MOLECULAR PHYSICS, 1998, VOL. 93, NO. 3, 501–509

Complex fluid behaviour of strongly asymmetric binary mixtures: thermodynamic properties of a generalized Lin–Taylor model

By J. M. ROMERO ENRIQUE, I. RODRÍGUEZ PONCE, L. F. RULL
Departamento de Física Atómica, Molecular y Nuclear, Area de Física Teórica
Universidad de Sevilla, Aptdo 1065, Sevilla, 41080, Spain

and UMBERTO MARINI BETTOLO MARCONI
Dipartimento di Matematica e Fisica and INFM, via Madonna delle Carceri,
Università di Camerino, 62032 Camerino, Italy

(*Received 18 August 1997; revised version accepted 13 October 1997*)

A detailed analysis is made of the lattice model of binary mixtures A–B, proposed a few years ago by Lin and Taylor. This model exhibits fluid–fluid immiscibility and a closed loop of immiscibility. Based on general arguments, the distinct possible behaviour is examined as a function of the coupling parameters, temperature and pressure in different lattices. The phase diagram is found to be richer than that reported previously, even in the square lattice case. The system, for attractive A–A interactions, shows the disappearance of one of the critical points for pressures lower than the A-pure system critical pressure. On the other hand, the mixture displays closed-loop behaviour without a low temperature immiscibility region for values of the interaction parameters $\varepsilon_{AA} < 0$ and $\varepsilon_{AB} < \varepsilon_{AA}/2$.

1. Introduction

In the last decade there has been an upsurge of interest in the physics of complex fluids. Among these, hydrogen bonded fluids play an important role, and present peculiar thermodynamic and structural properties which render them very different from simple fluids. Like ordinary fluids, they can exist in different phases and transform from one phase to another or coexist. It is known that the phase diagram of fluid mixtures can be very complex because, in addition to the familiar liquid–gas transition, the system can demix into phases of different composition.

Hydrogen-bonded fluids and their mixtures display a striking difference with respect to normal fluids, namely the presence of closed loops of immiscibility. Such special behaviour is due to the existence of short range and highly orientation dependent interactions which cause the molecules to associate. The presence of closed loops contrasts with one's intuitive idea that at low temperature order always prevails and thus that distinct phases separate as $T \to 0$. Surprisingly, phase separation instead starts at some finite temperature, and it is only upon further heating that the mixture becomes perfectly miscible. A well known example of a closed-loop phase diagram is provided by the binary mixture nicotine–water [1]. Instructive introductions to this area can be found in [2–5]. About sixty years ago Hirschfelder and coworkers [6] explained this reentrant miscibility by noting that hydrogen bonding favours mixing at low temperatures, but becomes ineffective as the temperature is raised above a certain lower critical temperature. Different lattice models have been proposed to study this behaviour, as can be seen in [4]. In the present paper we shall study and extend the lattice model of associating mixtures which was proposed by Lin and Taylor (LT) in [7] and [8].

We completed the study of these models by considering cases which were not analysed previously, and discovered that the morphology of its phase diagram is richer than that reported earlier. In particular, we found that in some cases the highest temperature at which the fluid is immiscible does not correspond to a critical point, but to the temperature at which the fluid becomes pure under conditions of fixed pressure. On the other hand, the system exhibits closed loop behaviour for values of the interaction parameters which were not considered in the Lin and Taylor studies.

We begin by recalling the LT binary mixture model. Each unit square cell consists of four triangular subunits and there are the following rules: (1) a pair of particles A or A–B cannot occupy the same unit square; (2) each triangular subunit can be occupied by at most one particle of type B (in other words, in a square cell left empty by particles A, it is possible to allocate at most four

0026–8976/98 $12·00

possible triangular B particles, one for each orientation of the triangles); (3) pairwise interactions exist between nearest neighbour A–A and A–B pairs, but not between pairs B–B. After summing over the occupation variables relative to particles B, the mixture can be mapped into an equivalent pure lattice gas model for species A only with renormalized temperature and concentration dependent interactions. Taking advantage of the isomorphism between a lattice gas and an Ising model, Lin and Taylor were able to provide an exact solution of the model in two dimensions. An exact solution of a closely related model with purely repulsive interactions had been discussed earlier by Frenkel and Louis [9], who found immiscibility at low temperatures instead of closed loops. This situation will appear in our discussion as a particular case of the model we solve.

The LT model is relevant because it shows that one can prove the existence of closed loops in the miscibility without introducing any uncontrolled approximations. The coexistence curves are obtained by cutting concentration–temperature slices in the thermodynamic space planes at fixed pressure, a situation which corresponds to experimental conditions in the laboratory.

Under suitable conditions one sees that the usual bell shaped coexistence curve becomes a closed loop plus a lower bell shaped curve. As a result of this complicated coexistence line, one may observe three critical points, two upper and one lower, instead of a single upper critical point. This is not, however, the only possibility. In fact the uppermost critical point may be suppressed and two different phases assume the same composition before their densities become equal. This leads to a first-order termination of the loop: the system turns pure, before it becomes critical. Moreover for some values of the coupling parameters, the lower portion of the coexistence curve can even disappear.

Physically, this behaviour occurs in the presence of a strong interaction between particles B and A. The direct A–A interaction is screened at low temperatures by particles B and the low temperature phases are B rich. The critical point of the pure fluid A is lowered because the effective A–A interaction is reduced by the screening. However, as the temperature increases the thermal fluctuations decrease the average number of associated A–B pairs and the interaction A–A becomes more effective and a demixing of the fluid can occur again, giving rise to a lower critical point. Finally, at sufficiently high temperatures the fluid becomes miscible again.

First we present the model and determine the corresponding thermodynamic functions, which are obtained from the exact mapping onto the Ising model. As far as coexistence properties are concerned, we need to consider only the solutions which correspond to zero magnetic field, H, in the associated Ising problem. After reducing the grand potential and the controlling fields of the model to dimensionless form, we study the phase diagram. This method leads to a natural way of classifying the solutions according to the sign of the interactions and of their relative strength. We illustrate explicitly the various cases with the help of the exact solutions for the square lattice case. Finally we present the conclusions.

2. The model

We begin by extending the lattice model of binary mixtures introduced by Lin and Taylor [7, 8] to D-dimensional lattices and coordination numbers υ. The mixture is composed of two species A and B. The A particles (corresponding to the squares in the LT model) are allowed to occupy any of the cells of the lattice at most once. Particles of the other type, named species B (corresponding to the triangles in the LT model), can occupy the cells left empty by particles A. Each unoccupied cell contains υ subcells, where every subcell shares a face with one of the nearest-neighbour cells. Single occupancy by particles B is allowed on the subcells. Each lattice cell can exist in $(2^{\upsilon}+1)$ different states: occupied by an A, completely empty or all the possibilities to be occupied by $1,\dots,\upsilon$ particles B. There are nearest-neighbour interactions between A–A pairs, $\varepsilon_{\mathrm{AA}}$. An interaction $\varepsilon_{\mathrm{AB}}$ between A–B pairs is present if the two partners have a face in common.

Assuming a grand canonical ensemble description, we shall refer to μ_{A} and μ_{B} as the chemical potentials relative to A and B, respectively. As usual, we define the fugacity z by

$$z = \mathrm{e}^{\beta\mu} \tag{1}$$

with $\beta = (k_{\mathrm{B}}T)^{-1}$ and T the absolute temperature of the system.

As shown in appendix A the grand canonical potential can be written as:

$$\Omega_{\text{mixture}} = Nk_{\mathrm{B}}T\left[\frac{\upsilon K}{2} - H - \upsilon\ln(1+z_{\mathrm{B}}) - \frac{1}{N}\ln Z_{D,\upsilon}(K,H)\right], \tag{2}$$

where N is the number of lattice cells, $Z_{D,\upsilon}$ is the canonical partition function of the Ising model, and H and K are defined by equation (A 9a,b) of appendix A.

The pressure of the mixture is given by

$$p = \frac{-\Omega_{\text{mixture}}}{V} = \frac{-\Omega_{\text{mixture}}}{N\sigma}, \tag{3}$$

and the densities of A and B particles take the forms

$$n_{\mathrm{A}} = \frac{m_{D,\upsilon}(K,H)+1}{2\sigma} \tag{4a}$$

and

$$
\begin{aligned}
n_{\mathrm{B}} &= \frac{z_{\mathrm{B}}}{N\sigma}\left(\frac{\partial \ln \Xi}{\partial z_{\mathrm{B}}}\right)_T \\
&= \frac{\upsilon}{4\sigma}\left[\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} + \frac{\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}} z_{\mathrm{B}}}{1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right] \\
&\quad - \frac{1}{2\sigma}\left[\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} - \frac{\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}} z_{\mathrm{B}}}{1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right] \\
&\quad \times \left[u_{D,\upsilon}(K,H) + \frac{H}{K} m_{D,\upsilon}(K,H)\right] \\
&\quad - \frac{\upsilon}{2\sigma}\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} m_{D,\upsilon}(K,H), \qquad (4b)
\end{aligned}
$$

where Ξ is the grand canonical partition function, σ is the hypervolume of a site of the lattice and $u_{D,\upsilon}$ and $m_{D,\upsilon}$ are the energy per site and the magnetization per site, respectively, of an Ising model in the presence of an external field.

For later convenience, we introduce the function $\tilde{C}(K,H)$:

$$\tilde{C}(K,H) = \frac{1}{N}\ln Z_{D,\upsilon}(K,H) + H - \frac{\upsilon}{2}K. \qquad (5)$$

Equations (3) and ($4a,b$) can be rewritten as

$$p = \frac{k_{\mathrm{B}}T}{\sigma}\left[\upsilon \ln(1+z_{\mathrm{B}}) + \tilde{C}(K,H)\right], \qquad (6a)$$

$$n_{\mathrm{A}} = \frac{m_{D,\upsilon}+1}{2\sigma}, \qquad (6b)$$

and

$$n_{\mathrm{B}} = \frac{\upsilon}{2\sigma}\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}}\left[\left(1+\frac{1}{\upsilon}\left(\frac{\partial \tilde{C}}{\partial K}\right)_H \frac{1-\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}{1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right) - m_{D,\upsilon}(K,H)\right]. \qquad (6c)$$

We also define $C(K)$ as $\tilde{C}(K, H=0)$. The key properties of $\tilde{C}(K,H)$ and $C(K)$ are derived in appendix B.

The mole fraction X_{A} of A particles is defined as

$$X_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}}+n_{\mathrm{B}}}. \qquad (7)$$

3. Phase diagram

In the present section we shall consider the conditions under which the model mixture displays coexistence between an A-rich phase, α, and a B-rich phase, β, i.e., immiscibility.

We will follow the procedure used in Lin and Taylor's work. For clarity we will show the results for the square lattice, where we have an explicit expression for $C(K)$, given by the Onsager solution (see, e.g. [11]), as shown originally by Lin and Taylor. Other closed expressions for $C(K)$ can be obtained for other two-dimensional lattices [12, 13]. In any case, the study is completely general and it is valid for any D-dimensional lattices, even if the expression for $C(K)$ is not known.

In order to have phase separation, from equation ($6b,c$) we see that in the Ising model we must fulfil the conditions: (a) $D \geqslant 2$, (b) $K > K_{\mathrm{c}}(D,\upsilon) > 0$, where K_{c} is the critical value of the coupling parameter. and (c) $H = 0$, the coexistence condition.

In principle, negative values of K are allowed in our system, but this condition leads to antiferromagnetism. In the generalized Lin–Taylor (GLT) model, as we can see from equation ($6b$), this situation would describe a different problem from the one we are studying, namely repulsive interactions mimic the features of the liquid–solid transitions. Thus we shall consider only the sector $K > 0$. When $H = 0$ and $K > K_{\mathrm{c}}(D,\upsilon)$, there are two coexistence states in the equivalent Ising model, with the same $u_{D,\upsilon}$ and opposite values of $m_{D,\upsilon}$.

From equation (A $9a$), the condition $H \equiv 0$ of the associated Ising model, leads to

$$z_{\mathrm{A}} = (1+z_{\mathrm{B}})^{\upsilon} \cdot \exp(\upsilon\beta\varepsilon_{\mathrm{AA}}/2). \qquad (8)$$

In order to study the states in coexistence, we invert equation (A $9b$):

$$z_{\mathrm{B}} = \frac{\exp\left(2K + \dfrac{\beta\varepsilon_{\mathrm{AA}}}{2}\right) - 1}{1 - \exp\left(2K - \beta\left(\varepsilon_{\mathrm{AB}} - \dfrac{\varepsilon_{\mathrm{AA}}}{2}\right)\right)}. \qquad (9)$$

When $\varepsilon_{\mathrm{AB}} = 0$, it is necessary to use a different inversion formula, as we shall see below.

The cases that allow values of $K > 0$ in the physical region of the parameters ($z_{\mathrm{B}} > 0$, $\beta > 0$) are, as we can see from equation (9), the cases with $\varepsilon_{\mathrm{AA}} < 0$ (and arbitrary $\varepsilon_{\mathrm{AB}}$), and the cases with $\varepsilon_{\mathrm{AA}} \geqslant 0$ and $\varepsilon_{\mathrm{AB}} > \varepsilon_{\mathrm{AA}}/2$. So, we shall restrict our study to these cases:

3.1. $\varepsilon_{\mathrm{AA}} \geqslant 0$ *and* $\varepsilon_{\mathrm{AB}} > \varepsilon_{\mathrm{AA}}/2$

In this case, both the A–A and A–B interactions are repulsive, as in the model studied by Frenkel and Louis [9]. We introduce the dimensionless pressure p^* and temperature T^* variables defined as

$$p^* = \frac{p\sigma}{\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{AA}}/2}, \qquad (10a)$$

and

$$T^* = \frac{k_{\mathrm{B}}T}{\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{AA}}/2}. \qquad (10b)$$

Substituting these definitions and equation (9) into ($6a$) with $H = 0$, we obtain the following expression:

$$p^* = T^*\left[\upsilon \ln\left(\frac{\exp(-s/T^*) - \exp(-1/T^*)}{\exp(-2K) - \exp(-1/T^*)}\right) + C(K)\right], \qquad (11)$$

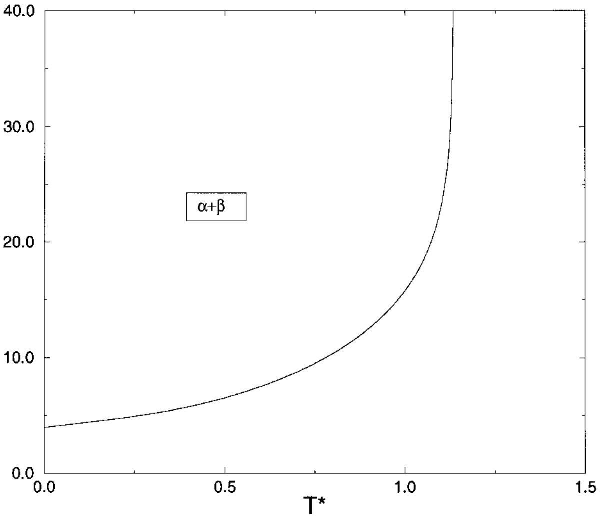

Figure 1. Plot of p_c^* versus T^* obtained from equation (11) for the two-dimensional Onsager solution of the Ising model for the cases $\varepsilon_{AA} \geqslant 0$ and $\varepsilon_{AB} > \varepsilon_{AA}/2$. The region between this curve and the $T^* = 0$ axis corresponds to the region of phase separation.

where the parameter s is

$$s = \frac{-\varepsilon_{AA}}{2\varepsilon_{AB} - \varepsilon_{AA}}. \tag{12}$$

Expression (11) defines the pressure as a function of T^* and K. At fixed temperature, the pressure p^* is a monotonically increasing function of K in the range allowed by equation (9), that includes positive and negative values of K; p^* displays a minimum value $T^*C(s/2T^*)$ at $K = s/(2T^*)$. Thus, if the pressure is greater than this minimum, one finds a single solution K for each value of T^*.

Furthermore, keeping K fixed and positive, the pressure is a monotonically increasing function also with respect to the temperature, and has a minimum value $p_m^* = -\upsilon s$ at $T^* = 0$, diverging at $T^* = 1/2K$.

With the help of these two properties, the values of pressure and temperature for which coexistence can be achieved are located between the critical line $p_c^*(T^*)$ (obtained by setting $K = K_c$) and the axis $T^* = 0$ (see figure 1). The mixture displays coexistence with a single upper critical point whenever $p^* > -\upsilon s$. For reduced pressures below this value the system is miscible. Since the ratio $\varepsilon_{AB}/\varepsilon_{AA} \to \infty$ when $s \to 0^-$, one needs only a small pressure $p^* > 0$ in order to induce immiscibility in such limit. On the other hand, when $s \to -\infty$ one has to force the system by applying greater and greater pressure in order to observe phase separation, since the minimum value of p^* which exhibits phase separation increases with s.

3.2. $\varepsilon_{AA} < 0$

In this case the interaction between particles A is attractive, but the interaction between particles A and B can be either attractive or repulsive. In this case component A undergoes a vapour–liquid phase separation below a certain critical temperature T_c^A of the pure model (that is, a single component system consisting of species A). The existence of this line implies the existence of new phase diagrams not mentioned in the Lin and Taylor paper.

We define the dimensionless pressure and temperature as:

$$p^* = \frac{-2p\sigma}{\varepsilon_{AA}}, \tag{13a}$$

and

$$T^* = \frac{-2k_B T}{\varepsilon_{AA}}. \tag{13b}$$

With these definitions, $T_c^{*A} = 1/(2K_c)$, at a dimensionless pressure $p_c^{*A} = C(K_c)/2K_c$.

Equation (6a) (with $H = 0$) can be rewritten with these definitions as

$$p^* = T^*\left[\upsilon \ln(1 + z_B) + C(K)\right] \tag{14}$$

If $\varepsilon_{AB} \neq 0$ we can use equation (9) to rewrite (14) as

$$\begin{aligned} p^* &= T^*\left[\upsilon \ln\left(\frac{\exp(-1/T^*) - \exp(-1/sT^*)}{\exp(-2K) - \exp(-1/sT^*)}\right) + C(K)\right] \\ &= g(T^*, K), \end{aligned} \tag{15}$$

where s is defined in equation (12). As in the preceding case, equation (15) defines the pressure as a function of T and K. The subdivisions of this case are the following.

3.2.1. $\varepsilon_{AA} < 0$ *and* $\varepsilon_{AB} > 0$

Physically this situation corresponds to a repulsive interaction AB. As in section 3.1, keeping the temperature fixed, the pressure is a monotonically positive increasing function of K. p^* has a minimum value $T^*C(1/2T^*)$ at $K = 1/(2T^*)$. Pressures greater than this minimum, for an assigned value of T^*, determine a single value of K.

Conversely, keeping K fixed, the pressure is a monotonically increasing function of the temperature, with a minimum value at $T^* = 1/(2K)$ given by $p^* = C(K)/(2K)$, diverging at $T^* = 1/(2sK)$.

The values of pressure and temperature where we find coexistence lie between the axis $T^* = 0$, the curve $p^* = T^*C(1/2T^*)$ and the critical line $p_c^*(T^*) = g(T^*, K_c)$ (figure 2(b)). The latter becomes a straight line when $\varepsilon_{AB} \to \infty$ (figure 2(a)). Below this line, it is not possible to find immiscibility states for every value of ε_{AA} and ε_{AB}.

For pressures greater than $p_m^* = C(K_c)/(2K_c)$, the system displays a bell shaped phase diagram which

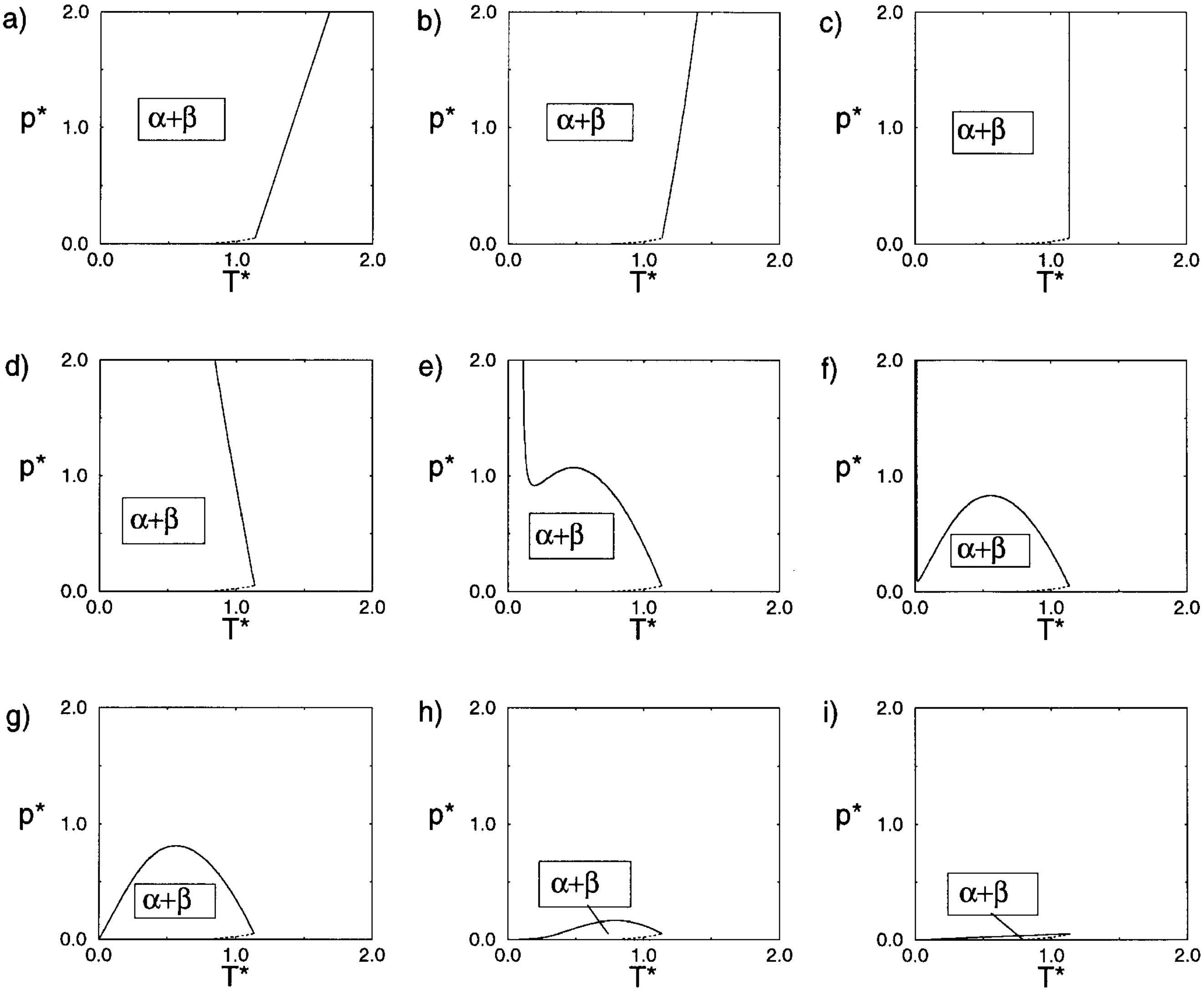

Figure 2. Plot of p_c^* against T^* using equation (14) and $\varepsilon_{AA} < 0$: (*a*) $\varepsilon_{AB} \rightarrow \infty$; (*b*) $\varepsilon_{AB} > 0$; (*c*) $\varepsilon_{AB} = 0$; (*d*) $\varepsilon_{AB} < 0$ and $|\varepsilon_{AB}| < |\varepsilon_{AB}^c| < |\varepsilon_{AA}|/2$; (*e*) $\epsilon_{AB} < 0$, $|\varepsilon_{AB}^c| < |\varepsilon_{AB}| < |\varepsilon_{AA}|/2$ and $p_m > C(K_c)/2K_c$; (*f*) as for (*e*) but $p_m < C(K_c)/2K_c$; (*g*) $\varepsilon_{AB} < 0$ and $|\varepsilon_{AB}| = |\varepsilon_{AA}|/2$; (*h*)$\varepsilon_{AB} < 0$ and $|\varepsilon_{AB}| > |\varepsilon_{AA}|/2$; and (*i*) $\varepsilon_{AB} \rightarrow -\infty$.

ends in an upper critical point. Below this pressure there is coexistence but no criticality. This happens because the system becomes pure A before the mixture turns critical. Thus one observes two pure phases of particles A in coexistence.

3.2.2. $\varepsilon_{AA} < 0$ *and* $\varepsilon_{AB} = 0$

In this case, there is no interaction between the two species A and B, so the only effect of particles B in the mixture is to reduce the volume available to particles A. Now equation (15) is not valid, since from (A 9 *b*) we obtain $K = 1/2T^*$. Thus, we must use equation (14), which defines the pressure as a function of the temperature and the fugacity of particles B. Because $z_B > 0$, for a specified temperature, all pressures greater than $p^* = T^* C(1/2T^*)$ are allowed. The values of pressure and temperature where there is coexistence are defined in a similar way as in section 3.2.1 (figure 2(*c*)), obtaining bell shaped phase diagrams which end in an upper critical point for pressures greater than $p_m^* = C(K_c)/2K_c$, and coexistence without criticality below this pressure, in the same sense as in section 3.2.1.

3.2.3. $\varepsilon_{AA} < 0$ *and* $\varepsilon_{AB} < 0$

In this case interactions A–A and A–B are both attractive, and we find the richest phase diagram behaviour, including closed loops of immiscibility.

At fixed T^*, equation (15) defines the pressure as a monotonically decreasing function of K in the interval allowed $(1/2sT^* < K \leqslant 1/2T^*)$, with a minimum value

$T^*C(1/2T^*)$ at $K = 1/(2T^*)$, diverging when $K \rightarrow 1/(2sT^*)$. As a consequence, the region of the (p^*, T^*) plane where there are coexistence states is, as in preceding cases, defined between the critical line $p^*_c(T^*)$, the curve $p^* = T^*C(1/2T^*)$, and the axis $T^* = 0$. But the different behaviour of $p^*_c(T^*)$, depending on the value of ε_{AB} fixed the value of ε_{AA}, leads to different types of phase diagram.

The first case is $|\varepsilon_{AB}| < |\varepsilon_{AA}|/2$ and corresponds to values of the parameter $s > 1$, so we obtain coexistence at low temperatures. The variety of phase diagrams that one can observe in this case is mirrored in the behaviour of the critical line. The latter cannot be obtained exactly for arbitrary lattices. However, from a knowledge of K_c and $C(K_c)$ this is possible. We shall consider the critical-line behaviour in all the cases represented in [10], Table I. For small values of $|\varepsilon_{AB}|$, the critical curve $p^*_c(T^*)$ is a monotonically decreasing function of T^* (figure 2(*d*)), and the phase diagram looks similar to those in sections 3.2.1 and 3.2.2, with the difference that the critical temperature decreases with p^*, instead of increasing, due to the opposite sign of the ε_{AB} interaction. The effect of applying a larger pressure is to favour mixing, hence the critical demixing point is lowered, while in the case with a repulsive ε_{AB} interaction (section 3.2.1) the critical point is driven towards higher values.

By increasing the value of $|\varepsilon_{AB}|$, there is a crossover value of this parameter, ε^c_{AB} at which a critical point of inflection appears, i.e., the first two derivatives of the critical pressure with respect to the temperature vanish. For $|\varepsilon^c_{AB}| < |\varepsilon_{AB}| < |\varepsilon_{AA}|/2$ the critical curve shows non-monotonic behaviour, with a local minimum, corresponding to the pressure p^*_m, followed by a local maximum p^*_M (figure 2(*e*)). The value of p^*_m becomes lower as $|\varepsilon_{AB}|$ increases, and can even be smaller than $C(K_c)/2K_c$, when $|\varepsilon_{AB}| \sim |\varepsilon_{AA}|/2$ (figure 2(*f*)). So for pressures greater than p^*_M, we have bell shaped phase diagrams with an upper critical point. For pressures between p^*_m and p^*_M a closed loop of immiscibility appears, which is characterized by an upper and a lower critical point, with $p^* > C(K_c)/2K_c$. Conversely, if $p^* < C(K_c)/2K_c$, one finds a loop with a single critical point, the lower one. In addition to the loop with one or two critical points, we have a bell shaped coexistence line at low temperatures which ends at an upper critical point. At p^*_m the lower upper critical point and the lower critical point coalesce into a double critical point, and we obtain a bottleneck shaped coexistence curve for lower values of the pressure, with an upper critical point for $p^* > C(K_c)/2K_c$ and none for lower pressures. These different types of behaviour with pressure are shown in figure 3.

The second case $|\varepsilon_{AB}| = |\varepsilon_{AA}|/2$ is important because it discriminates between two different types of behaviour, $|\varepsilon_{AB}| > |\varepsilon_{AA}|/2$ and $|\varepsilon_{AB}| < |\varepsilon_{AA}|/2$, with an attractive interaction between unlikeparticles. As in the former case, we consider the behaviour of the critical line $p_c(T_c)$. At $T^* = 0$ this function vanishes and has a positive derivative. As a consequence, there is no coexistence at low temperatures. If the derivative at $T^* = 1/2K_c$ has a negative value, we shall have non-monotonic behaviour. This is obtained if the expression

$$f(K_c) = \frac{C(K_c)}{2K_c} - \frac{\upsilon}{e^{2K_c} - 1} \tag{16}$$

has a negative value. When this happens it can be shown that the critical line has a single maximum (figure 2(*g*)). We have evaluated $f(K_c)$ in the different cases presented in table 1, obtaining a negative value, as is expected since in the first case just described we have obtained non-monotonic behaviour. Let us call the value of the pressure at the maximum p^*_M. For pressures greater than p^*_M the system is completely miscible. For pressures between p^*_M and $C(K_c)/2K_c$ we obtain closed loops of immiscibility with an upper and a lower critical point, and for pressures lower than $C(K_c)/2K_c$ we obtain closed loops with only a lower critical point, because the upper critical point has disappeared, ending the coexistence region when system becomes pure component A.

Table 1. Critical parameters of the Ising model for different lattices (see text).

Lattice	D	υ	K_c	$C(K_c)$	$\frac{2\upsilon K_c}{\exp(2K_c) - 1}$	$u_{D,\upsilon}(K_c, 0)$
Honeycomb	2	3	0.6585	0.037 34	1.446	-1.1547
Kagomé	2	4	0.4666	0.041 65	2.420	-1.4880
Square	2	4	0.4407	0.048 322	2.493	-1.4142
Triangular	2	6	0.2747	0.055 63	4.502	-2.0000
Diamond	3	4	0.3698	0.0938	2.701	-0.864
Simple cubic	3	6	0.2217	0.113	4.768	-0.9852
Body-centered cubic	3	8	0.1575	0.126	6.806	-1.080
Face-centered cubic	3	12	0.1021	0.129	10.817	-1.470

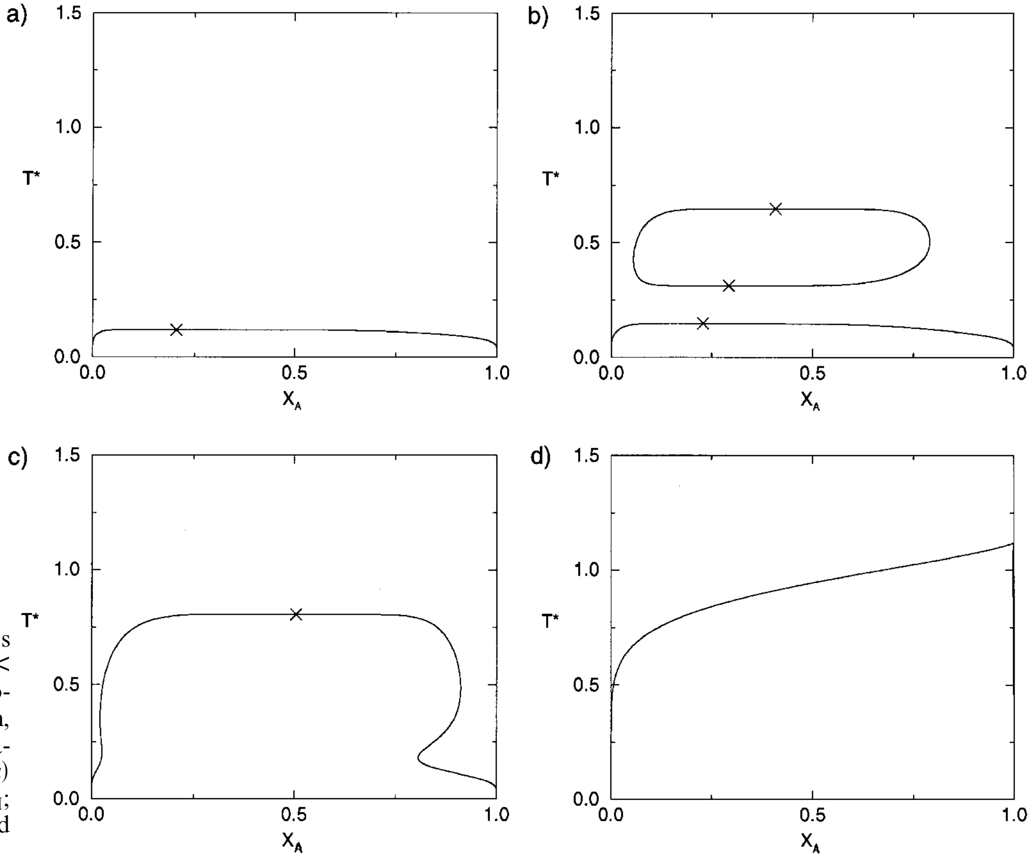

Figure 3. Coexistence curves for $\varepsilon_{AB} = 9/20\varepsilon_{AA}$ with $\varepsilon_{AA} < 0$ obtained from the two-dimensional Onsager solution, with crosses showing the location of the critical points: (*a*) $p^* > p_M$; (*b*) $p_m < p^* < p_M$; (*c*) $C(K_c)/2K_c < p^* < p_m$; and (*d*) $p^* < C(K_c)/2K_c$.

The third case is $|\varepsilon_{AB}| > |\varepsilon_{AA}|/2$ and corresponds to values of $s < 0$, so K can be lower than zero, which can lead to a solid–liquid-like transition at high pressures. The types of phase diagram behaviour are determined by studying the shape of the critical line for every lattice considered in table 1. For values of $|\varepsilon_{AB}|$ near $|\varepsilon_{AA}|/2$ the qualitative features of the critical line are similar to the critical line in the second case (figure 2(*h*)), and similar phase diagram behaviour is obtained, as in figure 4, for different pressures. When $|\varepsilon_{AB}|$ is increased, there is a value of this parameter, ε^C_{AB}, where the critical line monotonically increases, and for $|\varepsilon_{AB}| > |\varepsilon^C_{AB}|$ the critical line is monotonic, and becomes a straight line when $|\varepsilon_{AB}| \to \infty$ (figure 2(*i*)). The phase diagram we obtain comprises closed loops without an upper critical point for $p^* < C(K_c)/2K_c$, and the system is completely miscible for $p^* > C(K_c)/2K_c$.

4. Conclusion

We have studied the properties of an asymmetric mixture as a function of the dimensionality and of the coupling strength between the components and the temperature. Our results show that the model can display a richer phase diagram than that reported previously. The predicted behaviour ranges from simple coexistence of two immiscible phases to closed loops of coexistence terminated by two critical points or to closed loops of immiscibility with a single lower critical point. Temperature versus composition phase diagrams are presented for a variety of situations. In a forthcoming study we

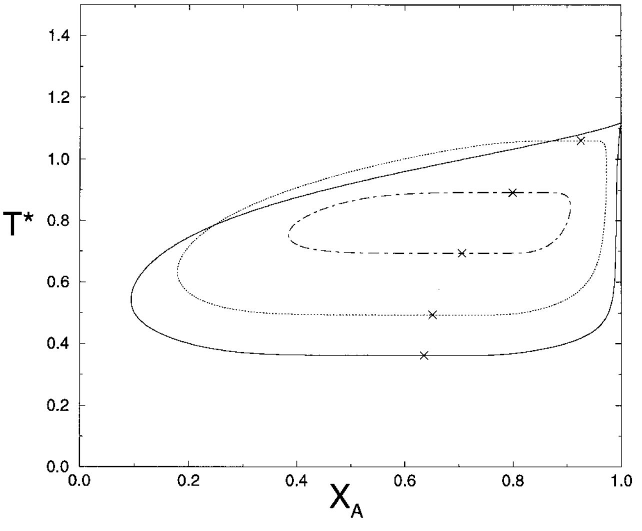

Figure 4. Coexistence curves for $\varepsilon_{AB} = \varepsilon_{AA}$ and $\varepsilon_{AA} < 0$: the continuous line corresponds to $p^* < C(K_c)/2K_c$; the dotted line indicates $p^*_M > p^*_1 > C(K_c)/2K_c$; and the dashed line shows $p^*_M > p^*_2 > p^*_1$.

shall address the issue of the inhomogeneous Lin–Taylor model with particular emphasis on its wetting behaviour. Finally, we remark that the presence of two or three critical points may lead to the unusual phenomenon of their coalescence. This possibility as we shall show elsewhere has interesting physical repercussions in the critical point behaviour [3].

L.F.R. wishes to acknowledge stimulating correspondence with Michael E. Fisher. We would like to thank Norman Carnahan and George Jackson for the critical reading of the manuscript. We also acknowledge support from European Union under contract C1*-CT94-0132, the DGICYT under contract PB94-1442 and Plan Andaluz de Investigación de la Junta de Andalucía and the Istituto Nazionale di Fisica Nucleare, Iniziativa F11.

Appendix A

Derivation of the grand canonical potential

We present the derivation of the grand potential used in the text, which follows Lin and Taylor's previous one.

The partition function for the mixture can be written as the following trace over the configurations of the system $\{n_i\}$:

$$\Xi = \sum_{\{n_i\}} \mathrm{e}^{\beta\mu_{\mathrm{A}}\sum_i n_i - \beta\varepsilon_{\mathrm{AA}}\sum_{\langle i,j\rangle} n_i n_j}\,\Xi_{\mathrm{B}}(\{n_i\}), \qquad (\mathrm{A}\ 1)$$

where n_i is an occupancy variable relative to the ith cell, which takes on the values one or zero if a particle A is present or not; the symbol $\langle i, j\rangle$ restricts the double sum to nearest neighbour cells only. $\Xi_{\mathrm{B}}(\{n_i\})$ is the partition function for particles B, subject to a fixed configuration of particles A.

Since the pairs B–B do not interact one can easily evaluate $\Xi_{\mathrm{B}}(\{n_i\})$.

$$\left[\sum_{l_{\mathrm{F}}=0}^{M_{\mathrm{F}}}\binom{M_{\mathrm{F}}}{l_{\mathrm{F}}}\mathrm{e}^{\beta\mu_{\mathrm{B}}l_{\mathrm{F}}}\right]\left[\sum_{l_{\mathrm{I}}=0}^{M_{\mathrm{I}}}\binom{M_{\mathrm{I}}}{l_{\mathrm{I}}}\mathrm{e}^{\beta\mu_{\mathrm{B}}l_{\mathrm{I}}}\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}l_{\mathrm{I}}}\right] = (1+z_{\mathrm{B}})^{M_{\mathrm{F}}}(1+z_{\mathrm{B}}\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}})^{M_{\mathrm{I}}}. \qquad (\mathrm{A}\ 2)$$

The total number M of subcells available to particles B has been divided into two classes: M_{F} represents the number of subcells which do not share a face with a cell occupied by A, while M_{I} is the number of those subcells where the particles B experience the A–B interaction.

The numbers M_{F} and M_{I} satisfy the relations:

$$M = M_{\mathrm{I}} + M_{\mathrm{F}} \qquad (\mathrm{A}\ 3a)$$

$$M_{\mathrm{I}} = \upsilon\sum_i n_i - 2\sum_{\langle i,j\rangle} n_i n_j, \qquad (\mathrm{A}\ 3b)$$

$$\begin{aligned} M_{\mathrm{F}} &= \upsilon N - \upsilon\sum_i n_i - M_{\mathrm{I}} \\ &= \upsilon N - 2\upsilon\sum_i n_i + 2\sum_{\langle i,j\rangle} n_i n_j. \end{aligned} \qquad (\mathrm{A}\ 3c)$$

Substituting these equalities into equation (A 1), the grand canonical partition function reads

$$\begin{aligned} \Xi = (1+z_{\mathrm{B}})^{\upsilon N}\sum_{\{n_i\}}\exp&\Big\{\Big[-\beta\varepsilon_{\mathrm{AA}} + 2\ln(1+z_{\mathrm{B}}) \\ &- 2\ln(1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}})\Big]\sum_{\langle i,j\rangle} n_i n_j\Big\} \\ &\times\exp\Big\{\Big[\beta\mu_{\mathrm{A}} - 2\upsilon\ln(1+z_{\mathrm{B}}) + \upsilon\ln(1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}})\Big]\sum_i n_i\Big\}. \end{aligned} \qquad (\mathrm{A}\ 4)$$

From equation (A 4) one concludes that the binary mixture is equivalent to a pure lattice gas model, after redefining the pair interaction and the chemical potential. The effective couplings of the 'equivalent' lattice gas depend upon the temperature, the fugacity of species B and the coupling strength A–B, according to the equations

$$(\beta\varepsilon)_{\mathrm{eff}} = \beta\varepsilon_{\mathrm{AA}} - 2\ln\left(\frac{1+z_{\mathrm{B}}}{1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right) = \frac{\varepsilon_{\mathrm{AA}}}{k_{\mathrm{B}}T^*}, \qquad (\mathrm{A}\ 5a)$$

$$(\beta\mu)_{\mathrm{eff}} = \beta\mu_{\mathrm{A}} - \upsilon\ln\left(\frac{(1+z_{\mathrm{B}})^2}{1+z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right) = \frac{\mu^*}{k_{\mathrm{B}}T^*}. \qquad (\mathrm{A}\ 5b)$$

These relations allow us to define a renormalized temperature T^* and chemical potential μ^* as functions of the real temperature and the chemical potential of the species A and B. The grand canonical potential can be written as

$$\begin{aligned} \Omega_{\mathrm{mixture}}(T,\mu_{\mathrm{A}},\mu_{\mathrm{B}}) &= -k_{\mathrm{B}}T\ln\Xi \\ &= -Nk_{\mathrm{B}}T\upsilon\ln(1+z_{\mathrm{B}}) + \frac{T}{T^*}\Omega_{\mathrm{lattice}}(T^*,\mu^*). \end{aligned} \qquad (\mathrm{A}\ 6)$$

Now, $\Omega_{\mathrm{lattice}}$ is not known exactly for arbitrary lattices and dimensionalities; nevertheless it can be calculated rigorously, whenever the corresponding Ising problem has a known solution. This is possible only for $D \leqslant 2$. To obtain the solution of our model it is convenient to transform from the occupation variables ($n_i = 0, 1$) to the Ising variables ($s_i = \pm 1$):

$$s_i = 2n_i - 1. \qquad (\mathrm{A}\ 7)$$

Substituting this relation in expression (A 4) we obtain

$$\Xi = \mathrm{e}^{NH - \frac{N\upsilon}{2}K}(1+z_{\mathrm{B}})^{N\upsilon}Z_{D,\upsilon}(K,H), \qquad (\mathrm{A}\ 8)$$

where the effective magnetic field H and the coupling are given by:

$$H = \frac{\beta\mu_{\mathrm{A}}}{2} - \upsilon\frac{\beta\varepsilon_{\mathrm{AA}}}{4} - \frac{\upsilon}{2}\ln(1 + z_{\mathrm{B}}), \qquad (\mathrm{A}\,9\,a)$$

$$K = \tfrac{1}{2}\ln\left(\frac{1 + z_{\mathrm{B}}}{1 + z_{\mathrm{B}}\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right) - \frac{\beta\epsilon_{\mathrm{AA}}}{4}, \qquad (\mathrm{A}\,9\,b)$$

and $Z_{D,\upsilon}$ is the canonical partition function of the associated Ising model. By taking the logarithm we obtain the grand potential and derive the thermodynamic properties of the model.

Appendix B
Properties of $\tilde{C}(K,H)$

In this appendix we study the behaviour of the function $\tilde{C}(K,H)$.

Let us write the Hamiltonian of the Ising model as:

$$\beta\mathcal{H} = -K\left[N_{++} + N_{--} - N_{+-}\right] - H(N_{+} - N_{-}), \qquad (\mathrm{B}\,1)$$

where N_{++}, N_{--} and N_{+-} represent the number of nearest-neighbour pairs of spin that are $(+1,+1)$, $(-1,-1)$ and $(+1,-1)$, respectively, and N_{+} and N_{-} are the numbers of spins with $s = +1$ and $s = -1$, respectively. Since

$$2N_{++} + N_{+-} = \upsilon N_{+} \qquad (\mathrm{B}\,2\,a)$$

and

$$2N_{--} + N_{+-} = \upsilon N_{-}, \qquad (\mathrm{B}\,2\,b)$$

Equation (B 1) can be written also as

$$\begin{aligned}\beta\mathcal{H} &= -4K\left(N_{++} - \frac{\upsilon N_{+}}{2}\right) - 2HN_{+} - \frac{\upsilon N}{2}K + HN \\ &= -\frac{\upsilon N}{2}K + HN + 2KN_{+-} - 2HN_{+}. \qquad (\mathrm{B}\,3)\end{aligned}$$

The function $\tilde{C}(K,H)$, which is proportional to the pressure of a pure fluid with interaction parameter given by equation (A 10 b) and chemical potential shift proportional to $2H$, can be expressed as

$$\begin{aligned}\tilde{C}(K,H) &= \frac{1}{N}\ln Z - \frac{\upsilon K}{2} + H \\ &= \frac{1}{N}\ln\left(\sum_{N_{+},N_{+-}} g(N_{+},N_{+-})\,\mathrm{e}^{-2KN_{+-}}\,\mathrm{e}^{2HN_{+}}\right). \qquad (\mathrm{B}4)\end{aligned}$$

The sum is over all configurations, and $g(N_{+},N_{+-})$ counts the number of states characterized by N_{+} up spins and N_{+-} up–down nearest pairs. As we can see, $\tilde{C}(K,H = \text{constant})$, is a monotonically decreasing function of K. When $K \to 0$, this function tends to $\ln(1 + \mathrm{e}^{2H})$, and in the thermodynamic limit, when $K \to \infty$, this function tends to $2H$ if $H > 0$ and to zero if $H < 0$.

$\partial\tilde{C}(K,H)/\partial K$ at H constant can be written as

$$\begin{aligned}\left(\frac{\partial\tilde{C}(K,H)}{\partial K}\right)_{H} &= \frac{-\beta U_{D,\upsilon}(K,H)}{NK} - \frac{\upsilon}{2} - \frac{H}{K}m_{D,\upsilon} \\ &= -\frac{2}{N}\langle N_{+-}\rangle_{K,H} \leqslant 0, \qquad (\mathrm{B}\,5)\end{aligned}$$

where $U_{D,\upsilon}$ is the internal energy of the associated Ising model, and $m_{D,\upsilon}$ is the magnetization per site. Physically, the derivative is proportional to the thermal average of the up–down nearest neighbour pairs. This function tends to zero when $K \to \infty$ (the only states with probability different from zero are those with $N_{+-} = 0$) and tends to $-2\upsilon/\left[(\mathrm{e}^{H} + \mathrm{e}^{-H})^{2}\right]$ when $K \to 0$.

It can be shown that $(\partial C/\partial K)_{H}$ is a monotonically increasing function with K, since its derivative respect to K, at H constant, is

$$\left(\frac{\partial^{2} C}{\partial K^{2}}\right)_{H} = \frac{4}{N}\left[\langle(N_{+-} - \langle N_{+-}\rangle)^{2}\rangle\right] \geqslant 0. \qquad (\mathrm{B}\,6)$$

Let us define $C(K) \equiv \tilde{C}(K, H = 0)$. The following relations hold:

$$C(K) \geqslant 0, \qquad (\mathrm{B}\,7\,a)$$

$$C(0) = \ln 2, \quad C(K \to \infty) = 0. \qquad (\mathrm{B}\,7\,b)$$

The derivatives of C with respect to K have the following properties:

$$C'(K) < 0, \qquad (\mathrm{B}\,7\,c)$$

$$C'(0) = \frac{-\upsilon}{2}, \quad C'(K \to \infty) = 0, \qquad (\mathrm{B}\,7\,d)$$

and

$$C''(K) > 0. \qquad (\mathrm{B}\,7\,e)$$

Thus, $C(K)$ varies from ln 2 to zero monotonically in the interval $0 < K < \infty$.

References

[1] Hudson, C. S., 1904, *Z. phys. Chem.*, **47,** 113.
[2] Jackson, G., 1991, *Molec. Phys.*, **72,** 1365.
[3] Wheeler, J. C., 1977, *Ann. Rev. phys. Chem.*, **28,** 411.
[4] Narayanan, T., and Kumar, A., 1994, *Phys. Rep.*, **249,** 135.
[5] Walker, J. S., and Vause, C. A., 1987, *Sci. Amer.*, **256,** 90.
[6] Hirschfelder, J., Stevenson, D., and Eyring, H ., 1937, *J. chem. Phys.*, **5,** 896.
[7] Lin, J. C., and Taylor, P. L., 1994, *Phys. Rev. Lett.*, **73,** 2863.
[8] Lin, J. C., and Taylor, P. L., 1994, *Phys. Rev.* E, **49,** 2058.
[9] Frenkel, D., and Louis, A. A., 1992, *Phys. Rev. Lett.*, **68,** 3363.
[10] Fisher, M. E., 1967, *Rep. Progr. Phys.*, **30,** 615.
[11] Plischke, M., and Bergersen, B., 1994, *Equilibrium Statistical Physics* (Singapore: World Scientific).
[12] Baxter, R. J., 1982, *Exactly Solved Models in Statistical Mechanics* (New York: Academic Press).
[13] Huang, K., 1987, *Statistical Mechanics* (New York: Wiley).