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## Phase transitions in lattice fluids II. Extended interactions

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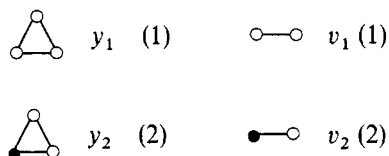
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**Abstract.** A study is made of a lattice fluid with interactions up to ninth neighbours. A simple approximation is used for the entropy and the internal energy is constructed in terms of a small number of basic configurations. The minimization of the free energy is performed using a numerical procedure described in a previous publication. The tail of the intermolecular potential is sufficiently extended to produce a full phase diagram showing both gas-liquid and liquid-solid transitions. The liquid-solid transition is second order, because of the particular lattice used, but otherwise the phase diagram is satisfactory. A direct application to monolayers is presented and a discussion of a possible biological application is given. The transition to a continuum model and methods of achieving more quantitatively realistic results are discussed.

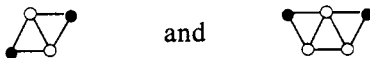
### 1. Introduction

The effect of introducing short-range attractive interactions in hard core lattice fluids has been described in a previous publication (Kaye and Burley 1974, to be referred to as I), where molecules were defined by the exclusion of first neighbours, and extended Kikuchi calculations used to include interactions on second and third neighbours. Although these interactions can produce a transition within the homogeneous disordered state, the ordering transition due to the hard core in all cases considered occurs at lower densities producing an overlap in which the ordered state is more stable. Therefore as in other calculations for this and similar models (Runnels *et al* 1970, 1971) there is only one transition, and no intermediate liquid-like phase.

The overlap between the two transitions had in fact been observed by Kikuchi (1951), who studied the first neighbour excluded problem on the triangular lattice using a single triangle as the primary subfigure. Although this subfigure can define the exclusion of first neighbours, it is not large enough to take directly into account any more distant interactions, and to include these, Kikuchi proceeded as follows. The notation here is the same as that of paper I. Using



as the relevant fraction variables, the probabilities of the configurations



with energies  $\epsilon_1$  and  $\epsilon_2$  respectively, can be constructed approximately as follows :

$$\begin{aligned}
 p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right) &= p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right) p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right) = \frac{p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right) p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right)}{p(\circ-\circ)} = \frac{p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right)}{p(\circ-\circ)} \frac{p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right) p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right)}{p(\circ-\circ)} \\
 &= y_2^2 y_1 / v_1^2. \tag{1} \\
 p\left(\begin{array}{c} \bullet \\ \circ \\ \bullet \end{array}\right) &= y_2^2 / v_1
 \end{aligned}$$

by a similar construction. These probabilities can then be used in an energy expression and a calculation similar to that of paper I, § 3, performed.

In cases where the energy can be expressed directly in terms of the primary fraction variables, the expression is a linear one, and on differentiation for equilibrium only constants are added to the basic equations to be solved. However, when the energy is expressed as above this is not so, and the resulting equations become very complicated. In Kikuchi's case, the use of a triangle as the primary subfigure leads eventually to an ordered calculation with only one equation, and this can be solved even with the non-linear energy factor. With larger primary subfigures however such an energy formulation would preclude an analytical solution.

Kikuchi found that both disordered and ordered transitions were produced by his model, but that in general the two overlapped, as in the case mentioned previously. However, by adopting a potential with  $\epsilon_2/\epsilon_1 = 2$ , ie with increasing interaction away from the core, Kikuchi obtained a separation of the two transitions and a phase diagram with three parts.

In lattice terms, the approach to a continuum involves progressive reduction in the mesh spacing, or an effective increase in the number of sites covered by each molecule. An ordered state would then be specified by the preferential occupation of one of an increasing number of sublattices. Kikuchi attributed the necessity for his 'unphysical' potential to the paucity of sublattices in the rather simple model. He argued that an overemphasis of the single energetic configuration tending to destroy the long-range order, that with the energy  $\epsilon_2$  above, is equivalent to an increase in the number of sublattices, and an approach to the continuum.

More recently, Orban *et al* (1968) have considered a square lattice model where the molecules are defined by the exclusion of first, second and third neighbours, with attractive interactions at fourth and fifth neighbours. The molecules here are five times the size of the lattice unit cell, and a Kikuchi calculation for the same model would involve five sublattices. Evidently this case goes some way towards fulfilling Kikuchi's requirements for a finer mesh, and more sublattices, and although these matrix calculations were limited to one rather narrow strip of 10 sites, they strongly indicated the appearance of a stable liquid phase without the need to specify an unphysical potential.

An alternative way to stabilize a liquid phase would be to return to the idea of Van der Waals and introduce an extended attractive tail into the potential, thereby increasing the internal energy of intermediate density disordered configurations so that their total free energy is lower than that of ordered ones at the same density. As already noted, the addition of extended interactions in a Kikuchi calculation by using relations such as equation (1) greatly complicates the equations to be solved and precludes an analytic solution with any but the simplest subfigures. However these interactions can be introduced with little additional difficulty into a numerical calculation of the type described in paper I (COFE). Using this method it is possible therefore to combine a study of the tail, already shown to be associated with a disordered condensation (Van Kampen 1964), with a Kikuchi calculation which contains enough geometric information to describe the hard core packing transition.

In addition to the effect of extended finite interactions described above, a result of Lebowitz and Penrose (1966) makes it possible to consider the effect of a Kac-Baker potential on the phase diagram of lattice fluids. This has recently been studied by Hall and Stell (1973), who used the collected data on several hard core lattice fluids to show that a phase diagram with two separate first-order transitions can be produced by the addition of such an infinitely weak and long-ranged potential. Their results are compared in § 4 with those of the rather different potential used in the following calculation.

## 2. A square lattice model with extended interactions

The molecular hard core is defined by first neighbour exclusion on the square lattice, and interactions up to the ninth neighbours are included in the attractive tail of the potential. A primary square subfigure was used in the Kikuchi calculation, and therefore the fraction variables and the relations between them are identical to those in § 3 of paper I.

However, since the present calculation must be a numerical one using the COFE procedure, the normalization is used to eliminate  $w_1$  from the spanning variable set so that all the fraction variables can be expressed in terms of the four independent variables  $w_2$  to  $w_5$ , as follows,

$$w_1 = 1 - 2w_2 - 2w_3 - w_4 - w_5$$

$$y_1 = 1 - w_2 - w_3 - w_4 - w_5$$

$$y_2 = w_2 + w_4$$

$$y_3 = w_3 + w_5$$

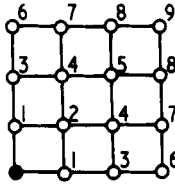
$$x_1 = 1 - w_2 - w_4$$

$$x_2 = w_2 + w_4$$

$$x_3 = 1 - w_3 - w_5$$

$$x_4 = w_3 + w_5.$$

The internal energy must now be formulated, with interactions extending to the ninth neighbour, and located as in figure 1 (for the complete ordered calculation there are of course two labellings for each extended configuration), and with first neighbours excluded, the probabilities of the remaining eight attractive configurations can be written



**Figure 1.** Location of interactions.

approximately in terms of the fraction variables based on the square as follows:

$$\begin{aligned}
 p_{12} \left( \begin{array}{cc} \circ^2 & \circ^1 \\ \bullet_1 & \circ_2 \end{array} \right) &= w_4 & p_{22} \left( \begin{array}{cc} \circ^2 & \circ^1 \\ \circ_1 & \bullet_2 \end{array} \right) &= w_5 \\
 p_{13} \left( \begin{array}{ccc} \circ^2 & \circ^1 & \circ^2 \\ \bullet_1 & \circ_2 & \bullet_1 \end{array} \right) &= w_2^2/y_1 & p_{23} \left( \begin{array}{ccc} \circ^2 & \circ^1 & \circ^2 \\ \circ_1 & \circ_2 & \circ_1 \end{array} \right) &= w_3^2/y_1 \\
 p_{14} \left( \begin{array}{ccc} \circ^2 & \circ^1 & \circ^2 \\ \bullet_1 & \circ_2 & \bullet_1 \end{array} \right) &= w_2 w_3/y_1 & p_{24} \left( \begin{array}{ccc} \circ^2 & \circ^1 & \circ^2 \\ \bullet_1 & \circ_2 & \circ_1 \end{array} \right) &= p_{14} \\
 p_{15} \left( \begin{array}{ccc} \circ^1 & \circ^2 & \bullet_1 \\ \circ^2 & \circ^1 & \circ^2 \\ \bullet_1 & \circ_2 & \circ_1 \end{array} \right) &= w_1^2 w_2^2 x_1/y_1^4 & p_{25} \left( \begin{array}{ccc} \circ^2 & \circ^1 & \bullet_2 \\ \circ^1 & \circ^2 & \circ^1 \\ \bullet_2 & \circ_1 & \circ_2 \end{array} \right) &= w_1^2 w_3^2 x_3/y_1^4 \\
 p_{16} \left( \begin{array}{cccc} \circ^2 & \circ^1 & \circ^2 & \circ^1 \\ \bullet_1 & \circ_2 & \circ_1 & \bullet_2 \end{array} \right) &= w_1 w_2 w_3/y_1^2 & p_{26} \left( \begin{array}{cccc} \circ^2 & \circ^1 & \circ^2 & \bullet_1 \\ \circ_1 & \circ_2 & \circ_1 & \circ_2 \end{array} \right) &= p_{16} \\
 p_{17} \left( \begin{array}{cccc} \circ^2 & \circ^1 & \circ^2 & \bullet_1 \\ \bullet_1 & \circ_2 & \circ_1 & \circ_2 \end{array} \right) &= w_1 w_2^2/y_1^2 & p_{27} \left( \begin{array}{cccc} \circ^2 & \circ^1 & \circ^2 & \circ^1 \\ \circ_1 & \circ_2 & \circ_1 & \bullet_2 \end{array} \right) &= w_1 w_3^2/y_1^2 \\
 p_{18} \left( \begin{array}{cccc} \circ^1 & \circ^2 & \circ^1 & \bullet_2 \\ \circ^2 & \circ^1 & \circ^2 & \circ^1 \\ \bullet_1 & \circ_2 & \circ_1 & \circ_2 \end{array} \right) &= w_1^4 w_2 w_3 x_1 x_3/y_1^7 & p_{28} \left( \begin{array}{cccc} \bullet_1 & \circ^2 & \circ^1 & \circ^2 \\ \circ^2 & \circ^1 & \circ^2 & \circ^1 \\ \circ_1 & \circ_2 & \circ_1 & \bullet_2 \end{array} \right) &= p_{18} \\
 p_{19} \left( \begin{array}{cccc} \circ^2 & \circ^1 & \circ^2 & \bullet_1 \\ \circ^1 & \circ^2 & \circ^1 & \circ^2 \\ \circ^2 & \circ^1 & \circ^2 & \circ^1 \\ \bullet_1 & \circ_2 & \circ_1 & \circ_2 \end{array} \right) &= w_1^7 w_2^2 x_1^2 x_3^2/y_1^{12} & p_{29} \left( \begin{array}{cccc} \bullet_2 & \circ^1 & \circ^2 & \circ^1 \\ \circ^1 & \circ^2 & \circ^1 & \circ^2 \\ \circ^2 & \circ^1 & \circ^2 & \circ^1 \\ \circ_1 & \circ_2 & \circ_1 & \bullet_2 \end{array} \right) &= w_1^7 w_3^2 x_1^2 x_3^2/y_1^{12}.
 \end{aligned} \tag{3}$$

The interaction could be extended indefinitely in this way, but since the forces between real molecules become negligible after a few molecular diameters, the range in this first calculation is restricted to the two extra interactive ‘rings’ represented by the above configurations. The energy associated with each neighbour is expressed relative to the close packing interaction  $\epsilon_2^\dagger$  by the relation

$$\epsilon_i = \epsilon_2 r_i \quad i = 3, \dots, 9 \tag{4}$$

† In paper I, § 3, the close packing interaction was labelled  $\epsilon_1$ . Here it is labelled  $\epsilon_2$  to fit the scheme in which the subscript refers to the neighbour.

in which set the  $r_i$  determine the shape of the interaction potential. The internal energy of the lattice is then

$$U = N\epsilon_2[(p_{12} + p_{22}) + \frac{1}{2}r_3(p_{13} + p_{23}) + r_4(p_{14} + p_{24}) + r_5(p_{15} + p_{25}) + \frac{1}{2}r_6(p_{16} + p_{26}) + r_7(p_{17} + p_{27}) + r_8(p_{18} + p_{28}) + r_9(p_{19} + p_{29})]. \quad (5)$$

Since the COFE procedure of paper I was formulated to deal with the linear energy expressions of a normal Kikuchi calculation, the procedure is slightly modified in this case. Equation (5) is used to incorporate explicitly the energy, its derivatives with respect to the independent variables (needed in the search for equilibrium), and its derivatives with respect to the density (needed to formulate the the pressure).

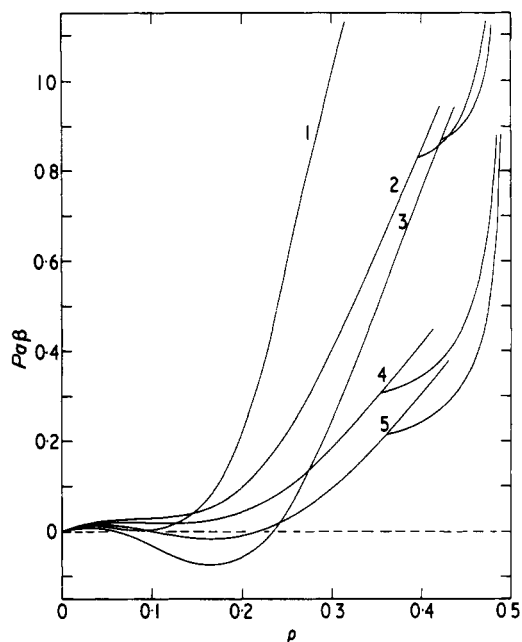
With a fixed temperature factor  $\epsilon_2\beta$  and a potential shape specified by the set  $r_i$ , the numerical procedure now provides the thermodynamic functions of the model as a function of the density. The onset of the disordered state as the density is lowered is marked by the disappearance of the asymmetry between equivalent pairs of fraction variables for the two sublattices. In practice once this transition was located, the disordered state was mapped out by using a separate and smaller calculation for an unlabelled lattice.

### 3. Results

Provided the attractive tail is not made extremely weak in comparison to the close packing interaction  $\epsilon_2$ , the effect of the added interactions on the disordered state is to produce a Van der Waals type of condensation at relatively low densities. This is illustrated in figure 2, which shows isotherms for potentials defined by three different sets  $r_i$ . Both ordered and disordered states are displayed, and as can be seen, the ordering transition is separate in all cases from the vapour-liquid transition, producing a stable liquid phase. Curves 2 and 3 of figure 2 refer to different temperatures for the same potential and correspond in a qualitative sense to the calculations of Kikuchi referred to in the introduction, in that the interaction increases at first with greater separation. The effect of using such a potential is to make the transition to an ordered state more difficult at lower temperatures, so that it occurs at higher densities and pressures, ie it requires greater mechanical compression. This was not observed by Kikuchi, who considered only one isotherm, and as shown in figure 2, it leads to a crossing of the two isotherms at different temperatures.

To avoid this, a potential must be used in which the interactions of the tail are always less than that of the close packing interaction, and curves 4 and 5 of figure 2 refer to such a potential. The lower temperature transition is now at lower pressure and the isotherms do not cross, although the lower temperature transition is still at rather higher density, indicating that the attractive tail is still rather too strong.

Accordingly a rather weaker attractive tail was chosen for the extensive calculations at different temperatures needed to elucidate the full diagram of state. The result of this calculation is shown in figures 3 and 4, along with the parameters  $r_i$  defining the potential. The extended interaction model shows all the broad characteristics of a real system, with gas, liquid and solid regions as indicated by the phase diagram of figure 5 and the low pressure detail of figure 6. Like that of real fluids the liquid vapour co-existence curve is asymmetrical (figure 6). The critical point is located at  $\eta_2 = 0.143$ ,



**Figure 2.** Square lattice, effect of extended interaction potentials† on the Van der Waals and order-disorder transitions.

Curve	$\eta_2$	$r_3$	$r_4$	$r_5$	$r_6$	$r_7$	$r_8$	$r_9$
1‡	0.707	3.0	2.8	2.6	2.4	2.2	2.0	1.8
2	0.25	1.4	1.2	1.0	0.8	0.6	0.4	0.2
3	0.1	1.4	1.2	1.0	0.8	0.6	0.4	0.2
4	0.15	0.9	0.8	0.7	0.6	0.5	0.4	0.3
5	0.1	0.9	0.8	0.7	0.6	0.5	0.4	0.3

† These are based on  $\eta_2$  and defined in equation (4).  $\eta_2 = \exp(\epsilon_2\beta)$ .

‡ For curve 1, the order-disorder transition is at  $Pa\beta \approx 1.9$ .

$\rho_c = 0.1$  and  $Pa\beta_c = 0.025$ , and the triple point is at  $\eta_2 = 0.0945 \pm 2$ ,  $\rho_1 = 0.28$ ,  $Pa\beta_1 = 0.011$ . As can be seen from figures 3 and 4, the melting transition is second order at all temperatures, unlike that of a real fluid.

#### 4. Discussion

It has been shown that the overlap of disordered and ordering transitions characteristic of short-range interactions in lattice fluids may be removed by including extended range interactions more like the tail of the real intermolecular potential. In doing this the ability to include non-linear factors in a numerical (COFE) calculation has been crucial. Except for the second-order liquid-solid transition, the  $p$ - $V$  plane of the resulting phase diagram is qualitatively the same as that of a simple inert element.

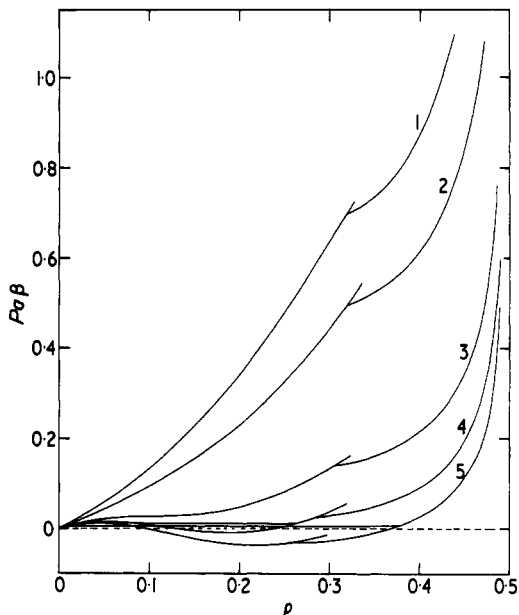


Figure 3. Pressure diagram for the extended interaction model; separate Van der Waals and ordering transitions. Curve 1,  $\eta_2 = 1.0$ ; curve 2,  $\eta_2 = 0.5$ ; curve 3,  $\eta_2 = 0.15$ ; curve 4,  $\eta_2 = 0.1$ ; curve 5,  $\eta_2 = 0.08$ . Extended interactions defined by:  $r_3 = 0.75$ ,  $r_4 = 0.65$ ,  $r_5 = 0.55$ ,  $r_6 = 0.45$ ,  $r_7 = 0.4$ ,  $r_8 = 0.35$ ,  $r_9 = 0.3$ .

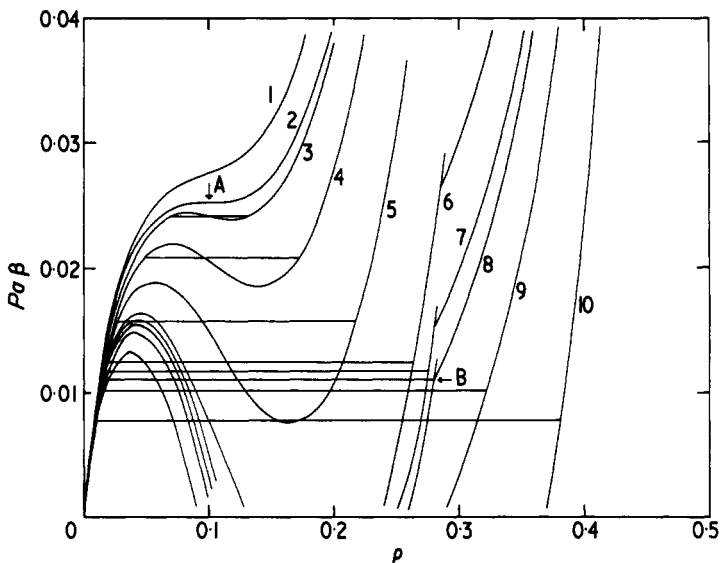
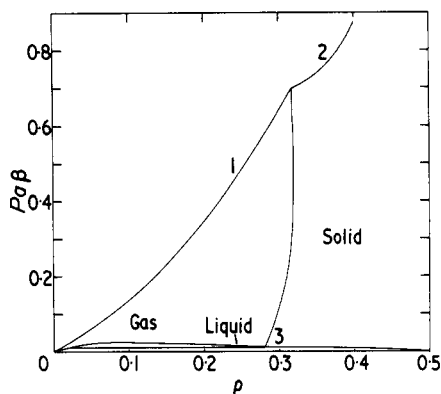


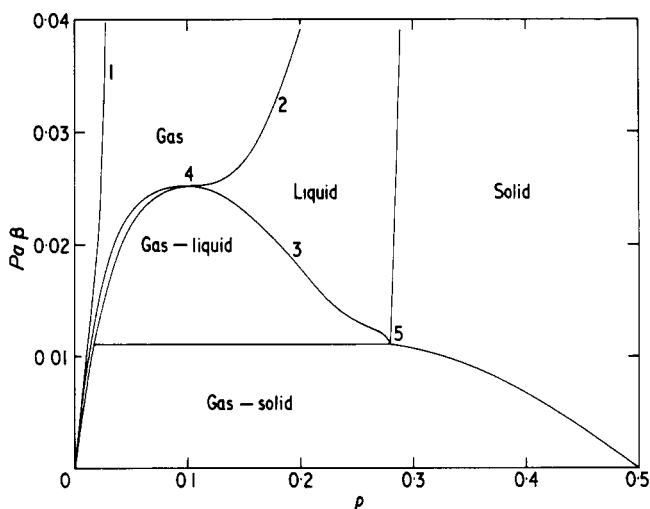
Figure 4. Low pressure detail of figure 3. A, critical point; B, triple point.

- |                                     |                                    |
|-------------------------------------|------------------------------------|
| 1, $\eta_2 = 0.15$                  | 6, $\eta_2 = 0.1$                  |
| 2, $\eta_2 = 0.143$ ( $T$ critical) | 7, $\eta_2 = 0.096$                |
| 3, $\eta_2 = 0.14$                  | 8, $\eta_2 = 0.0945$ ( $T$ triple) |
| 4, $\eta_2 = 0.13$                  | 9, $\eta_2 = 0.09$                 |
| 5, $\eta_2 = 0.115$                 | 10, $\eta_2 = 0.08$ .              |





**Figure 5.** Phase diagram for the extended interaction model. Curve 1, disordered isotherm, infinite temperature; curve 2, ordered isotherm, infinite temperature; 3, triple point.



**Figure 6.** Low pressure detail of figure 5. Curve 1, disordered isotherm, infinite temperature; curve 2, disordered isotherm, critical temperature; curve 3, liquid-vapour coexistence curve; point 4, critical point; point 5, triple point (for locations of points 4 and 5 see text).

However when a Kac-Baker potential is added to the hard core of the same model (Hall and Stell 1973), the phase diagram has a first-order solid-fluid transition and no liquid-gas transition. This result is in fact very similar to that produced by a single attraction on second neighbours, where the fluid-solid transition rapidly becomes first order, with the ordered state stable at low densities (cf paper I, Runnels *et al* 1970†). The liquid-gas transition lacking in this and the Kac-Baker case can be produced, in a purely disordered calculation, by the addition of a third neighbour attraction (cf paper I),

† In both these cases the infinite temperature solid-fluid transition is found to be second order with *finite* compressibility, and therefore a critical temperature exists at which the order of the transition changes. In the calculations of Hall and Stell the infinite temperature transition is assumed to have an *infinite* compressibility and there is therefore no such critical temperature.

but even in this case it is cancelled out by an overlapping, more stable, ordered state. The separation achieved with the present model depends on the relative strengths of the interactions in the extended tail. This is essentially because the first neighbour exclusion generates only two sublattices. Half the possible interactions of any molecule are therefore with others on the same sublattice, tending to stabilize ordered configurations, and compared to models nearer the continuum there are relatively few interactions favouring disordered configurations. If the tail interactions are made strong enough to produce a first-order transition to the solid, the liquid state disappears. The second-order liquid–solid transition is therefore a consequence of adjusting the potential to preserve the separate liquid state, and the lack of a liquid–gas transition in the Kac–Baker case probably also relates to this dependence of the liquid–gas transition on potential shape.

This interpretation implies that the separation of transitions will be easier in models with larger hard cores, where there are more sublattices and a smaller proportion of interactions between molecules on the same sublattice. When the exclusions on the square lattice are extended to third neighbours, there are five sublattices, and the model does have two separate first-order transitions when an attractive potential is added (Hall and Stell 1973, Orban *et al* 1968).

In view of the above, it is interesting to note Hall and Stell's suggestions that the separate liquid–gas transition is related to the hard core shape, since it is this which determines the actual details of the sublattice structure. Bearing in mind also that even infinite temperature transitions become first order as more neighbours are excluded (Bellemans and Nigam 1967, Orban and Bellemans 1968), it is clear that the results will be improved as lattice models closer to the continuum are considered.

Although the averaging inherent in the present description of the distant interactions is probably an adequate description of the smeared out distant potential, the discrete nature of the interactions in a lattice model presents more problems for the closer ranges. Here the smooth interaction field is not at all well represented by the geometrical specificity of close neighbours, and one of the dangers in a lattice energy formulation is that by overemphasizing one particular interaction, artificial slots in the interaction field can be created which may stabilize ordered configurations not defined by any geometrical packing of the hard core, and which are completely unphysical. This is unlikely to happen if the close packing interaction is always the strongest, as in these calculations. Some effects of short-range interactions on the liquid–vapour coexistence curve will be studied in a subsequent publication. A possible improvement requires a closer approach to a smooth interaction potential, and therefore, as in the case of the ordering transition, this will come about as more neighbours are excluded and the mesh size of the lattice effectively reduced (cf Hoover *et al* 1964). It should be emphasized here that unlike cell theories, the present lattice fluids are discrete analogues of the continuum, which they are capable of approaching by a progressive reduction of mesh size.

In allowing extended range and non-linear energy factors to be introduced, the COFE procedure overcomes a large obstacle to the complete but approximate modelling of systems more complex than the much studied simple lattice gas or hard core fluid. Any model which can be defined within the span of a given primary subfigure can probably now be tackled in a numerical Kikuchi calculation. Such calculations will at first be simple approximations giving only qualitative results (in a subsequent paper the application to dimers and trimers will be described), but since most systems of interest are complex, their usefulness seems assured (cf the application of mean field approximations to a wide variety of problems, Brout 1968).

In a possible direct application of the present model, the existence is noted of a physical system whose phase diagram closely resembles that of figure 5, with a second-order transition to the solid phase. The system is that of insoluble monomolecular layers of long chain paraffin molecules with hydrophilic head groups on an aqueous substrate. Typical examples, on which much experimental work has been done, are the long chain fatty acids, stearic acid, myristic acid, etc. In these layers the hydrophobic chains are known to be approximately perpendicular to, and therefore most distant from, the aqueous surface. A general phase diagram for such monolayers, taken from Harkins (1943) is shown in figure 7, which can be immediately compared with that of figure 5. Further discussion of these monolayer phenomena can be found in a review by Gaines (1966).

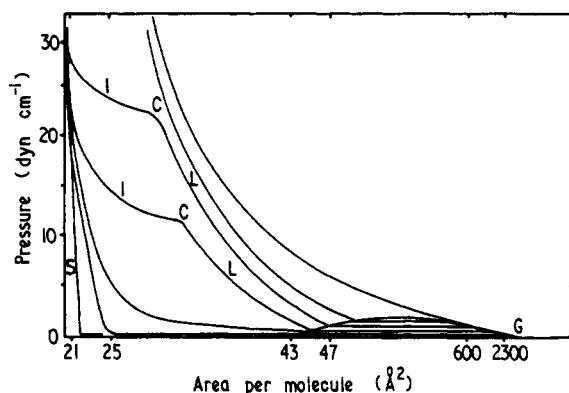


Figure 7. General phase diagram for monolayers (from Harkins 1943). S, solid phase; I, 'intermediate liquid'; L, 'liquid expanded' phase; G, gas.

In this field of study one of the major problems has always been the interpretation of the second-order transition labelled C in figure 7. Because of the high compressibility on the high density (low area per molecule) side of the transition, the shoulder region labelled I in the figure has been called an intermediate liquid, the term solid being reserved for the high density part of the diagram where the isotherms finally steepen.

The classical interpretation of this transition is that of Langmuir (1933) who suggested that at C the disorder characteristic of the liquid disappears and close packed islands of solid monolayer begin to appear, and that the solid is eventually reached when these islands coalesce to produce a uniform solid phase.

Kirkwood (1943) has offered the alternative interpretation that the transition is essentially orientational, associated with the hindered rotation of monolayer molecules whose cross section is in fact asymmetrical.

The similarity of Langmuir's phenomenological interpretation and that for the order-disorder transition of hard molecules (cf Gaunt and Fisher 1965) is striking. However, if a monolayer model is proposed essentially as a planar system of parallel interacting cylinders, their behaviour would be expected to be the same as that of a system of interacting continuum discs with a first-order liquid-solid transition, whereas in the monolayer system it is of second order.

It has already been noted that a transition is weakened in a system which is more loosely packed (eg the square lattice). This is also true of 'network melting' described

by Ubbelohde (1965) in which the packing of molecules is restricted by directional bonds between molecules. In a sense this is equivalent to the case of molecules with an asymmetrical or 'rough' cross section, which also limits the relative orientations of closely packed molecules.

It seems probable therefore that Langmuir's interpretation is essentially correct, but that the first-order transition which we would expect of smooth cylindrical molecules is weakened by the asymmetrical or rough cross section of real monolayer molecules, essentially as suggested by Kirkwood. The relatively high compressibility of the 'intermediate liquid' is simply a correlate of the weak nature of the transition, representing the slow break up of the crystal as melting is approached, and need not be distinguished as a separate phase.

Lattice models such as those described in this chapter necessarily describe 'rough' molecules and it is possible that a continuation of such studies will represent an important theoretical contribution to the understanding of monolayers.

And since the basic structural unit of biological membranes is known to be a planar double layer, each sheet of which is similar to the monolayers described above, and with experimental evidence (cf Engelman 1970) of an ordering transition in real membranes at a temperature close to the 'in vivo' temperature of the organism concerned, it is also possible that lattice studies such as those of this paper will prove useful in biophysical work.

## References

- Bellemans A and Nigam R K 1967 *J. chem. Phys.* **46** 2922-35  
Brout R 1968 *Statistical Physics, Phase Transitions and Superfluidity* vol. 1, ed. M Chretien (New York: Gordon and Breach) p 4  
Engelman D M 1970 *J. molec. Biol.* **47** 115-7  
Gaines G L 1966 *Insoluble Monolayers at Liquid-Gas Interfaces* (New York: Wiley, Interscience)  
Gaunt D S and Fisher M E 1965 *J. chem. Phys.* **43** 2840-63  
Harkins W D 1943 *Publ. Am. Ass. Advmt. Sci.* No 21 (*Surf. Chem.*) 40  
Hall C K and Stell G 1973 *Phys. Rev. A* **7** 1679-89  
Hoover W G, Alder B J and Ree F H 1964 *J. chem. Phys.* **41** 3528-33  
Kaye R D and Burley D M 1974 *J. Phys. A: Math., Nucl. Gen.* **7** 843-58  
Kikuchi R 1951 *J. chem. Phys.* **19** 1230-41  
Kirkwood J G 1943 *Publ. Am. Ass. Advmt. Sci.* No 21 (*Surf. Chem.*) 157-60  
Langmuir I 1933 *J. chem. Phys.* **1** 756-76  
Lebowitz J L and Penrose O 1966 *J. math. Phys.* **7** 98-113  
Orban J and Bellemans A 1968 *J. chem. Phys.* **49** 363-70  
Orban J, Van Craen J and Bellemans A 1968 *J. chem. Phys.* **49** 1778-83  
Runnels L K, Craig J R and Streiffer H R 1971 *J. chem. Phys.* **54** 2004-13  
Runnels L K, Salvant J P and Streiffer H R 1970 *J. chem. Phys.* **52** 2352-8  
Ubbelohde A R 1965 *Melting and Crystal Structure* (Oxford: Clarendon)  
Van Kampen N G 1964 *Phys. Rev.* **135** A362-9