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# Phase transitions in mixed adsorbed layers: Effect of repulsion between “hard squares” and “point particles”

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# Phase transitions in mixed adsorbed layers: Effect of repulsion between “hard squares” and “point particles”

## **Abstract**

It is shown that repulsive interactions between larger “hard squares” and smaller “point particles” in a mixed adlayer model modify the hard-square order–disorder transition and can produce phase separation.

## **Disciplines**

Biological and Chemical Physics | Mathematics

## **Comments**

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## NOTES

## Phase transitions in mixed adsorbed layers: Effect of repulsion between “hard squares” and “point particles”

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There exist extensive studies of ordering and phase transitions in commensurately adsorbed layers involving a *single* adspecies.<sup>1</sup> These studies were often motivated by applications to surface reactions, where it is in fact the behavior of *mixed* adlayers of reactants that is more relevant (but little studied). The classic example of such a surface reaction is catalytic CO oxidation, where adsorbed CO and O coexist on a surface, and react through a Langmuir–Hinshelwood mechanism.<sup>2,3</sup> In these reaction systems, superlattice ordering of adspecies is common [e.g., due to very strong nearest-neighbor (NN) O–O repulsions], as are significant interactions between distinct reacting adspecies (e.g., NN CO–O repulsions).<sup>4,5</sup>

During reaction, the state of the adlayer is driven out of equilibrium by adsorption and reaction processes occurring at a rate comparable to (or faster than) diffusion of some adspecies (e.g., O). However, it appears that ordering transitions in such nonequilibrium adlayers can be qualitatively similar to those in corresponding equilibrium systems.<sup>6</sup> Thus, to develop the limited understanding of such systems, and to provide a benchmark for studies of reaction systems, we consider a simple canonical equilibrium model: adlayers on a square lattice consisting of a mixture of “hard squares,” representing O, and “point particles,” representing CO. There are infinite NN repulsions between the hard squares (HS), no interactions between the point-particles (PP), and HS and PP interact via NN repulsions,  $E \geq 0$ .

The system is parametrized by partial coverages  $\theta_{\text{HS}}$  and  $\theta_{\text{PP}}$ , or activities  $z_{\text{HS}}$  and  $z_{\text{PP}}$ , and by  $\beta$  denoting the inverse temperature. If  $\beta E = 0$ , distribution of hard-squares is unaffected by the presence of the point particles, and is given by that of pure hard squares with activity  $z = z_{\text{HS}}/(1 + z_{\text{PP}})$ . In this case, there is a transition from short range to long range  $c(2 \times 2)$  order in the distribution of hard-squares as  $z$  increases above 3.796 26, or as  $\theta_{\text{HS}}$  increases above 0.3677 43 (cf. Ref. 7).

For  $\beta E \gg 1$ , the population of point-particles adjacent to

hard squares is negligible. The model can be visualized as mixture of hard discs with radii satisfying  $1 - \sqrt{2}/2 \leq r_{\text{PP}} \leq \frac{1}{2}$  and  $\frac{1}{2} \leq 1 - r_{\text{PP}} \leq r_{\text{HS}} \leq \sqrt{2}/2$  in units of the lattice constant (see Fig. 1). The grand partition function has the form

$$Z = \sum_{\{n_{\text{HS}}\}} \sum_{n_{\text{PP}}} (z_{\text{HS}})^{n_{\text{HS}}} (z_{\text{PP}})^{n_{\text{PP}}} \binom{N'}{n_{\text{PP}}} \\ = \sum_{\{n_{\text{HS}}\}} (z_{\text{HS}})^{n_{\text{HS}}} (1 + z_{\text{PP}})^{N'}. \quad (1)$$

The first sum is over all allowed configurations of various numbers,  $n_{\text{HS}}$ , of hard squares. The second is over the number,  $n_{\text{PP}}$ , of point particles, which are randomly distributed on  $N'$  allowed sites (not occupied by or adjacent to a HS particle). If  $n_{\text{HS}}^j$  is the HS occupancy of site  $j$ , and  $j_\alpha$  for  $\alpha = 1, \dots, 4$  denote the four neighbors of  $j$ , then site  $j$  is allowed (disallowed) if  $f_j = (1 - n_{\text{HS}}^j) \prod_\alpha (1 - n_{\text{HS}}^{j_\alpha}) = 1(0)$ , so  $N' = \sum_j f_j$ . Expanding  $f_j$  as a sum of products of occupation numbers in this expression for  $N'$  allows  $Z$  to be mapped onto the form of the partition function for a *single-species* hard-square model with *attractive* second NN, third NN, and quartet interactions, and *repulsive* triplet interactions. Denoting these by  $E_2$ ,  $E_3$ ,  $E_q$ , and  $E_t$ , respectively, one finds that  $\beta' E_2 = -2 \ln(1 + z_{\text{PP}})$ , and  $E_3 = E_q = -E_t = E_2/2$ , with  $\beta'$  the inverse temperature.

Thus, our basic observation is that the site-exclusion effect between the hard squares and the coadsorbed point particles should be similar to that of introducing longer-range attractive interactions between hard-squares (assuming that these dominate the triplet repulsions). In particular, this interspecies repulsion may induce phase separation or demixing of the distribution of hard-squares into coexisting “condensed”  $c(2 \times 2)$  and “dilute” phases. There are many other examples of this so-called entropy-driven phase separation (and of mapping dual species or decorated lattice-gas models to interacting single species models).<sup>8</sup>

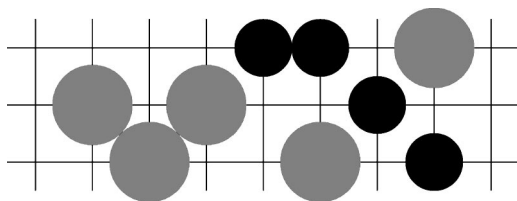


FIG. 1. Illustration of the mixed species model.

To confirm the above speculation, we apply the transfer matrix method, combined with finite-size scaling, which does reveal and allow precise determination of the tricritical point for phase separation (as well as other aspects of the phase diagram).<sup>9,10</sup> Results are presented in Fig. 2, where we show the phase diagram in the  $\theta_{\text{HS}}-u_{\text{PP}}$  plane, where  $u_{\text{PP}} = z_{\text{PP}}/(1+z_{\text{PP}})$  is the reduced activity for point particles. There is a tricritical point where the second-order  $c(2 \times 2)$  ordering transition becomes a first-order demixing transition. Using the method proposed by Bartelt *et al.*<sup>10</sup> we estimate the tricritical point at  $u_{\text{PP}}=0.780(2)$ ,  $u_{\text{HS}}=0.9427(3)$ ,  $\theta_{\text{PP}}=0.38(1)$ , and  $\theta_{\text{HS}}=0.20(1)$ , using strip widths up to 14. For  $u_{\text{PP}} < u_{\text{PP}}^t$ , a line of order-disorder transitions in the hard-square distribution extends from the tricritical point down to the classic hard-square critical coverage of  $\theta_{\text{HS}}=0.3677$  (see above), as  $u_{\text{PP}} \rightarrow 0$ .

It is natural to compare behavior in our mixed adlayer model (viewed as a single-species interacting hard-square

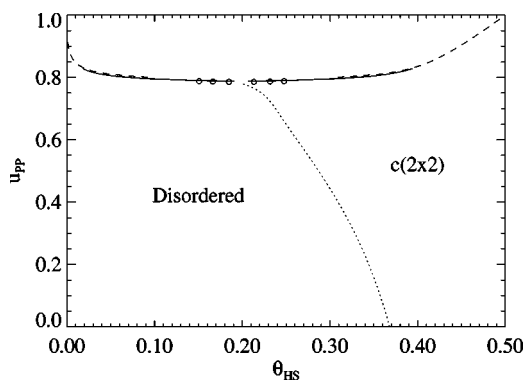


FIG. 2. Estimated  $u_A-\rho_B$  phase diagram for the mixed species problem. The dashed line is obtained from finite-size-scaling of strip sizes 6–8–10, and the solid line is from sizes 8–10–12, and the open circle from sizes 10–12–14. Details of the method can be found in Ref. 10. The dotted line shows the second-order  $c(2 \times 2)$  ordering transition, obtained by the method of Nightingale (Ref. 11) using strip sizes 10 and 12.

model) against that of Baxter's generalized hard-square model,<sup>12</sup> which has just second NN attractions,  $E_2$  (beyond NN exclusion). For the latter, various aspects of the phase diagram are known exactly, including the tricritical coverage of  $\theta_{\text{HS}}^t = (5 - \sqrt{5})/10 \approx 0.2763$ . The "height" of the tricritical point satisfies  $\beta E_2 = 1.656$  vs 3.03 for our model. Thus, the combined effect of the third NN, triplet, and quartet interactions in our model is to weaken phase separation (relative to pure attractive second NN interactions).

A similar binary hard core ("hard hexagons") model on a triangular lattice has been studied recently.<sup>13,14</sup> There, the main issue is the existence of a dense disordered (liquid) phase. As it can be seen from Fig. 2, the second-order transition (dotted) line connects to the tricritical point, supporting the claim of Ref. 14 that there is no gas-liquid phase transition. Numerical calculations show that the transition belongs to the Ising universality class, despite the many-particle interactions in the equivalent single-species model.

In summary, we have shown that repulsive interspecies interactions produce phase separation in a mixed adlayer model. This is consistent with experimental observations of island formation<sup>4</sup> and theoretical determinations of CO-O repulsions.<sup>5</sup> This behavior would also strongly influence chemical diffusion of the adspecies.<sup>15</sup>

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