Regions of analyticity in a model three-component solution

Dale A. Huckaby and Jacek M. Kowalski*
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129
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A model for a three-component solution is considered in which the bonds of a square or cubic lattice are covered by 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}. It is shown there is no demixing transition in the model if $\epsilon_{AB} \leq (\epsilon_{AA}+\epsilon_{BB})/2$.

Several years ago Wheeler and Widom[1] introduced a lattice model of a three-component solution containing rodlike molecules of types AA, BB, and AB. Each bond of the lattice is covered by a single molecule. The ends of molecules near a common lattice site are allowed to interact, thereby contributing to the configurational energy of the system. A typical configuration for such a system is illustrated in Fig. 1 for the square lattice.

Under the simplifying assumption that an A and a B end near a common site repel infinitely ($\epsilon_{AB} \to \infty$), and that like ends do not interact ($\epsilon_{AA}=\epsilon_{BB}=0$), the model has only two reduced activities as thermodynamic variables and, as it was shown,[1] can be easily mapped onto the standard Ising model on the same lattice. This allows the translation of the well-known closed form results for the $2d$ Ising model and all the existing information about critical behavior of the $3d$ Ising model into the corresponding results for the three-component model.

We shall investigate the situation which occurs when finite interactions ϵ_{AA}, ϵ_{BB}, and ϵ_{AB} are allowed. For simplicity we shall consider the model only on the square and simple cubic lattices. The generalization to other types of lattices is straightforward.

As was mentioned by Wheeler and Widom,[1] the model with finite interactions can be formulated as an Ising model on a decorated lattice. The decorated lattice Λ_2 corresponding to the model on the square lattice is illustrated in Fig. 2. The d-dimensional lattice Λ_d is a line graph; i.e., it can be covered by a set of complete graphs such that each vertex of Λ_d 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 single point is also a complete graph which can be used in a covering set to provide double covering of sites at the boundary.)

As is apparent from Fig. 2, the complete graphs C_2 and C_4 form a covering set for Λ_2. Similarly, C_2 and C_6 form a covering set for Λ_3. Hence, the complete graphs C_2 and C_{2d} form covering sets for Λ_d, where each site of Λ_d is covered by a vertex from one C_2 and from one C_{2d} graph.

We found it convenient to describe the model in terms of lattice gas rather than Ising variables. We let $t_i=+1$ ($t_i=0$) indicate that site $i \in \Lambda_d$ is occupied by an A-type (B-type) molecular end. We can, formally, then write the grand canonical partition function for the model on Λ_d as

$$\Xi_{\Lambda_d} = \sum_{\{t_i\}} e^{-H(\{t_i\})/kT} , \tag{1}$$

where the Hamiltonian is given as

$$H_{\Lambda_d}(\{t_i\}) = \sum_{(i,j)\subset C_{2d}} \{\epsilon_{AA} t_i t_j + \epsilon_{BB}(1-t_i)(1-t_j) + \epsilon_{AB}[(1-t_i)t_j + t_i(1-t_j)]\}$$
$$- \sum_{(i,j)\subset C_2} \{\mu_{AA} t_i t_j + \mu_{BB}(1-t_i)(1-t_j) + \mu_{AB}[(1-t_i)t_j + t_i(1-t_j)]\} . \tag{2}$$

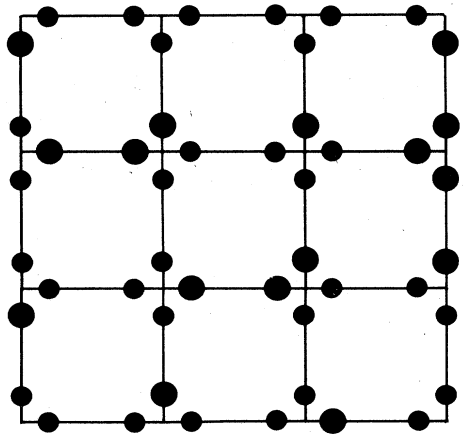

FIG. 1. Configuration of molecules on the square lattice.

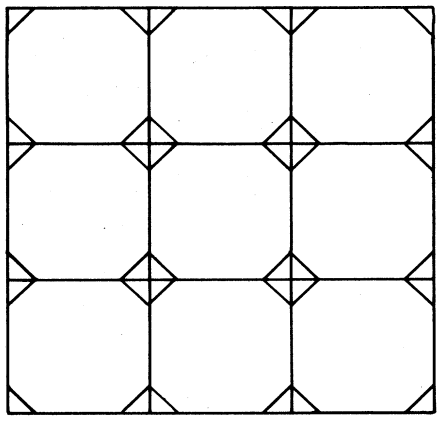

FIG. 2. Line graph associated with the square lattice.

Here, C_{2d} and C_2 refer to complete graphs of the covering set of Λ_d. Since vacant sites are not allowed, the chemical potentials μ_{AA}, μ_{BB}, and μ_{AB} are all infinite; however, differences such as $\mu_{AB}-\mu_{AA}$ or $\mu_{AB}-\mu_{BB}$ are finite thermodynamic variables which determine the relative concentrations of the three molecular species at equilibrium.

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

$$H'_{\Lambda_d}(\{t_i\}) = J \sum_{(i,j)\subset C_{2d}} t_i t_j + \mu \sum_{(i,j)\subset C_2} t_i t_j - h \sum_{i\in\Lambda_d} t_i \ , \quad (3)$$

where $J=\epsilon_{AA}+\epsilon_{BB}-2\epsilon_{AB}$, $\mu=2\mu_{AB}-\mu_{AA}-\mu_{BB}$, and

$$h=(2d-1)(\epsilon_{BB}-\epsilon_{AB})-\mu_{BB}+\mu_{AB} \ .$$

Hence, the Wheeler-Widom model is equivalent to a lattice gas on a line graph composed of complete graphs C_2 and C_{2d}, each of which has a different coupling constant.

Heilmann[2] has shown that the partition function for a repulsive lattice gas on a line graph with equal couplings within each complete graph of the covering set is zero only when $z=\exp(h/kT)$ is real and negative. Hence, the partition function is never zero for physical values of h so long as $J\geq 0$ and $\mu\geq 0$.

Using an idea of Runnels and Hubbard,[3] Ruelle[4] obtained an alternative proof of Heilmann's result which provided the following useful extension. If the couplings on line segments C_2 of the covering set are attractive, the partition function is never zero when $\mathrm{Re}z\geq 0$. The partition function is, therefore, never zero for physical values of h so long as $J\geq 0$ and $\mu\leq 0$.

The Heilmann and Ruelle results, therefore, prove that the thermodynamic functions for the Wheeler-Widom model are analytic so long as $\epsilon_{AB}\leq(\epsilon_{AA}+\epsilon_{BB})/2$.

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*Permanent address: Institute of Physics, Wrocław Technical University, Wrocław, Poland.

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