in the lower temperature range intersect. This behaviour is displayed by the isotherms in the right-hand part of figure 5.

In water there are density maxima on isobars in the liquid phase below the critical point as well as in the supercritical region. In our model this occurs for $\epsilon/w = \frac{1}{4}$ but

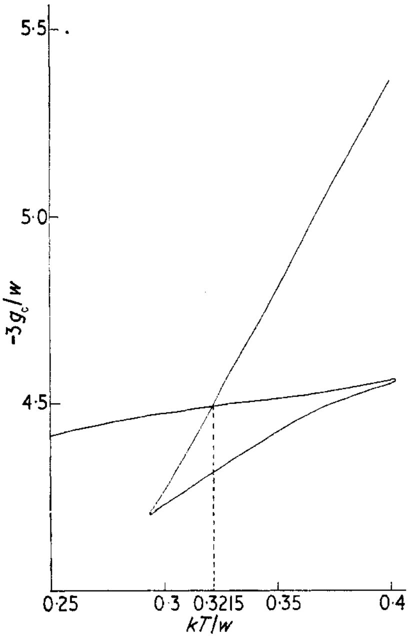

Figure 4. Chemical potential $(-3g_c/w)$–temperature curve for $\epsilon/w = 0$, $pa_0/w = 1/300$, first-order triangle approximation.

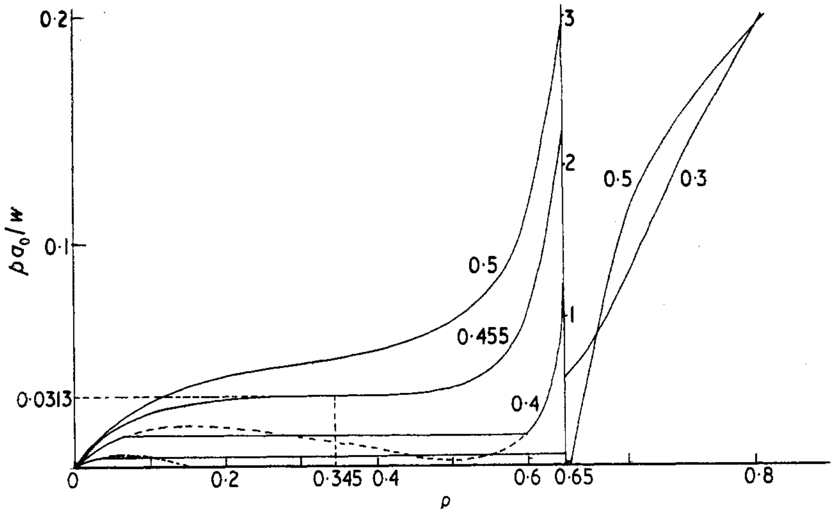

Figure 5. Pressure–density curves at constant temperature for $\epsilon/w = 0$, first-order triangle approximation. Each curve is labelled with the value of kT/w. Note that the scale of the diagram is changed for $\rho > 0{\cdot}65$ to display intersecting isotherms.

not for $\epsilon/w = 0$, which is physically reasonable since in water the non-bonding interactions comprehended in our parameter ϵ are of considerable importance. Anomalous density behaviour in water ceases at a pressure between 1500 and 2000 atmospheres (Bridgman 1949, Eisenberg and Kauzmann 1969) while the critical pressure is 218·3 atmospheres so that the ratio p_0/p_c is between 7 and 9. For the present model with $\epsilon/w = 0$ the accurate value of p_0/p_c is 84 while with the first-order (triangle) approximation p_0/p_c is 32. On the other hand with $\epsilon/w = \frac{1}{4}$ it can be seen from figure 3 that the first-order (triangle) approximation gives a value of p_0/p_c between $\frac{15}{4}$ and $\frac{25}{4}$ while the accurate value would presumably be rather higher. It thus again appears that the model's behaviour is closer to that of water with $\epsilon/w = \frac{1}{4}$ than with $\epsilon/w = 0$. However, it should be remarked that the anomalous behaviour of water is, as would indeed be expected, more complicated than that of the model, since at 1500 atmospheres there is a density minimum as well as a maximum in the isobar.

From a theoretical point of view the chief defect in the present model is that, as well as the long-range order implicitly imposed by using a triangular lattice of sites for the molecules, there is an additional degree of 'sublattice' long-range order resulting from the assumed differences between molecular pair interactions when both the members are on honeycomb lattice sites and when one member is on an interstitial site. This defect will be removed in the next paper of the series where there is no distinction between the sites of the triangular lattice and the open structure appears as a form of short-range order. However, the present paper has demonstrated that a very simple interstitial model with restricted directional bonding properties can show density and critical behaviour qualitatively similar to that of fluid water.

Acknowledgments

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Appendix

We relate the properties of the interstitial bonded fluid model for the case $\epsilon = 0$, when the distributions on sublattices a and b are uncorrelated, with those of the Ising model on the honeycomb lattice. If M_a denotes the number of molecules on the $\frac{2}{3}N$ sites of sublattice a and $N_\mathrm{mm}{}^{(\mathrm{a})}$, $N_\mathrm{mh}{}^{(\mathrm{a})}$, $N_\mathrm{hh}{}^{(\mathrm{a})}$ respectively denote the numbers of molecule–molecule, molecule–hole and hole–hole nearest-neighbour pairs on sublattice a then (disregarding boundary effects)

$$2N_\mathrm{mm}{}^{(\mathrm{a})}+N_\mathrm{mh}{}^{(\mathrm{a})} = 3M_\mathrm{a} = 3(\tfrac{2}{3}N)\rho_\mathrm{a} = 2N\rho_\mathrm{a} \tag{A1}$$

$$2N_\mathrm{hh}{}^{(\mathrm{a})}+N_\mathrm{mh}{}^{(\mathrm{a})} = 3(\tfrac{2}{3}N-M_\mathrm{a}) = 2N(1-\rho_\mathrm{a}). \tag{A2}$$

If $\Omega^{(\mathrm{a})}$ denotes the number of configurations on sublattice a for given values of M_a and $N_\mathrm{mm}{}^{(\mathrm{a})}$ then, using (A1) and (A2), the free energy of the assembly on sublattice a is

$$\begin{aligned}\tfrac{2}{3}Nf_\mathrm{c}{}^{(\mathrm{a})} &= -kT\ln\Omega^{(\mathrm{a})}-wN_\mathrm{mm}{}^{(\mathrm{a})}\\ &= \tfrac{1}{4}Nw-Nw\rho_\mathrm{a}-kT\ln\Omega^{(\mathrm{a})}+\tfrac{1}{4}wN_\mathrm{mh}{}^{(\mathrm{a})}-\tfrac{1}{4}w(N_\mathrm{mm}{}^{(\mathrm{a})}+N_\mathrm{hh}{}^{(\mathrm{a})}).\end{aligned} \tag{A3}$$

Now the configurational free energy of an Ising ferromagnet on a honeycomb lattice of $\frac{2}{3}N$ sites, identical with sublattice a, is

$$\tfrac{2}{3}Nf_\mathrm{c}{}^{*} = -kT\ln\Omega^{(\mathrm{a})}+JN_\mathrm{mh}{}^{(\mathrm{a})}-J(N_\mathrm{mm}{}^{(\mathrm{a})}+N_\mathrm{hh}{}^{(\mathrm{a})}) \tag{A4}$$

where the labels 'm' and 'h' now denote the 'up' and 'down' positions of an Ising dipole and J is the Ising interaction constant (see, for instance, Domb 1960). Comparing (A3) and (A4) and identifying J and $\frac{1}{4}w$, equation (5.2) follows.

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