Triangular lattice gas with first- and second-neighbor exclusions: Continuous transition in the four-state Potts universality class

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Using phenomenological renormalization (transfer-matrix scaling), we have reexamined the phase transition of a triangular lattice gas with particles having both nearest- and second-nearest-neighbor exclusions. Widely accepted classical studies indicated that disordering of the ordered ["$p(2\times2)$"] state is first order. In contradiction, we show that the transition is *second order;* its exponents are consistent with the four-state Potts model universality class, in accord with its Landau-Ginzburg-Wilson Hamiltonian classification.

In the study of lattice-gas melting transitions, hard-core limits have provided useful benchmarks. For a triangular lattice with just nearest-neighbor exclusions, the hard-hexagon model, Baxter's celebrated solution[1] finds a continuous transition in the three-state Potts universality class. This critical behavior is predicted by the Landau-Ginzburg-Wilson (LGW) Hamiltonian classification scheme.[2] A natural extension of this triangular lattice problem is to consider next-nearest-neighbor as well as nearest-neighbor exclusions. LGW arguments indicate that, if second order, the melting of the ordered phase should lie in the four-state Potts universality class.[2] Two much-cited[2,3,4] numerical studies of this model—by Orban and Bellemans[5] (OB) and by Runnels, Craig, and Streiffer[6] (RCS) a decade and a half ago—concluded that this transition (as well as those of hard-core particles with larger-range exclusions) is first order. Using the phenomenological renormalization, or transfer-matrix scaling, method (PR/TMS) developed by Nightingale,[7] we demonstrate that the transition of the hard-hexagon model with second-neighbor exclusions is indeed second order and in the four-state Potts universality class. We also discuss how modern ideas of finite-size scaling reconcile the results of OB and RCS with our findings.

Our attention was drawn to this problem by studies of gas atoms chemisorbed on the close-packed faces of fcc and hcp metallic single crystals.[8] The top layer of metallic atoms are a triangular lattice and as temperature is lowered the adsorbed atoms are often found to form a $p(2\times2)$ overlayer,[9] i.e., a Bravais net with primitive vectors parallel to and twice the length of those of the substrate. This overlayer pattern is a realization of the ordered state of the present problem.[10] To investigate the physical systems, we used a lattice-gas model with a wide variety of pairwise interactions (including just nearest- and second-neighbor repulsions) between the adsorbed atoms; our calculations used PR/TMS,[11] Monte Carlo finite-size scaling,[11,12] and explicit Monte Carlo simulation of the structure factor.[13] We found second-order transitions, with critical behavior consistent with the LGW-predicted four-state Potts model. The Monte Carlo and renormalization-group study by Glosli and Plischke[14] also suggested the transition is second order. Thus, the results of OB and RCS seemed curious.

In the present problem of infinite nearest- and second-nearest-neighbor repulsions, it has been rigorously established[15] that a $p(2\times2)$ ordered state forms at sufficiently high activity $z\equiv\exp(x)$, where $x\equiv\mu/kT$ is the reduced chemical potential. Using the well-established transfer-matrix technique,[16,17] we have calculated the correlation length ξ associated with this order for infinite strips of sites with even widths $n=4,6,\ldots,16$:[18]

$$\xi^{-1}(n,x)=(1/\sqrt{3})\ln|\lambda_0^{\{n\}}/\lambda_1^{\{n\}}| \ , \tag{1}$$

where $\lambda_0^{\{n\}}$ is the largest eigenvalue and $\lambda_1^{\{n\}}$ becomes degenerate with it when there is long-range $p(2\times2)$ order.[19] The unusual prefactor, needed for Eq. (4), arises because the spacing between rows in the infinite direction is $(\sqrt{3}/2)$ times the lattice constant and we considered the transfer matrix between pairs of rows. The density $\rho(n,x)=n^{-1}d\lambda_0^{\{n\}}/dx$. From the usual finite-size scaling formula, we obtain the estimate $\tilde{x}_c$ (of x_c):

$$\xi(n,\tilde{x}_c)/n=\xi(n+2,\tilde{x}_c)/(n+2) \ . \tag{2}$$

Approximations to ν were obtained using

$$\left(\frac{n+2}{n}\right)^{1+1/\nu}=\frac{\partial\xi(n+2,\tilde{x}_c)}{\partial x}\Big/\frac{\partial\xi(n,\tilde{x}_c)}{\partial x} \ . \tag{3}$$

The exponent η was obtained from the amplitude of the correlation length using the conjecture of Derrida and De Seze;[20]

$$\eta=(n/\pi)\xi^{-1}(n,\tilde{x}_c) \ . \tag{4}$$

The results are presented in Table I. (For comparison of ρ with OB and RCS, one must multiply by 4, the inverse of the close-packed density.)

While the convergence of ν and η is clearly slow and makes extrapolation to the infinite n limit problematic, such behavior is expected for the four-state Potts model. This model has $\nu=\frac{2}{3}$ and $\eta=\frac{1}{4}$. Blöte and Nightingale[21,22] ob-

TABLE I. Results using finite-size scaling [Eqs. (2)–(4)].

$n,n+2$	$\tilde{x}_c$	$\rho(n+2,\tilde{x}_c)$	ν	η
4,6	1.728 25	0.185 80	0.7007	0.2388
6,8	1.762 94	0.187 41	0.6985	0.2262
8,10	1.764 98	0.187 51	0.7132	0.2251
10,12	1.762 52	0.187 32	0.7173	0.2269
12,14	1.760 86	0.187 20	0.7164	0.2284
14,16	1.759 89	0.187 14	0.7143	0.2296

TABLE II. Exponents using three-point fit of reduced compressibility and two-point fit of susceptibility. $\tilde{x}_c$ is evaluated for strips of width $n-2$ and n.

n	$(\partial/\partial x)\rho(n,\tilde{x}_c)$	$\nu(n,n+2,n+4)$	$\chi(n,\tilde{x}_c)$	$\eta(n,n+2)$
6	0.1224	0.74	5.5689	. . .
8	0.1540	0.72	10.2114	0.110
10	0.1833	0.72	15.5671	0.203
12	0.2113	0.72	21.6038	0.210
14	0.2382		28.4683	
16	0.2643		. . .	

served similar convergence problems in the four-state Potts model, which they attributed to the known presence of a marginal eigenvalue. Their "best estimate"[21] of ν was 0.7177, which is comparable to our results. For η their result[21,22] is 0.2728; the deviation similar to ours. Our values are distinctly different from those of a "discontinuity fixed point"[23] ($\nu=1/d=\frac{1}{2}$ and $\eta=0$), which characterize the obtainable exponents at first-order transitions.

Exponent estimates can also be obtained by directly scaling $\partial\rho/\partial x$ (i.e., the specific heat, or equivalently here, the compressibility[24]) and the susceptibility. Finite-size scaling theory[25] predicts that the (reduced) compressibility at the infinite system critical point should increase with increasing strip size as $n^{\alpha/\nu}$. Likewise the critical susceptibility χ_c should increase as $n^{\gamma/\nu}$. These numbers, evaluated at the estimated critical points of Table I, appear in Table II. The susceptibility here is defined by the structure factor evaluated at one of the reciprocal lattice vectors of the $p(2\times 2)$ structure. It was computed by numerically differentiating the partition function with respect to an appropriate staggered field Δ (which favors alternate rows running in the close-packed finite direction): $\chi(n,x)=n^{-1}\partial^2\ln\lambda_0^{(n)}/\partial^2\Delta$.

By fitting the susceptibilities to the form $cn^{\gamma/\nu}$ using data from strips of width n and $n+2$, and reduced compressibilities to the form $c_0+c_1n^{\alpha/\nu}$ using strips of width n, $n+2$, and $n+4$, we obtain estimates of the exponents ν and η through the relations $d\nu=2-\alpha$ and $\gamma/\nu=2-\eta$. These estimates appear in Table II. Again, given the poor convergence associated with the four-state Potts model, the results are consistent with a four-state Potts continuous transition.[26] In a first-order transition, the susceptibility and the compressibility calculated in this way are predicted to diverge exponentially in n,[21] obviously not the case here.

As more exclusions are added to the model, the Lifshitz condition is violated, so that LGW symmetry considerations can no longer be used to make predictions about the nature of the phase transition.[2] More complicated sorts of phase transitions become possible. For example, Ostlund's model calculations[27] show melting via an intermediate floating phase if the number of exclusions exceeds a specified value. Thus, it is no longer clear that the standard prediction[5,6] of first-order transitions for multiple exclusions is correct. In the limit of infinite range exclusions, viz., the hard disk model, there is no long-range positional order. While the hard disk transition is accepted as first order, there is controversy when more general interactions exist.[28]

We must still account for the original classification[5,6] as first order of the triangular lattice gas with first- and second-neighbor exclusions. We note that OB and RCS treated the identical transfer matrices that we use in PR/TMS, but without finite-size scaling[6,20,25] to analyze results. Their empirical extrapolation procedure to infinite strip width was acknowledged[5b,16] to invite possible error. Explicitly, they considered the densities $\rho_<$ and $\rho_>$ at the two points of inflection of $\partial\rho/\partial x$. OB then linearly extrapolated $\rho_>$ vs n^{-1} and $\rho_<$ vs n^{-2}. Since the intercepts (at $n\to\infty$) clearly do not meet, OB concluded the transition was first order. According to finite-size scaling,[25] rounding of a phase transition occurs when ξ is of order the size of the system, i.e., $\xi(\rho_{\gtrless})\approx n$. From the definitions of the exponents α and ν,

$$\xi(x_{\gtrless})\propto|z_{\gtrless}-z_c|^{-\nu}\propto|\rho_{\gtrless}-\rho_c|^{-\nu/(1-\alpha)}\ . \tag{5}$$

Hence, $\rho_>-\rho_<$ should decay as $n^{-(1-\alpha)/\nu}$.[29] For the four-state Potts model $(1-\alpha)/\nu=\frac{1}{2}$. We thus surmise that OB's analysis would have identified the four-state Potts transition as first order. (Our log-log plot of OB's values of $\rho_>-\rho_<$ yields an exponent of -0.6.) For the hard-hexagon model, where $(1-\alpha)/\nu=\frac{4}{5}$, Runnels and Combs[16] extrapolated again with -0.75 and correctly identified the transition as second order. We finally note that even OB recognized that Chesnut's Monte Carlo calculations,[30] cited by OB for corroboration, involved very small lattices. Moreover, determining with modern Monte Carlo capabilities the known order of a Potts transition for $q=4,5,6$ (Ref. 31)—and more generally distinguishing weakly first-order transitions from second order—is a subtle problem that usually requires computation on several lattices of different size and subsequent finite-size scaling analysis.[32]

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[8]T. L. Einstein, in *Chemistry and Physics of Solid Surfaces IV,* edited by R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1982), p. 251. Effective exclusion can arise when adsorption of the gas atoms is strongly site specific and when their hard-core radius exceeds the spacing between adsorption sites. Examples include Cl/Ag(100) [D. E. Taylor, E. D. Williams, and R. L. Park, J. Vac. Sci. Technol. A **2**, 895 (1984)] and Se/Ni(100) [P. Bak, P. Kleban, W. N. Unertl, J. Ochab, G. Akinci, N. C. Bartelt, and T. L. Einstein (unpublished)].

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