

# Phase Separation in Binary Hard-Core Mixtures: An Exact Result

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We prove the existence of a first-order, entropy-driven demixing transition in a simple lattice model for a hard-core mixture. The existence of this transition follows from the fact that this lattice model can be mapped onto an Ising model with nearest-neighbor interactions for which the phase behavior is known. The same mapping leads to a very simple interpretation of the entropic contribution of the solvent to the interaction parameter  $\chi$  in the Flory-Huggins theory of polymer solutions.

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The phase stability of a liquid mixture is determined by the (Gibbs) free energy of mixing. This free energy is the sum of an entropic and an enthalpic contribution. For a long time, it was believed that enthalpic interactions are essential for fluid-fluid phase separation in simple ("atomic") mixtures. This belief was partly based on the early work of Lebowitz and Rowlinson [1], who studied the phase behavior of binary mixtures of dissimilar hard spheres within the Percus-Yevick (PY) approximation. Lebowitz and Rowlinson found that, at least within the PY approximation, hard spheres of arbitrary size ratio will mix in all proportions in the fluid phase. The implication of this result was that entropic effects are not enough to cause a miscibility gap in a simple fluid mixture.

In a recent Letter, Biben and Hansen [2] have used a more sophisticated analytical theory for dense fluid mixtures. Unlike the PY approximation, this theory is found to predict that an asymmetric binary hard-sphere mixture should phase separate if the sizes of the two spheres are sufficiently dissimilar (typically, if the size ratio is less than 0.2). This result is clearly of considerable fundamental interest. However, as in the case of Ref. [1], it is based on an approximate theory for the hard-sphere mixture. Hence, one may wonder to what extent the result found in Ref. [2] depends on the approximations that are used to compute the equation of state of the mixture. Clearly, it would be highly desirable to have a model system of a binary mixture for which the existence of a purely entropic demixing transition can be proven exactly.

In this Letter we show that this can, indeed, be done. We construct a simple lattice model of binary hard-core mixture. By transforming to a grand-canonical ensemble, we can map this binary hard-core mixture onto a one-component lattice gas with attractive nearest-neighbor interactions. This mapping is of interest because the one-component lattice gases can, in turn, be mapped onto Ising-like models for which, in some cases, the phase behavior is known exactly. To illustrate our approach, first consider a trivial model system, namely, a square lattice with at most one particle allowed per square. Apart from the fact that no two particles can occupy the same square face, there is no interaction between the particles. For a

lattice of  $N$  sites, the grand-canonical partition function is

$$\Xi = \sum_{\{n_i\}} \exp \left( \beta \mu \sum_i n_i \right). \quad (1)$$

The sum is over all allowed sets of occupation numbers  $\{n_i\}$  and  $\mu$  is the chemical potential. Next, we include "small" hard particles that are allowed to sit on the links of the lattice (see Fig. 1). These small particles are excluded from the edges of a square that is occupied by a large particle.

For a given configuration  $\{n_i\}$  of the large particles, one can then exactly calculate the grand-canonical partition function of the small particles. Let  $M = M(\{n_i\})$  be the number of free spaces accessible to the small particles. Then clearly

$$\Xi_{\text{small}}(\{n_i\}) = \sum_{l=0}^M \frac{M! z_s^l}{l!(M-l)!} = (1 + z_s)^{M(\{n_i\})}, \quad (2)$$

where  $z_s$  is the fugacity of the small particles.  $M$  can be written as

$$M(\{n_i\}) = 2N - 4 \sum_i n_i + \sum_{(ij)} n_i n_j, \quad (3)$$

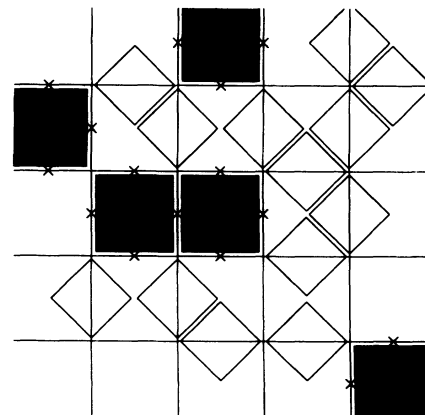


FIG. 1. Exactly solvable lattice-gas model for a mixture of large (black squares) and small (white squares) hard particles. The crosses indicate which small-particle sites are excluded by the presence of large particles.

where  $2N$  is the number of links on the lattice and the second sum is over nearest-neighbor pairs and comes from the fact that when two large particles touch, one link is doubly excluded [3]. The total partition function for the "mixture" is

$$\Xi_{\text{mixture}} = \sum_{\{n_i\}} \exp \left( [\beta\mu - 4\ln(1+z_s)] \sum_i n_i + \ln(1+z_s) \sum_{\langle ij \rangle} n_i n_j \right), \quad (4)$$

where we have omitted a constant factor  $(1+z_s)^{2N}$ . Equation (4) is simply the expression for the grand-canonical partition function of a one-component lattice-gas Ising model with a shifted chemical potential and an effective nearest-neighbor attraction with an interaction strength  $\ln(1+z_s)/\beta$ . As is well known, this lattice model can again be transformed to a 2D Ising spin model that can be solved in the zero-field case [4,5]. In the language of our mixture model, no external magnetic field means

$$(1+z_s)^2 = z_l, \quad (5)$$

where  $z_l = \exp(\beta\mu)$ , the large-particle fugacity. The order-disorder transition in the Ising model then corresponds to phase separation in the language of our model. This demixing is purely entropic, just like the transition predicted by [2] for the hard-sphere mixture. In fact, the mapping described above can also be carried through when energetic interactions between the large particles are included. However, for the sake of clarity, we will restrict ourselves to thermal hard-core mixtures.

Of course, there is a wide variety of lattice models for hard-core mixtures that can be mapped onto one-component systems with effective attraction. The model discussed above is only special in the sense that it can be mapped onto a model that is exactly solvable. In particular, from the known results for the 2D Ising model (see, e.g., [6]), it is straightforward to evaluate the composition of the coexisting phases along the entire coexistence line. This coexistence curve is shown in Fig. 2.

One important question that is raised by the work of Biben and Hansen [2] is whether the demixing transition is of the fluid-fluid or the fluid-solid type. The phase transition in the square-lattice model that we discussed above provides no answer to this question, as there is no distinction between "liquid" and "solid" in a lattice gas on a square, or simple-cubic, lattice. There are, however, slightly more complex lattice models that do have a distinct solid and fluid phase. An example is a mixture of large and small hard hexagons on a triangular lattice. This model can be solved exactly in the limit that only small or large hexagons are present. In the latter case, Baxter [7] has shown that the system undergoes a fluid-solid transition. To our knowledge, the phase behavior of the mixture cannot be computed analytically. However, we have performed preliminary computer simulations on this model that show a clear demixing transition. Thus far, however, we have not found evidence of a fluid-fluid

transition in this system.

Yet, from the above mapping, it is immediately obvious that a fluid-fluid transition does, in fact, occur in another hard-core mixture, namely, that of a mixture of hard-core monomers and polymers on a lattice. To this end, we consider once again our model of a mixture of large and small hard squares (cubes, in 3D) on a square (cubic) lattice, i.e., the model that could be mapped onto the one-component lattice gas with nearest-neighbor interactions. We now construct "polymers" by connecting  $N$  large squares (cubes), while the solvent is represented by the small particles. The simplest polymers are made by connecting  $N$  large particles by nearest-neighbor bonds only. A grand-canonical summation over all configurations of the small particles yields a very simple expression for the (canonical) partition function of the polymers, namely,

$$Z_{\text{polymers}} = \sum_{\{n_i\}} \exp \left( \frac{J}{k_B T} \sum_{\langle ij \rangle} n_i n_j \right), \quad (6)$$

with  $J \equiv k_B T \ln(1+z_s)$  and where the sum is over all acceptable (i.e., nonoverlapping) configurations of the hard-core polymers. Equation (6) is precisely the expression for the partition function of the Flory-Huggins lattice model [8]. This model has been studied extensively both using approximate analytical theories, in particular the well-known Flory-Huggins theory and modifications thereof (for a critical review see [9]) and, more recently,

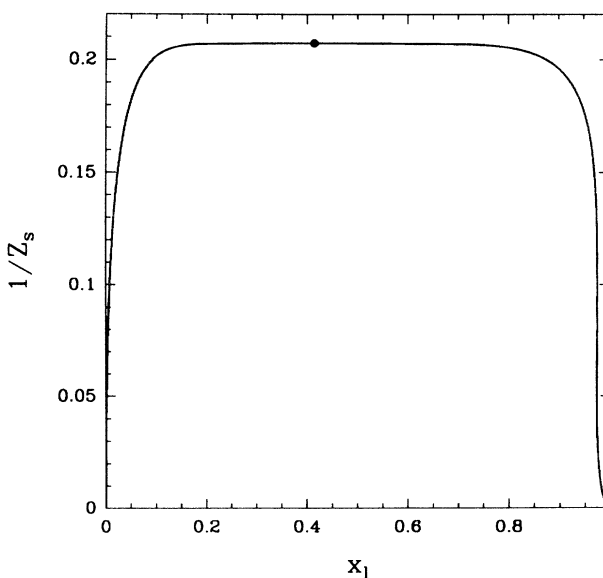


FIG. 2. Phase diagram of the model system shown in Fig. 1.  $X_l$  denotes the molar fraction of large squares;  $z_s$  is the fugacity of small squares. The drawn curve indicates the composition of coexisting phases. Note that this curve is asymmetric. In particular, the critical point (indicated by a black dot) is located at  $X_l = 2^{1/2} - 1$ . Along the coexistence curve the fugacities of the large and small particles are related through Eq. (5).

by direct numerical simulations (see, e.g., [10,11]). Traditionally, the coupling constant  $J$  has been interpreted as a purely *energetic* interaction. In contrast, in the context of the model that we consider,  $J$  is of completely entropic origin. We can now translate the results that have been obtained for the Flory-Huggins lattice-gas model directly to our hard-core mixture. This means that many effects that in the past were interpreted as originating from energetic attractions can also be obtained from purely entropic effects. In particular, the existence of a first-order fluid-fluid phase separation in this model provides direct proof that a purely entropic demixing transition exists in a hard-core polymer-solvent mixture. Our analysis also yields a very simple "entropic" interpretation of other, closely related phenomena, such as polymer collapse in a "poor" solvent. It is, perhaps, worth pointing out that in our model, the solvent molecules are smaller than the monomeric units of the polymer. In contrast, in the original Flory-Huggins lattice model, there is no such size asymmetry. We can, however, construct a hard-core lattice model where solvent and monomeric units occupy the same volume. It can be shown that the solvent-induced polymer collapse will also occur in such a "symmetric" model system.

Finally, we note that the Flory-Huggins theory for polymer solutions yields the following (approximate) expression for the free energy of a polymer solution,

$$\frac{F_{\text{mix}}}{k_B T} = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi), \quad (7)$$

where  $\phi$  is the fraction of the volume occupied by polymer, while the parameter  $\chi$  is related to the coupling constant  $J$  of the original lattice model by

$$\chi = \frac{1}{2} (J/k_B T) n_b = \frac{1}{2} n_b \ln(1 + z_s), \quad (8)$$

where  $n_b$  is the coordination number of the lattice. If, as was assumed in the original Flory-Huggins theory,  $J$  is due to energetic interactions, then  $\chi$  should vary as  $1/T$ . However, in the present (extreme) interpretation of the same lattice-gas model, the parameter  $\chi$  would be *completely independent of temperature*. There is, in fact, a large body of experimental data that shows that, for many polymer solutions,  $\chi$  has a large, if not dominant, entropic (i.e., temperature-independent) part. In fact, several theories exist that give explicit expressions for the entropic contribution to  $\chi$  both in incompressible polymer blends [9] and in compressible polymer solutions [12]. Schweizer and Curro [13] have used the RISM (reference interaction-site model) approximation [14] to estimate the (purely entropic)  $\chi$  parameter of a blend of hard-core, off-lattice polymers. The picture that we have sketched above is not in conflict with any of these theories. Rather, it provides a very simple and intuitively clear explanation why the  $\chi$  of a polymer solution should be expected to have a large entropic part.

Thus far, we have only discussed how, in lattice models, hard-core repulsion between particles of disparate sizes may lead to phase separation. Although the exact result that we have obtained applies to a lattice model, the physical mechanism that drives such a demixing transition is also present in off-lattice binary mixtures: The fraction of the volume that is accessible to the small particles increases when the large particles cluster.

In summary, we have demonstrated the existence of an entropically driven demixing transition in simple hard-core lattice models. By mapping hard-core mixtures onto lattice models with nearest-neighbor attraction, we clearly show how the entropy associated with hard-core *repulsion* may pose as an effective *attraction*. Although the effect that we discuss is by no means the only example of "attraction through repulsion," it may well be the simplest.

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