

## Three-Phase Equilibrium in a Binary Hard-Core Lattice Model

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A binary lattice model with hard-repulsive interactions is presented consisting of hexagons and points on a two-dimensional triangular lattice. This is the first model with hard interactions only to show gas, liquid, and solid phases. The phase diagram is calculated.

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For monatomic simple fluids the occurrence of a gas-liquid phase separation requires the presence of interparticle attractions [1]. Similarly it was generally believed that the fluid-fluid phase separation in binary mixtures also requires enthalpic interactions. However, recently Biben and Hansen provided an indication for a spinodal instability for binary hard-sphere mixtures with diameter ratios larger than 5 [2]. Subsequently, Frenkel and Louis presented an exactly solved model that shows the phase separation [3]. They studied a binary hard-core lattice model that can be mapped onto a one-component lattice gas with attractive nearest-neighbor interactions. The latter model is known to show gas-liquid phase separation. This example demonstrates that the effective attraction between the larger particles induced by the addition of small, hard-repulsive particles leads to a fluid-fluid phase separation of the gas-liquid type.

In monatomic systems with hard-repulsive interactions a fluid-solid transition can occur as well. An example is the hard-sphere system [4–6]. When long-range attractions are added, a gas-liquid phase separation can be induced, leading to three-phase equilibrium (see, for instance, Refs. [7] and [8]). The question now arises whether binary hard-core mixtures exist that show three-phase equilibrium. In this Letter we demonstrate that this is indeed the case.

As a starting point a system of hard hexagons on a triangular lattice is used. Baxter has solved this model and he has shown it to have a continuous freezing transition at  $\rho_c = N_1/N = 0.27639$  and  $z_c = 11.09017$ , where  $N_1$  is the number of hard hexagons,  $N$  the number of lattice points, and  $z_c$  the activity [9,10]. In addition to hard hexagons, our lattice model also contains points that are allowed to be placed on any lattice site not occupied by hexagons (see Fig. 1). The resulting lattice model appears to have received little attention so far. Frenkel and Louis performed some preliminary computer simulations. Although they observed a clear demixing, they did not find evidence for a fluid-fluid transition [3]. We show that addition of points to a hard hexagon system does indeed induce a gas-liquid transition, whereas the freezing transition remains present.

We consider the semigrand canonical partition function  $\Xi(N_1, z_2, N)$  for a system at activity of points  $z_2$ :

$$\Xi(N_1, z_2, N) = \sum_{N_2=0} z_2^{N_2} Z(N_1, N_2, N), \quad (1)$$

where  $N_2$  is the number of points and  $Z(N_1, N_2, N)$  is the canonical partition function. Introducing the number of free lattice points,  $N_f$ , we can write

$$Z(N_1, N_2, N) = \sum_{N_f} \frac{N_f!}{(N_f - N_2)! N_2!} \mathcal{C}(N_f, N_1, N), \quad (2)$$

where  $\mathcal{C}(N_f, N_1, N)$  denotes the number of realizations of  $N_f$  free lattice sites at fixed  $N_1$  and  $N$ . Clearly,

$$\sum_{N_f} \mathcal{C}(N_f, N_1, N) = Z^0(N_1, N), \quad (3)$$

where  $Z^0(N_1, N)$  is the canonical partition function of the pure hard hexagon model. Substituting Eqs. (2) and (3) into Eq. (1) and interchanging the summations over  $N_2$  and  $N_f$ , we obtain

$$\begin{aligned} \Xi(N_1, z_2, N) &= Z^0(N_1, N) \sum_{N_f} p(N_f | N_1, N) (1 + z_2)^{N_f} \\ &= Z^0(N_1, N) \Xi'(N_1, z_2, N), \end{aligned} \quad (4)$$

where  $p(N_f | N_1, N)$  is the probability density function for  $N_f$  at fixed  $N_1$  and  $N$ , given by

$$p(N_f | N_1, N) = \mathcal{C}(N_f, N_1, N) / Z^0(N_1, N).$$

In order to calculate thermodynamic properties of the

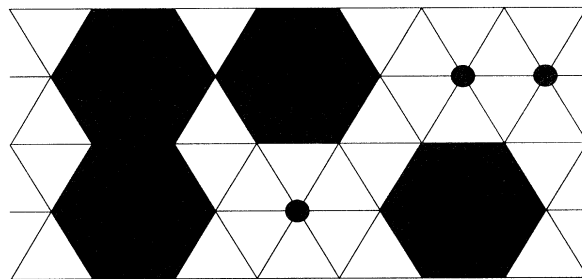


FIG. 1. Schematic of triangular lattice with hard hexagons and points.

mixture we write

$$\begin{aligned}\Omega(N_1, z_2, N) &= -k_B T \ln \Xi \\ &= F^0(N_1, N) - k_B T \ln \Xi'(N_1, z_2, N),\end{aligned}\quad (5)$$

where  $F^0(N_1, N)$  is the Helmholtz free energy of the pure hard hexagon model. It is now straightforward to evaluate  $\mu_1$ , the chemical potential of hard hexagons,

$$\mu_1 = \left( \frac{\partial \Omega}{\partial N_1} \right)_{z_2, N} = \mu_1^0 - k_B T \frac{\partial \sigma}{\partial \rho_1}, \quad (6)$$

and the pressure  $P$ ,

$$P = - \left( \frac{\partial \Omega}{\partial N} \right)_{N_1, z_2} = P^0 + k_B T \left( \sigma - \rho_1 \frac{\partial \sigma}{\partial \rho_1} \right), \quad (7)$$

with  $\sigma = \ln \Xi' / N$ ,  $\rho_1 = N_1 / N$ , and  $\mu_1^0$  and  $P^0$  the corresponding values for the hard hexagon model. As can be seen from Eqs. (5)–(7), calculation of thermodynamic properties of mixtures of hard hexagons and points only requires information about properties of the pure hard hexagon model.

For  $\mu_1^0$  and  $P^0$  Baxter's results are used [10]. A Monte Carlo approach can be used for calculating  $p(N_f | N_1, N)$ . A regular simulation will yield good statistics for  $p$  only for a limited range of  $N_f$ . To circumvent this problem the method of cumulants can be used to calculate  $\sigma$  [11]:

$$\begin{aligned}\sigma &= f(\rho_1) \ln(1 + z_2) + \frac{1}{2} g(\rho_1) [\ln(1 + z_2)]^2 \\ &\quad + \frac{1}{6} h(\rho_1) [\ln(1 + z_2)]^3 \dots\end{aligned}\quad (8)$$

with

$$\begin{aligned}f &= \langle N_f \rangle / N, \\ g &= \langle (N_f - \langle N_f \rangle)^2 \rangle / N, \\ h &= \langle (N_f - \langle N_f \rangle)^3 \rangle / N.\end{aligned}$$

A lattice of size  $L \times L = N$  was used with periodic boundary conditions. In Fig. 2 (lower curve) we plot  $\sigma / \ln(1 + z_2)$  for  $L = 24$  using only the first term of Eq. (8). Unfortunately  $h$  did not appear to be small compared to  $g$ , and therefore no further attempts were made to obtain accurate results using this method.

An alternative way to apply Eq. (4) is to measure the full distribution  $p(N_f | N_1, N)$  using a sampling scheme that allows for an accurate determination of the wings of this distribution. For this purpose we use the umbrella sampling technique [12,13]. Details about the implementation used here can be found in Ref. [14]. Results for  $L = 24$  are shown in Fig. 2. For comparison some calculations have been performed with  $L = 48$  showing that the finite-size effect is rather small.

In order to apply Eqs. (6) and (7) a 9-degree polynomial in  $\rho_1$  was fitted to  $\sigma / \ln(1 + z_2)$ , calculated with um-

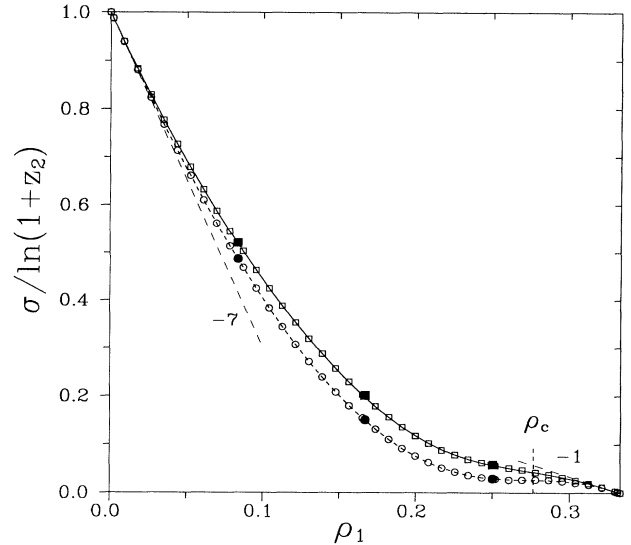


FIG. 2. Simulation results for  $\sigma / \ln(1 + z_2)$ , drawn for  $z_2 = 1.4$  (squares) and first-cumulant approximation Eq. (8) (circles). Open symbols:  $L = 24$ ; full symbols:  $L = 48$ . Full and short-dashed lines are polynomial fits of order 9. Limiting slopes  $-7$  and  $-1$  are indicated by medium-dashed lines and the critical density  $\rho_c$  by a vertical dashed line.

brella sampling and  $L = 24$ , under the constraint that the two limiting slopes at  $\rho_1 = 0$  and  $\rho_1 = 1/3$  would have their values in the thermodynamic limit,  $-7$  and  $-1$ , respectively. Coexistence was calculated by equating both  $\mu_1$  and  $P$  for the two phases. The resulting phase diagram is presented in Fig. 3 as a function of the activities  $z_1$  and  $z_2$ . A different representation of the re-

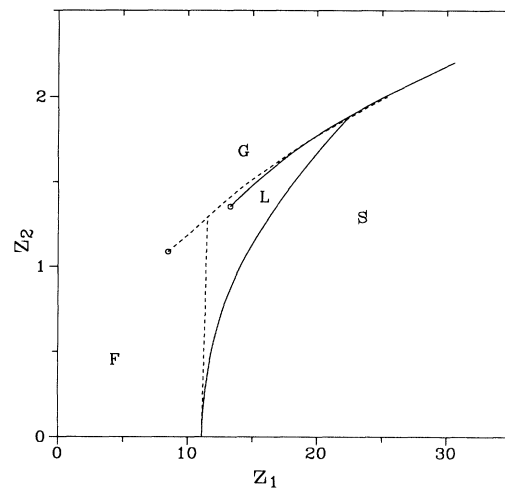


FIG. 3. Phase diagram of hard hexagon and point mixtures obtained from simulation results with  $L = 24$  using exact result Eq. (4) (full line) and first-cumulant approximation Eq. (8) (dashed line). Critical points are indicated by circles and the fluid, gas, liquid, and solid phases by their first letter.

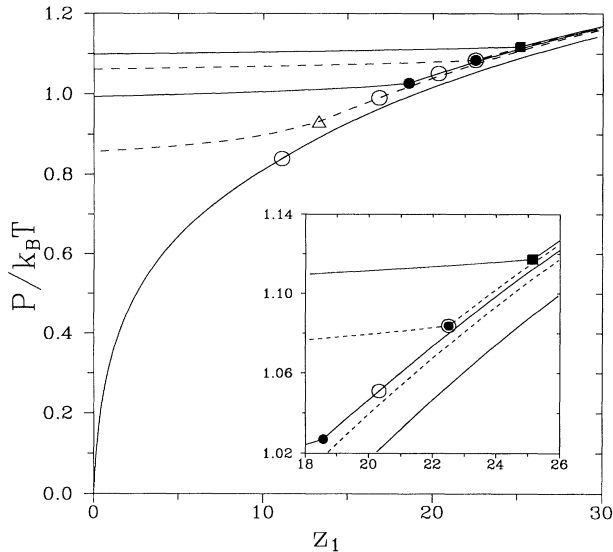


FIG. 4. Pressure as a function of  $z_1$  for  $z_2 = 0$  (bottom), 1.355, 1.7, 1.89, and 2 (top). Open circles: continuous freezing transition; triangle: critical point; full circles: gas-liquid transition; square: gas-solid transition. The region near the triple point is enlarged in the inset.

sults is given in Fig. 4, where the pressure is plotted as a function of  $z_1$ , for a few values of  $z_2$ . A gas-liquid transition indeed occurs, the critical point being at  $z_1 = 13.3$  and  $z_2 = 1.36$ . The freezing transition remains present, leading to a triple point at  $z_1 = 22.5$  and  $z_2 = 1.89$ . A systematic study of the finite-size effect on these values has not been carried out yet.

The nature of the freezing transition cannot be established due to the low resolution of the present calculations. If  $(\partial^2 \sigma / \partial \rho_1^2)_{\rho_1 = \rho_c} > 0$ , the freezing transition would become first order; otherwise it would remain continuous. From the present data it appears that

$(\partial^2 \sigma / \partial \rho_1^2)_{\rho_1 = \rho_c} = 0$ . For comparison the phase diagram resulting from the first-cumulant approximation is included in Fig. 3. It is seen to overestimate the tendency to phase separate. Because in this approximation  $(\partial \sigma / \partial \rho_1)_{\rho_1 = \rho_c} \approx 0$ , the freezing transition remains practically at fixed  $z_1$ .

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