Eutectic point in a simple lattice gas model

M. Sandhoff, H. Pfnnır and H.-U. Everts
Institut für Theoretische Physik, Universität Hannover
Appelstraße 2, 30167 Hannover, Germany
†Institut für Festkörperphysik, Universität Hannover
Appelstraße 2, 30167 Hannover, Germany

Abstract

We investigate the phase diagram and the critical properties of the adsorbate system sulfur/ruthenium(0001) in the coverage region $\frac{1}{4} < \Theta < \frac{1}{3}$ by means of Monte-Carlo simulations of a simple lattice gas model on a triangular lattice. The model contains only repulsive nearest and next-nearest neighbor interactions. Combining results obtained by using both Glauber and Kawasaki kinetics in the simulations we identify two tricritical points, three coexistence regions and a eutectic point in the phase diagram of the system. Our results agree with the findings of recent experimental work on S/Ru(0001). Furthermore we are able to add certain details to the experimentally observed phase diagram.

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The comparison of experimental phase diagrams and of experimental data for the critical properties of adsorbed layers with the results of computer simulations of appropriate lattice gas models can provide detailed information about the effective lateral interactions between the adsorbed particles. However, the reliability of this method depends on the validity of the lattice gas description for the system to be considered. Therefore, this point requires careful experimental tests. The inadequacy of the lattice gas description may be the reason for the quantitative disagreement between the simulated [1] and the experimental [2] phase diagrams of some systems.

For the system S/Ru(0001), careful investigations [3, 4, 5] have revealed that for coverages $0 < \Theta < \frac{1}{2}$ the S atoms are attached to well defined surface sites. For $0 < \Theta < \frac{1}{3}$ only the the hcp site is occupied while for higher coverages, $\frac{1}{3} < \Theta < \frac{1}{2}$, one finds adsorbate atoms on the fcc site as well. Thus, for coverages up to $\Theta = \frac{1}{2}$ the description of the system by lattice gas models appears to be justified. Hence, for this system the comparison between Monte-Carlo (MC) simulations of such models and the rather complex experimentally observed phase diagram shown in Fig. 1 is well founded. Apart from the existence of five different commensurate structures the most interesting features

*Email: sandhoff@kastor.itp.uni-hannover.de
of the phase diagram of S/Ru(0001) are the striped domain wall phase and the coexistence region of two ordered structures which covers a large area in the interval $\frac{1}{4} < \Theta < \frac{1}{3}$. To our knowledge, this is the first adsorbate system in which such a prominent coexistence region has been observed. In view of the complexity of this phase diagram it may seem questionable whether the experimental observations can be reproduced in detail by a reasonably simple lattice gas model.

In this letter we shall demonstrate by means of MC simulations that, in fact, a surprisingly simple lattice gas model suffices for a quantitative description of the experimental phase diagram for coverages $\frac{1}{4} \leq \Theta \leq \frac{1}{3}$ for which the coexistence region (region C) is observed. This area is bounded on the left by the homogeneous $p(2 \times 2)$ phase (B) and by the homogeneous $(\sqrt{3} \times \sqrt{3})$ phase on the right (D) (Fig. 1). The ideal coverages (also referred to as critical coverages) of the two phases are $\Theta = \frac{1}{4}$ and $\Theta = \frac{1}{3}$ resp.. The coexistence region consists of homogeneous islands with $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})$ order.

The lattice gas model with the smallest number of parameters which is able to produce these two structures is

$$\mathcal{H}_{LG} = \varphi_1 \sum_{nn} c_i c_j + \varphi_2 \sum_{nnn} c_i c_j.$$  \hspace{1cm} (1)

As usual, $c_i = 0, 1$ denotes the occupation of the lattice site $i$, and the sums run over the $N \times N$ sites of the triangular lattice for nearest (nn) and next nearest neighbors (nnn).

Positive coupling constants $\varphi_i$ for the first- and second-nearest neighbor interactions stabilize the $p(2 \times 2)$ structure at $\Theta = \frac{1}{4}$ (Refs. [6, 7]), while the existence of the $(\sqrt{3} \times \sqrt{3})$ structure requires that $\varphi_2/\varphi_1 < \frac{1}{5}$, see Ref. [8]. The formation of $p(2 \times 2)$ islands at low coverages, Fig. 1, indicates that in a realistic lattice gas model for S/Ru(0001) a weak attractive third neighbor interaction has to be included. As we have checked this interaction is of little importance for coverages $\Theta > \frac{1}{4}$. Therefore we ignore it in the present work. Similar models have been considered in previous numerical studies of adsorbate systems on square lattices [9] and of systems on triangular lattices [10, 12, 13]. For the parameter ratio $\varphi_2/\varphi_1 = \frac{1}{10}$, a Monte-Carlo simulation of the model (1) has been performed by Glosli and Plischke [6], but a number of questions remained unresolved in their work.

Commonly, simulations have been performed with the use of Glauber kinetics i.e. for constant chemical potential $\mu$ (Ref. [14]). This requires that a term $\mu \sum c_i$ is added to the hamiltonian (1) in order to control the coverage $\Theta = \frac{1}{N^2} \sum_i c_i$. Practically, with this technique it turns out to be rather difficult to tune to a coverage that deviates significantly from the ideal coverages. In a Monte-Carlo run the system tends to jump between the competing ideal structures, and very long runs are necessary to achieve accurate statistics. Furthermore, this simulation technique does not directly mimic the experimental situation. The experiments are done at constant coverage and not at constant chemical potential. Thus it appears appropriate to use Kawasaki kinetics [15] which conserves the coverage.

To obtain a detailed picture of the phase diagram in the intermediate region between the ideal coverages $\Theta = \frac{1}{4}, \frac{1}{3}$ we combine results from both types of simulation techniques.

As a measure for long range order of the $p(2 \times 2)$ type and of the $(\sqrt{3} \times \sqrt{3})$ type we use appropriate order parameters $\Psi_{p(2 \times 2)}$ and $\Psi_{(\sqrt{3} \times \sqrt{3})}$ for which explicit expressions can be found in Refs. [7] and [16]. In particular, these quantities allow the independent measurement of the fraction of these structures which constitute the coexistence region.

To characterize the nature of the phase transitions, we calculate the susceptibilities
\( \chi_{p(2 \times 2)}, \chi_{(\sqrt{3} \times \sqrt{3})} \) and the specific heat \( c \),

\[
\chi = \frac{N^2}{k_B T} \left( \langle \Psi_N^2 \rangle - \langle \Psi_N \rangle^2 \right)
\]

(2)

\[
c = \frac{N^2}{k_B T^2} \left( \langle \varepsilon_N^2 \rangle - \langle \varepsilon_N \rangle^2 \right).
\]

(3)

Here \( \varepsilon \) is the energy per site and \( \langle \ldots \rangle \) denotes the average over Monte-Carlo sweeps. The critical divergences of \( c \) and \( \chi \) in the infinite system appear as maxima for finite \( N \). From the size dependence of these maxima the critical exponents \( \alpha, \gamma, \nu \) and the transition temperature \( T_c \) can be determined \[17, 18\].

In simulations at constant chemical potential the coverage \( \Theta \) fluctuates as a function of the temperature

\[
\Delta \Theta := \frac{N^2}{k_B T} \left( \langle \Theta_N^2 \rangle - \langle \Theta_N \rangle^2 \right).
\]

(4)

The quantity \( \Delta \Theta \) does not necessarily couple to the order parameter. However, it is clearly of interest for first order phase transitions: While the chemical potential and the temperature have to be equal in both phases the coverage jumps discontinuously at the transition.

In our simulations we work with triangular lattices with periodic boundary conditions. The lattice sizes vary between 12 \( \times \) 12 and 60 \( \times \) 60 sites. Because of the different unit cells of the \( p(2 \times 2) \) and of the \( (\sqrt{3} \times \sqrt{3}) \) structures we have to change the linear dimension \( N \) in steps of 12 to avoid frustration by boundary effects. Each data point is obtained from 600 000 to 1 200 000 Monte-Carlo sweeps.

The ratio of the order-disorder transition temperatures at the ideal coverages \( \Theta = \frac{1}{4}, \frac{1}{3} \) measured in the experiment \[3\] is used to fix the coupling constant \( \varphi_2 \) in units of \( \varphi_1 \). As usual we set \( \varphi_1 = 1 \) and measure all energies in units of this nn coupling. This allows the direct comparison of results from both types of simulations. Agreement with the experiment is established with \( \varphi_2 = 0.123 \).

At the coverages \( \Theta = \frac{1}{4}, \frac{1}{3} \) both kinetics can be used for the determination of critical properties because the chemical potential is practically constant across the transition temperature. By comparison of the critical exponents with the results obtained from the experiment and with the values predicted by the Landau rules \[13, 20\] we are able to check our routines. Our finite size analysis reveals that Glauber kinetics and Kawasaki kinetics lead to identical results for both coverages: The maximum of the specific heat at \( \Theta = \frac{1}{4}(\frac{1}{3}) \) has a size dependence \( c_{n_{\text{max}}} \sim N^{\frac{\alpha}{\nu}} \) with \( \frac{\alpha}{\nu} = 1.10 \pm 0.1(0.50 \pm 0.06) \), see Fig. 2, while the susceptibility \( (\chi_{n_{\text{max}}} \sim N^{\frac{\gamma}{\nu}}) \) yields \( \frac{\gamma}{\nu} = 1.95 \pm 0.2(1.65 \pm 0.2) \). These exponents are comparable with the exact values of the \( q = 4 (q = 3) \) Potts model \( \frac{\alpha}{\nu} = 1(0.4), \frac{\gamma}{\nu} = 1.75(1.73) \) (Ref. \[21\]) and with the experimental values. Previous simulations of lattice gas models with \( p(2 \times 2) \) and \( (\sqrt{3} \times \sqrt{3}) \) symmetries have yielded similar differences between the lattice gas exponents and the Potts exponents \[10, 11, 8, 12, 13\].

As we have discussed above, Kawasaki kinetics is the appropriate tool to analyze the ordered structures in the intermediate coverage region, \( \frac{1}{4} < \Theta < \frac{1}{3} \), and the boundaries between these structures. For sufficiently low temperatures we find that particles added to the \( p(2 \times 2) \) structure do not appear as point defects but as islands of \( (\sqrt{3} \times \sqrt{3}) \) order. Due to the interfacial tension this minority phase forms hexagons in a sea of the ideal \( p(2 \times 2) \) phase (majority phase). At \( \Theta \simeq 0.292 \simeq \frac{1}{3}(\frac{1}{4} + \frac{1}{3}) \) both domains occupy half the available area. Above \( \Theta = 0.292 \) the roles are interchanged, i.e. the denser \( (\sqrt{3} \times \sqrt{3}) \)
structure becomes the majority phase which surrounds islands of \( p(2 \times 2) \) phase. The coexistence line of the region III, Fig. (3), in which the \( p(2 \times 2) \) and the \((\sqrt{3} \times \sqrt{3})\) structure coexist, is determined by the disappearance of the order parameter measuring the minority domains.

Clearly the boundaries of region III must end at the ideal coverages for \( T = 0 \). We are unable to confirm this for \( \Theta < 0.27 \) and \( \Theta > 0.31 \) because the area covered by the minority phase is too small.

To avoid Fisher renormalization \([22]\) we investigate the order-disorder transition of the majority phases, \( p(2 \times 2) \) and \((\sqrt{3} \times \sqrt{3})\) resp., with Glauber kinetics. Paths of constant \( \mu \) are shown in Fig. (2). As \( \Theta \) approaches \( \Theta = 0.292 \) the N-dependence of the finite-size peak in the specific heat \( c \sim N^{\frac{\nu}{\nu}} \) deviates significantly from the Potts values \( \frac{\nu}{\nu} = 1, \frac{5}{2}, \text{ resp.} \) For \( \mu = -0.50 \), label a, which corresponds to the ideal coverage \( \Theta = \frac{1}{3} \), the exponent is 1.10, see above. For \( \mu = -0.58 \) we find 1.33 (label b) and on the path \( \mu = -0.68 \) we obtained 1.67 (label c). As \( \Theta \) approaches \( \Theta = 0.292 \) from higher coverages \( \frac{\nu}{\nu} \) increases from 0.5 for \( \mu = -0.98 \), to 1.1 for \( \mu = -0.74 \) (paths d - f). This behavior of \( \frac{\nu}{\nu} \) is indicative of the existence of tricritical points on the order to disorder transition lines. In the interval between these tricritical points \( \Theta^{(1)}_{tr} < \Theta < \Theta^{(2)}_{tr} \), the transition is a fluctuation induced first order transition. While the coverage remains close to the ideal coverages \( \Theta = \frac{1}{3}, \frac{1}{5} \text{ resp.} \) on lines of constant chemical potential which cross the phase boundary outside the interval \( \Theta^{(1)}_{tr} < \Theta < \Theta^{(2)}_{tr} \), it changes rapidly on lines \( \mu = const. \) that cross the phase boundary within this interval. On these last lines the coverage develops large fluctuations. This is seen in Figs. (4) and (5) where we plot \( \Delta \Theta \) versus \( kT \). Evidently, for \( \Theta^{(1)}_{tr} < \Theta < \Theta^{(2)}_{tr} \) the peaks in \( \Delta \Theta \) scale with a power of the system size. By contrast, \( \Delta \Theta \) is structureless in the vicinity of the ideal coverages, where the transition is of second order. The insets in Fig. (4) and Fig. (5) display the jump in coverage on lines of constant \( \mu \) and give an estimate of the width of regions I, II in which the \( p(2 \times 2) \) phase and the \((\sqrt{3} \times \sqrt{3})\) phase coexist with the lattice gas phase. From this point of view the maxima of the specific heat and of the susceptibilities obtained from simulations are to be considered as averages over these coexistence regions. The determination of the tricritical points from finite size results is difficult since the exponents \( \frac{\nu}{p}, \frac{\nu}{\nu} \) increase smoothly when \( \Theta \) is varied between the ideal coverages and \( \Theta = 0.292 \). In general, the tricritical points are the lower (upper) end points of the coexistence regions I and II. We determine the boundaries of these coexistence regions by extrapolating the points of maximum curvature of the graphs \( \Theta(T) \) shown in Fig. (4) and Fig. (5). This provides the estimate for the locations of the tricritical points in Fig. (3).

The two upper boundaries of the coexistence regions I,II must meet the boundary of the coexistence region III in one point, i.e. at \( \Theta = 0.292 \). Otherwise the region III would have a coexistence line with the lattice gas phase at which three phases coexist. This would contradict Gibbs’ phase rule \([19]\) which, for a two component system with three phases, allows only for a triple point. This point is well known for binary alloys in 3d and is called eutectic point. We check the first order nature of the phase transition at the eutectic point with simulations for constant \( \Theta \). For symmetry reasons the chemical potential is constant on the line of constant coverage \( \Theta = 0.292 \). Thus, in contrast to the general case \( \Theta \neq 0.292 \), calculations of critical exponents on this line are not affected by Fisher renormalization \([22]\). At the eutectic point our simulations yield the following size dependence of the specific heat and the susceptibilities: \( c \sim N^{1.8}, \chi_{p(2\times2)} \sim N^{1.32}, \chi_{\sqrt{3} \times \sqrt{3}} \sim N^{1.52} \). For first order transitions these thermodynamic quantities are predicted to diverge as \( N^2 \) with the system size \([23]\). The reason for the discrepancy
between this theoretical prediction and our numerical values for the exponents of the susceptibilities is visible in Fig. 4. While the positions of the peaks of the specific heat, $c_N^{(\text{max})}$, increase linearly with $\ln(N)$, the peaks of the susceptibilities, $\chi_N^{(\text{max})}$, curve upwards as function of $\ln(N)$. This means that with our system sizes we have not yet reached the scaling regime. In fact, the data for $\chi_{p(2 \times 2)}$ and $\chi_{(\sqrt{3} \times \sqrt{3})}$ are based on effective system sizes $N_{\text{eff}} < \frac{N}{2}$ because for $\Theta = 0.292$ the $p(2 \times 2)$ and the ($\sqrt{3} \times \sqrt{3}$) structures cover less than half the lattice.

In summary, we have shown that the simple lattice gas model (1) yields a surprisingly rich phase diagram in two dimensions which closely resembles phase diagrams commonly observed in three dimensional substitutional binary alloys. It accounts for all details of the experimental phase diagram in the coverage region $\frac{1}{4} \leq \Theta \leq \frac{1}{3}$. This includes the in particular coexistence regions I and II. These regions and their structure could not be determined with certainty in the experiment although their existence had been inferred from the structure of the experimental phase diagram in the vicinity of $\Theta = 0.292$. Finally, we note that the topology of the phase diagram found in this study can be expected to occur more generally for systems with threefold symmetry provided the lateral interactions decrease with distance comparably fast as in our model.

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Figure Captions

Figure 1: Experimental phase diagram of the system S/Ru(0001) [24]. A: $p(2 \times 2)$ islands + lattice gas. E': $(\sqrt{3} \times \sqrt{3})$ + line defects. Regions A, E and E’ are not considered in the simulation.

Figure 2: Specific heat $c$ for fixed coverage $\Theta = \frac{1}{4}$; the curves correspond to the system sizes $24 \times 24$, $36 \times 36$, $48 \times 48$ and $60 \times 60$. The inset displays the linear fit through the maxima of $c_N$.

Figure 3: Calculated phase diagram. Solid lines: boundaries of different regions. Region I {II}: coexistence of the disordered phase with the $p(2 \times 2)$ {$(\sqrt{3} \times \sqrt{3})$} phase. Region III: coexistence of $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})$. Tricritical points: $\Theta_{tr}^{(1)} = 0.256$, $kT_{tr}^{(1)} = 0.173$; $\Theta_{tr}^{(2)} = 0.324$, $kT_{tr}^{(2)} = 0.170$ marked by •. Dotted lines: maxima of specific heat $c$ for constant $\Theta$. Dash dotted lines: paths of $\mu = const.$.

Figure 4: Coverage fluctuations $\Delta \Theta$ at first order phase transitions for three different values of $\mu$ corresponds to the labels (a - c) in Fig. (3). Curves are shown for the same system sizes as in Fig. (2).

Figure 5: Same as in Fig. 4 but for $\Theta > 0.292$.

Figure 6: Specific heat $c$ (a); susceptibilities $\chi_{p(2\times2)}$, $\chi_{(\sqrt{3}\times\sqrt{3})}$ (b) at the eutectic point. Insets: positions of the maxima of $c$, $\chi_{p(2\times2)}$ and $\chi_{(\sqrt{3}\times\sqrt{3})}$ as functions of the lattice size $N$. System sizes are in Fig. (3).
Phase diagram S / Ru(0001)

- **disordered**
- **p(2x2)-islands**
- **p(2x2)**
- **c(2x4)**
- **√3 x √3R30°**
- **p(2x2) + √3**
- **(√7 x √7)R19.1°**
- **“fluid”**

Temperature [K] vs. Coverage [ML]
\[ \ln(c_N) = \ln(c_N^{\text{max}}) \]

Slope = 1.10
lattice gas phase (disordered)

coexistence region
$p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})$
\[ \ln(c_N^{(\text{max})}) \]

Slope = 1.78
