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LETTER TO THE EDITOR

Exact two-phase coexistence surface for a three-component soiution on the square lattice

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Abstract. A model three-component system is considered in which the bonds of a square lattice are covered by rod-like molecules of types AA, BB, and AB. The ends of molecules which are first neighbours to each other at a common lattice site interact with energies ε_{AA}, ε_{BB}, and ε_{AB}. The model is equivalent to an Ising model on the 4–8 lattice. The plait line and the two-phase coexistence surface in temperature–composition space are calculated exactly.

Wheeler and Widom [1] introduced a lattice model of a three-component solution in which each bond of a lattice is covered by a rod-like molecule of type AA, BB, or AB. The ends of molecules near a common lattice site interact with energy ε_{AA} if both ends are of type A, ε_{BB} if both ends are of type B, and ε_{AB} if one end is of type A and the other end is of type B.

Under the simplifying assumptions $\varepsilon_{AB} \to \infty$ and $\varepsilon_{AA} = \varepsilon_{BB} = 0$, the model can be mapped onto the standard Ising model on the same lattice. The bulk [1] and interfacial properties [2] of this simplified version of the model have been investigated. With the introduction of anisotropic couplings, the model has been used to study the roughening transition [3]. By adding an interaction between neighbouring AB molecules, the model can be used to study microemulsions [4]. A six-component version of the model has also been studied [5].

The model with general finite interactions ε_{AA}, ε_{BB}, and ε_{AB} was shown to have no phase transitions if $\varepsilon_{AB} \leq (\varepsilon_{AA} + \varepsilon_{BB})/2$ [6]. For certain ranges of the interaction energies and chemical potentials, the Peierls argument [7] was used to prove the existence of phase separation or of long-range order at sufficiently low temperatures for the model on the square and simple cubic lattices [8].

The exact two-phase coexistence surface in temperature–composition space has been obtained for the model with general finite interactions on the honeycomb lattice [9]. In the present letter the exact two-phase coexistence surface in temperature–composition space is obtained for a modified version of the model with general finite interactions on the square lattice.

A typical molecular configuration for the model on the square lattice is illustrated in figure 1. In the modified version, the ends of molecules near a common vertex which are on neighbouring perpendicular bonds interact with finite energies ε_{AA}, ε_{BB}, and ε_{AB}. This defines a variation of the general model considered earlier [6, 8] in that only *first-neighbour* molecular ends near a common vertex are considered to interact.

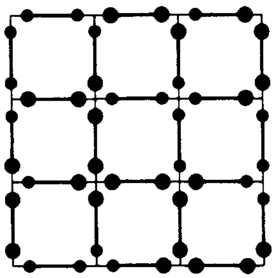

Figure 1. A molecular configuration on the square lattice. Molecular ends of type A and B are represented by balls of two different sizes.

Using the method previously described [8, 9], the present model on the square lattice can be shown to be equivalent to an Ising model on the 4-8 lattice (see figure 2).

If we let $S_i = +1$ ($S_i = -1$) indicate that a site i of a 4-8 lattice containing N sites is occupied by a type A (type B) molecular end, then the canonical partition function for the equivalent Ising model is given as

$$Z_{4\text{-}8} = \sum_{\{S_i\}} \exp\left[-H_{4\text{-}8}(\{S_i\})/kT\right] \tag{1}$$

where

$$H_{4\text{-}8} = J_I \sum_{(i,j)\subset \mathscr{S}} S_i S_j + \mu_I \sum_{(i,j)\subset \mathscr{C}} S_i S_j - h_I \sum_{i\in 4\text{-}8} S_i \tag{2}$$

and

$$\begin{aligned} J_I &= (\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB})/4 \\ \mu_I &= (2\mu_{AB} - \mu_{AA} - \mu_{BB})/4 \\ h_I &= (\varepsilon_{BB} - \varepsilon_{AA})/2 - (\mu_{BB} - \mu_{AA})/4. \end{aligned} \tag{3}$$

The sets $\mathscr{S}$ correspond to simple squares in the 4-8 lattice, and the sets $\mathscr{C}$ correspond to the links between squares (see figure 2).

In the present calculation, we consider primarily the case $J_I < 0$, $\mu_I < 0$, and $h_I = 0$. For this range of parameters, phase separation into AA-rich and BB-rich phases occurs at sufficiently low temperatures. For other ranges of the parameters J_I, μ_I, and h_I, other types of ordered phases occur in the model at sufficiently low temperatures. In fact, ordered low-temperature phases occur in the present modified version of the

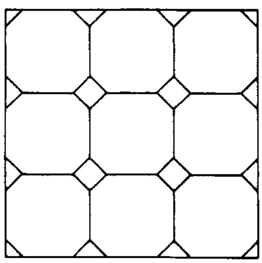

Figure 2. The 4-8 lattice.

model even if $J_l > 0$. The result of [6], which proves such phases do not occur in the original model with finite interactions if $J_l > 0$, does not apply to the modified version of the model, for the equivalent Ising representation is not on a line graph.

The mole fractions of AA, BB, and AB molecules in the model can be calculated from the relationships [9]

$$\begin{aligned} &X_{\mathrm{AA}} + X_{\mathrm{BB}} + X_{\mathrm{AB}} = 1 \\ &|X_{\mathrm{AA}} - X_{\mathrm{BB}}| = I_{4\text{-}8} \\ &X_{\mathrm{AB}} = (1 - \sigma_{4\text{-}8})/2. \end{aligned} \tag{4}$$

Here

$$I_{4\text{-}8} = |\langle S_i \rangle_{i \in 4\text{-}8}|$$

is the magnetisation of an Ising model on the 4-8 lattice and

$$\sigma_{4\text{-}8} = \langle S_i S_j \rangle_{i,j \subset \mathscr{C}}.$$

(Note that $S_i S_j = 1$ if an AA or BB molecule covers $\mathscr{C}$ and $S_i S_j = -1$ if an AB molecule covers $\mathscr{C}$.)

The 4-8 lattice is a lattice of the 'chequered type' for which the zero field ($h_l = 0$) Ising partition function has been obtained exactly [10]. Upon simplification of the general prescription for the partition function of an Ising model on a chequered type lattice [10, 11], we obtained for the 4-8 lattice the simple expression

$$\ln \lambda_{4\text{-}8} = \lim_{N \to \infty} \frac{1}{N} \ln Z_{4\text{-}8} = \frac{1}{32\pi^2} \int_0^{2\pi} \int_0^{2\pi} \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \ln\{2^4[\alpha + 2\beta(\cos\omega_1 + \cos\omega_2) + 2\delta(\cos(\omega_1 + \omega_2) + \cos(\omega_1 - \omega_2))]\}. \tag{5}$$

If we let $R = -J_l/kT$, $L = -\mu_l/kT$, $C_1 = \cosh 2R$, $S_1 = \sinh 2R$, $C_2 = \cosh 2L$, $S_2 = \sinh 2L$, then α, β, and δ are given as

$$\begin{aligned} &\alpha = 4C_1^2 S_1^2 S_2^2 + 4(C_1^2 + C_2)^2 \\ &\beta = -2S_1^2 S_2 (C_1^2 + C_2) \\ &\delta = -S_1^2 S_2^2. \end{aligned} \tag{6}$$

An exact expression for $\sigma_{4\text{-}8}$ is obtained by first noting that

$$\sigma_{4\text{-}8} = 2 \frac{\partial}{\partial L} \ln \lambda_{4\text{-}8} \bigg|_R . \tag{7}$$

Letting $I = 8 \ln(\lambda_{4\text{-}8} 2^{-1/2})$, we obtain

$$\sigma_{4\text{-}8} = \frac{1}{4} \left[\frac{\partial I}{\partial \alpha} \frac{\partial \alpha}{\partial L} + \frac{\partial I}{\partial \beta} \frac{\partial \beta}{\partial L} + \frac{\partial I}{\partial \delta} \frac{\partial \delta}{\partial L} \right] \bigg|_R . \tag{8}$$

The integrals $\partial I/\partial \alpha$, $\partial I/\partial \beta$, and $\partial I/\partial \delta$ were obtained using the method of Hurst [12, 13]. The integral $\partial I/\partial \delta$ for the 4-8 lattice, although not given in [12] or [13], can be calculated using the methods therein or obtained by noting from equation (5) that

$\alpha\,\partial I/\partial\alpha+\beta\,\partial I/\partial\beta+\delta\,\partial I/\partial\delta=1$. The results are

$$\frac{\partial I}{\partial\alpha}=2K(k)/[\pi(\alpha-4\delta)]$$

$$\frac{\partial I}{\partial\beta}=\frac{-4(\alpha+2\beta)K(k)+4(\alpha+4\beta+4\delta)\Pi_1(\nu,k)}{\pi(\alpha-4\delta)(\beta+2\delta)} \tag{9}$$

$$\frac{\partial I}{\partial\delta}=\frac{2(\alpha\beta-2\alpha\delta+4\beta^2)K(k)-4\beta(\alpha+4\beta+4\delta)\Pi_1(\nu,k)}{\pi\delta(\alpha-4\delta)(\beta+2\delta)}+\frac{1}{\delta}$$

where

$$K(k)=\int_0^{\pi/2}(1-k^2\sin^2\theta)^{-1/2}\,\mathrm{d}\theta$$

$$\Pi_1(\nu,k)=\int_0^{\pi/2}(1+\nu\sin^2\theta)^{-1}(1-k^2\sin^2\theta)^{-1/2}\,\mathrm{d}\theta$$

$$k^2=16(\beta^2-\alpha\delta)/(\alpha-4\delta)^2 \tag{10}$$

$$\nu=4(\beta+2\delta)/(\alpha-4\delta).$$

An exact expression for $\sigma_{4\text{-}8}$ then follows immediately from equations (6)-(10).

The exact spontaneous magnetisation of a ferromagnetic Ising model on the 4-8 lattice ($R>0$, $L>0$, $h_l=0$) has been conjectured by Lin *et al* [14] to be given as

$$I_{4\text{-}8}=F(1-\kappa^2)^{1/8} \tag{11}$$

where

$$F=(1+\mathrm{e}^{-2L}C_1^{-2})^{-1/2}$$

$$\kappa^2=\{[2t_1t_2(1-t_1^2)]^4+[(1+2t_1^2t_2^2+t_1^4)^2-16t_1^4t_2^2][1-2t_1^2t_2^2+t_1^4]^2\}[2t_1t_2(1+t_1^2)]^{-4} \tag{12}$$

$$t_1=\tanh R$$

$$t_2=\tanh L.$$

Equation (11) reproduces the exact low-temperature series expansion for $I_{4\text{-}8}$ up to at least twelfth order [14]. An incorrect formula for $I_{4\text{-}8}$, previously published by Lin and Fang [15], did not contain the factor F.

An equation relating R_c and L_c along the line of critical points can be obtained from an examination of the partition function given by equation (5). The symmetry of the integrand in equation (5) ensures that $\ln\lambda_{4\text{-}8}$ is an even function of R and of L. The argument of the logarithm of the integrand is non-negative, but has a minimum value of zero on the critical line. This minimum value occurs at $\omega_1=\omega_2=0$ if $L_c>0$ and at $\omega_1=\omega_2=\pi$ if $L_c<0$. After some algebra we obtain the simple result

$$\exp(-2|L_c|)+1=\sqrt{2}\tanh 2|R_c|. \tag{13}$$

For the 4-8 lattice with a single coupling constant $L_c=R_c>0$, we obtain

$$\exp(2R_c)=\{2+\sqrt{2}+\sqrt{10+8\sqrt{2}}\}/2=4.015\ldots \tag{14}$$

a result given numerically by Utiyama [10]. Equation (13) for the case $R_c>0$, $L_c>0$ can also be obtained from equation (11) by setting $I_{4\text{-}8}=0$.

For plotting purposes, we define the reduced parameters $\mu' = |\mu_l/J_l|$ and $T' = kT/|J_l|$. Figure 3 contains a plot of μ'_c against T'_c as given by equation (13). The maximum value of T'_c, which occurs as $\mu'_c \to \infty$, is given from equation (13) as

$$\max T'_c = 2/\ln(\sqrt{2}+1) = 2.269 \ldots . \tag{15}$$

Hence, for the case $R > 0$ and $L > 0$, phase separation into an AA-rich and a BB-rich phase does not occur if $T' > 2.269 \ldots$.

Equation (13) and the exact expression for σ_{4-8} can be combined to yield a formula for X_{AB} along the critical line. Letting $\tau = \sqrt{2} \tanh 2|R_c|$ (see equation (13)), we obtain the exact result

$$X^c_{AB} = \frac{1}{2}\left[1 \mp \coth 2|L_c| \pm \frac{4}{\pi(2-\tau)}\left(\frac{\tau-1}{\tau+1}\right)^{1/2} \cos^{-1}(1/\tau)\right]. \tag{16}$$

The upper signs are to be used for $L > 0$, the lower signs for $L < 0$.

For the case $L > 0$, a plot of X^c_{AB} against T'_c (the plait line) is given in figure 4. The maximum value of X^c_{AB}, which occurs as $T'_c \to 0$, is given by equations (13) and (16) for $L > 0$ as

$$\max X^c_{AB} = (2-\sqrt{2})/4 = 0.1464 \ldots . \tag{17}$$

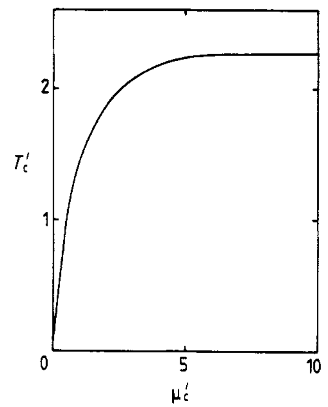

Figure 3. A plot of T'_c against μ'_c at the plait point. $\mu'_c \to \infty$ as $T'_c \to 2/\ln(\sqrt{2}+1) = 2.269 \ldots$.

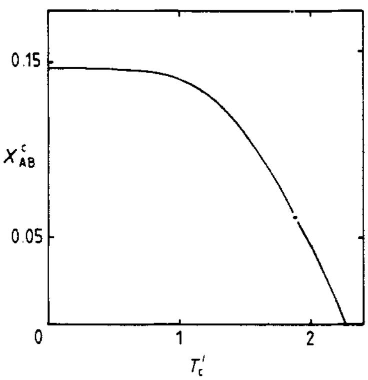

Figure 4. A plot of X^c_{AB} against T'_c along the plait line. The maximum value of X^c_{AB} is $(2-\sqrt{2})/4 = 0.1464 \ldots$, which occurs as $T'_c \to 0$. As $T'_c \to 2/\ln(\sqrt{2}+1) = 2.269 \ldots$, $X^c_{AB} \to 0$.

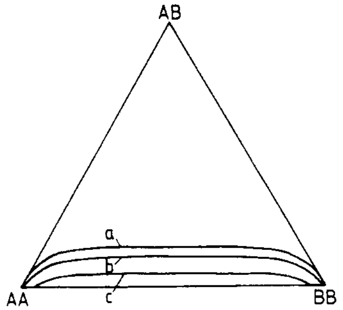

Figure 5. Isothermal coexistence curves at the temperature $T'_{(a)} \to 0$, $T'_{(b)} = 1.5$, $T'_{(c)} = 2.0$. The coexistence curve shrinks to a point at $T' = 2.269\ldots$.

Hence there is no phase separation into AA-rich and BB-rich phases if $X_{AB} > 0.1464\ldots$. The presence of AB molecules thus greatly enhances the miscibility of AA and BB molecules.

Using equations (4) and (8)-(12), we obtained isothermal coexistence curves for the model. Three such curves are illustrated in figure 5. As $T' \to 0$, the model is equivalent to an Ising model on the square lattice with coupling constant L. The coexistence curve as $T' \to 0$ is the same as the coexistence curve for the original model studied by Wheeler and Widom [1] for which $J_l \to -\infty$. (As $\mu' \to \infty$, $X_{AB} \to 0$ and the model becomes equivalent to an Ising model on the square lattice with coupling constant R.)

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