Journal of Statistical Physics, Vol. 45, Nos. 1/2, 1986

Exact Solution of a Three-Component System on the Honeycomb Lattice

Dale A. Huckaby[1] **and Masato Shinmi**[1]

Received January 22, 1986; final May 7, 1986

A model three-component system is considered in which the bonds of a honeycomb lattice are covered by rodlike molecules of types AA, BB, and AB. The ends of molecules near a common lattice site interact with energies ε_{AA}, ε_{BB}, and ε_{AB}. The model is equivalent to an Ising model on the 3-12 lattice. Exact results are obtained for the two-phase coexistence curves in the isothermal composition plane.

KEY WORDS: Ising model; phase transitions; three-component; honeycomb lattice.

1. INTRODUCTION

Wheeler and Widom[1] introduced a lattice model of a three-component solution in which each bond of the lattice is covered by a rodlike 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. A typical molecular configuration for the model on the honeycomb lattice is illustrated in Fig. 1.

Under the simplifying assumption that a type A and a type B molecular end near a common site repel infinitely ($\varepsilon_{AB} \to \infty$), and that like ends do not interact ($\varepsilon_{AA} = \varepsilon_{BB} = 0$), the model has only two reduced activities as thermodynamic variables and can be easily mapped onto the standard Ising model on the same lattice. The bulk and interfacial properties of this special case of the model have been previously studied.[1,2]

---

[1] Department of Chemistry, Texas Christian University, Fort Worth, Texas, 76129.

0022-4715/86/1000-0135$05.00/0

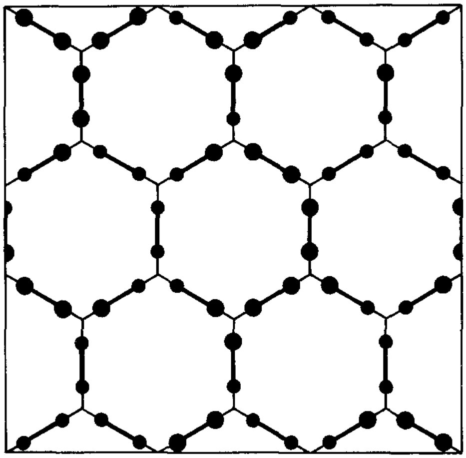

Fig. 1. Configuration of molecules on the honeycomb lattice. The type A and type B molecular ends are represented by balls of two different sizes.

In the present paper we study the model on the honeycomb lattice with general finite interactions ε_{AA}, ε_{BB}, and ε_{AB}. Exact results are obtained for the two-phase coexistence curves in the isothermal composition plane.

2. ISING REPRESENTATION OF THE MODEL

As has been shown previously,[3,4] the model with general finite interactions is equivalent to an Ising model on a line graph. (A line graph is a graph Λ that can be covered by a set of complete graphs such that each vertex of Λ is covered by exactly two complete graphs. A complete graph C_v is a graph containing v vertices together with links joining every pair of vertices.)

The line graph Λ associated with the model on the honeycomb lattice is called the 3–12 lattice and is illustrated in Fig. 2. Each site of the 3–12 lattice is covered by a vertex from one C_3 and from one C_2 graph.

If we let $S_i = +1$ ($S_i = -1$) indicate that site $i \in \Lambda$ is occupied by a type A (type B) molecular end, then we can formally write the grand canonical partition function for the model on the 3–12 lattice Λ as

$$\Xi_\Lambda = \sum_{\{S_i\}} \exp[-H_\Lambda(\{S_i\})/kT] \tag{1}$$

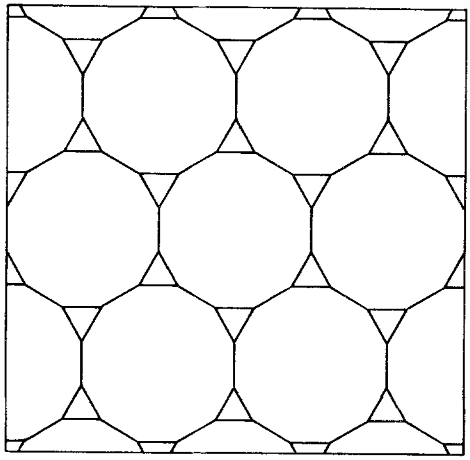

Fig. 2. The 3-12 lattice, each site of which is covered by one C_3 graph and one C_2 graph.

where the Hamiltonian is given as

$$\begin{aligned} H_A(\{S_i\}) = \sum_{(i,j) \subset C_3} & \{\varepsilon_{AA}(1+S_i)(1+S_j) + \varepsilon_{BB}(1-S_i)(1-S_j) \\ & + \varepsilon_{AB}[(1-S_i)(1+S_j) + (1+S_i)(1-S_j)]\}/4 \\ & - \sum_{(i,j) \subset C_2} \{\mu_{AA}(1+S_i)(1+S_j) + \mu_{BB}(1-S_i)(1-S_j) \\ & + \mu_{AB}[(1-S_i)(1+S_j) + (1+S_i)(1-S_j)]\}/4 \end{aligned} \tag{2}$$

Collecting terms in Eq. (2), we see that the Hamiltonian, except for a constant term, can be written as

$$H'_A(\{S_i\}) = J_I \sum_{(i,j) \subset C_3} S_i S_j + \mu_I \sum_{(i,j) \subset C_2} S_i S_j - h_I \sum_{i \in A} S_i \tag{3}$$

where $J_I = (\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB})/4$, $\mu_I = (2\mu_{AB} - \mu_{AA} - \mu_{BB})/4$, and $h_I = (\varepsilon_{BB} - \varepsilon_{AA})/2 - (\mu_{BB} - \mu_{AA})/4$. The general Wheeler–Widom model on the honeycomb lattice is thus equivalent to an Ising model on the 3-12 lattice. Since vacant sites are not allowed, the model is considered in the limit where the chemical potentials μ_{AA}, μ_{BB}, and μ_{AB} all tend to infinity; however, differences such as $\mu_{AB} - \mu_{AA}$ or $\mu_{AB} - \mu_{BB}$ are finite thermodynamic variables.

By studying the zeros of the grand canonical partition function of the equivalent lattice gas on the line graph, it was proved[3] that there are no phase transitions in the model if $J_I \geqslant 0$. The Lee–Yang circle theorem[5] ensures there are no phase transitions in the model if $J_I < 0$, $\mu_I < 0$, and $h_I \neq 0$.

In the present paper we shall present exact results for the model on the honeycomb lattice for the case $J_I < 0$, $\mu_I < 0$, and $h_I = 0$. For this range of parameters, phase separation into an AA-rich and a BB-rich phase occurs at sufficiently low temperatures.

3. EXACT COEXISTENCE CURVES

In order to study the Wheeler–Widom model on the honeycomb lattice, we first obtain the canonical partition function for the equivalent Ising model on the 3-12 lattice, $Z_{3\text{-}12}(R, L)$, where $R = -J_I/kT$ and $L = -\mu_I/kT$. Syozi[(6),2] has related $Z_{3\text{-}12}(R, L)$ for a 3-12 lattice containing $3N$ sites to the partition function $Z_{\mathrm{H}}(K)$ for an Ising model on a honeycomb lattice which contains N sites. His method is outlined in Appendix A. The result is

$$Z_{3\text{-}12}(R, L) = A^N Z_{\mathrm{H}}(K) \tag{4}$$

where

$$A^4 = e^{-4R}(e^{4R} + 3)(e^{4R} - 1)^3 \sinh^3 2L/\sinh^3 2K \tag{5}$$

The parameters K, L, and R are related as

$$\coth K = \coth L\,(e^{4R} + 3)/(e^{4R} - 1) \tag{6}$$

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

$$\begin{aligned} X_{AA} + X_{BB} + X_{AB} &= 1 \\ |X_{AA} - X_{BB}| &= I_{3\text{-}12} \\ X_{AB} &= (1 - \sigma_{3\text{-}12})/2 \end{aligned} \tag{7}$$

Here

$$I_{3\text{-}12} = |\langle S_i \rangle_{i \in A}|$$

is the magnetization of the 3-12 lattice and

$$\sigma_{3\text{-}12} = \langle S_i S_j \rangle_{i,j \subset C_2}$$

(Note that $S_i S_j = 1$ if an AA or a BB molecule covers C_2 and $S_i S_j = -1$ if an AB molecule covers C_2.)

[2] See also the references in Ref. 6, especially Refs. 7 and 8.

An exact expression for $\sigma_{3\text{-}12}$, derived in Appendix B, is

$$\sigma_{3\text{-}12} = [2\alpha K_1(\kappa) \sinh 2K - \cosh 2K]/(3 \sinh 2L) + \coth 2L \tag{8}$$

where, letting $z = \exp(-2K)$

$$\alpha = (1 - z^4)(z^2 - 4z + 1)/[\pi |1 - z^2| (1 - z)^4] \tag{9}$$

$$K_1(\kappa) = \int_0^{\pi/2} (1 - \kappa \sin^2 \phi)^{-1/2} \, d\phi \tag{10}$$

$$\kappa = 16z^3(1 + z^3)(1 - z)^{-3}(1 - z^2)^{-3} \tag{11}$$

From Eq. (6) we find z explicitly in terms of L and R as

$$z = \frac{e^{-2L}(e^{4R} + 1) + 2}{e^{4R} + 1 + 2e^{-2L}} \tag{12}$$

The spontaneous magnetization of the 3-12 lattice is given by the exact expression

$$I_{3\text{-}12} = \frac{(e^{4R} + 3)^{1/2}(e^{4R} - 1)^{1/2}(1 - \kappa)^{1/8}}{e^{4R} + 1 + 2e^{-2L}} \tag{13}$$

Equation (13) is used to determine the coexistence curves in the model. A derivation of Eq. (13) will be published elsewhere.[9]

We now consider the range of parameters $J_I < 0$, $\mu_I < 0$, $h_I = 0$. Equation (6) indicates that this case corresponds to a ferromagnetic ($K > 0$) Ising model on the honeycomb lattice. Since the ferromagnetic Ising model on the honeycomb lattice has a critical point at $\exp(2K_c) = 2 + \sqrt{3}$,[10] then from Eqs. (4) and (6), the critical parameters L_c and R_c for the Ising model on the 3-12 lattice are related as

$$\coth L_c = \sqrt{3}\,(e^{4R_c} - 1)/(e^{4R_c} + 3) \tag{14}$$

The critical point in the three-component solution model is called a plait point.

For plotting purposes, we define the reduced parameters $\mu' = \mu_I/J_I$ and $T' = -kT/J_I$. Figure 3 gives a plot of μ'_c versus T'_c for the Wheeler–Widom model on the honeycomb lattice. The maximum possible value of T'_c, which occurs when $\mu'_c \to \infty$, is given by Eq. (14) as

$$\max T'_c = 4/\ln(3 + 2\sqrt{3}) = 2.143... \tag{15}$$

Equations (7) and (13)–(15) imply that if $T'_c < 2.143...$, phase separation into an AA-rich and a BB-rich phase occurs if μ' is sufficiently

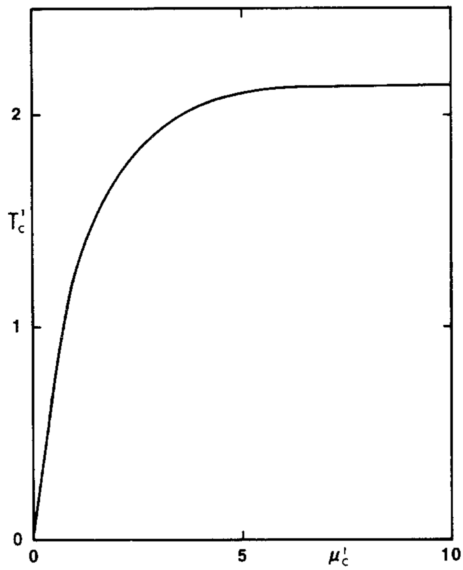

Fig. 3. A plot of T'_c versus μ'_c at the plait point. $\mu'_c \to \infty$ as $T'_c \to 4/\ln(3+2\sqrt{3}) = 2.143...$.

large. Likewise, at a fixed $\mu' > 0$, phase separation occurs at sufficiently low temperatures (see Fig. 3). In a previous paper,[4] we used the Peierls argument to prove that this type of phase separation also occurs in the model on the square and simple cubic lattices.

Using Eqs. (7)–(13), we have plotted isothermal coexistence curves for the model in Fig. 4. As $T' \to 0$, the model becomes equivalent to an Ising model on the honeycomb lattice with $K = L$ [see Eq. (6)]. The coexistence curve in this low-temperature limit is the same as the coexistence curve obtained for the special case of the model studied by Wheeler and Widom[1,2] for which $J_I \to -\infty$. This is also the coexistence curve at constant μ' as $\mu' \to 0$.

As $\mu' \to \infty$, $X_{AB} \to 0$ and the model becomes equivalent to an Ising model on the Kagomé lattice with coupling constant R. The limiting form of the spontaneous magnetization of the Kagomé lattice[11] yields, as $T' \to \max T'_c = 2.143...$,

$$|X_{AA} - X_{BB}| \sim A_c(1 - T'/\max T'_c)^{1/8} \tag{16}$$

where A_c is a constant.

At the plait point, it follows from Eqs. (7)–(12) and (14) that $X^c_{AA} = X^c_{BB}$ and

$$X^c_{AB} = \frac{1}{2}\left(1 - \frac{3\cosh 2L_c - 2}{3\sinh 2L_c}\right) \tag{17}$$

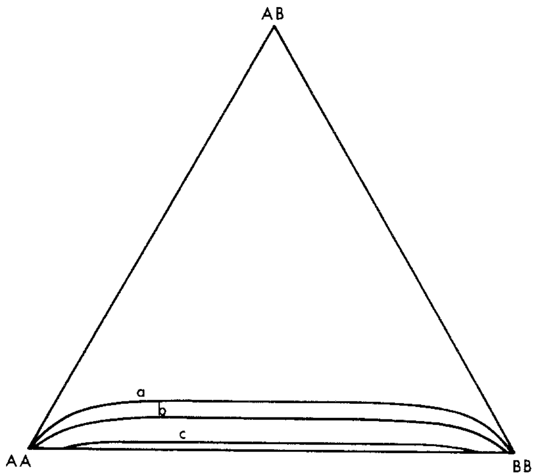

Fig. 4. Isothermal coexistence curves at the temperature $T'_{(a)} \to 0$, $T'_{(b)} = 1.5$, $T'_{(c)} = 2.0$. The coexistence curve shrinks to a point at $T' = 2.143...$.

where L_c is given by Eq. (14) as a function of $T'_c = R_c^{-1}$. A plot of X^c_{AB} versus T'_c is given in Fig. 5. As $T'_c \to \max T'_c$, $X^c_{AB} \to 0$ linearly in T'_c. The maximum value of X^c_{AB} occurs as $T'_c \to 0$. Equations (14) and (17) yield

$$\max X^c_{AB} = (9 - 4\sqrt{3})/18 = 0.1151... \tag{18}$$

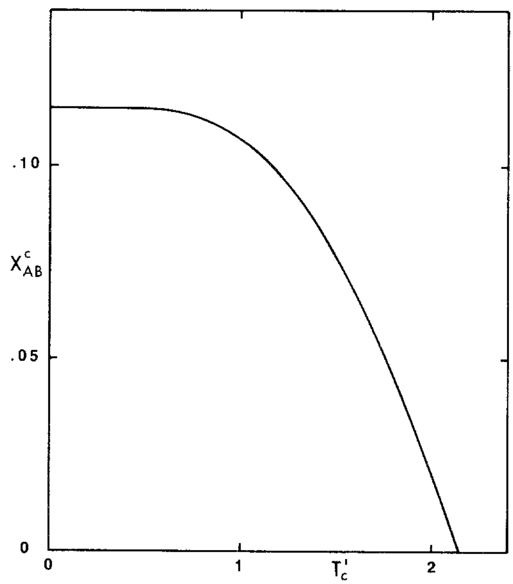

Fig. 5. A plot of X^c_{AB} versus T'_c at the plait point. The maximum value of X^c_{AB} is $(9 - 4\sqrt{3})/18 = 0.1151...$, which occurs as $T'_c \to 0$. As $T'_c \to 2.143...$, $X^c_{AB} \to 0$.

Hence, there is no phase separation into AA-rich and BB-rich phases in a system for which $X_{AB} > 0.1151$. The presence of AB molecules thus greatly enhances the miscibility of AA and BB molecules.

The case $J_I < 0$, $\mu_I > 0$, $h_I = 0$, corresponding to an antiferromagnetic ($K < 0$) Ising model on the honeycomb lattice, can also be solved by the above method. For this range of parameters an ordered phase, consisting mainly of AB molecules, occurs at sufficiently low temperatures. In this phase most of the sites of one sublattice of the honeycomb lattice are surrounded by type A molecular ends, the sites of the other sublattice being surrounded by type B molecular ends.[1,4]

APPENDIX A. CALCULATION OF $Z_{3\text{-}12}(R, L)$

We shall here outline Syozi's[6] method for calculating the partition function for an Ising model on the 3-12 lattice (see Fig. 2) with a coupling R between pairs of spins on C_3 and a coupling L between spins on C_2.

Using the star-triangle transformation, the partition function for the 3-12 lattice containing $3N$ sites can be related to the partition function for an Ising model on a doubly decorated honeycomb lattice (DDH) containing $4N$ sites as

$$Z_{3\text{-}12}(R, L) = \Delta^{-N} Z_{\mathrm{DDH}}(L_1, L)$$

where

$$\Delta^4 = e^{4R}(e^{4R} + 3)^2$$

Here L_1 is the coupling between a spin on a honeycomb lattice site and a spin on a neighboring decorated site. The parameters L_1 and R are related as

$$e^{4R} = 2 \cosh 2L_1 - 1$$

Using the multiple decoration and iteration transformation,[6] one can in turn relate $Z_{\mathrm{DDH}}(L_1, L)$ to the partition function for an Ising model on the honeycomb lattice (H) containing N sites as

$$Z_{\mathrm{DDH}}(L_1, L) = I^{3N/2} Z_{\mathrm{H}}(K)$$

where

$$I^2 = 4 \sinh 2L \sinh^2 2L_1 / \sinh 2K$$

Here K is the coupling constant between neighboring spins on the honeycomb lattice.

Equations (4)–(6) of Section 3 relating $Z_{3\text{-}12}(R, L)$ to $Z_{\mathrm{H}}(K)$ then follow immediately.

APPENDIX B. AN EXACT EXPRESSION FOR $\sigma_{3\text{-}12}$

If $Z_{3\text{-}12}(R, L)$ is the partition function of an Ising model on a 3-12 lattice containing $3N$ sites as given in Appendix A, then

$$\sigma_{3\text{-}12} = \langle S_i S_j \rangle_{i,j \subset C_2} = \frac{1}{3N/2} \frac{\partial}{\partial L} \ln Z_{3\text{-}12}(R, L) \bigg|_R$$

From Eqs. (4)–(6),

$$\sigma_{3\text{-}12} = \left[\frac{2}{3N} \frac{d}{dK} \ln Z_H(K) - \coth 2K \right] \frac{\partial K}{\partial L} \bigg|_R + \coth 2L$$

The internal energy per spin for the Ising model on the honeycomb lattice is given as

$$U_{\mathrm{H}} = -\frac{kTK}{N} \frac{d}{dK} \ln Z_{\mathrm{H}}(K)$$

Houtappel[10] has obtained the exact expression

$$U_{\mathrm{H}}/kT = -K[\coth 2K + \alpha K_1(\kappa)]$$

where α, κ, and $K_1(\kappa)$ are defined in Eqs. (9)–(11). A calculation of $\partial K/\partial L|_R$ using Eq. (6) yields the exact result

$$\sigma_{3\text{-}12} = [2\alpha K_1(\kappa) \sinh 2K - \cosh 2K]/(3 \sinh 2L) + \coth 2L$$

ACKNOWLEDGMENTS

This research was supported by the Robert A. Welch Foundation, grant P-446. M. S. is a Robert A. Welch Foundation Predoctoral Fellow.

REFERENCES

1. J. C. Wheeler and B. Widom, *J. Am. Chem. Soc.* **90**:3064 (1968).
2. B. Widom, *J. Phys. Chem.* **88**:6508 (1984).
3. D. A. Huckaby and J. M. Kowalski, *Phys. Rev. A* **30**:2121 (1984).
4. D. A. Huckaby, J. M. Kowalski, and M. Shinmi, *J. Phys. A* **18**:3585 (1985).

5. T. D. Lee and C. N. Yang, *Phys. Rev.* **87**:410 (1952).
6. I. Syozi, in *Phase Transitions and Critical Phenomena*, Vol. 1, C. Domb and M. S. Green, eds. (Academic Press, New York, 1972).
7. I. Syozi, *Rev. Kobe Univ. Mercantile Marine* **2**:21 (1955).
8. M. E. Fisher, *Phys. Rev.* **113**:969 (1959).
9. D. A. Huckaby, *J. Phys. C*, in press.
10. R. M. F. Houtappel, *Physica* **16**:425 (1950).
11. S. Naya, *Prog. Theor. Phys.* **11**:53 (1954).