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Critical exponents in the Lin–Taylor model of asymmetrical associating binary mixtures

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The critical behaviour of an associating fluid mixture, the so called Lin–Taylor model, has been studied, with focus on the critical exponents which characterize different points on the critical manifold. In general the critical behaviour of the mixture is found to be Ising-like, but there are some special situations: when two ordinary critical points merge into a double critical point or three critical points coalesce at a critical inflection point. A check has been made on the validity of the relations between critical exponents and predictions from the scaling laws.

1. Introduction

An understanding of the thermodynamic properties of fluid mixtures has substantial technological and industrial relevance. The presence of different kinds of molecule makes the behaviour of such systems more complicated than that of one-component fluids. Indeed, as well as the usual liquid–gas phase separation one may observe liquid phases corresponding to different concentrations. In most cases these regions of immiscibility end on a line of critical solution points (CSP), i.e., a 1-dimensional manifold in the global phase diagram [1]. The topology of the critical manifold can be used as a classification criterion of the phase diagram behaviour of binary fluid mixtures [2]. Recently, associating binary mixtures have attracted much interest, due to their peculiar properties. In fact, unlike standard mixtures, the miscibility curves corresponding to a given value of the pressure acting on the fluid may appear as closed loops. In other words, as the temperature is lowered the system phase separates into two liquids, but upon further cooling the mixture becomes miscible again. Such a phenomenon is due to a subtle interplay between the energy and the entropy and is observed in solutions like nicotine–water [3]. Few models have been introduced to study these reappearing phases. We have recently studied the phenomenology of the Lin–Taylor lattice gas mixture. In the present paper we consider in detail the critical exponents of such a model and show that almost everywhere on the critical line they are Ising-like, with the exception of what happens near special points. Since the coexistence region can end in high temperatures at an upper critical solution point (UCSP) or begin in low temperatures at a lower critical solution point (LCSP), when varying the parameters that characterize the mixture (pressure or couplings between the particles), a number of critical points can merge. So, two or three critical points can coalesce in a double critical point (DCP) or a critical inflection point (CIP), respectively. Such behaviour can be characterized as in the one-component case by a set of critical exponents. Experimental results [4] indicate Ising-like critical behaviour of the binary fluid mixtures, in complete agreement with the theoretical predictions based on renormalization group analysis and studies of lattice models. The latter is specially useful in the study of the criticality of hydrogen bonded binary fluid mixtures that present peculiar phase diagrams such as closed loops of immiscibility [5], allowing the appearnce of DCP and CIP. One of the first lattice models that takes account of the directional interaction was proposed some years ago by Barker and Fock [6]. However, most of the models proposed for the study of these systems are decorated lattice models [7], that are isomorphic with Ising models. Previous studies on lattice models [8–10] showed different critical behaviour for the DCP and CIP, characterized by the doubling and tripling of the critical exponent β. However, other critical exponents have been analysed only in [10], using a model that cannot be studied exactly, but in the framework of a renormalization group method.

Our aim is to observe the critical behaviour of a model that can be studied exactly, in order to test previous results and theoretical predictions such as the scaling relations between the critical exponents.

2. The Lin–Taylor model of binary mixtures

We shall investigate the properties of a lattice model of asymmetrical binary mixtures with directional interactions that was proposed few years ago by Lin and Taylor [11, 12]. Subsequent work [13, 14] completed and extended the study of the phase diagram of the model to arbitrary lattices, with special emphasis towards the appearance of islands of immiscibility.

Let us consider a binary mixture of interacting particles in a D-dimensional latice (with coordination number υ). The first kind of particle (that we will call A particles) can occupy any lattice cell that is not occupied by other A or B particles. In addition, each cell contains υ subcells of equal size, one for each face of the cell, which are available to species B when the mother cell is not occupied by A. Multiple occupation of the subcells is forbidden. There is a nearest-neighbour pairwise interaction between particles A, with a coupling value $\varepsilon_{\mathrm{AA}}$ and a binary interaction $\varepsilon_{\mathrm{AB}}$ for each edge contact between particles A and B.

The grand canonical partition function of this system can be mapped onto an Ising model [12, 14] with renormalized coupling parameters. In fact, given a value of the temperature T and the chemical potentials μ_A and μ_B, respectively, of particles A and B, the pressure (that it is related to the grand canonical potential) can be written as

$$p = \frac{k_B T}{\sigma}\left[\upsilon \ln(1+z_{\mathrm{B}}) + H - \frac{\upsilon}{2}K + \frac{1}{N}\ln Z^{\mathrm{Ising}}_{D,\upsilon}(K,H)\right]. \tag{1}$$

In this expression, N is the total number of cells of hypervolume σ, $z_{\mathrm{B}} = e^{\beta\mu_{\mathrm{B}}}$ is the fugacity of particles B, and $Z^{\mathrm{Ising}}_{D,\upsilon}(K,H)$ is the (canonical) partition function of the corresponding Ising model with the effective coupling K and the effective magnetic field H given by

$$K = \frac{1}{2}\ln\left(\frac{1+z_{\mathrm{B}}}{1+z_{\mathrm{B}}\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right) - \frac{\beta\varepsilon_{\mathrm{AA}}}{4}, \tag{2}$$

$$H = \frac{\beta\mu_{\mathrm{A}}}{2} - \upsilon\frac{\beta\varepsilon_{\mathrm{AA}}}{4} - \frac{\upsilon}{2}\ln(1+z_{\mathrm{B}}). \tag{3}$$

The mole fraction is given as

$$x_{\mathrm{A}} = \frac{1+m_{\mathrm{D},\upsilon}(K,H)}{f_1(z_{\mathrm{B}},T,H) + f_2(z_{\mathrm{B}},T)m_{D,\upsilon}(K,H)}, \tag{4}$$

where $m_{D,\upsilon}$ is the magnetization per site of the Ising model, and f_1 and f_2 are defined as

$$\begin{aligned} f_1(z_{\mathrm{B}},T,H) = 1 &+ \frac{\upsilon}{2}\left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} + \frac{z_{\mathrm{B}}\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}{1+z_B\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right) \\ &- \left(u_{D,\upsilon}(K,H) + \frac{H}{K}m_{D,\upsilon}(K,H)\right) \\ &\times \left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} - \frac{z_{\mathrm{B}}\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}{1+z_{\mathrm{B}}\,\mathrm{e}^{-\beta\varepsilon_{\mathrm{AB}}}}\right), \end{aligned} \tag{5}$$

$$f_2(z_{\mathrm{B}},T) = 1 - \frac{\upsilon z_{\mathrm{B}}}{1+z_{\mathrm{B}}}, \tag{6}$$

with $u_{D,\upsilon}$ the energy per site of the Ising model in units of $J \equiv K/\beta$. The function f_1 and f_2 satisfy the inequality $f_1 \geqslant f_2$, being equal if and only if z_{B} vanishes.

In order to obtain immiscibility, e.g. coexistence between two phases of different mole fractions, it is necessary that $D > 1$, $H = 0$ and $K > K_{\mathrm{c}}$, where K_{c} is the corresponding critical value of the Ising coupling parameter. Taking $m = |m_{D,\upsilon}(K,H=0)|$, the corresponding mole fractions are

$$x^{\pm}_{\mathrm{A}} = \frac{1 \pm m}{f_1 \pm f_2 m}, \tag{7}$$

with $f_1 = f_1(z_{\mathrm{B}},T,H=0)$ and $f_2 = f_2(z_{\mathrm{B}},T)$.

The states of the mixture with effective parameters $H = 0$ and $K = K_{\mathrm{c}}$ correspond to the critical solution points, since the non-analyticity of the grand canonical potential is directly related to the behaviour of the Helmholtz free energy of the Ising model at its critical point. The projection of the critical solution points over the (p,T) plane is the critical solution line (CSL), which depends on the values of the couplings values ε_{AA} and ε_{AB} [12–14].

3. The critical exponents in the Lin–Taylor model

In this section we shall determine the critical exponents that characterize the critical behaviour inside the coexistence region. We choose a critical solution point that corresponds to a pressure p and a temperature T_{c}. First we shall study the behaviour, as a function of the temperature, of the effective Ising coupling constant K near the critical point inside the coexistence region, keeping fixed the value of the pressure p. Thus we set $H \equiv 0$. If $\varepsilon_{\mathrm{AB}}$ is equal to zero, then $K = -\beta\varepsilon_{\mathrm{AA}}/4$ and $(1 - K_{\mathrm{c}}/K) = -(T/T_{\mathrm{c}} - 1)$. If $\varepsilon_{\mathrm{AB}} \neq 0$, the pressure p can be considered as a function of T and K using equations (1) and (2). If we impose p to be constant, by the well known implicit function theorem we can write

$$\left(\frac{\mathrm{d}K}{\mathrm{d}T}\right) = -\left[\left(\frac{\partial p}{\partial T}\right)_{K,H=0} \Big/ \left(\frac{\partial p}{\partial K}\right)_{T,H=0}\right], \tag{8}$$

where the denominator of this expression is nonzero [14]. This expression can be rewritten as

$$\left(\frac{\mathrm{d}K}{\mathrm{d}T}\right) = -\left[\left(\frac{p}{T} + T\left(\frac{\partial (p/T)}{\partial T}\right)_{K,H=0}\right) \Big/ \left(\frac{\partial p}{\partial K}\right)_{T,H=0}\right]. \tag{9}$$

Taking account of equations (1) and (2) and the fact that the pressure is constant, it is clear that the numerator of this expression is a regular function of both T and K, in the region of physically acceptable parameters. Consequently, the dependence of K with respect to the temperature close to the critical point is determined by the characteristics of the CSL at the critical point. So, if the critical point is not at a relative extremum (maximum or minimum) or an inflection point of the CSL, e.g., the critical point is an UCSP or a LCSP, the relation is linear:

$$\left(1-\frac{K_{\rm c}}{K}\right) \approx \frac{T_{\rm c}}{K_{\rm c}}\left(\frac{\mathrm{d}K}{\mathrm{d}T}\right)_{T=T_{\rm c}}\left(\frac{T}{T_{\rm c}}-1\right). \tag{10}$$

The critical point that corresponds to a relative extremum is a DCP. The case of the maximum will not be studied, since it corresponds to the disappearance of an island of immiscibility, merging its UCSP and LCSP at the DCP. Consequently, there is no coexistence region neither below nor above the DCP. The minimum of the CSL corresponds to a DCP where the LCSP of an island of immiscibility coalesces with the UCSP point of the low temperature immiscibility region [12, 14]. The relation between K and T near the DCP is

$$\left(1-\frac{K_{\rm c}}{K}\right) \approx -\frac{T_{\rm c}^2}{2K_{\rm c}}\left[\left(\frac{\partial^2 p}{\partial T^2}\right)_{K,H=0} \Big/ \left(\frac{\partial p}{\partial K}\right)_{T,H=0}\right]_{\rm DCP} \times \left(\frac{T}{T_{\rm c}}-1\right)^2. \tag{11}$$

On the other hand, the inflection point of the CSL corresponds to the merging of three critical points at a CIP. In this case K is cubic with respect to the temperature shift:

$$\left(1-\frac{K_{\rm c}}{K}\right) \approx -\frac{T_{\rm c}^3}{6K_{\rm c}}\left[\left(\frac{\partial^3 p}{\partial T^3}\right)_{K,H=0} \Big/ \left(\frac{\partial p}{\partial K}\right)_{T,H=0}\right]_{\rm CIP} \times \left(\frac{T}{T_{\rm c}}-1\right)^3. \tag{12}$$

The derivative of $z_{\rm B}$ respect to the temperature T, fixed p and $H=0$ reads

$$\frac{\mathrm{d}z_{\rm B}}{\mathrm{d}T} = \frac{-1}{k_{\rm B}T^2}\left[2p\sigma + \left(-u_{D,\upsilon}-\frac{\upsilon}{2}\right) \times \left(\frac{\varepsilon_{\rm AA}}{2} - \varepsilon_{\rm AB}\frac{z_{\rm B}\,\mathrm{e}^{-\beta\varepsilon_{\rm AB}}}{1+z_{\rm B}\,\mathrm{e}^{-\beta\varepsilon_{\rm AB}}}\right)\right] \Big/ \left[\frac{2\upsilon}{1+z_{\rm B}} + \left(-u_{D,\upsilon}-\frac{\upsilon}{2}\right)\left(\frac{1}{1+z_{\rm B}} - \frac{\mathrm{e}^{-\beta\varepsilon_{\rm AB}}}{1+z_B\,\mathrm{e}^{-\beta\varepsilon_{\rm AB}}}\right)\right]. \tag{13}$$

From this expression it is clear that the derivatives of $z_{\rm B}$ with respect to the temperature at the DCP and CIP are negative (they appear when $\varepsilon_{\rm AA}/2 < \varepsilon_{\rm AB} < 0$ [12, 14] and $-u_{D,\upsilon} - \upsilon/2$ is bounded between $-\upsilon/2$ and 0 [14]). In a similar way it can be shown that it is also negative at the critical point of the pure A system, since $\varepsilon_{\rm AA} < 0$ and $z_{\rm B} = 0$.

After ascertaining the dependence of K and $z_{\rm B}$ on T near the critical point, the behaviour of the order parameter $M^{\pm} = (x_{\rm A}^{\pm} - x_{\rm Ac})/x_{\rm Ac}$ can be studied, as can be seen from appendix A, equation (A 1). Close enough to the critical point, we can write the following asymptotic expression for $M^{\pm}$:

$$M^{\pm} \approx M_0^{\rm linear}\left(\frac{T}{T_{\rm c}}-1\right) \pm \left(1-\frac{f_2^{\rm c}}{f_1^{\rm c}}\right) m + o\left(u_{D,\upsilon}-u_{D,\upsilon}^{\rm c}, m^2, |T-T_{\rm c}|^2, |T-T_{\rm c}|m\right), \tag{14}$$

where $M_0^{\rm linear}$ is defined as

$$M_0^{\rm linear} = -x_{\rm Ac}\left(\frac{\upsilon}{2}-u_{D,\upsilon}^{\rm c}\right)\left(T\frac{\mathrm{d}z_{\rm B}}{\mathrm{d}T}\right)^{\rm c}\frac{1}{(1+z_{\rm B}^{\rm c})^2} - x_{\rm Ac}\left(\frac{\upsilon}{2}+u_{D,\upsilon}^{\rm c}\right)\left(T\frac{\mathrm{d}z_{\rm B}}{\mathrm{d}T}+z_{\rm B}\frac{\varepsilon_{\rm AB}}{k_{\rm B}T}\right)^{\rm c} \times \frac{\mathrm{e}^{-\beta_{\rm c}\varepsilon_{\rm AB}}}{(1+z_{\rm B}^{\rm c}\,\mathrm{e}^{-\beta\varepsilon_{\rm AB}})^2}, \tag{15}$$

and the index c indicates that the function is evaluated at the critical point. The term $u_{D,\upsilon} - u_{D,\upsilon}^{\rm c}$ is not considered explicitly in equation (14). When $z_{\rm B}^{\rm c} = 0$, such a term disappears, and when $z_{\rm B}^{\rm c}$ is different from zero, this term goes to zero as $(K - K_{\rm c})^{1-\alpha_{\rm I}}$, with $\alpha_{\rm I}$ the heat capacity critical exponent of the Ising model. Close to the critical point, it becomes negligible with respect to m, that goes as $(K - K_{\rm c})^{\beta_{\rm I}}$, where $\beta_{\rm I}$ is the corresponding critical exponent (see table 1) of the Ising model.

The linear term in equation (14) is negligible if $z_{\rm B}^{\rm c} \neq 0$ and the dependence of m on the temperature near the critical point is characterized by an exponent lower than 1. Under these conditions the coexistence curve is symmetrical with respect to $x_{\rm Ac}$ close to the critical point,

Table 1. Critical exponents of the Ising model [17]

Exponent	$D = 2$	$D = 3$	$D \geqslant 4^{a}$
$\alpha_I = \alpha'_I$	0 (log)	0.119 ± 0.006	0
β_I	$\frac{1}{8}$	0.326 ± 0.004	$\frac{1}{2}$
$\gamma_I = \gamma'_I$	$\frac{7}{4}$	1.239 ± 0.003	1
δ_I	15	4.80 ± 0.05	3
η	$\frac{1}{4}$	0.024 ± 0.007	0
$\nu_I = \nu'_I$	1	0.627 ± 0.002	$\frac{1}{2}$

[a] Logarithm corrections appear for $D = 4$ [18].

and the critical exponent β can be obtained easily: for an UCSP or a LCSP it is β_I, for a DCP it is $2\beta_I$, and for a CIP it is $3\beta_I$.

The conditions mentioned above are not verified in three cases: (a) the pure A vapour–liquid critical point, (b) a CIP for $D \geqslant 4$, and (c) a DCP for $D > 4$. For these three cases the critical exponent $\beta = 1$. In the first case the term on m disappears since $f_1^{\mathrm{c}} = f_2^{\mathrm{c}} = 1$. Consequently, the critical point corresonds to a cuspidal point of the coexistence curve and is dominated near the critical point by the linear term. Something similar happens in case (b), with the difference that near the critical point $m \sim |T - T_{\mathrm{c}}|^{3/2}$ (for $D = 4$ a logarithmic correction must be added [18]). For case (c) the term in m has a linear dependence on $|T - T_{\mathrm{c}}|$ near the critical point ($2\beta_I = 1$). The effect of the linear term on equation (14) is to modify the slope of the branches of the coexistence curve near the critical point (no longer symmetrical).

We shall focus our study on the dimensionalities of physical interest, namely $D = 2$ and $D = 3$.

The entropy per particle of the state with a mole fraction x_{Ac} can be obtained from the entropy per particle of the coexisting states (see appendix B), and reads:

$$\frac{s}{k_{\mathrm{B}}} = \left[(x_{\mathrm{Ac}} - 1)\ln z_{\mathrm{B}} - \nu x_{\mathrm{Ac}} \ln(1 + z_{\mathrm{B}})\right] - \left[1 - \frac{f_2}{f_1^{\mathrm{c}}}\right]\frac{T}{z_{\mathrm{B}}}\left(\frac{\partial z_{\mathrm{B}}}{\partial T}\right)_{p,H=0}. \tag{16}$$

Since $C_{p,x_{\mathrm{Ac}}} = T(\partial s/\partial T)_{p,x_{\mathrm{Ac}}}$, and taking into account equation (13), we see that the singular part of the heat capacity $C^{\mathrm{sing}}_{p,x_{\mathrm{Ac}}}$ stems from the term $(\partial^2 z_{\mathrm{B}}/\partial T^2)_{p,H=0}$. After some algebra, $C^{\mathrm{sing}}_{p,x_{\mathrm{Ac}}}$ takes the form

$$C^{\mathrm{sing}}_{p,x_{\mathrm{Ac}}} \approx 2x_{\mathrm{Ac}}\frac{T_{\mathrm{c}}^2}{K_{\mathrm{c}}^2}\left(\frac{\partial K}{\partial T}\right)^2 C^{\mathrm{I}}_{H=0}, \tag{17}$$

where $C^{\mathrm{I}}_{H=0}$ is the heat capacity of the Ising model at $H = 0$. The exponent α' is equal to α'_I for an UCSP and a LCSP. However, for a DCP or a CIP the divergence of the heat capacity disappears and then the critical exponent $\alpha' = 0$. Following Fisher [15], a critical exponent for the singular part α'_s can be defined. From equation (17) the exponent α'_s is found to be $2\alpha'_I - 2$ for a DCP, and $3\alpha'_I - 4$ for a CIP.

Taking into account the Gibbs–Duhem relation, we can write the response function as

$$\chi \equiv \left(\frac{\partial x_{\mathrm{A}}}{\partial(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})}\right)_{T,p} = -x_{\mathrm{A}}\left(\frac{\partial x_{\mathrm{A}}}{\partial \mu_{\mathrm{B}}}\right)_{T,p}. \tag{18}$$

The singular part of the response function can be related to the magnetic susceptibility of the Ising model and reads

$$\chi^{\mathrm{sing}} \approx \frac{x_{\mathrm{Ac}}}{2k_{\mathrm{B}}T_{\mathrm{c}}}\left(1 - \frac{f_2^{\mathrm{c}}}{f_1^{\mathrm{c}}}\right)^2 \chi^{\mathrm{I}}, \tag{19}$$

where $\chi^{\mathrm{I}} = (\partial m/\partial H)_K$. From equation (19) we obtain that the critical exponent γ' is equal to γ'_I for the UCSP and LCSP, to $2\gamma'_I$ for a DCP and to $3\gamma'_I$ for a CIP.

Finally, we derive the exponents related to the correlation length, ν' and η The correlation functions can be written as

$$G_{\mathrm{AA}}(i,j) = \langle N_{\mathrm{A}}(i)N_{\mathrm{A}}(j)\rangle - \langle N_{\mathrm{A}}(i)\rangle\langle N_{\mathrm{A}}(j)\rangle, \tag{20}$$

$$G_{\mathrm{AB}}(i,jt) = \langle N_{\mathrm{A}}(i)N^{t}_{\mathrm{B}}(j)\rangle - \langle N_{\mathrm{A}}(i)\rangle\langle N^{t}_{\mathrm{B}}(j)\rangle, \tag{21}$$

$$G_{\mathrm{BB}}(is,jt) = \langle N^{s}_{\mathrm{B}}(i)N^{t}_{\mathrm{B}}(j)\rangle - \langle N^{s}_{\mathrm{B}}(i)\rangle\langle N^{t}_{\mathrm{B}}(j)\rangle, \tag{22}$$

where $N_{\mathrm{A}}(i)$ is the number of particles A per unit volume of cell i, and $N^{\mathrm{s}}_{\mathrm{B}}(i)$ is the number of particles B per unit volume in subcell s of the cell i. It can be shown that

$$G_{\mathrm{AA}}(i,j) = \frac{1}{4\sigma^2}G^{\mathrm{I}}_2(i,j) \tag{23}$$

$$\begin{aligned} G_{\mathrm{AB}}(i,jt) = \frac{1}{8\sigma^2}\Bigg[&\left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} - \frac{z_{\mathrm{B}}\theta}{1+z_{\mathrm{B}}\theta}\right) \\ &\times (G^{\mathrm{I}}_3(j,l,i) - G^{I}_2(i,l)) \\ &- \left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} + \frac{z_{\mathrm{B}}\theta}{1+z_{\mathrm{B}}\theta}\right)G^{\mathrm{I}}_2(i,j)\Bigg], \end{aligned} \tag{24}$$

$$\begin{aligned} G_{\mathrm{BB}}(is,jt) = \frac{1}{16\sigma^2}\Bigg[&\left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} - \frac{z_{\mathrm{B}}\theta}{1+z_{\mathrm{B}}\theta}\right)^2 \\ &\times (G^{\mathrm{I}}_4(i,k,j,l) + G^{\mathrm{I}}_2(k,l) \\ &- G^{\mathrm{I}}_3(j,l,k) - G^{I}_3(i,k,l)) \\ &+ \left(\left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}}\right)^2 - \left(\frac{z_{\mathrm{B}}\theta}{1+z_{\mathrm{B}}\theta}\right)^2\right) \\ &\times (G^{\mathrm{I}}_2(i,l) + G^{\mathrm{I}}_2(j,k) - G^{\mathrm{I}}_3(j,l,i) \\ &- G^{\mathrm{I}}_3(i,k,j)) \\ &+ \left(\frac{z_{\mathrm{B}}}{1+z_{\mathrm{B}}} + \frac{z_{\mathrm{B}}\theta}{1+z_{\mathrm{B}}\theta}\right)^2 G^{\mathrm{I}}_2(i,j)\Bigg], \end{aligned} \tag{25}$$

where $\theta = e^{-\beta\varepsilon_{AB}}$, and k and l are the nearest-neighbour cells corresponding to subcell is and jt, respectively. The functions G^{I}_{2}, G^{I}_{3} and G^{I}_{4} are the correlation functions of two, three and four spins in the Ising model:

$$G^{I}_{2}(i,j) = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle \tag{26}$$

$$G^{I}_{3}(i,j,k) = \langle s_i s_j s_k \rangle - \langle s_i s_j \rangle \langle s_k \rangle \tag{27}$$

$$G^{I}_{4}(i,j,k,l) = \langle s_i s_j s_k s_l \rangle - \langle s_i s_j \rangle \langle s_k s_l \rangle \tag{28}$$

In the two-dimensional case, the asymptotic expressions of the correlation functions for $r = |i - j| \gg 1$ and $K > K_c$ decay as $\exp(-r/\xi)/r^2$, where ξ is the correlation length of the Ising model [15]. In the 3-dimensional case, the expansion series show a similar scenario. The correlation functions also decay as $\exp(-r/\xi)$, while the correlation length diverges as $(K - K_c)^{-\nu_I}$. As a consequence, the critical exponent ν' is equal to the Ising value ν'_I for an UCSP and a LCSP, and is $2\nu'_I$ and $3\nu'_I$ for a DCP and a CIP, respectively.

Just at the critical point, the leading dependence on the distance is determined by G^{I}_{2} [15], that varies as $1/r^{D-2+\eta}$, hence, the critical exponent η is always equal to the Ising value η_I.

Now we are able to check the scaling relations between the critical exponents that we have obtained [15]:

$$\alpha' + 2\beta + \gamma' = 2, \tag{29}$$

$$\gamma' = \nu'(2 - \eta), \tag{30}$$

$$D\nu' = 2 - \alpha'. \tag{31}$$

It is clear that these relations are verified for UCSP and a LCSP, but not for the DCP and the CIP. However, if we substitute the critical exponent α' by α'_s, we obtain another set of scaling relations [15] that are valid for all types of critical point. Such a result is in agreement with that obtained previously in [10].

4. Conclusion

The critical behaviour of the Lin and Taylor model has been analysed. This model is relevant because it presents special critical solution points such as DCP and CIP for certain values of the pressure and coupling parameters between the particles. The critical exponents $\alpha'(\alpha'_s)$, β, γ', ν' and η corresponding to $D = 2$ and $D = 3$ have been obtained explicitly. In general, the critical behaviour is Ising-like, with the exception of the DCP and the CIP, where two and three critical points merge, respectively. A new type of critical behaviour appears in these cases, characterized in each case by a new set of critical exponents: $\alpha' = 0$ $(\alpha'_s = 2\alpha'_I - 2)$, $\beta = 2\beta_I$, $\gamma' = 2\gamma'_I$, $\nu' = 2\gamma'_I$ and $\eta = \eta_I$ for a DCP, and $\alpha' = 0$ $(\alpha'_s = 3\alpha'_I - 4)$, $\beta = 3\beta_I$, $\gamma' = 3\gamma'_I$, $\nu' = 3\nu'_I$ and $\eta = \eta_I$ for a CIP. The appearance of these new sets is related to the tangential approach to the critical line imposed by the constraint p = constant [1]. The scaling relations $\alpha'_s + 2\beta + \gamma' = 2$, $\gamma' = 2$, $\gamma' = \nu'(2 - \eta)$ and $D\nu' = 2 - \alpha'_s$ hold true for all the critical points, suggesting that the rest of the critical exponents can be obtained using other scaling relations.

The results obtained are in agreement with the critical behaviour obtained with other binary mixture models [8–10]. However, Landau–Ginzburg theory violates the scaling laws for the DCP and CIP, as was pointed out by Narayanan and Kumar [16]. Such a discrepancy could be solved by the distinction between α' and α'_s.

Finally, we must remark that the critical exponents depend strongly on the constraint we have used to obtain the phase diagrams. For example, if we had assumed T to be constant, t would have been replaced by $p/p_c - 1$. Then, all the critical exponents for $D = 2$ and $D = 3$ would be Ising-like, since $K - K_c$ can be shown to be proportional to $p - p_c$, provided that $T = T_c$.

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Appendix A

Definition of critical exponents in binary mixtures

As in the simple fluid case, the critical exponents characterize the anomalous behaviour of the mixture near a critical point [1, 4]. We define the order parameter of the mixture as

$$M = \frac{|x_A - x_{Ac}|}{x_{Ac}}, \tag{A 1}$$

where x_A is the component A mole fraction, and x_{Ac} its critical value. The corresponding conjugate field is

$$h = \frac{\Delta - \Delta_c}{\Delta_c} \tag{A 2}$$

where Δ is the difference in the chemical potential between the two components $\mu_A - \mu_B$, and Δ_c its value at the critical point. We introduce a reduced temperature shift according to

$$t = \begin{cases} T/T_c - 1 & \text{if UCP, DCP or CIP,} \\ 1 - T/T_c & \text{if LCP,} \end{cases} \qquad \text{(A 3)}$$

where T_c is the critical value of the absolute temperature T. For $|t| \ll 1$, and for fixed pressure p, we define the critical exponents as follows.

Exponents α *and* α'

The divergence of the heat capacity is characterized by the exponents α and α':

$$C_{p,X_{Ac}} \equiv T\left(\frac{\partial s}{\partial T}\right)_{p,X_{Ac}} = \begin{cases} \dfrac{A}{\alpha}(t^{-\alpha} - 1) & t > 0, \\ \dfrac{A'}{\alpha'}((-t)^{-\alpha'} - 1) & t < 0, \end{cases} \qquad \text{(A 4)}$$

with $s = S/(N_A + N_B)$ the entropy per particle, and A and A' the critical amplitudes. If α or α' is equal to zero, the corresponding divergence is logarithmic.

Exponent β

The behaviour of the order parameter near the critical point follows the relation

$$M = M_0|t|^{\beta} \qquad t < 0, \text{ coexistence,} \qquad \text{(A 5)}$$

where M_0 is the order parameter critical amplitude.

Exponents γ and γ'

The response function diverges near the critical point as

$$\chi \equiv \left(\frac{\partial X_A}{\partial \Delta}\right)_{T,p} = \begin{cases} \chi_0 t^{-\gamma} & t > 0, M = 0, \\ \chi_0'(-t)^{-\gamma'} & t < 0, \text{coexistence,} \end{cases} \qquad \text{(A 6)}$$

where the critical amplitudes are χ_0 and χ_0'. The response function can be related to the osmotic compressibility χ_{osm} by the relation [4]

$$\chi_{osm} \approx \frac{1}{X_A}\left(\frac{\partial X_A}{\partial \pi}\right)_T = \frac{v}{X_A^2}\chi + \frac{1}{X_A}\left(\frac{\partial X_A}{\partial p}\right)_{\Delta,T}. \qquad \text{(A 7)}$$

In this expression π is the osmotic pressure, and v is the mean specific volume.

Exponent δ

This critical exponent characterizes the behaviour of the order parameter along the critical isotherm with its conjugate field:

$$h = h_0 M |M|^{\delta - 1} \qquad t = 0, \qquad \text{(A 8)}$$

where h_0 is the corresponding critical amplitude.

Exponents υ *and* υ'

The correlation length for the order parameter fluctuations behaves as follows near the critical point:

$$\xi = \begin{cases} \xi_0 t^{-\upsilon} & t > 0, M = 0, \\ \xi_0'(-t)^{-\upsilon'} & t < 0, \text{coexistence,} \end{cases} \qquad \text{(A 9)}$$

with ξ_0 and ξ_0' the critical amplitudes.

Exponent η

This critical exponent defines the decay of the correlation function with the distance at the critical point:

$$G_{ij}(r, t = 0, h = 0) = G_{ij}^0 r^{-(D-2+\eta)} \qquad r \to \infty, \qquad \text{(A 10)}$$

where D is the dimensionality of the space, and G_{ij}^0 the critical amplitudes.

Appendix B

Calculation of the entropy per particle at $X_A - X_{Ac}$

In order to evaluate the heat capacity at constant pressure p and mole fraction X_{Ac} in the coexistence region, we need the entropy per particle.

The entropy can be evaluated using the relation $S = -(\partial \Omega / \partial T)_{V,\mu_A,\mu_B}$. So, the entropy of the coexisting phases can be written as

$$S^{\pm} = \frac{N}{2} k_B \Big[(f_3 \pm f_4 m) - \ln z_B (f_1 \pm f_2 m) \Big], \qquad \text{(B 1)}$$

where N is the total number of lattice cells, m is the absolute value of the Ising magnetization, f_1 and f_2 are defined by the equations (5) and (6), and f_3 and f_4 are defined by

$$f_3 = 2\beta p \sigma + \left(-u_{D,\upsilon} - \frac{\upsilon}{2}\right)\left(\frac{\beta\varepsilon_{AA}}{2} - \beta\varepsilon_{AB}\frac{z_B e^{-\beta\varepsilon_{AB}}}{1 + z_B e^{-\beta\varepsilon_{AB}}}\right)$$

$$- \upsilon \ln(1 + z_B) + \ln z_B, \qquad \text{(B 2)}$$

$$f_4 = -\upsilon \ln(1 + z_B) + \ln z_B, \qquad \text{(B 3)}$$

and the entropy per particle of the coexisting phases will be $s^{\pm} = (2S^{\pm})/(N[f_1 \pm f_2 m])$.

The entropy of the system is $S_{p,X_{Ac}} = (N_A^+ + N_B^+)s^+ + (N_A^- + N_B^-)s^-$, where $N_A^{\pm}$ and $N_B^{\pm}$ correspond to the number of particles A and B; the entropy per particle of the system is

$$s = rs^+ + (1 - r)s^-, \qquad \text{(B 4)}$$

where $r = (N_A^+ + N_B^+)/(N_A^+ + N_A^- + N_B^+ + N_B^-)$. On the other hand, it is easy to see that r can be obtained also from the relation

$$X_A^c = \frac{1}{f_1^c} = rX_A^+ + (1 - r)X_A^-, \qquad \text{(B 5)}$$

where $x_A^{\pm}$ are the coexisting mole fractions defined in the equation (7). After some algebra the entropy per particle can be rewritten as

$$\frac{s}{k_B} = -\ln z_B + \frac{f_4}{f_1^c} + \left(1 - \frac{f_2}{f_1^c}\right)\frac{f_3 - f_4}{f_1 - f_2}. \tag{B 6}$$

Taking into account that, from the equation (13), the derivative of z_B with respect to the temperature along the coexistence curve can be expressed as

$$\frac{dz_B}{dT} = \frac{-z_B}{T}\frac{f_3 - f_4}{f_1 - f_2}, \tag{B 7}$$

we obtain equation (16).

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