PHYSICAL REVIEW E VOLUME 49, NUMBER 3 MARCH 1994

Exact results for phase separation in an asymmetric model of an interacting binary mixture

Jian-Cheng Lin and P. L. Taylor
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079

(Received 9 November 1993)

We obtain exact coexistence curves for a two-dimensional lattice model of an asymmetric binary mixture of large and small molecules (squares and triangles, respectively), in which there is an energy cost ϵ for edge contact between a square and a triangle. For phase separation to occur, the coupling parameter $e^{-\beta\epsilon}$ must be smaller than a critical value. As ϵ varies, the model interpolates between the two hard-square systems formed when $\epsilon = 0$ or $\epsilon = \infty$. Phase separation occurs only for sufficiently large ϵ. A high packing density is also necessary to drive the demixing process.

PACS number(s): 61.20.Gy, 82.60.Lf, 05.50.+q, 61.25.Hq

Phase separation in binary mixtures has been studied in a wide variety of contexts [1–8]. The two components, A and B, say, become miscible when entropic effects are sufficient to overcome any existing enthalpic effects caused by attractive or repulsive forces between the constituents [3,4]. In an interesting recent paper, Frenkel and Louis [8] described an exact calculation that showed phase separation to occur in a two-dimensional lattice model even in the absence of any energy of interaction between the constituents other than the infinite energy of repulsion defining the hard-square nature of their model. In their model, square molecules A were placed in a square lattice, and smaller diamond-shaped molecules B could occupy sites overlapping two squares unoccupied by molecules of type A. While the central result of their work was that phase separation occurred when only hard-core interactions were present, their analysis also led to exact solutions when an energy ϵ_{AA} was associated with the presence of two A-type molecules on nearest-neighboring squares.

In the present paper we discuss a variant of the model of Frenkel and Louis in which an exact solution can be obtained when repulsive interactions ϵ_{AB} between squares and small molecules are included. This is of interest because it interpolates between the two hard-core models corresponding to $\epsilon_{AB} = 0$ and $\epsilon_{AB} = \infty$. It is also useful to note the relative effects of ϵ_{AA} and ϵ_{AB} on demixing in a system in which the packing number, defined as the fraction of the lattice area covered by molecules, is less than unity. An exact calculation in which the effects of ϵ_{AA} and ϵ_{AB} are separately observable illustrates the importance of free volume in determining whether phase separation occurs.

Our model is similar to that of Frenkel and Louis [8], and consists of a mixture of large molecules A (black squares) and small molecules B (shaded triangles) on a two-dimensional square lattice as shown in Fig. 1. Each black square is allowed to occupy any of the squares on the lattice, the chemical potential is μ for this species, and there is no energy cost for contact between the black squares (for simplicity we postpone consideration of the effects of the coupling ϵ_{AA}). Multiple occupancy by the black squares is forbidden. Each unoccupied square on the lattice is then further divided into four triangles. Each of these triangles can be occupied by at most one small particle B (the shaded triangles) with a fugacity z_B, and there is no energy cost for contact between shaded triangles. A repulsive coupling, ϵ, between the small and large molecules is introduced for each edge contact between the black squares and the shaded triangles. Energy costs for point contact between the squares and the triangles are neglected. The difference between our model and that of Ref. [8] lies in the size and shape of molecules B (triangles rather than diamonds consisting of pairs of bonded triangles) and the presence of the A-B interaction.

In the absence of the B particles, the grand-canonical partition function for the large particles is

$$\Xi_A = \sum_{\{n_i\}} \exp\left[\beta\mu \sum_i n_i\right] , \tag{1}$$

where β is the inverse temperature, n_i takes the value zero (unoccupied) or one (occupied) and thus describes the occupancy of the square at position i, and the sum is

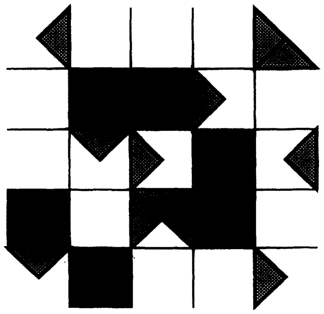

FIG. 1. A phase-separation lattice model for a mixture of large molecules A (black squares) and small molecules B (shaded triangles). The energy cost for the edge contact between the small and large molecules is ϵ.

©1994 The American Physical Society

over all the possible occupation configurations. Given a configuration of occupancy $\{n_i\}$ on a lattice of N squares, the grand-canonical partition function for particles B is

$$\Xi_B(\{n_i\}) = \sum_{l_1=0}^{M_I} \sum_{l_2=0}^{M_F} C_{l_1}^{M_I} C_{l_2}^{M_F} z_B^{l_1+l_2} e^{-\beta\epsilon l_1}$$

$$= (1 + z_B e^{-\beta\epsilon})^{M_I} (1 + z_B)^{M_F} \ , \qquad (2)$$

where

$$M_I = 4\sum_i n_i - 2\sum_{(i,j)} n_i n_j \qquad (3)$$

is the total number of triangles available for occupancy by the B that have edge contact with the large particles, and

$$M_F = 2\left(2N - 4\sum_i n_i + \sum_{(i,j)} n_i n_j\right) \qquad (4)$$

is the total number of triangles available for occupancy by B that have no edge contact with the large particles. Here $C_l^M = \frac{M!}{l!(M-l)!}$ is the combinatorial factor. Thus the grand-canonical partition function for the mixture is

$$\Xi_{\text{mixture}} = (1 + z_B)^{4N} \sum_{\{n_i\}} \exp\left\{ [2\ln(1 + z_B) - 2\ln(1 + z_B e^{-\beta\epsilon})] \sum_{(i,j)} n_i n_j \right\}$$

$$\times \exp\left\{ [\beta\mu - 8\ln(1 + z_B) + 4\ln(1 + z_B e^{-\beta\epsilon})] \sum_i n_i \right\} \ . \qquad (5)$$

By means of the transformation $n_i = \frac{s_i+1}{2}$, the above partition function is mapped into the partition function of the two-dimensional Ising model with coupling $K \equiv \beta J = \frac{1}{2}\ln\frac{1+z_B}{1+z_B e^{-\beta\epsilon}}$ and external field $h \equiv \beta H = \frac{1}{2}\ln\frac{z_A}{(1+z_B)^4}$, where $z_A \equiv \exp(\beta\mu)$ is the fugacity of the large particles. The coexistence curves can be obtained from the exact solution [9–11] of the two-dimensional Ising model with no external field, as was done in Ref. [8]. Along the coexistence curves, the two fugacities thus obey the relation $z_A = (1 + z_B)^4$. For squares of unit area, we find the number density n_A of large molecules, defined as $\sum_i n_i/N$, to be

$$n_A = \frac{m_{2\text{D}} + 1}{2} \ , \qquad (6)$$

and the number density of small molecules to be

$$n_B = \frac{z_B}{N}\frac{\partial \ln \Xi_{\text{mixture}}}{\partial z_B}$$

$$= \left(\frac{1}{1+\eta} + \frac{\theta}{\theta+\eta}\right)$$

$$-\frac{1}{2}\left(\frac{1}{1+\eta} - \frac{\theta}{\theta+\eta}\right) u_{2\text{D}} - \frac{2}{1+\eta} m_{2\text{D}} \ , \qquad (7)$$

where $\theta \equiv e^{-\beta\epsilon}$, where $\eta \equiv 1/z_B$ is the reciprocal of the fugacity of the small particles, and where $u_{2\text{D}}$ and $m_{2\text{D}}$ are the energy per site and spontaneous magnetization per site of the zero-field two-dimensional Ising model, respectively [9–11]. We have plotted the coexistence curves in the η-X_A plane for various values of θ in Fig. 2. Here $X_A \equiv \frac{n_A}{n_A+n_B}$ is the molar fraction of the large particles. The line of critical points can be determined from the exact result $K_c = \frac{1}{2}\ln(1 + \sqrt{2})$, which yields

$$1 = (1 + \sqrt{2})\theta + \sqrt{2}\eta \ . \qquad (8)$$

Since at a critical point $m_{2\text{D}} = 0$ and $u_{2\text{D}} = -\sqrt{2}$, the molar fraction of large molecules is

$$X_A|_{K=K_c} = \frac{1}{1 + (2+\sqrt{2})\frac{1}{1+\eta} + (2-\sqrt{2})\frac{\theta}{\theta+\eta}} \ . \qquad (9)$$

Figure 2 shows that when the coupling ϵ decreases (θ increases), the two-phase region in η-X_A shrinks, decreasing the tendency to phase separation. When θ reaches a value $\theta_c = \sqrt{2} - 1$ [see Eq. (8)], the two-phase region vanishes and no phase separation occurs. Let us look at the two limits ("hard" and "soft" limits) of the present model, corresponding to two models of hard-core mixtures. While the first (hard) model, in which $\epsilon \to \infty$,

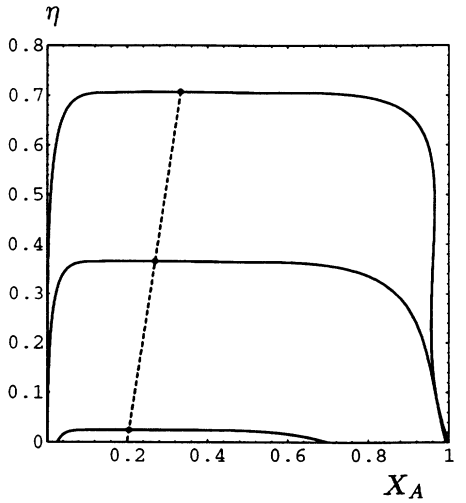

FIG. 2. This shows the coexistence curves (solid curves) with various values of θ (from top to bottom, θ = 0, 0.2, and 0.4, respectively) in the η-X_A phase plane. The dots and the dashed line represent the critical points and the projection, in the η-X_A phase plane, of the line of critical points, respectively.

can undergo a phase separation, the second (soft) one, in which $\epsilon \to 0$, cannot. This difference results from a corresponding difference in the possible packing arrangments. In the second model an edge contact between large and small particles is permitted, while such a contact in the first one does not occur because of the infinite repulsive force between particles of different type. When the contacts between unlike particles are forbidden, the loss of avaible area has a strong effect on the entropy of the system. It is this steric hindrance that plays the key role in yielding a phase separation in the mixture. For a mixture with fixed numbers of large and small particles, a configuration that shows phase separation needs a smaller area (or has a larger packing number) than a homogeneous phase, which needs a larger area (or has a smaller packing number). Hence by increasing the packing number of the mixture (or decreasing the area of the system) more configurations that show homogeneity will be eliminated, decreasing their competition with phase-separation-favored configurations. At a critical packing number where the configurations that favor phase separation become dominant, demixing will occur. The phase separation behavior of a mixture of hard spheres displays similar behavior, and it is no surprise that such a mixture has no phase separation for a low packing number [5] but shows a phase-separated character at higher packing numbers [6]. Increasing the coupling ϵ has the effect of increasing the amount of excluded area (from zero to 1/4 in this model), and thus to increase the tendency to phase separation.

As mentioned above, for the steric hindrance to play a role in phase separation the mixture has to have enough particle contacts. This can be seen more clearly in Fig. 3, in which we plot the coexistence curves in the θ-X_A plane for various values of η. For η larger than a critical value $\eta_c = 1/\sqrt{2}$ [see Eq. (8)], where the mixture is in the lower pressure region, the two-phase zone disappears, and there is no phase separation. Thus for phase separation to occur, the packing number of the mixture must be greater than $\frac{3}{4}$. (Again, the packing number is $\xi \equiv \sum n_\alpha S_\alpha$, where the sum is over the subscript α which represents large or small particles and S_α is the area of the particle α, and represents the fraction of the area of the lattice covered by molecules.) This result to some extent resolves the disagreement between the works of Refs. [5] and [6], as we see that these two studies were concerned with different packing densities. Lebowitz and Rowlinson [5] used the Percus-Yevick approximation, which is valid at low packing densities, and found mixing in all proportions of small and large hard spheres, while Biben and Hansen [6] used a theory appropriate to dense fluid mixtures.

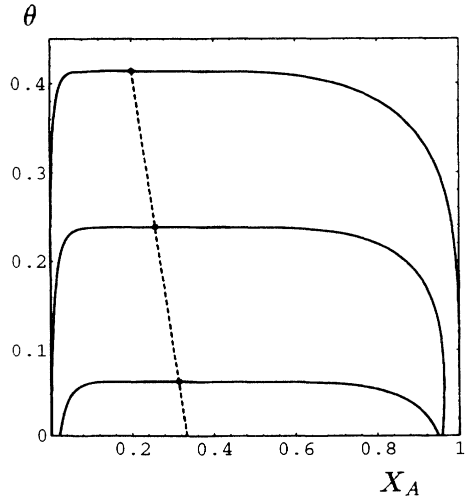

FIG. 3. This illustrates the coexistence curves (solid curves) for various values of η (from top to bottom, $\eta = 0$, 0.3, and 0.6, respectively) in the θ-X_A phase plane. The dots and the dashed line represent the critical points and the projection, in the θ-X_A phase plane, of the line of critical points, respectively.

The model we have treated can also be used to shed some light on the effects of polymerization on phase separation, as it can be thought of in terms of a mixture of monomers (triangles) and oligomers (squares consisting of four tightly bound triangles) with a degree of polymerization of 4. The asymmetrical shape of the phase diagrams can be observed in Figs. 2 and 3. We can generalize the model to include the degree of polymerization as a parameter. To this end, we first divide squares that are not occupied by a large molecule into k^2 smaller squares, and then further divide each of those smaller squares into four small triangles. Each of those triangles can then be occupied by at most one small molecule. The system thus constructed is a crude model for a mixture of monomers and branched polymers with degree of polymerization $4k^2$. In this case, one can verify that the k-dependent M_I and M_F are given by

$$k\left(4\sum_i n_i - 2\sum_{(i,j)} n_i n_j\right)$$

and

$$2\left(2k^2 N - 2k(k+1)\sum_i n_i + k\sum_{(i,j)} n_i n_j\right),$$

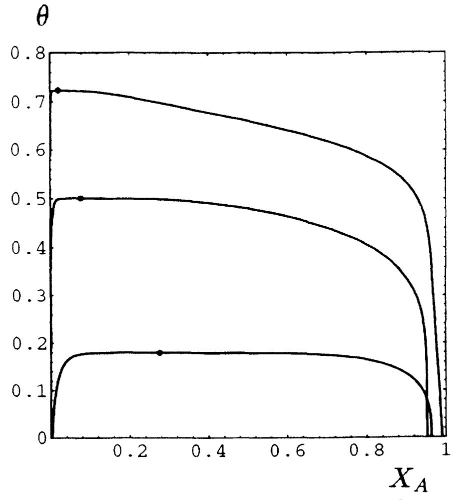

FIG. 4. This shows the coexistence curves for various values of k (from bottom to top, $k = 1$, 2, 4, respectively) and with $\eta = 0.4$ in the θ-X_A phase plane. The dots represent the critical points.

respectively. We have plotted coexistence curves in the θ-X_A plane for a fixed value of η and various values of k in Fig. 4. One can observe that increasing the degree of polymerization increases the tendency to phase separation, as is predicted in a mixture of monomers and linear polymers by the Flory-Huggins mean-field theory [7,12]. The equation that describes the projection of the critical surface at fixed k onto the η-θ plane is given by

$$1 = \left[(\sqrt{2}+1)^{\frac{1}{k}} - 1\right]\eta + (\sqrt{2}+1)^{\frac{1}{k}}\theta \, . \qquad (10)$$

The corresponding critical values (i.e., θ_c and η_c) are still larger than zero and smaller than unity, but increase and eventually reach unity as k tends to infinity. An asymptotic analysis indicates that when k tends to infinity, the mixture is always in the two-phase region as long as neither θ nor η is equal to unity.

As in the case of the system studied by Frenkel and Louis, it is possible in our model to introduce interactions ϵ_{AA} between the large molecules and still obtain exact solutions. The effective coupling parameter K that appears in the equivalent Ising model is now

$$K = \tfrac{1}{2}\ln\frac{1+z_B}{1+z_B e^{-\beta\epsilon}} - \tfrac{1}{4}\beta\epsilon_{AA} \, . \qquad (11)$$

This is quite different from the combination $\frac{1}{2}\beta(\epsilon - \frac{1}{2}\epsilon_{AA})$ that appears when there is no free volume. However, if we take the limit of an incompressible system by increasing the fugacity z_B of the small particles to infinity, then the simpler form for K is restored.

In conclusion, we have obtained exact coexistence curves for a model describing an asymmetric mixture of interacting particles. Consideration of the effects of increasing the repulsive interaction energy ϵ between A and B particles from zero to infinity shows that both ϵ and the packing density must be sufficiently large if demixing is to occur.

This work was supported by the NSF Science & Technology Center Program under Grant No. DMR 89-20147.

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1989), Vol. 8.

[2] F. S. Bates, Science **251**, 898 (1991), and references therein.

[3] A. de Kuijper, B. Smit, J. A. Schouten, and J. P. J. Michels, Europhys. Lett. **13**, 679 (1990).

[4] G. I. Kerley, J. Chem. Phys. **91**, 1204 (1989).

[5] J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).

[6] T. Biben and J. P. Hansen, Phys. Rev. Lett. **66**, 2215 (1991).

[7] J. C. Lin and P. L. Taylor, Mol. Cryst. Liq. Cryst. **237**, 25 (1993).

[8] D. Frenkel and A. A. Louis, Phys. Rev. Lett. **68**, 3363 (1992).

[9] L. Onsager, Phys. Rev. **65**, 117 (1944).

[10] C. N. Yang, Phys. Rev. **85**, 808 (1952).

[11] L. E. Reichl, *A Modern Course in Statistical Physics* (University of Texas Press, Austin, 1980), p. 291.

[12] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).

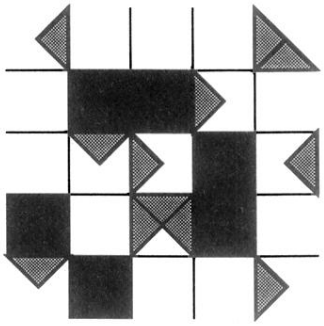

FIG. 1. A phase-separation lattice model for a mixture of large molecules A (black squares) and small molecules B (shaded triangles). The energy cost for the edge contact between the small and large molecules is ϵ.