Extent of exponent variation in a hard-square
lattice gas with second-neighbor repulsion

Wolfgang Kinzel

Institut für Festkörperforschung der Kernforschungsanlage Jülich Postfach 1913, 5170 Jülich, West Germany

M. Schick

Department of Physics, University of Washington, Seattle, Washington 98195
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The critical exponents of a class of transitions observable in adsorbed systems have been predicted to be nonuniversal. The extent of this variation for physical systems is of obvious experimental interest. We calculate this extent in a model which exhibits such a transition and which may be appropriate to physisorption on square substrates, a lattice gas with nearest-neighbor exclusion and second-neighbor repulsion. We apply phenomenological scaling methods to strips of finite width and find an ordered phase near density $\frac{1}{4}$ characterized by a thermal exponent y_T which varies with density from 0.9 to at least 1.5. For completeness, the case of a second-neighbor attraction is also considered. The expected universality of the resultant transition is obtained and its tricritical point located.

I. INTRODUCTION

Adsorbed systems provide physical realizations of many theoretical models and thereby permit experimental verification of current ideas of critical phenomena.[1] One of the most unusual models which can be realized in this way is the two-dimensional x-y model with cubic anisotropy which is of particular interest due to the nonuniversality of its critical exponents.[2] Thus the critical exponents of an adsorbed system which undergoes a transition in this class depend upon the interactions within the system and the external pressure.

Recent activities in chemisorption studies encourage the belief that experiments to detect this variation in critical exponents are feasible. These activities include the studies[3] of O chemisorbed on W(110) in which continuous transitions are observed which are predicted[1,4] to be in the above universality class and the low-energy-electron-diffraction studies[5] of O chemisorbed on Ni(111) which show that measurement of critical exponents in chemisorbed systems is possible.

A crucial factor in the observability of the variation in the critical exponents is the extent of this variation. This will of course depend upon the interactions and thus the particular system of interest. Preparatory to the calculation of this magnitude in the O/W(110) system characterized by a centered-rectangular ($C2\ mm$) substrate and interactions which extend to third or fourth neighbors,[3] we have considered the simpler system of particles adsorbed on a square ($P4\ mm$) substrate with nearest-neighbor exclusion and second-neighbor repulsion. The Hamiltonian of the lattice gas, subject to a chemical potential μ, is

$$H = \sum w_{ij} n_i n_j - \mu \sum_i n_i \ ,$$ (1.1)

where the first sum is over all pairs of sites, $i \neq j$, n_i is the occupation number of the ith site and takes the values 0, 1 and the interaction w_{ij} is given by

$$w_{ij} \to \infty, \quad i,j \text{ nearest neighbors} \ ,$$

$$w_{ij} = \begin{cases} w, & i,j \text{ next nearest neighbors} \\ 0, & \text{otherwise}. \end{cases}$$ (1.2)

This model has the virtue that it may be applicable to physisorption on square substrates[6] such as MgO, and that some aspects of it have been studied previously.[7-10] In particular, Binder and Landau[7] have studied a more general version of the above model in which the nearest-neighbor repulsion is taken to be finite. If the ratio of the second- to first-neighbor interaction be denoted R, the problems we have studied correspond to $\lim R \to 0+$ or $\lim R \to 0-$ depending on whether w is repulsive or attractive. In the former case one expects qualitatively the same features as obtained in Ref. 7 for $R = \frac{1}{4}$. At low coverages corresponding to negative values of μ the system is disordered at all temperatures. For larger chemical potentials in the range $4w > \mu > 0$ and sufficiently low temperatures the system is ordered. At zero temperature this order is characterized by rows

or columns in which every other site is occupied alternating with empty rows or columns. There is no long-range order between the half-filled rows so that the system has an entropy of order $A^{1/2}$ where A is the number of lattice sites. Although this entropy is infinite in the thermodynamic limit, it is not extensive. We shall denote this state (2×1). It is the transition to this state from the disordered state which is predicted to be nonuniversal[1] and which is of greatest interest to us. For all $\mu > 4w$ and sufficiently low temperatures a simpler ordered phase exists in which second-neighbor sites are preferentially occupied. This state is denoted $(\sqrt{2} \times \sqrt{2})$. The transition to it from the disordered state is in the universality class of the ferromagnetic Ising model.[1]

For the case of attractive second-neighbor interactions, the only ordered phase which exists is the $(\sqrt{2} \times \sqrt{2})$ phase which occurs for $0 > \mu > 2w$ at sufficiently low temperatures. The transition is continuous and in the ferromagnetic Ising class for small $|\mu|$ and first order for large $|\mu|$. A tricritical point separates the two regimes. The transition to this phase has been studied by Runnels, Salvant, and Streiffer.[8] They proceeded by calculating from the largest eigenvalue of the transfer matrix the thermodynamic properties of a sequence of semi-infinite strips of width M and then inferring the behavior of the infinite width system. At the time, there was no theory to guide these inferences. Subsequently, such a theory of finite-size scaling was developed.[11] Nightingale[12] has recently employed it to extract excellent estimates of the thermodynamic functions of the infinite system from transfer-matrix calculations such as those of Runnels et al.[8] It is this approach, called phenomenological scaling, which we have employed with strips of width $M \leq 14$. Accounts of general transfer-matrix methods[13] and phenomenological scaling[12] are available in the literature as well as a description of the particular methods we have employed.[14] Therefore we simply restate the few relevant formulas here.

From the largest and second-largest eigenvalues in magnitude of the transfer matrix of a semi-infinite strip of width M, $\Lambda_0^{(M)}$ and $\Lambda_1^{(M)}$, the lattice-gas density $n(\tilde{T}, \tilde{\mu})$ and correlation length $\xi_M(\tilde{T}, \tilde{\mu})$ are obtained from

$$n = \frac{\tilde{T}}{M} \frac{\partial}{\partial \tilde{\mu}} \ln \Lambda_0^{(M)}(\tilde{T}, \tilde{\mu}) \ , \tag{1.3}$$

$$\xi_M^{-1} = \ln|\Lambda_0^{(M)}/\Lambda_1^{(M)}| \ . \tag{1.4}$$

Here $\tilde{T}$ and $\tilde{\mu}$ are the reduced temperature and chemical potential $\tilde{T} \equiv T/w$, $\tilde{\mu} \equiv \mu/w$, and Boltzmann's constant has been set to unity. An approximation to the phase boundary $\tilde{T}_c(\tilde{\mu})$ of the infinite system is obtained from the solution of

$$\xi_M(\tilde{T}_c, \tilde{\mu})/M = \xi_{M'}(\tilde{T}_c, \tilde{\mu})/M' \ , \tag{1.5}$$

where M and M' are different strip widths. The approximation improves with increasing M and M'. The thermal exponent y_T follows from

$$\left(\frac{M}{M'}\right)^{y_T+1} = \frac{\partial \xi_M(\tilde{T}, \tilde{\mu})}{\partial \tilde{T}} \bigg/ \frac{\partial \xi_{M'}(\tilde{T}', \tilde{\mu})}{\partial \tilde{T}'} \ , \tag{1.6}$$

where the partial derivatives are evaluated at $\tilde{T}_c(\tilde{\mu})$.

II. RESULTS

A. Transition to the $(\sqrt{2} \times \sqrt{2})$ phase

The transition to the $(\sqrt{2} \times \sqrt{2})$ structure is first order for sufficiently large negative chemical potential and continuous otherwise. The first-order nature of the transition is quite apparent from isotherms $n(\tilde{\mu})$ calculated from Eq. (1.3), at least for temperatures sufficiently below the tricritical point which divides the regions of first-order and continuous transitions. It is seen from the abrupt increase in the compressibility upon entering the two-phase coexistence regime. The value of the chemical potential on the phase boundary for a given temperature can be determined from the value at which the calculated compressibility, which is always finite for a finite system, reaches it maximum. A series of isotherms are shown in Fig. 1 of Ref. 8. The phase boundary in the region of continuous transition is obtained from Eq. (1.5). The combined results of Ref. 8 and of our calculation for the phase boundary are shown in Fig. 1. Note that the point $w/T = 0$, $\mu/T = 1.333$ corresponds to the hard-square model with nearest-neighbor exclusion only.[15] Values for the critical exponent are obtained from Eq. (1.6). The results for temperatures near the tricritical point obtained from comparing strip widths M'/M of $\frac{4}{6}$ and $\frac{8}{10}$ are shown in Fig. 2. The values of y_T obtained in that region in which the transition is actually first order are meaningless, however, as the assumption of long-range correlations which underlies the derivation of Eqs. (1.4) and (1.5) is invalid. In the limit of infinite strip width we expect y_T to be equal to unity, the ferromagnetic Ising value, for all temperatures down to the tricritical point and then to jump discontinuously to the larger tricritical value which is strongly indicated[16] to be 1.8. Figure 2 shows how this behavior is approximated. It is interesting to observe the improvement in the approximation with increasing strip width, an improvement which causes the curves obtained from different values M'/M to cross. We identify the value at which these curves cross as an approximate value of the tricritical thermal exponent y_T^t. The coordinates of the intersection of the $\frac{8}{10}$ and $\frac{10}{12}$ results (not shown) are $y_T^t = 1.7$ and $w/T = -1.62$ which is the tricritical temperature shown in Fig. 1 in-
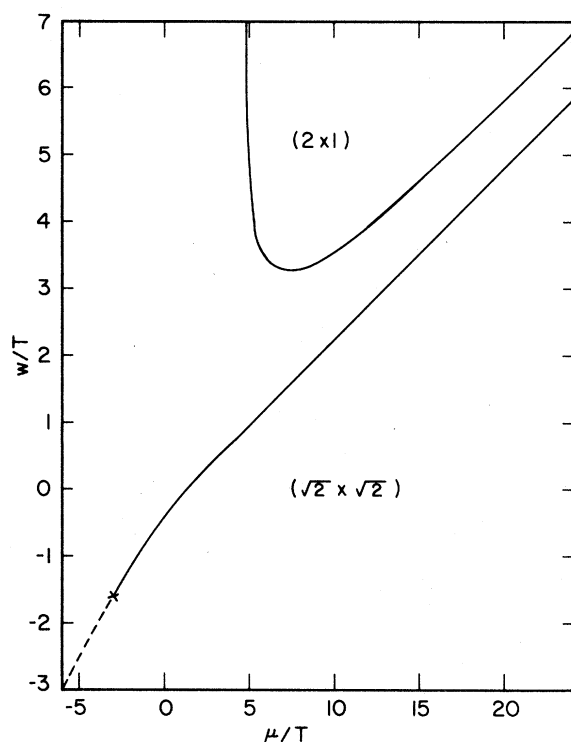
FIG. 1. Phase diagram of the square lattice gas with nearest-neighbor exclusion and second-neighbor interaction w. Solid lines denote continuous transitions, the dashed line a first-order transition, and the cross the tricritical point.

FIG. 2. Results for the thermal exponent from two approximations are shown for negative w and for temperatures near the tricritical point.

dicated by a cross. We believe this to be an improvement over the tricritical temperature $w/T = -0.4$ inferred in Ref. 8.

B. Transition to the (2×1) phase

The transition to the (2×1) phase is everywhere continuous and the phase boundary obtained from Eq. (1.5) is shown in Fig. 1. We find the asymptote on the left, which corresponds to the logarithm of the critical fugacity of a gas with first- and second-neighbor exclusion to be given by $\mu/T = 4.70$. The corresponding density is $n = 0.240$. Again we believe these results obtained with transfer-matrix methods and the benefit of finite-size scaling to be more accurate than the earlier results[9] of 5.3 and 0.238 obtained by transfer-matrix methods alone. Parenthetically we remark that the power of the phenomenological scaling approach is demonstrated by the ease with which the existence of a transition in this particular system is ascertained, an existence which had previously been in some doubt.[10] Further, the fact that the second largest eigenvalue of the transfer matrix occurs in the subblock spanned by functions which
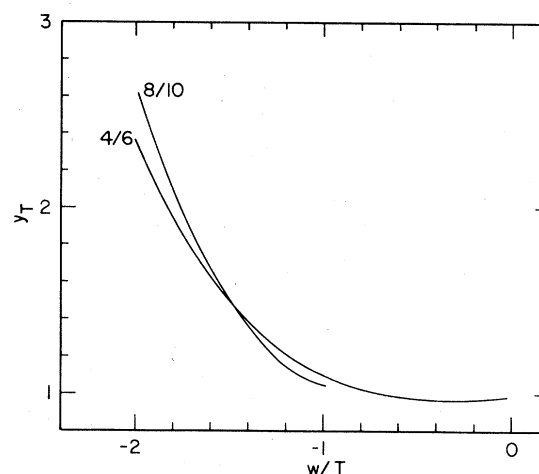
transform as the unit representation identifies the ordered state as (2×1) rather than (2×2).

The region of large chemical potentials where the two different ordered phases are in proximity is also of interest. We find the (2×1) phase boundary asymptote to be $w = \mu/4 + 0.84$ while that of the $(\sqrt{2} \times \sqrt{2})$ phase to be $w = \mu/4 - 0.21$. Thus the disordered phase between them extends down to zero temperature as anticipated in Ref. 7. This region in the temperature-density plane is shown in Fig. 3(a). Note that the disordered phase exists over a finite-density range contrary to the expectation expressed[17] in Ref. 7. Also of interest in Fig. 3(a) is the decrease of the density at the $(\sqrt{2} \times \sqrt{2})$ phase boundary with increasing temperature. This is a consequence of our result that the transition to this phase at $T = 0$ occurs at a density $n = 0.3987$. For $T \gg w$ the critical density must approach that of the gas with nearest-neighbor exclusion only which is[15] $n = 0.3678$, hence the negative slope.

The thermal exponent y_T obtained from Eq. (1.6) is shown in Fig. 4 versus μ/w. For the $(\sqrt{2} \times \sqrt{2})$ transition, $\mu/w > 4$, results for increasing strip width approach unity. In particular, as $\mu/w \rightarrow 4+$, y_T obtained from strip widths $\frac{10}{12}$ equals unity to within 0.1%. Further, the variation of the approximate y_T with μ/w is small. In the case of nearest-neighbor exclusion only, the same approach also yields unity to excellent accuracy.[15] Thus the expected universality is obtained.

Results for the exponent of the transition to the (2×1) phase are completely different. Convergence of the successive approximations is rapid for small values of μ/w but becomes slower as this ratio approaches $4 -$. The asymptotic values of y_T are
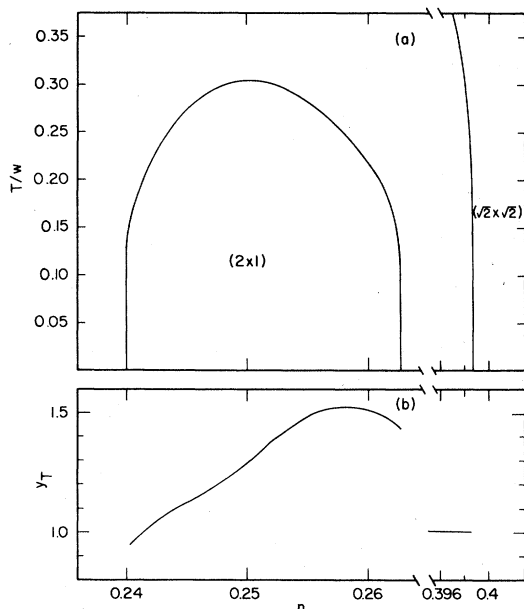
FIG. 3. (a) Phase diagram in the temperature-density plane. Note the break in the density scale. (b) Values of the thermal exponent obtained from comparison of strips of width $\frac{10}{12}$ vs density. In contrast to the nonuniversal values obtained for the (2×1) phase, note the universal value obtained at the right for the $(\sqrt{2} \times \sqrt{2})$ phase.
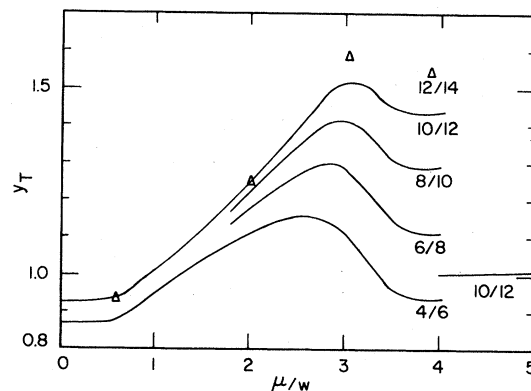

FIG. 4. Sequence of approximations for the thermal exponent of the nonuniversal transition vs reduced chemical potential. Four values obtained by comparing widths $\frac{12}{14}$ are shown by triangles. Only a single approximation for the universal transition is shown for clarity.

nonuniversal as predicted.[1] For the case of first- and second-neighbor exclusion, $\mu/w \rightarrow 0 +$, $y_T \rightarrow 0.925$ which produces a cusp in the compressibility in agreement with the results of Ref. 9. The thermal exponent of the infinite system increases initially with μ/w but, as is clear from Fig. 4, its value becomes increasingly difficult to extract from our approximate calculations. It is possible that y_T increases monotonically with μ/w and approaches the value 2 indicative of a first-order transition as μ/w approaches 4 corresponding to the zero-temperature transition of $n = 0.262$ of Fig. 3(a). That no first-order transition occurs at finite temperature, however, has been as-

certained by examining the isotherms. The results for y_T obtained from strip widths $\frac{10}{12}$ are shown versus density in Fig. 3(b). Even if y_T does not extend to 2 as surmised above but has only the variation shown in Fig. 3(b), it is clear that the corresponding variation in $v = y_T^{-1}$, from 1.09 to 0.66, and in $\alpha = 2(1 - v)$, from -0.17 to 0.68, should be measurable in scattering or specific-heat experiments, respectively. We are thus encouraged to carry out a similar study on a system under current experimental study, such as O/W(110).

[1]See, for example, the review by M. Schick, in *Phase Transitions in Surface Films,* edited by J. G. Dash and J. Ruvalds (Plenum, New York, 1980), and references therein. In particular, E. Domany, M. Schick, J. S. Walker, and R. B. Griffiths, Phys. Rev. B <u>18</u>, 2209 (1978).

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[17] In particular, whereas we believe the zero-temperature results shown in Fig. 14(a) of Ref. 7 are correct, analogous results of Fig. 15(a) are incorrect.