Phase transitions in lattice fluids. I. Short-range interactions

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Abstract. The phase transitions of lattice fluids with molecules defined by first-neighbour exclusion, and interacting at short range, are considered using extended Kikuchi approximations. On the square lattice, a second-neighbour interaction does not produce a disordered low-density transition, but does make the packing transition first order below a critical temperature $\epsilon\beta = -1.05$. The resulting phase diagram therefore has only generalized fluid and solid regions. In a Kikuchi double-square calculation with third-neighbour interaction a disordered transition is produced, but this overlaps with the ordered state and again there is no stable intermediate liquid phase. Short-range interactions produce qualitatively the same effect on the triangular and simple cubic lattices. Particularly for the ordered state, the large sets of non-linear equations produced by an analytical treatment of extended Kikuchi approximations have limited the range of possible calculations. We have found numerical solution of these equations successful only with very good initial guesses, and therefore we have used a numerical optimization procedure in which linear constraints can be applied to minimize the free energy directly, producing a procedure through which Kikuchi calculations can be to a large extent automated, and large problems successfully attempted.

1. Introduction

In hard core lattice fluids, molecules are represented by occupied vertices which exclude from occupancy one or more neighbouring vertices, and it is now well established that these models possess an order–disorder transition akin to that of continuum hard discs or spheres, and to the fluid–solid transition of real fluids. The transition arises solely from geometrical packing effects due to the hard core, and in the case where no other interactions are considered (effectively at infinite temperature), much work has been done using the Kikuchi method (Burley 1961, 1965), the matrix method (Ree and Chesnut 1966, Runnels and Combs 1966, Runnels et al 1967), and series expansions (Gaunt and Fisher 1965, Gaunt 1967). The result is that, for first neighbours excluded, the infinite temperature transition is now well characterized for most lattices (a tabular summary can be found in Kaye 1973). Less extensive work has been done on models with more extended hard cores (Bellemans and Nigam 1967, Orban and Bellemans 1968, Runnels et al 1971).

The gas–liquid transition on the other hand depends on attractive interactions between molecules, and even the simplest lattice fluid with no exclusions (a transformation of the Ising ferromagnet, cf Fisher 1967) displays this type of transition when attractive interactions between nearest neighbour pairs are included.

In a recent paper, Hall and Stell (1973) have collected together most of the recent results from the above papers. They utilize this material, which concerns short-range interactions, by adding a long-range tail. There are no new results for short-range interactions so in the present work, which is concerned solely with such interactions, comparisons will only be made with the original papers. The value of Hall and Stell's work is in considering whether or not the addition of a long-range tail will produce a realistic phase diagram. A similar problem is considered in a subsequent publication (Kaye and Burley 1974), and comparisons with the Hall and Stell results are more appropriately made there.

In this paper we extend previous Kikuchi calculations on the first neighbour excluded model by using larger primary Kikuchi figures, in order both to improve the quantitative results for the infinite temperature transition, and to include interactions and therefore the possibility of both transitions in the same model. In the first instance a relatively simple calculation based on a primary square figure is used to study the effect of a single attractive interaction between second neighbours in the case of the square lattice model. A larger calculation using a primary double square is then used to improve the quantitative results and to introduce a second interaction between third neighbours. In this case the Kikuchi calculation cannot be carried through analytically, and consequently we have developed a numerical procedure (cf § 5) which has proved to be a powerful method for the larger Kikuchi calculations, and made tractable several new problems.

Similar calculations are then performed for the same model on the triangular and simple cubic lattices, again to investigate the effect of a single interaction, and in the former case also to extend Kikuchi calculations for the infinite temperature transition, in order to investigate the discrepancy between the Kikuchi results and that obtained by series and matrix methods.

2. Model

In order to illustrate the model and the solution technique, a square lattice of N sides and area per molecule a is considered. Molecules are defined by an occupied vertex with first neighbour exclusion, so that the effective molecular area is $2a$. At maximum density the molecules fully occupy one of two possible interpenetrating sublattices, as shown in figure 1, and the existence of an ordered state at lower densities is characterized by a continued imbalance in the occupancy of these two sublattices, as opposed to a disordered state in which the lattice is fully homogeneous. In a Kikuchi calculation the lattice is described in terms of the configurations of *small* subfigures of the lattice, and consequently to include the possibility of distinguishing between ordered and disordered states, the two sublattices have to be labelled. For a detailed discussion of this point see Kaye (1973).

In the triangular and simple cubic lattices the model is similarly defined except that there are now different possible sublattices and labellings.

3. Single-square calculations

The lattice is described in terms of the probabilities (fraction variables) of the primary and secondary subfigures shown in table 1. The degeneracy of each subfigure, shown in
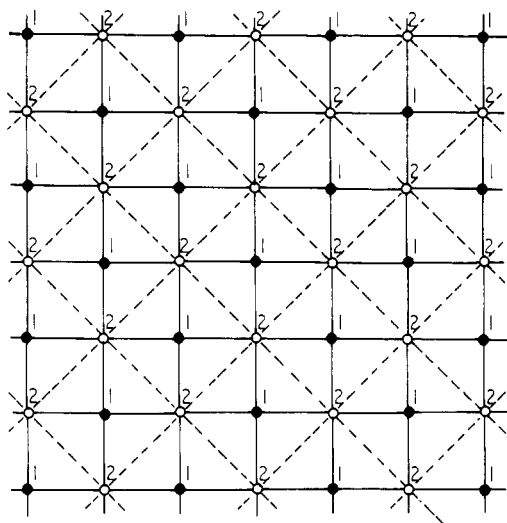
Figure 1. Labelling of the square lattice to describe the ordered state, producing two interpenetrating sublattices. ● Fully occupied sublattice representing ordered maximum density state. ⋰ Molecular 'boundaries'.

Table 1.

brackets alongside it, takes into account the symmetry of the figure with respect to the lattice, and the single interaction is also shown in the table.

There exist the following relations between the primary and secondary fraction variables (fv):

$$
\begin{aligned}
y_1 &= w_1 + w_2 + w_3 & x_1 &= y_1 + y_3 \\
y_2 &= w_2 + w_4 & x_2 &= y_2 \\
y_3 &= w_3 + w_5 & x_3 &= y_1 + y_2 \\
& & x_4 &= y_3
\end{aligned}
\tag{1}
$$

and there is a normalization among the 5 spanning variables (w_i)

$$\psi = w_1 + 2w_2 + 2w_3 + w_4 + w_5 - 1 = 0, \tag{2}$$

which reduces the number of independent variables to 4.

Following the method and notation of Kikuchi (cf Burley 1972 or Kaye 1973), the total number of configurations of an ensemble of L identical and independent lattices can be expressed in terms of the fraction variables by

$$G_L = \left(\frac{(\circ\!\!-\!\!\circ)^2}{\left(\begin{smallmatrix}\circ & \circ \\ \circ & \circ\end{smallmatrix}\right)(\circ)^{1/2}} \right)^{N/L}, \tag{3}$$

and the entropy of a single lattice as

$$S = \frac{k}{L} \ln G_L. \tag{4}$$

From the primary fraction variables the total energy of the lattice is

$$U = N(w_4 + w_5)\epsilon_1, \tag{5}$$

and the molecular density

$$\rho = \tfrac{1}{2}(x_2 + x_4); \qquad 0 \leqslant \rho \leqslant \tfrac{1}{2}. \tag{6}$$

The appropriate grand thermodynamic potential gives

$$Pa\beta = \frac{S}{kN} - \frac{U\beta}{N} + \rho\mu\beta, \tag{7}$$

where $\beta = 1/kT$ and μ is a potential for the exchange of molecules and unoccupied lattice sites. Since S, U and ρ are all available in terms of the spanning variables, this expression can now be maximized. Rather than use the normalization to reduce the number of variables immediately, it is convenient for obtaining the pressure to maximize with respect to all the spanning variables, using a Lagrange multiplier on equation (2) as follows,

$$\frac{\partial Pa\beta}{\partial w_i} + \lambda \frac{\partial \psi}{\partial w_i} = 0 \qquad i = 1, \ldots, 5. \tag{8}$$

Eliminating λ and μ from the 5 resulting equations which define equilibrium gives

$$\lambda = -\ln\left(\frac{y_1^2}{(x_1 x_3)^{1/2} w_1} \right), \tag{9}$$

and

$$\mu\beta = \ln\left(\frac{y_1^4 w_2^4 x_2}{x_1 w_1^4 y_2^4} \right), \tag{10}$$

and 3 relations between the 5 spanning variables

$$w_1 w_4 \eta_1 = w_2^2 \tag{11}$$

$$w_1 w_5 \eta_1 = w_3^2 \tag{12}$$

$$w_5 y_2^2 (x_1 x_4)^{1/2} = w_4 y_3^2 (x_2 x_3)^{1/2} \tag{13}$$

where the temperature variable is defined by

$$\eta_1 = \exp(\epsilon_1 \beta). \tag{14}$$

With equation (2) these relations serve to determine all the spanning variables in terms of one parameter, conveniently taken as the density. From equation (8) it is easily shown that the pressure is given by

$$Pa\beta = -\lambda, \tag{15}$$

and all the other thermodynamic functions then follow from equations (5)–(7).

With the sublattices made equivalent, the disordered solution follows easily. Equation (13) becomes an identity and equations (11) and (12) are identical, and the one remaining equation then provides a quadratic solution,

$$Pa\beta = 2\ln(1-2\rho) - \ln(1-\rho) - \ln(1-2\rho-2w_2), \tag{16}$$

where w_2 satisfies

$$w_2^2(2-\eta_1^{-1}) - w_2 + (\rho - 2\rho^2) = 0. \tag{17}$$

The full ordered solution is more difficult, and it is inconvenient to solve directly in terms of the density. However a solution is possible by rewriting the equations in terms of reduced fraction variables (fv_i'), where

$$fv_i' = \frac{fv_i}{w_4}, \tag{18}$$

and using a fixed parameter w_2/w_4 in place of the density. All the fraction variables can then be calculated in terms of this parameter via a quartic equation.

The results from both ordered and disordered solutions are described in § 6.

4. Double-square calculations

In order to introduce a second interaction ϵ_2, and at the same time improve the approximations, the configurations of a double square are now used as the primary variable set. Using the C scheme of Kikuchi and Brush (1967) for this subfigure,

$$G_L = \left(\frac{(\circ\!\!-\!\!\circ\!\!-\!\!\circ)^{1/2} \left(\begin{smallmatrix} \circ & \circ \\ \circ & \circ \end{smallmatrix} \right)}{(\circ\!\!-\!\!\circ) \left(\begin{smallmatrix} \circ & \circ & \circ \\ \circ & \circ & \circ \end{smallmatrix} \right)} \right)^{N/L} \tag{19}$$

and so the necessary function variables are those in table 2, with the relations

Table 2.

Diagram	Label			Diagram	Label		
	z_1	(1)			w_1	(1)	
	z_2	(2)			w_2	(2)	
	z_3	(2)			w_3	(2)	
	z_4	(1)			w_4	(1)	ϵ_1
	z_5	(1)			w_5	(1)	ϵ_1
	z_6	(2)	ϵ_1		v_1	(1)	
	z_7	(2)	ϵ_1		v_2	(2)	
	z_8	(1)	ϵ_2		v_3	(1)	
	z_9	(1)	ϵ_2		v_4	(1)	ϵ_2
	z_{10}	(2)			v_5	(1)	
	z_{11}	(1)	$2\epsilon_1+\epsilon_2$		v_6	(2)	
	z_{12}	(1)	$2\epsilon_1+\epsilon_2$		v_7	(1)	
					v_8	(1)	ϵ_2
					y_1	(1)	
					y_2	(1)	
					y_3	(1)	

$$w_1 = z_1 + z_2 + z_3$$
$$w_2 = z_2 + z_8 + z_{10} = z_4 + z_6\dagger$$
$$w_3 = z_5 + z_7 = z_3 + z_9 + z_{10}\dagger$$
$$w_4 = z_6 + z_{11}$$
$$w_5 = z_7 + z_{12}$$
$$v_1 = z_1 + 2z_3 + z_4 + z_9$$
$$v_2 = z_2 + z_6 + z_{10}$$
$$v_3 = z_5 + 2z_7 + z_{12}$$
$$v_4 = z_8 + z_{11}$$
$$v_5 = z_1 + 2z_2 + z_5 + z_8$$
$$v_6 = z_3 + z_7 + z_{10}$$
$$v_7 = z_4 + 2z_6 + z_{11}$$
$$y_1 = v_1 + v_2 = v_5 + v_6\dagger$$
$$y_2 = v_2 + v_4 = v_7\dagger$$
$$y_3 = v_6 + v_8 = v_3\dagger.$$

(20)

Of the 5 extra relations marked by †, two are independent and can be used to reduce the number of spanning variables for this problem to 10. The normalization is then

$$\psi = z_1 + 3z_2 + 3z_3 + z_6 + z_7 + 2z_8 + 2z_9 + 4z_{10} + z_{11} + z_{12} - 1 = 0, \quad (21)$$

and the energy and density are given by

$$U = N\epsilon_1(z_6 + z_7 + z_{11} + z_{12}) + N\epsilon_2(z_8 + z_9 + z_{11} + z_{12}), \quad (22)$$

$$\rho = \tfrac{1}{2}(z_2 + z_3 + z_6 + z_7 + z_8 + z_9 + 2z_{10} + z_{11} + z_{12}); \qquad 0 \leqslant \rho \leqslant \tfrac{1}{2}. \quad (23)$$

In a disordered solution, the number of spanning variables is reduced to 6, and an analytic solution following the lines of § 3 was obtained. However in the ordered case there are 9 equations to be solved, and it has not been found possible to do this analytically. A numerical procedure has been used therefore, which is described below.

5. A numerical procedure for large scale Kikuchi calculations

The Newton–Raphson method has been used to solve the sets of equations coming from Kikuchi calculations (Kikuchi 1966), but where the number of independent variables is high, or where good initial guesses for them are not available, the method fails, largely because of overshooting the constraints on the fraction variables

$$0 \leqslant fv_i \leqslant \frac{1}{\alpha_i}, \quad (24)$$

where α_i represents the degeneracy of the general fraction variable.

We have therefore developed a numerical procedure that can be used for all Kikuchi problems, with the advantage that only one computer program has to be written, to which different data sets defining specific problems can be supplied. The method is essentially a numerical analogue of the usual canonical method of statistical mechanics (ie the Helmholtz free energy replaces the potential of equation (7)), and will be referred to by the shorthand COFE (constrained optimization of free energy).

In a problem which has q spanning variables, the normalization is used to express all variables, and via the methods of § 3 the entropy, internal and free energies, in terms of $q-1$ independent variables, one of which is chosen, if possible, to be the density. The derivatives of the free energy with respect to the independent variables are then calculated, and holding the density constant, a numerical method of Fletcher (1968) is used to maximize the general term of the canonical sum with respect to the remaining $q-2$ variables, whilst applying the constraints of equation (24). A successful optimization gives the equilibrium values of the independent variables and that of the canonical sum, which is equated with its maximum term. All the thermodynamic functions can then be calculated.

In practice all the details of a particular problem, including the degeneracy factor G_L, the constraints on the fraction variables, the energy expression and the temperature factors $\epsilon_i\beta$, are codified in a set of matrices. With the density and temperature factors specified, these matrices are used to formulate a sub-procedure which calculates values for the general term of the canonical sum for any feasible set of the remaining independent variables. With an initial guess for these variables, the maximization is performed, and from an initial solution calculation over the whole range of density and temperature

is incorporated into the procedure by using previous solutions in a cubic extrapolation to provide guesses for subsequent ones.

Apart from its generality the COFE procedure has proved powerful, providing solutions so far to problems with up to 29 independent variables. Its success is largely due to the Fletcher optimization method. Developed from that of Davidon (1959), it is both more efficient and also allows *linear* equality or inequality constraints to be applied to the independent variables. Without this facility a procedure such as COFE has not been feasible, since previous maximization methods such as that of Davidon search over an unbounded variable space and lead to calculations with negative fraction variables which effectively stops the search.

6. Square lattice results

The effect of introducing a single interaction into the primary square calculation is shown in figure 2. For $\eta_1 = 1$ (ie at infinite temperature), the result of Burley (1961) is reproduced, with a discontinuous second-order transition to an ordered state at $\rho = 0.317$, the compressibility of both phases at this point remaining finite. In this context, 'discontinuous' means the sharp change of slope at the transition which occurs in a Kikuchi calculation, as opposed to the 'continuous' change which results from series and matrix calculations. As the temperature is lowered, the transition moves to lower densities, with a corresponding increase in the compressibility of the ordered state at the
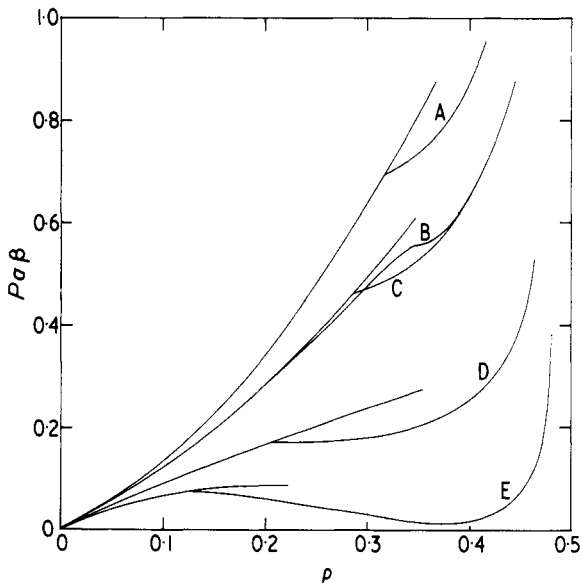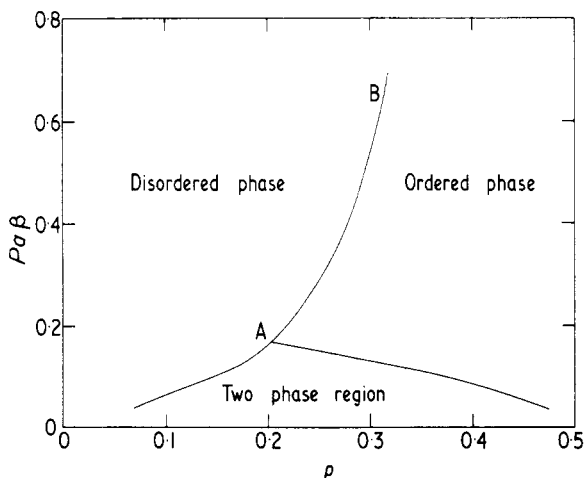

Figure 2. Single-square approximation, the effect of temperature on the order–disorder transition. Comparison with Fisher's exact isotherm. (Since we count twice as many interactions as Fisher, we use $\eta_1 = 1/\sqrt{2}$, corresponding to half the interaction energy in his calculation.) Curve A, $\eta_1 = 1.0$, pure hard core case (cf Burley 1961). $Pa\beta$ and ρ at transition 0.693 and 0.317 respectively. Curve B, exact isotherm of Fisher (1963). Transition at $(0.559, \sqrt{2}/4)$, with $dP/d\rho = 0$. Curve C, $\eta_1 = 1/\sqrt{2}$. Transition at (0.465, 0.288). Curve D, $\eta_1 = 0.35$, critical temperature. Transition at (0.169, 0.202), with $dP/d\rho = 0$. Curve E, $\eta_1 = 0.2$, low temperature case.

transition, until at a critical temperature $\eta_c = 0.35$, the compressibility of the ordered state becomes infinite. Below this temperature the transition is first order with a co-existence line located using the criterion of equal exchange potentials μ. As can be seen from the free energy diagram (figure 3), the ordered state is stable at the higher densities. Also shown in figure 2 is the single exact isotherm of Fisher (1963), for a slightly modified version of the model in which only half the possible interactions are included. With only one interaction ϵ_1, the disordered isotherm does not have any transition (Van der Waals type of loop), and consequently there is only the direct transition for a generalized fluid to the ordered solid, with a $P-V$ diagram which is shown in figure 4.
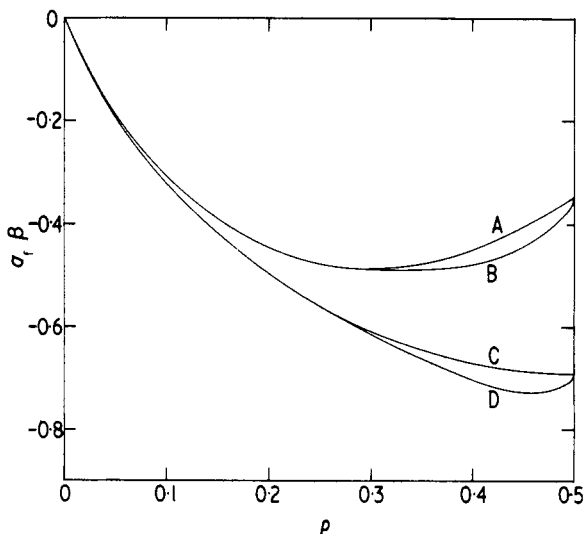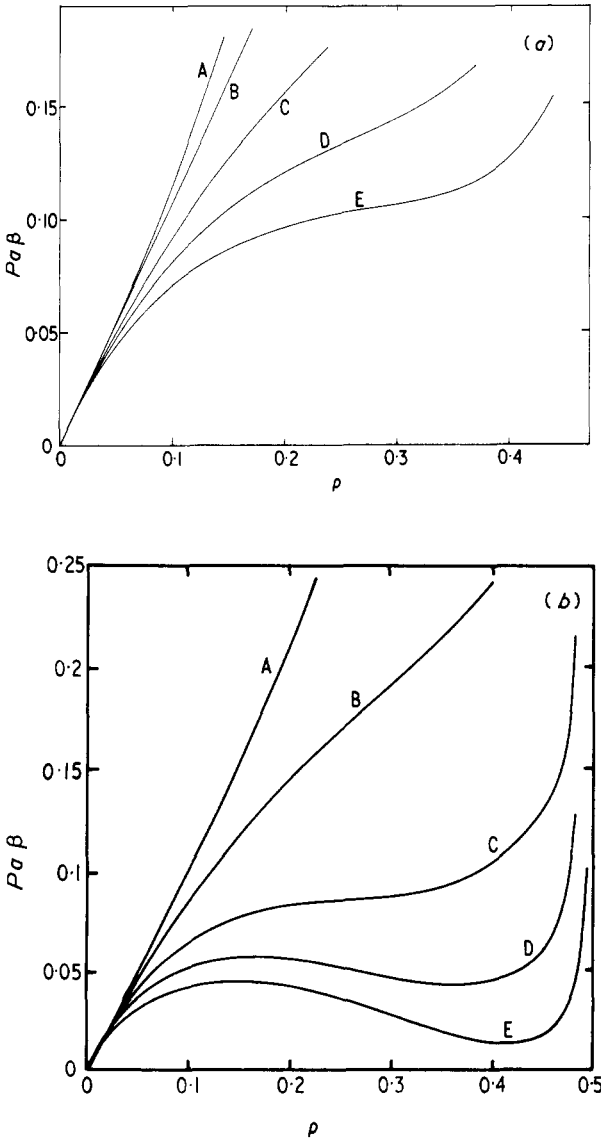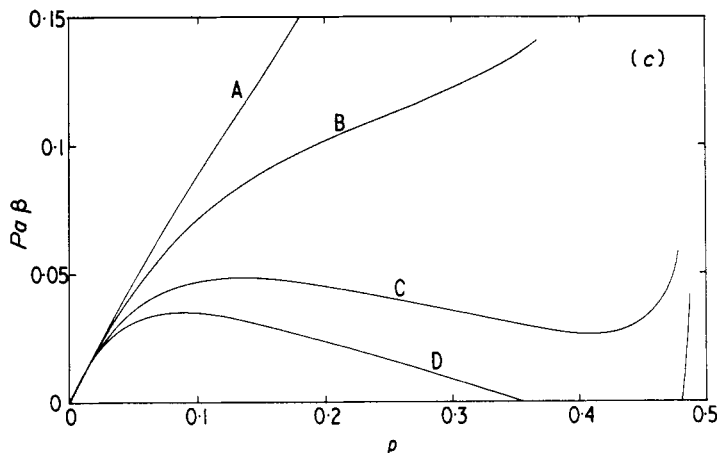

Figure 3. Single-square approximation, ordered and disordered free energy curves. Curve A, $\eta_1 = 1/\sqrt{2}$, disordered state; curve B, $\eta_1 = 1/\sqrt{2}$, ordered state; curve C, $\eta_1 = 0.5$, disordered state; curve D, $\eta_1 = 0.5$, ordered state. a_f is the Helmholtz free energy per lattice site.
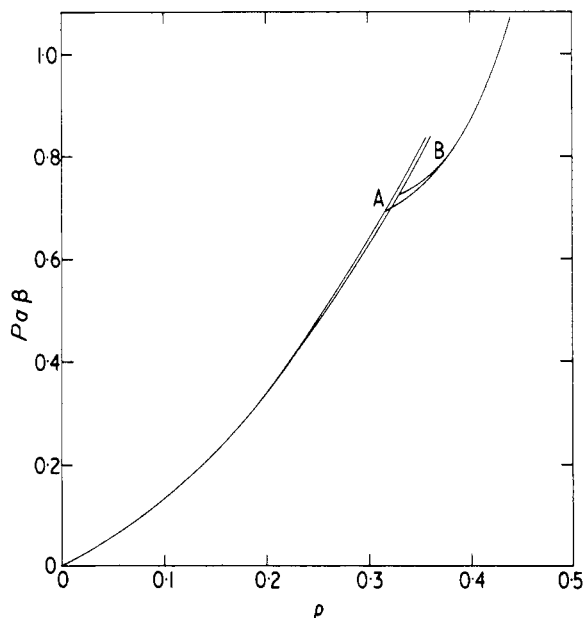

Figure 4. Single-square approximation, diagram of state. A Critical point, $\eta_1 = 0.35$, $\rho = 0.2$, $Pa\beta = 0.168$. B Infinite temperature, $\eta_1 = 1.0$, $\rho = 0.317$, $Pa\beta = 0.693$.

The inclusion of the second interaction ϵ_2 in the double-square calculation at once makes possible a disordered Van der Waals type of transition. This becomes possible for $\eta_1 \lesssim 0.5$, and is shown in figure 5. For the infinite temperature case, the result of the numerical calculations for the full ordered state is shown in figure 6. The larger subfigure brings an improvement in the estimate of the transition density from 0.317 in the single square calculation to $\rho = 0.33$ in the present case. A complete ordered calculation was also performed for the case $\eta_1 = \frac{1}{4}$, $\eta_2 = 1/\sqrt{2}$, for which the disordered state (figure 5) shows a pronounced Van der Waals loop. As can be seen in figure 7, the more stable ordered state undergoes a transition to a disordered state at a density of about 0.1, so overlapping the Van der Waals loop and leaving only one transition. It is first order, and the coexistence line is located as before.
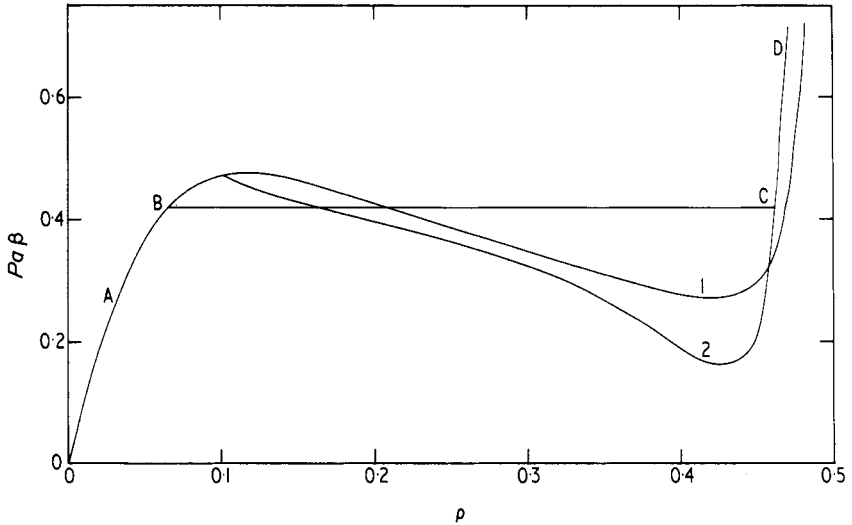
Figure 5. Double-square approximation, disordered isotherms for two interactions. (*a*) $\eta_1 = 0.5$. Curve A, $\eta_2 = \sqrt{2}$ (repulsion); curve B, $\eta_2 = 1.0$ (infinite temperature); curve C, $\eta_2 = 0.71$; curve D, $\eta_2 = 0.58$; curve E, $\eta_2 = 0.5$. (*b*) $\eta_1 = \frac{1}{3}$, η_2 as in (*a*). (*c*) $\eta_1 = 0.25$, η_2 as in (*a*).

Figure 6. Infinite temperature ordering transition comparison of approximations. Curve A, double-square approximation, $\rho_t = 0.33$, $Pa\beta_t = 0.725$; curve B, single-square approximation, $\rho_t = 0.317$, $Pa\beta_t = 0.693$. Matrix method: Runnels and Combs (1966), $\rho_t = 0.371$, $Pa\beta_t = 0.792$; series expansions: Gaunt and Fisher (1965), $\rho_t = 0.370$, $Pa\beta_t = 0.792$.

Although the inclusion of an extra interaction produces a Van der Waals loop in the disordered curve, this transition is not stable and the overall qualitative behaviour is the same as that calculated using the simpler Kikuchi square, so that a phase diagram similar to that of figure 4 is to be expected from these larger calculations. Accordingly

Figure 7. Double-square approximation, overlap of transitions. Curve 1, disordered state: $\eta_1 = 0.25$, $\eta_2 = 1/\sqrt{2}$; curve 2, ordered state: $\eta_1 = 0.25$, $\eta_2 = 1/\sqrt{2}$. Stable curve ABCD.

we have not, in the double-square case performed calculations to locate precisely the critical temperature at which the transition changes from second to first order, nor have we attempted to draw an accurate phase diagram.

The double-square calculation does however give a clear idea of how the Van der Waals loop is affected by changes in the potential, and some useful qualitative results can be seen. Even though these loops are overlapped by the ordered state, in more sophisticated models, the two transitions can be separated. A more detailed study of the dependence of the coexistence curve on the potential will be made in a further publication.

7. Other lattices

Calculations for the same model on the triangular and simple cubic lattices are similar to those above and consequently we omit detailed descriptions.

In the triangular case a two triangle subfigure was used to incorporate a single interaction between second neighbours, and since there are three close packed sub-lattices, threefold labelling of the lattice is necessary. In a calculation with seven spanning variables an analytic solution using reduced variables (cf equation (18)) can be obtained, and an ordered state found in which two sublattices are equivalent but different from the third. The disordered state, with all sublattices equivalent, is easily calculated. In the infinite temperature case the result of Burley (1965) is reproduced, in which the transition is first order. At lower temperatures the single interaction produces a disordered Van der Waals loop, but as in the square lattice, the lowering of the density and pressure with temperature of the ordering transition leads to an overlap, and only the latter is stable. The resulting phase diagram is very similar to that of the square lattice, except for the position and nature of the infinite temperature transition, and the consequent lack of a critical point.

COFE calculations using a ▽△ were also performed, with the same interaction between second neighbour, and the results are shown in figure 8, along with those of the simpler
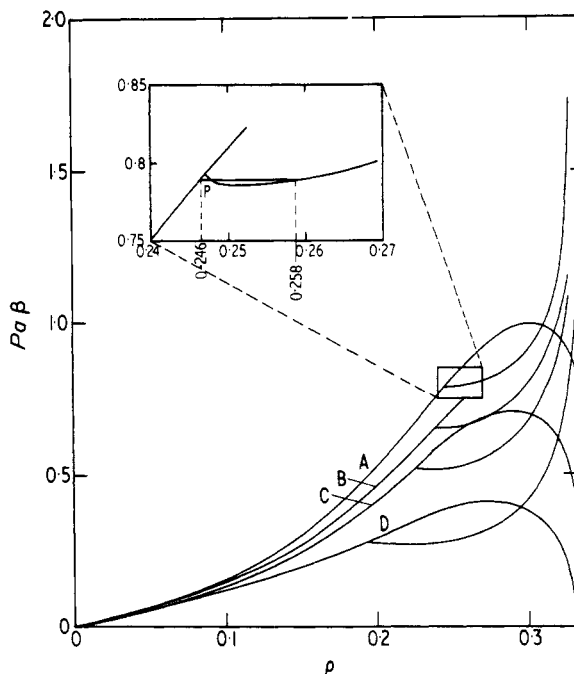
Figure 8. ▽△ approximation, pressure diagram. Order–disorder transition and the effect of temperature. Curve A, $\eta_1 = 1.0$; inset, $\rho_G = 0.246$, $\rho_S = 0.258$, $Pa\beta_t = 0.79$ at the transition; curve B, $\eta_1 = 0.9$; curve C, $\eta_1 = 0.8$; curve D, $\eta_1 = 0.6$. Kikuchi ▽ $\rho_G = 0.228$, $\rho_S = 0.257$, $Pa\beta_t = 0.736$; matrix method: Runnels and Combs (1966), second-order transition, $\rho_t = 0.279$, $Pa\beta_t = 0.843$; series expansion: Gaunt (1967), second-order transition, $\rho_t = 0.277$, $Pa\beta_t = 0.839$.

calculation, and other methods. In the infinite temperature case the extent of the density discontinuity is much reduced in the improved approximation, and at lower temperatures the effect on the transition is qualitatively the same as that calculated using the simpler figure again with no separate disordered transition.

First neighbour exclusion on the simple cubic lattice produces a maximum density configuration which can be considered as one of two possible FCC sublattices, so that a twofold labelling is necessary to describe the ordered state. We have performed calculations using both a square and a cube as the primary subfigure, although as in the triangular lattice we do not describe these in detail since they are similar to those already described. In the former case an interaction ϵ_1 across the diagonal of a square is included, and analytic solutions for both states are possible, following the lines of § 3. In the latter case a second interaction ϵ_2 across the diagonal of a cube can be included, and the ordered state now has to be solved using the COFE procedure. Clearly if $\epsilon_2 \ll \epsilon_1$ there exists the possibility of an intermediate stable ordered state which would be a BCC sublattice of the basic simple cubic lattice. There are four possible BCC sublattices, so that to describe this intermediate state four distinguishable types of lattice site would have to be labelled. Since the maximum density state would necessarily be a FCC one, this model could possibly describe transitions between different high-density ordered states, but since the fourfold labelling greatly increases the number of fraction variables, this problem must remain as a separate project.

The results for the simple cubic lattice are similar to those of the square lattice, with no separate liquid state, and are here only briefly summarized. The ordering transition is second order at infinite temperature, and in the square calculation is located at $\rho = 0.1904$, as found by Burley (1961). This is improved slightly to $\rho = 0.2$ in the cube calculation. The transition becomes first order at lower temperatures, and mapped in the square calculation, the phase diagram is similar to that in figure 4, with the critical point located by $\eta_1 = 0.75$, $\rho = 0.13$ and $Pa\beta = 0.15$.

8. Discussion

For the infinite temperature cases, new estimates of the ordered state transition points have been obtained using subfigures larger than those of previous Kikuchi calculations (Burley 1961, 1965). As can be seen in figures 6 and 8 the new calculations move the transition towards the higher densities and pressures of the matrix and series results, which are more accurate in locating the transition point. Also from these figures, and from figure 2 where Fisher's exact isotherm is compared with its Kikuchi equivalent, it may be seen that the larger subfigure brings an improvement only near to the transition, the calculation being accurate at low or high densities. This aspect of Kikuchi calculations is well known and arises from the fact that near the transition molecular correlations play a delicate and critical role, and can only be accurately described by the Kikuchi calculations within the limited range of the primary subfigure.

The infinite temperature transition of the triangular lattice is of particular interest, since the matrix and series methods predict a second-order transition with zero slope in the isotherm but no density discontinuity. Although the transition remains first order in both of the Kikuchi calculations above, the density gap of the $\triangledown\triangle$ calculation becomes much smaller than that in the two-triangle case. For the two-triangle calculation

$$\rho_G = 0.684\rho_0, \qquad \rho_S = 0.771\rho_0$$

where in the larger $\triangledown\triangle$ calculation

$$\rho_G = 0.738\rho_0, \qquad \rho_S = 0.774\rho_0,$$

which represents a density discontinuity of only some 5%. Kikuchi has also performed these latter calculations (in a private communication to DMB), and obtains results very close to those quoted above.

It is still possible that the transition on the triangular lattice is first order, with a very small density discontinuity. However as can be seen above the better approximation greatly weakens the transition, and in the following argument it seems as though even larger Kikuchi calculations will eventually produce a second-order transition with an infinity in the isothermal compressibility. Looking in detail at the transition (detail of figure 8), it can be seen that near the transition, the loop in the ordered state is very flat and that as the density of the ordered state decreases, the pressure and its gradient both decrease monotonically up to a point, labelled P in the figure, where the gradient becomes zero. This point is very close to the eventual order–disorder contact, which is effected by a short upward spike of the ordered isotherm. It is this spike which makes the transition first order, so it is important to realize that this spike also represents the most unreliable part of the whole Kikuchi calculation, since it occurs at the point where the small subfigure approximation forces the calculation into a discontinuous description of the transition between the two phases. It is quite possible that this spike is therefore an

artefact and that the transition is in reality second order, with $dP/d\rho = 0$, as indicated by series and matrix calculations. This is confirmed by preliminary calculations using a $\triangledown\triangledown\triangledown$ subfigure by one of us (DMB), which indicate a further reduction in the density gap at the transition.

When there is an attractive interaction only between second neighbours, that is between molecules touching as in the close packed configuration, there is in addition to the entropic advantage of regular packing at high densities, an energetic advantage, since only close packed configurations have finite internal energy. Accordingly the ordered state is stable at lower densities, and the transition becomes analogous to that of a normal fluid below the triple point, with direct condensation from vapour to solid.

In the case of the square lattice these results are qualitatively in agreement with those of Runnels *et al* (1970), except that there the matrix method was used, and the second-order transition is continuous. Bearing in mind that the Kikuchi single-square calculation is the simplest which can describe the model, and the great difficulty of extrapolating to an infinite lattice in the matrix calculations, the difference between η_c for the latter (estimated at 0·67) and for the present calculations is not serious and does not detract from the qualitative observations above.

Even when the disordered state alone does exhibit a Van der Waals transition; as in the square lattice with a second interaction, or the triangular lattice, the ordered state overlaps this 'would-be' transition and is stable to lower densities. This same lack of a liquid-like phase was also observed by Runnels *et al* (1971) when considering molecules defined by the exclusion of first and second neighbours on the triangular lattice, with one interaction between third neighbour. The direct condensation of vapour to solid in these models is a consequence of the fact that all the energetically favourable configurations also represent occupation of particular sublattices, whereas the existence of a stable liquid-like phase depends on disordered or homogeneous configurations with sufficient energy to induce local condensation.

In order to overcome this difficulty it is likely that much more extended interactions will have to be introduced, requiring Kikuchi calculations of a much greater complexity. In this development the numerical procedure of § 5 is crucial, and in a further publication (Kaye and Burley 1974), its application to such an extended problem will be described. In this context it may be noted that the usefulness of the Kikuchi method has been greatly extended by the development of a numerical solution procedure. It is not now limited to small primary subfigures and so can be used (without complex analytic manipulations) on a wide variety of lattice problems. In doing this its primary role would be to provide qualitative information, although more exact results could be obtained at the expense of more extensive computations. It may also be noted here that in the Kikuchi method, a disorded calculation can be performed, and a transition located, even if ultimately it is unstable. This enables both transitions to be followed as the interaction potential is modified, and conditions to be established under which a separation would take place. Like the COFE procedure, this facility turns out to be crucial for more sophisticated calculations, and does not exist in other methods.

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