# Phase diagram of the triangular Ising model: Renormalization-group calculation with application to adsorbed monolayers\*

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We study a triangular Ising model subject to nearest-neighbor pair interactions K, an external magnetic field H, and triangular three-spin interactions P. K > 0 (<0) corresponds to ferromagnetic (antiferromagnetic) coupling. The phase diagram and thermodynamics are invariant under  $(K, H, P) \leftrightarrow (K, -H, -P)$ . A simple position-space renormalization group is formulated, based on three interpenetrating three-spin cells, which preserves the three-sublattice symmetry of the antiferromagnetic phase. The complete (K, H, P) phase diagram consists of five interconnecting transition surfaces (two secondorder and three first-order), which bound the four single-phase regions ( $\uparrow \uparrow \uparrow$ ,  $\uparrow \uparrow \downarrow$ ,  $\downarrow \downarrow$ , and  $\downarrow \downarrow \downarrow$ ). The edges of these surfaces form loci of second-order, critical-endpoint, and Baxter-Wu transitions. When P = 0, this system is known to provide a useful model of the order-disorder transition in monolayer films adsorbed on a hexagonal substrate. Calculation of the magnetization M(K,H) and heat capacity  $c_M(K,H)$ of the Ising model allows quantitative comparison with experimental data for helium on graphite. The observed dependence  $T_c(n)$  of the transition temperature on coverage is well fit with a single effective antiferromagnetic pair interaction. The corresponding calculated heat capacities (*no* additional adjustable parameters) are in remarkable agreement with experimental data near and below  $T_c$ .

## I. INTRODUCTION

The two-dimensional Ising model with nearestneighbor antiferromagnetic coupling is of experimental interest because it provides a reasonable model for the order-disorder transition which occurs in many physisorbed monolayer films. The particular case of helium adsorbed on graphite has been studied extensively.<sup>1-3</sup> The hexagonal basal planes of the graphite substrate form a triangular lattice of preferred adsorption sites. The diameter of a helium atom is somewhat larger than the lattice spacing, so there is a repulsive nearestneighbor interaction u. At high temperature and low coverage n (relative to the number of adsorbtion sites), the helium atoms move quite freely over the substrate.<sup>4</sup> At low temperature and coverage  $n \approx \frac{1}{3}$ , an ordered phase is observed<sup>1,2,5</sup> (Fig. 1), in which helium atoms occupy next-nearest-neighbor sites. The transition between ordered and disordered phases takes place when  $k_{\rm B}T$  is comparable in magnitude to the near-neighbor repulsion. Whenever the helium atoms are well localized to adsorbtion sites,<sup>6</sup> it is attractive to model the system by a lattice gas,<sup>7</sup> in which each adsorbtion site *i* is either empty  $(n_i = 0)$  or or full  $(n_i = 1)$ . The average density  $n \equiv \langle n_i \rangle$  is controlled by a chemical potential  $\mu$ . The equivalence of such a lattice gas to an Ising model is well known<sup>7,8</sup>: The appropriate reduced Hamiltonian is

$$-\beta \mathcal{K}_{0} = K \sum_{\langle ij \rangle} S_{i} S_{j} + H \sum_{i} S_{i} + NC , \quad S_{i} = \pm 1 , \quad (1.1)$$

where  $\langle ij \rangle$  indicates a nearest-neighbor pair, N is the total number of lattice sites,  $\beta \equiv 1/k_BT$ ,  $n_i = \frac{1}{2}(1+S_i)$ ,  $K = -\frac{1}{4}\beta u$ ,  $H = \frac{1}{2}[\beta \mu - 3\beta u - \ln(\lambda_T^2/v_0)]$ , and the spin-independent constant term  $C = \frac{1}{2}[\beta \mu - \frac{3}{2}\beta u - \ln(\lambda_T^2/v_0)]$ . In the foregoing,  $\mu$  is the (d=2)chemical potential of the helium adatom,  $\lambda_T$  is their thermal wavelength  $(\lambda_T^2 = 2\pi\hbar^2\beta/m)$ , and  $v_0$ is the area of the primitive cell of the substrate



FIG. 1. Basal plane of a graphite substrate with adsorbed helium atoms shown to scale. The adatoms are represented in a characteristic  $n = \frac{1}{3}$  array.

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FIG. 2. Schematic phase diagram for the triangular Ising model (1.1) for positive and negative nearest-neighbor interactions. The thermodynamics is invariant under  $H \leftrightarrow -H$ , so the figures are symmetric about H=0.

surface. There is in the physical monolayer problem an additional longer-ranged Van der Waals attraction. This leads to further-neighbor ferromagnetic interactions in the corresponding Ising model; however, it is a comparatively weak effect and will be ignored in what follows.<sup>9</sup> Further discussion of the connection between the adsorbtion problem, the lattice gas, and the Ising model is given in Appendix A.

The Ising model (1.1) on the triangular lattice is exactly soluble when H = 0 but not otherwise for both<sup>10</sup> K > 0 (ferromagnetic) and  $K < 0^{11}$  (antiferromagnetic, corresponding to the adsorbtion problem). When K > 0,<sup>10</sup> there is a critical point at  $K = K_{\text{Onsager}} = 0.2747$ , H = 0, and for  $K > K_{\text{Onsager}}$ the K axis forms a first-order phase boundary between the ferromagnetically aligned phases **\*\*\*** (for H > 0) and  $\ddagger \ddagger \ddagger$  (for H < 0) (Fig. 2). When K < 0,<sup>11</sup> the situation is more complicated. Recall that a triangular lattice of side a may be regarded as composed of three equivalent interpenetrating triangular sublattices, A, B, and C, each of side  $a\sqrt{3}$ . The points of each sublattice (e.g., A) are second neighbors of each other but have nearest neighbors entirely on the other sublattices (e.g., B and C). The exact solution<sup>11</sup> at H = 0 (i.e.,  $n = \frac{1}{2}$ for the lattice gas) exhibits paramagnetic behavior at all finite T but has a ground state with infinite degeneracy (finite entropy per spin at T = 0) at the energy  $-\beta E_0/N = -|K| + C$ . This degeneracy encompasses not only the six aligned-sublattice "antiferromagnetic" configurations,  $\uparrow \uparrow \downarrow$  (i.e.,  $A = \uparrow$ ,  $B = \uparrow, C = \downarrow$ ),  $\uparrow \downarrow \uparrow$ ,  $\downarrow \uparrow \uparrow$ ,  $\uparrow \downarrow \downarrow$ ,  $\uparrow \downarrow \downarrow$ , and  $\downarrow \downarrow \uparrow$ , but also, for example, those states derived from them by flipping an arbitrary number of nonadjacent spins on the majority sublattices (A and B in the case of  $\uparrow \uparrow \downarrow$ ). For  $H \ge 0$   $(n \ge \frac{1}{2})$  less is known: Simple energy arguments suffice to prove that for |H/K| > 6the ground state is ferromagnetic ( $\uparrow \uparrow \uparrow$  for H > 0and  $\mathbf{i} \mathbf{i} \mathbf{i}$  for  $H \leq 0$ , so here, as for H = 0, one expects no phase transition at finite temperature. However, a weak magnetic field (0 < |H/K| < 6)breaks the infinite degeneracy while still favoring the antiferromagnetic configurations, leaving a threefold degenerate ground state (+++, +++, and  $\ddagger \uparrow \uparrow$  for H > 0;  $\uparrow \downarrow \downarrow$ ,  $\ddagger \uparrow \downarrow$ , and  $\ddagger \downarrow \uparrow$  for H < 0). In this range of fields one, therefore, expects a phase transition at finite temperature  $K_c^{-1}(H/K)$  between paramagnetic and antiferromagnetic domains (Fig. 2). Each antiferromagnetic domain is, in fact, a region of coexistence of three symmetrical phases, each associated with one of the corresponding degenerate ground states. The ordered phase has, accordingly, the same threefold symmetry exhibited by the three-state Potts model.<sup>12</sup> It has been argued by Alexander<sup>13</sup> that the transitions should belong to the same universality class.

Monte Carlo results<sup>14</sup> confirm the structure of Fig. 2; however, previous analytic approximations,<sup>15</sup> which have been of the mean-field type, yield a finite transition temperature at H = 0 in disagreement with the exact result,<sup>11</sup> presumably because they are unable to handle the large fluctuations connected with the ground-state degeneracy. In this paper, we treat the thermodynamics of the Hamiltonian (1.1) via the position-space renormalization-group methods of Niemeijer and van Leeuwen<sup>16</sup> and others.<sup>17-21</sup> Our recursion relations, although exceedingly simple, succeed in preserving the symmetry of the antiferromagnetic phases and lead to a phase diagram in agreement with Fig. 2 and the arguments outlined above. Using these recursion relations, we are in a position to make reasonably quantitative calculations of all thermodynamic properties of the triangular Ising model (both  $K \ge 0$  and  $K \le 0$ ) and, via the latticegas analog, of the corresponding properties of adsorbed helium.

In order to preserve the three-sublattice antiferromagnetic symmetries in the calculation it is necessary to use clusters of three (or more) renormalization-group (RG) "cells." As is well known,<sup>16,17</sup> the RG method introduces "cell-spin interactions," not present in the initial Hamiltonian (1.1). The most important of these for our purposes<sup>22</sup> is a three-spin interaction between the spins at the vertices of each elementary triangle. Our three-cell (nine-spin) approximate recursion relations preserve the form of the following generalization of (1.1):

$$-\beta \Im C(K, H, P, C; \{S\}) = K \sum_{\langle ij \rangle} S_i S_j + H \sum_i S_i$$
$$+ P \sum_{\langle ijk \rangle} S_i S_j S_k + NC, \quad (1.2)$$

where  $\langle ijk \rangle$  denotes the vertices of an elementary triangle. The fixed point corresponding to the ferromagnetic transition occurs at  $P^*=0$ ; however, the fixed point corresponding to the antiferromagnetic (Potts) transition occurs at a finite value of P\*. In addition to the ferromagnetic and antiferromagnetic critical surfaces the three-dimensional (K, H, P) phase diagram of (1.2) contains another locus of criticality with no analog in (1.1): The problem of pure three-spin interactions (K = H = 0)corresponds to a special case of the eight-vertex model<sup>23</sup> which has been solved exactly by Baxter and Wu<sup>24</sup> and exhibits a special "Baxter-Wu" (BW) critical point at  $P = \pm P_{BW}$ ,  $P_{BW} = 0.4407$ . For |P| $< P_{BW}$ , the system is paramagnetic, while for P  $> P_{\rm BW}$  there is first-order coexistence of  $\uparrow \uparrow \uparrow$  with the three antiferromagnetic phases of the +++ form (for  $P \leq -P_{BW} \ddagger \ddagger$  coexists with the three  $\ddagger \ddagger$ phases). Imbro and Hemmer<sup>25</sup> and Den Nijs and coworkers<sup>26</sup> have examined the crossover between ferromagnetic and Baxter-Wu critical behavior within a renormalization-group context quite similar to ours. They have not yet applied their calculation to the antiferromagnetic regime (K < 0) applicable to helium nor do they map out the full (K, H, P) phase diagram. We comment further on their results in Sec. III B.

In Sec. II we motivate and develop our approximate recursion relations. Section III contains results: Section IIIA treats the properties of the original Ising model (1.1). We find excellent agreement with Monte Carlo data<sup>14</sup> and the exact results.<sup>11</sup> Comparison via the lattice-gas analog with experimental data on helium monolayers is extremely encouraging: A single adjustable parameter (the nearest-neighbor helium-helium repulsion  $u = -4k_BTK$ ) produces quantitative fits to both the phase diagram and the measured heatcapacity profiles at a variety of densities. Section IIIB explores the behavior of the generalized Hamiltonian (1.2). We map out the full, global phase diagram, find all fixed points, and calculate corresponding critical behavior. Section IV summarizes our principal conclusions.

## **II. SYMMETRIES AND RECURSION RELATIONS**

In this section, we set up the RG and approximate recursion relations which underlie the results presented in Sec. III. It is not our objective to perform the most elaborate and accurate calculation possible. Rather, we aim to find the *minimum*<sup>27</sup> input required to capture the qualitative behavior outlined in Sec. I. The virtue of simplicity should be transparency. Indeed, our calculation requires at most a modest desk-top minicomputer and much of it can be carried through by hand. It is gratifying, of course, that many results do turn out quite quantitative.

The success of the renormalization-group method<sup>16-21</sup> rests on the fact that the recursion relations for the coupling constants induced by spatial rescaling are analytic in form and can, therefore, safely be approximated without destroying the nonanalyticities associated with critical behavior. We employ the cell-cluster, position-space formulation of Niemeijer and van Leeuwen<sup>16, 17</sup> (NvL). As has been emphasized by van Leeuwen, <sup>28</sup> it is crucial that the cell cluster and cell spin be chosen in such a way that the symmetries of the ordered state be preserved (otherwise, nonanalyticities may be forced into the recursion relations!). With this in mind we summarize here some important symmetry properties to be built into our RG transformations: (a) All eight ordered states (not just  $\uparrow \uparrow \uparrow$  and  $\downarrow \downarrow \downarrow$ ) should be preserved. This requires that the three-sublattice structure be preserved under rescaling. (b) The complete symmetry between the A, B, and C sublattices should be respected. Finally, (c) parity should be preserved by the transformation. In crudest form this is just the condition that the thermodynamics be invariant under the mapping

$$(K, H, P) \leftarrow (K, -H, -P) \tag{2.1}$$

in (1.2), which follows from reversal of all spins under the thermodynamic trace. A more detailed version applies to the separate sublattices: Consider the Hamiltonian

$$-\beta \mathcal{K} = K_{AB} \sum_{\langle ij \rangle} S_i^A S_j^B + K_{AC} \sum_{\langle ik \rangle} S_i^A S_k^C$$
$$+ K_{BC} \sum_{\langle jk \rangle} S_j^B S_k^C + H_A \sum_i S_i^A$$
$$+ H_B \sum_j S_j^B + H_C \sum_k S_k^C$$
$$+ P \sum_{\langle ijk \rangle} S_i^A S_j^B S_k^C + \text{const.}, \qquad (2.2)$$

where i, j, and k run over the sublattices A, B, and C, respectively. Equation (2.2) generalizes (1.2) to sublattice inequivalence and incorporates the fact that an elementary triangle has one vertex on each of the three sublattices. The thermody-



FIG. 3. Sites of the triangular lattice grouped into interpenetrating three-spin cells. Our calculation uses a single three-cell cluster, which contains nine spins altogether.

namics of this model is specified by the seven coupling variables. It is apparent (e.g., by reversal of spins on sublattice A) that the following symmetry holds:

$$(K_{AB}, K_{AC}, K_{BC}, H_A, H_B, H_C, P)$$
  
 $\rightarrow (-K_{AB}, -K_{AC}, K_{BC}, -H_A, H_B, H_C, -P).$  (2.3)

Successive application of (2.3) and its cyclic analogs for sublattices *B* and *C* reproduces (2.1). If (2.1) [or (2.3)] is true for the original couplings, then it should remain true for the renormalized coupling, after rescaling.

To implement the NvL method<sup>29</sup> it is necessary to choose an elementary spin cell, a cell cluster, and a spin projection, all in such a way that the above symmetries are built in. A minimum of three cells is necessary, if the sublattices are to remain distinct [point (a)]. Triangular symmetry of the lattice requires that there be at least three spins per cell. Our recursion relations are based on the cluster of three interpenetrating threespin cells<sup>30,31</sup> illustrated in Fig. 3. Note that each cell contains spins from a single sublattice and that the three cells are treated with complete symmetry [point (b)]. In calculating recursion relations from this cell cluster we employ periodic boundary conditions so that our calculation is entirely equivalent to periodic continuation of one  $3 \times 3$  block shown<sup>32</sup> in Fig.3. Because there are only three cells, the renormalization of a Hamiltonian of the form (1.2) leads to a new Hamiltonian of identical form,<sup>33</sup> only with renormalized couplings, K', H', P', and C'. Formally,

 $\exp\bigl[-\beta \mathcal{K}(K',H',P',C';\{S'\})\bigr]$ 

$$= \sum_{\{S\}} \mathcal{O}(\{S'\}, \{S\}) \exp[-\beta \mathcal{K}(K, H, P, C; \{S\})]$$
$$= e^{9^{C}} Z(S'_{A}, S'_{B}, S'_{C}; K, H, P), \qquad (2.4)$$

where  $\mathcal{O}$  is the spin projection which we make precise below. Once the "partial partition functions"  $Z(S'_A, S'_B, S'_C; K, H, P)$  are known, the recursion relations follow immediately. Denoting  $\bigstar$  and  $\bigstar$  spins by "+" and "-", respectively, and suppressing (K, H, P) dependence,

$$K' = \frac{1}{24} \ln \left( \frac{Z(+++)Z(---)}{Z(+--)Z(+--)} \right) = K'(K, H, P),$$
(2.5a)

$$H' = \frac{1}{8} \ln \left( \frac{Z(+++)Z(++-)}{Z(---)Z(+--)} \right) = H'(K, H, P) , \quad (2.5b)$$

$$P' = \frac{1}{48} \ln \left( \frac{Z(+++)Z^{3}(+--)}{Z(---)Z^{3}(+--)} \right) = P'(K, H, P), \quad (2.5c)$$

$$C' = 3C + \frac{1}{24} \ln[Z(+++)Z(---)Z^{3}(++-)Z^{3}(+--)]$$
  
= 3C + R(K, H, P). (2.5d)

For work at low temperatures it is sometimes convenient to employ the strong-coupling variables

$$x = \exp\left[\frac{2}{3}(H+6P)\right], \quad y = \exp\left[\frac{2}{3}(H-6P)\right],$$
  
$$z = \exp\left[\frac{2}{3}(6K-H-6P)\right]. \quad (2.6)$$

Recursion relations for these variables read,

$$x' = [Z(+++)Z(+--)/Z(---)Z(++-)]^{1/6}, \quad (2.7a)$$

$$y' = [Z(++-)/Z(+--)]^{1/3},$$
 (2.7b)

$$z' = [Z(---)/Z(+--)]^{1/3},$$
 (2.7c)

where the partial partition functions are taken to be expressed in terms of x, y, and z.

It remains only to define the spin projection. In order to preserve under rescaling the *full* partition function

$$Z(K, H, P, C) = \sum_{\{S'\}} Z(\{S'\}; K', H', P', C')$$
$$= Z(K', H', P', C'), \qquad (2.8)$$

it is sufficient that

$$\sum_{\{S'\}} \mathfrak{O}(\{S'\}, \{S\}) = 1.$$
 (2.9)

If  $\mathcal{O}$  is fully symmetric in the three sublattices [point (b)], then  $\mathbb{Z}(\{S'\})$  is invariant under permutation of its spin arguments. In order to preserve the parity symmetry (2.1) [point (c)] it suffices that

$$\mathscr{O}(\{-S'\};\{-S\}) = \mathscr{O}(\{S'\};\{S\}), \qquad (2.10)$$

which implies

$$Z(\{-S'\}; K, H, P) = Z(\{S'\}; K, -H, -P).$$
(2.11)

Equation (2.11) guarantees via (2.5) that

$$K'(K, -H, -P) = K'(K, H, P),$$
  
 $H'(K, -H, -P) = -H'(K, H, P),$  (2.12)

P'(K, -H, -P) = -P'(K, H, P),

so that, if  $(K, H, P) \rightarrow (K', H', P')$  under rescaling, then  $(K, -H, -P) \rightarrow (K', -H', -P')$ . Thus, the RG flows, the phase diagram, and all thermodynamic quantities have the symmetry (2.1). It is a special case of (2.12) that the K axis is an invariant subspace under RG flow in the sense that (K, 0, 0) $\rightarrow (K', 0, 0)$ . The more detailed parity (2.3) requires

$$\begin{split} & \mathscr{O}(-S'_{A},S'_{B},S'_{C};\{-S_{A},S_{B},S_{C}\}) \\ & = \mathscr{O}(S'_{A},S'_{B},S'_{C};\{S_{A},S_{B},S_{C}\}) \,, \quad (2.13) \end{split}$$

and similarly for the B and C sublattices. This has consequences analogous to (2.12) in the larger space of couplings (2.2). In particular it implies

$$Z(-S'_{A}, -S'_{B}, S'_{C}; 0, 0, P)$$
  
=  $Z(S'_{A}, S'_{B}, S'_{C}; 0, 0, P),$  (2.14)

which shows via (2.5) that (0, 0, P) - (0, 0, P'), so the P axis is also an invariant subspace.

The projection  $\mathcal{P}$  is standardly constructed as a product over single cells

$$\mathcal{O}\left(\{S'\};\{S\}\right) = p\left(S'_{A};\{S_{A}\}\right) p\left(S'_{B};\{S_{B}\}\right) p\left(S'_{C};\{S_{C}\}\right) . \quad (2.15)$$

The most-general form of the single-cell projection  $p(S'; \{S\})$  consistent with symmetry and parity is<sup>18</sup>

$$p(S'; \{S\}) = \frac{1}{2} [1 + \frac{1}{2}u(S_1 + S_2 + S_3 + S_1S_2S_3)S' + \frac{1}{2}v(S_1 + S_2 + S_3 - 3S_1S_2S_3)S'], \quad (2.16)$$

where the parameters u and v must remain in the interval  $-\frac{1}{2} \le u, v \le \frac{1}{2}$ , if the projection is to be non-negative. Equations (2.15)-(2.16) give a spin projection satisfying (2.9)-(2.14). In what follows we shall normally and unless otherwise stated use the "majority-rule"<sup>16,17</sup> (MR) projection  $u = v = \frac{1}{2}$ , which is equivalent to the direct assignment S'  $= \operatorname{sgn}(S_1 + S_2 + S_3)$ . It follows from (2.4) that the majority-rule partial partition functions are

$$Z_{MR}(+++) = \exp(27K + 9H + 18P) + 9 \exp(15K + 7H + 6P)$$
$$+ 27 \exp(7K + 5H + 2P)$$
$$+ 18 \exp(3K + 3H - 2P)$$

$$+9\exp(3K+3H+6P)$$
, (2.17a)

$$Z_{MR}(++-) = \exp(-9K + 3H - 18P) + 6 \exp(-9K + H - 6P)$$
  
+ 3 exp(3K + 5H - 6P)  
+ 9 exp(-5K - H - 2P)  
+ 18 exp(-K + 3H - 2P)  
+ 18 exp(-K + H + 2P)  
+ 9 exp(-K + H - 6P). (2.17b)

The remaining partial partition functions may be read off from (2.17) using (2.11).

In addition to the MR projection we shall make occasional use of a spin projection which is not of the product form (2.15). The most-general such projection which treats all nine spins symmetrically and satisfies (2.9), (2.10), and (2.13) has 24 free parameters. Variation of most of these parameters does not improve noticeably upon the results of majority rule, which we shall mainly report. A slight advantage is sometimes gained by a particular, minor reassignment of some of the mixed-spin configurations among the partial partition functions. We refer to this as our "generalized" (G) projection. In place of (2.17) it gives

$$Z_{G}(+++) = Z_{MR}(+++) + 18 \exp(-K + H + 2P)$$
  
- 18 exp(3K + 3H - 2P), (2.18a)  
$$Z_{G}(++-) = Z_{MR}(++-) - 18 \exp(-K + H + 2P)$$
  
+ 12 exp(-K - H - 2P)

+ 
$$6 \exp(3K + 3H - 2P)$$
. (2.18b)

The RG recursion relations which we exploit in the remainder of this paper are based on (2.5) in conjunction with either (2.17) or (2.18). The methodology for extraction of fixed points, critical exponents, phase boundaries, and thermodynamic functions follows now-standard lines.<sup>16-21,34</sup>

## **III. RESULTS**

## A. Antiferromagnetic transition, comparison with <sup>4</sup>He monolayers

We begin this survey with those results most directly related to the experimental monolayer-ordering transitions, which motivated this study. The global (K, H, P) phase diagram is discussed in Sec. III B. The (T, H) phase boundaries of the antiferromagnetic version of the simple Hamiltonian (1.1) [see Fig. 2(b)] are determined by the intersection of the half-plane P = 0, K < 0 with the special surfaces of the global (K, H, P) phase diagram. Two symmetrical [via (2.1)] lobes of critical surface intersect the P = 0, K < 0 half-plane, thus determining two symmetrical  $(H \leftrightarrow -H)$  loci of critical points, one of which is depicted in Fig. 4. The Monte-Carlo phase-boundary points<sup>14</sup>

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FIG. 4. Antiferromagnetic phase boundaries for the Hamiltonian (1.1). Results for two different approximations (MR and G) are shown. Data points and error bars refer to the Monte Carlo calculation of Ref. 14.

results and quite quantitatively with the results of the G projection (2.18). Note that in agreement with exact results<sup>11</sup> (but in contrast to previous analytic approximations<sup>15</sup>) the phase boundary is depressed to T = 0 when H = 0. It is straightforward to calculate the entropy per spin  $s_0$  at T = H = 0. Both MR and G projections give  $s_0 = 0.324$  compared to the exact result<sup>35</sup>  $s_0 = 0.323...$ , so our simple RG succeeds in handling the ground-state degeneracy mentioned in Sec. I to within better than 0.4%. Finally, we remark that the slope of the phase boundary in Fig. 4 near H/|K|=6 is related to the critical fugacity  $z_c$  at which the triangular lattice gas with infinite nearest-neighbor repulsion undergoes its ordering transition<sup>36</sup>: If  $H/|K|=6-a/|K|+\cdots$ , then the slope  $a=\frac{1}{2}\ln z_c$ . Gaunt<sup>37</sup> finds  $z_c=11.05$  from series expansions. This yields a= 1.20, in excellent agreement with the Monte Carlo points but only modest agreement with our a= 0.91 from both MR and G projections.

In adsorbed monolayer experiments it is the density rather than the chemical potential which is controlled. To make contact with the experimental phase diagram it is, therefore, necessary to calculate the magnetization  $M(T,H) = \langle S_i \rangle$  along the phase boundary of Fig. 4 and then to use the relation

$$n = \frac{1}{2} [1 + M(H, T)]$$
(3.1)

between the lattice-gas density and the magnetization to find the critical temperature  $T_c(n)$ . It is well known by now how to perform such calculations within the RG context: One simply follows the free energy<sup>19</sup> or its derivatives<sup>38</sup> along each trajectory. The low-density region  $n < \frac{1}{2}$  relevant to physical monolayer systems corresponds<sup>39</sup> to H < 0. Points on the phase boundary flow to the critical fixed point AF (see Table I), located at  $K^* = H^* = -\infty$ ,  $P^* = -0.113$  ( $6K^* - H^* - 6P^* = -0.91$ ), which governs

TABLE I. Critical fixed-point parameters from the majority rule [MR projection (2.17)]. Because of the symmetry (2.1) fixed points not on the K axis occur in pairs  $(K^*, H^*, P^*) \rightarrow (K^*, -H^*, -P^*)$ . Directional data are given for fixed points located at  $K^* = \pm \infty$ . Certain exact results are shown in square brackets for comparison.

Fixed points		Location $(K^*, H^*, P^*)$		ConditionsEi $(K^* = \pm \infty \text{ only})$		envalue exponents y	
F	Ferromagnetic	(0.185, 0, 0)	0) 01 <sup>a</sup>		1.45	0.64, -1.06	
BW	Baxter-Wu	(0, 0, 0)	$\pm 0.741$ )		2.00 <sup>°</sup> ,	0.55, -0.63	
R		$(0.508, \pm 1.48)$	$\pm 0.92$		$2.00^{\circ}$ ,	0.90, 0.30	
S	Critical endpoint	(∞, ∓∞,	±∞)	$-6K^{*\pm}H^{*\pm}6P^{*=}0.90$ $H^{*+}2P^{*=\pm}0.34$	$2.00^{f}$ ,	0.96, -∞	
AF	Antiferromagnetic (Potts)	( <b>-∞</b> , ±∞,	±0.113)	$6K^{\pm}H^{\pm}6P^{\pm}-0.91$	0.96.	$-0.26, -\infty$	
AF	T=0 Antiferromagnetic	$(-\infty, \pm \infty),$	±∞)	$6K^{*\pm}H^{*\pm}6P^{*=}-0.47$ $H^{*}-6P^{*=}=0.98$	×°,	1.00, -0.55	
Т	"Tricritical"	$(-\infty, \pm \infty,$	±∞)	$6K^{*\pm}H^{*\pm}6P^{*=}2.1$ $H^{*-}6P^{*=\mp}2.16$	∞,	1.76, 0.69	
B	"Bicritical"	$(-\infty, 0,$	0)		0.46.	0.20 0.48	
Q	"Multicritical"	(-∞, ±∞,	±∞)	$6K^{*\pm}H^{*\pm}6P^{*=}-\infty$ $H^{*}-6P^{*=}0$	∞,	0.46, 0.15	

<sup>a</sup> Reference 10.

<sup>b</sup> Reference 8.

<sup>c</sup> Not integer.

<sup>d</sup> Reference 24.

<sup>e</sup> References 24 and 49.

<sup>f</sup> Integer.



FIG. 5. Order-disorder transition temperature of the triangular lattice gas as a function of coverage n [Eq. (3.1)]. No transition occurs in this (MR) calculation for n < 0.24.

the antiferromagnetic (Potts) transition. Points in the ordered phase ( $\uparrow \downarrow \downarrow$ ) flow to a sink at  $K^* = -\infty$ ,  $H^* = -\infty$ ,  $P^* = \infty$ , while those in the disordered phase  $(\ddagger \ddagger)$  flow to a sink at  $K^* = \infty$ ,  $H^* = -\infty$ ,  $P^* = 0$ . The phase diagram  $T_c(n)$  based on the MR projection is shown in Fig. 5. We note in passing that the minimum density at which the lattice gas orders is n = 0.24 (MR and G), which compares favorably with Gaunt's<sup>37</sup> series estimate of n = 0.227. The region near the peak of Fig. 5 is shown in detail in Fig. 6 along with data points for <sup>4</sup>He on Grafoil<sup>2</sup> and for <sup>4</sup>He on ZYX UCAR (an improved Grafoillike substrate) from Bretz's recent work.<sup>40</sup> Our maximum transition temperature occurs at a density of n = 0.337, offset by entropic contributions from the energetically most favorable density n



FIG. 6. Detail of Fig. 5 showing region near the peak  $n_{max} = 0.337$ . Data points are for <sup>4</sup>He on Grafoil: circles, cell A; triangles, cell B; both from Bretz *et al.*, Ref. 2; squares, Bretz, Ref. 40; inverted triangle, Hering *et al.*, Ref. 2.

=  $\frac{1}{3}$ . This maximum (mistakenly placed at *exactly*  $n = \frac{1}{3}$ ) is often<sup>2,40</sup> used as a fiducial in calibrating the total area of the experimental cell, so in plotting the experimental points we have taken the liberty of "recalibrating" the "experimental density" so the maximum occurs at  $n_{exp} = 0.337$ . (Of course, this is a very small effect, since the offset from  $n = \frac{1}{3}$  is only 1%.) The maximum experimental transition temperature then fixes

$$|J|/k_B = 2.08 \,^{\circ}\mathrm{K}$$
, (3.2)

which we have used for all the data.<sup>41</sup> This corresponds to a nearest-neighbor <sup>4</sup>He-<sup>4</sup>He repulsion of u = 8.32 °K, which is not physically unreasonable.<sup>42</sup> Our procedure forces agreement with experiment at the maximum. Agreement (in Fig. 6) away from the maximum is a crude but satisfactory test of the theory.

We have also calculated<sup>19,38</sup> the heat capacity per site  $c_M$  of the Ising model at constant magnetization, which corresponds to the constant-area heat capacity *per particle* of the lattice gas according to

$$C_V/k_B N_{\text{part}} = c_M/nk_B.$$
(3.3)

This relation includes the configurational contribution to the lattice-gas heat capacity and omits the contribution arising from the kinetic energy. It is derived and discussed in Appendix A. By adjusting H to keep M constant, we have calculated the heat capacity (3.3) as a function of  $k_BT/|J|$  for a number of densities n near the maximum of Fig. 6. These curves are shown as Figs. 7-11, along with the corresponding experimental <sup>4</sup>He data from Refs. 2 and 40. In plotting the experimental data we have used the value (3.2) of J, thus superposing the position of the peaks in Fig. 8. Theory then predicts with no additional adjustable parameter peak positions for  $n \neq 0.337$  plus magnitude and



FIG. 7. Heat capacity per particle at constant coverage. Data from Bretz *et al.*, Ref. 2 for densities somewhat below the maximum  $n_{max} = 0.337$  of Fig. 6.



FIG. 8. Heat capacity per particle at constant coverage. The curve is calculated from Eq. (3.3) at the maximum n of Fig. 6. Data points for <sup>4</sup>He on Grafoil are from Bretz *et al.*, Ref. 2.

shape for all n. Agreement is more than satisfactory for the older Grafoil data<sup>2</sup> (Figs. 7-10), although it is clear that the model systematically overestimates heat capacities near but above the ordering transition. This discrepancy presumably represents a failure of the strictly local Ising-model-lattice-gas picture as the adatoms delocalize and become increasingly mobile at higher temperatures (see also Ref. 42 and Appendix A). At temperatures much higher than the ordering transition  $c_{\rm M} \rightarrow 0$ , while the experimental  $C_{\rm V}/k_{\rm B}N_{\rm part} \rightarrow 1$  (d = 2 classical gas), so the curves must cross again. Figure 10 is of interest because it indicates that the specific-heat singularity should be increasingly difficult to observe as the density gets further from the value 0.337. This is in complete accord with experimental observations.<sup>2</sup> Our calculations at higher densities show that a secondary maximum in the specific heat emerges at a temperature greater than that of the transition. As the singularity will be difficult to observe, this secondary maximum may be incorrectly identified as signal-



FIG. 9. Heat capacity per particle at constant coverage. Data from Bretz *et al.*, Ref. 2 for densities somewhat above the maximum.



FIG. 10. Heat capacity per particle at constant coverage. Data from Ref. 43 for a density above the maximum.

ing the transition itself. Such a maximum can be observed in the experimental data<sup>43</sup> shown in Fig. 10 at  $k_B T/|J|=1.4$ . Unfortunately, there is a lacuna in the data at the expected transition temperature.

The actual singular behavior of the heat capacity at the ordering transition is controlled by the one relevant ("thermal") eigenvalue at the antiferromagnetic fixed point. Table I shows  $y_{\tau} = 0.956$ , implying  $\alpha = 2(1 - y_T^{-1}) = -0.093$ , which (being negative) is not Fisher renormalized<sup>44</sup> along paths of constant M. This weak singularity is quite consistent with the older data (Figs. 7-9), which was originally interpreted as logarithmic; however, it stands in disagreement with  $\alpha = 0.36$  quoted by Bretz<sup>40</sup> for the UCAR data of Fig. 11. The ordering transition is expected<sup>13</sup> to be in the three-state Potts model universality class, so one might hope for a direct check on our calculated value of  $\alpha$ . Three-state Potts exponents have been calculated by a number of authors; however, disagreement among the published values precludes any firm comparison: Straley and Fisher<sup>45</sup> give  $\alpha = 0.05$ 



FIG. 11. Heat capacity per particle at constant coverage. Data for <sup>4</sup>He on the improved Grafoil substrate ZYX UCAR from Ref. 40 at  $n=n_{max}$ . Theoretical curve shown is the same as Fig. 8.



FIG. 12. Perspective view of the global (K, H, P) phase diagram of the triangular Ising model (1.2). Firstorder surfaces are shown shaded. Parameters of the fixed points shown are collected in Table I. Lines of constant K are plotted at intervals of 0.2 from K=-0.6to K=+0.6.

 $\pm 0.10$  from low-temperature series, Kim and Joseph<sup>46</sup> quote  $\alpha = 0.26$  from high-temperature series, while Berker and Wortis<sup>34</sup> and Burkhardt *et al.*<sup>47</sup> have done position-space RG calculations and find  $\alpha = 0.19$  and  $\alpha = 0.34$ , respectively.

## B. Global phase diagram

We turn now to the behavior of the general Hamiltonian (1.2). Figure 12 is a perspective plot of the global (K, H, P) phase diagram obtained by using the majority-rule projection (2.17). Constant-K cross-sections are shown in Figs. 14-17. Figures 13 and 18 depict the situation at  $K = -\infty$  and  $K = +\infty$ , respectively. In all plots we adhere to the convention of showing first-order phase boundaries with



FIG. 13. Constant-K cross section of the global phase diagram (MR) at  $K = -\infty$ . Note that axes are labeled by the reduced variables H/|K| and P/|K|. First-order boundaries are dashed, while higher-order boundaries are shown with solid lines. Parameters of the various fixed points are collected in Table I.



FIG. 14. Constant-K cross sections of the global phase diagram in the antiferromagnetic region K=-1.0 to K=0.0 by steps of 0.2. First-order phase boundaries are dashed; higher-order are solid. The dots are tricritical points. They lie on the line BW-T and map to BW under MR recursion relations.

dashed lines and higher-order phase boundaries with solid lines. Critical fixed points and corresponding eigenvalue exponents are collected in Table I.

The phase diagram (see Fig. 12) consists of two halves, identical by (2.1) under inversion in the K axis. The left-hand half consists of a rounded surface entirely in the  $H \ge 0$ ,  $P \le 0$  quadrant for  $K \ge 0$ but bulging over for  $K \le 0$  into the  $H \le 0$ ,  $P \le 0$  and  $H \ge 0$ ,  $P \ge 0$  quadrants. This surface completely encloses the **+++** phase.<sup>48</sup> It is bisected by a line running down the ridge-line from S (at  $K = +\infty$ , Fig. 18) to R and thence down the front of the surface through the point BW on the P axis and on to T (at  $K = -\infty$ , Fig. 13). To the left of the line S-R-BW-T (i.e., on the front in Fig. 12 and shown shaded) the surface is a locus of first-order transitions between the **+++** and **+++** phases. To the right of S-R-BW-T the surface (unshaded and seen most clearly as the front of the image surface enclosing  $\dagger$   $\dagger$  on the right of Fig. 12) is a locus of



FIG. 15. Constant-K cross section of the global phase diagram at K=0.1 in the ferromagnetic region. The dots are tricritical points on the line R-BW.



FIG. 16. Constant-K cross section of the global phase diagram at K=0.185 in the ferromagnetic region. This cross section includes the ferromagnetic fixed point F. The two dots at the ends of the isolated dashed line are ferromagnetic critical points on the line R-F-R and map to F under the recursion relations.

second-order transitions (between **\*\*\*** and **\*\*\***) governed by the antiferromagnetic (Potts) fixed point AF at  $K = -\infty$  (Fig. 13). The parameters of the fixed point AF are listed in Table I and were discussed in Sec. IIIA. The two rounded surfaces described above are connected by a third, rather planar surface, which is confined to K > 0, contains the segment of the K axis above F, and meets the rounded surfaces along the special lines S-R. This surface (also shaded in Fig. 12) is a locus of firstorder transitions between **††** and **†††**. It is bounded at the lower edge by the special line R-F-R. The intersection of these three interconnected surfaces with the K = 0 plane has already been displayed in Fig. 14. Figures 19 and 20 show intersections with the planes P = 0 and H = 0, respectively.

The dimensionless couplings K, H, and P of the Hamiltonian (1.2) contain the temperature and are



FIG. 17. Constant-K cross section of the global phase diagram at K=0.65 in the ferromagnetic region, somewhat above R. The dots are critical endpoints. They lie on S-R and map to S under recursion relations.



FIG. 18. Constant-K cross section of the global phase diagram (MR) at  $K=+\infty$ . Note that the axes are labeled by the reduced variables H/K and P/K. First-order boundaries are dashed, while higher-order boundaries are shown with solid lines. Parameters of the various fixed points are collected in Table I.

related to the corresponding temperature-independent interaction energies by

$$K = J/k_B T$$
,  $H = B/k_B T$ ,  $P = p/k_B T$ . (3.4)

Decreasing the temperature T at fixed interaction energies corresponds in Fig. 12 to moving radially outward from the origin. Some typical (B,T)phase diagrams at fixed J and p are shown schematically in Figs. 21 and 22. Various ratios p/Jsample different regions of the global phase diagram.

We turn now to the special lines R-F-R and S-R-BW-T. Figures 23-25 exhibit projections of these lines and indicate the direction of RG flows along them. R-F-R is the domain of the fixed point F and represents a line of ferromagnetic critical points, described in our MR calculation



FIG. 19. Intersection of the global phase diagram with the H-K plane (P=0). The ferromagnetic fixed point F appears at the top center. Antiferromagnetic critical lines map to the fixed point AF.



FIG. 20. Intersection of the global phase diagram with the P-K plane (H=0). The fixed points F and BW appear on the axes.

by the exponents given in Table I. When H=P=0, the critical coupling is known exactly:  $K_c = 0.275$ , compared with our  $K^* = 0.185$ . Our two relevant ferromagnetic eigenvalue exponents are also in poor agreement with the exact results shown. Indeed, it appears<sup>31</sup> that low-order calculations with "open" cells (such as Fig. 3) appropriate to represent the *anti*ferromagnetic situation give far worse results for *ferro* magnetic properties than calculations of equivalent order using compact cells.<sup>16,17</sup>

The segment *R*-*S* flows to the fixed point *S* and is a locus of critical endpoints, along which the antiferromagnetic (Potts) critical surface meets the two first-order surfaces at finite angle. The eigenvalue exponents belonging to *S* show typical critical-endpoint structure,<sup>34</sup> combining a leading y = 2= *d* (characteristic of all first-order transitions)<sup>49</sup> with a  $y_T = 0.96$  in coincidence with the thermal exponent of AF.

The remaining segment R-BW-T is a locus of tricritical points, defining the smooth joining of the first- and second-order parts of the rounded surfaces. In our approximations, R-BW-T is the domain of the Baxter-Wu point BW, located on the



FIG. 21. Temperature-magnetic-field phase diagrams: Antiferromagnetic interaction (J < 0). Phase boundaries are shown schematically for different ratios of the exchange energy |J| to the three-spin interaction p: (a) p=0, (b)  $0 , (c) <math>0 < \frac{1}{2} |J| < p$ , (d) |J| = 0. Plots for  $p \rightarrow -p$  would simply be reflected about B = 0 by the general symmetry (2.1). Note that the  $\ddagger \ddagger \ddagger and \ddagger \ddagger \ddagger = 0$ .

P axis. As mentioned in Sec. I, the exact BW critical coupling is known,<sup>24</sup>  $P_c = 0.4407$ . Agreement with our  $P^* = 0.741$  is poor; but, our leading eigenvalue exponent is only 7% larger than the conjectured exact value<sup>50</sup> of 1.875. There is, however, an interesting and, we believe, open question concerning the connectivity of the fixed points R, F, BW, and T. Two other groups<sup>25,26</sup> have used RG methods to study the flows about the Baxter-Wu point and into the ferromagnetic region (neither of Refs. 25 and 26 treats the K < 0 region, which has been our primary focus). Imbro and Hemmer<sup>25</sup> use a simple linear transformation<sup>51</sup> on the Hamiltonian (1.2). den Nijs et al.<sup>26</sup> use a cluster of six<sup>52</sup> rather compact four-spin cells in a calculation which includes a number of further-neighbor and many-spin couplings in addition to those appearing



FIG. 22. Temperature -magnetic-field phase diagrams: Ferromagnetic interaction (J > 0). Phase boundaries are shown schematically for different ratios of the exchange energy J to the three-spin interaction p: (a) 0 < J < 0.37p, (b) 0.37p < J < 0.55p, (c)  $0.55p < J < \frac{3}{2}p$ , (d)  $0 < \frac{2}{3}p < J$ , and (e) p = 0.



FIG. 23. Projections on the P-K plane (H=0) of the special lines of the global phase diagram (Fig. 12). Fixed points are labeled and directions of flow between them are indicated.

in (1.2). Results are summarized in Table II. Both groups find a third *relevant* eigenvalue (cf. our  $y_3 = -0.63$  in MR), indicating flow *outward* from BW in all *three* directions. Neither Ref. 25 nor Ref. 26 plots a global phase diagram; however, they have both traced a critical line flowing directly from BW to the ferromagnetic fixed point F (cf. our R-F-R). Our phase diagram would have this structure, if (a) the fixed point R were brought down to coincide with BW and (b) the flow along BW-T were reversed from ours, so the fixed point T controlled the tricritical line.

Both our present phase diagram and the one suggested by the above considerations are physically reasonable and we know no simple way of deciding between them. The most technically sophisticated calculation is certainly that of Ref. 26; however, the question hinges on the relevance or irrelevance of the third BW eigenvalue. All position-space RG calculations are notably and increasingly unreliable for subdominant exponents. In an attempt



FIG. 24. Projections on the H-P plane (K=0) of the special lines of the global phase diagram (Fig. 12). Fixed points are labeled and directions of flow between them are indicated.



FIG. 25. Projections on the H-K plane (P=0) of the special lines of the global phase diagram (Fig. 12). Fixed points are labeled and directions of flow between them are indicated.

to clarify this point we made two additional BW calculations, using (i) the generalized (G) transformation described by the projection (2.18) and (ii) the general single-cell projection (2.16) with u = 0.500, v = 0.565 (cf.  $u = v = \frac{1}{2}$  for MR). The choice of parameters in (ii) was made to fit the exact BW thermal exponent  $y_T = 1.5$ . This necessitated going *outside* the range of non-negative projections [see after (2.16)], and (unlike G) the resulting projection becomes unphysical beyond the immediate neighborhood of BW. Results are summarized in Table II. In both cases there is dramatic improvement in the location of  $P^*$  and in the leading eigenvalues; however, the ambiguity in the sign of  $y_3$  persists.

Finally, we comment on the remaining three critical fixed points in Table I, AF', B, and Q, which are all located at  $K = -\infty$  (Fig. 13) and have no domain at finite couplings. AF' is distinct from T(as shown in Table I) and has as its domain the line B-AF' less the point B. The close correspondence of the exponents y = 0.96 of AF and y = 1.00of AF' suggests that AF' is just a special, zerotemperature version of the antiferromagnetic fixed point AF. The fixed points B and Q are related and rather interesting. To understand them we need only consider turning on an attractive second-nearest-neighbor interaction. It is easy to show that at zero temperature and P = 0 the phase diagram consists of regions of two-phase equilibrium between **†††** and **††‡**, between **††‡** and *↓↓↓* and *↓↓↓*. The first and last of these two-phase regions ends in a tricritical point as in the similar problem on the square lattice.<sup>21</sup> The second two-phase region is peculiar to the triangular system. It exists on the H = 0axis and terminates at the bicritical point B which is located at a finite temperature  $T_B$  which depends on the strength of the second-neighbor coupling. When this strength vanishes, as in our calculation,

Majority rule	Generalized	Single-cell $u = 0.500, v = 0.565$	Ref. 25	Ref. 26	Exact <sup>a</sup>
P <sub>c</sub> 0.741	0.473	0.458	1.37	0.49	0.441
y <sub>H</sub> 2.00	1.91	1.91	1.37	1.94	1.875
$y_T 0.55$	1.12	1.50	1.59	1.24	1.500
$y_3 - 0.63$	-0.40	1.32	1.23	0.40	???

TABLE II. Baxter-Wu point and its eigenvalue exponents: Comparison of various calculations. Our results are shown in the first three columns. Details of the RG projections are given in the text.

<sup>a</sup> References 24 and 49.

 $T_B$  must vanish. In the larger K, H, P space the domain of B is a line of bicritical points which terminates at zero temperature at the multicritical point Q. These expectations are confirmed in the physical space P = 0 by the Monte Carlo calculation of Mihura and Landau,<sup>53</sup> a calculation which includes a second-neighbor attraction. In addition they find that the specific heat exponent of the bicritical transitions appears to be negative. This is in accord with our thermal eigenvalue  $y_T = 0.46$  of Table I from which  $\alpha = 2(1-y_T^{-1})$  is -2.3.

## IV. SUMMARY

We have constructed a simple renormalizationgroup applicable to the triangular Ising model (1.2)with either ferromagnetic or antiferromagnetic coupling. Our recursion relations are based on three interpenetrating cells of three spins each and are particularly chosen to preserve the symmetry of the antiferromagnetic (Potts) phases. The calculated antiferromagnetic phase diagram at vanishing three-spin coupling is in excellent agreement with exact and Monte Carlo results and provides a good one-parameter (J) fit via the latticegas model to experimental data on <sup>4</sup>He submonolayers. We compute heat-capacity curves which (with no additional parameters) are in reasonable agreement with <sup>4</sup>He data near and below the ordering transition. Finally, we have mapped out for the first time a full global (K, H, P) phase diagram. In addition to the antiferromagnetic phenomena, this contains ferromagnetic and tricritical behavior, plus the Baxter-Wu transition at H = K = 0. Our results for  $K \ge 0$  (ferromagnetic region) are numerically inferior to those for K < 0 but provide a generally plausible description. There remain, however, unresolved questions concerning the correct interconnectivity of the Baxter-Wu and ferromagnetic fixed points.

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## APPENDIX A

According to the usual equivalence<sup>8</sup> the grand free energy of the classical nearest-neighbor triangular lattice gas is related to the magnetic free energy of the corresponding Ising model by

$$-k_B T \lim_{V \to \infty} (\ln \Xi/V) = -\frac{k_B T}{v_0} \lim_{N \to \infty} \left( \frac{1}{N} \ln \operatorname{Tr} e^{-\beta \mathcal{X}_0} \right), \quad (A1)$$

with the Ising Hamiltonian  $\mathcal{K}_0$  displayed in (1.1). The heat capacity per unit area  $c_V$  of the gas at constant areal density is then related to the heat capacity per site  $c_M$  of the Ising model at constant magnetization by

$$c_{V} = (1/v_{0})(k_{B}n + c_{M})$$
 (A2)

The experimental quantity which it is conventional to display is  $C_{\nu}/k_B N_{part}$ , the constant-area heat capacity *per particle* in units of  $k_B$ ,

$$C_{v}/k_{B}N_{part} = v_{0}c_{v}/nk_{B} = 1 + c_{M}/nk_{B}.$$
 (A3)

The first term on the right-hand side of (A3) is the heat capacity which arises from the translational kinetic energy of a noninteracting classical gas, while the second term is the so-called "configurational" heat capacity due to the pair interactions.

Equation (A3) correctly represents the high-temperature (ideal classical d=2 gas) asymptote of the experimental data, since  $c_M \rightarrow 0$  as  $T \rightarrow \infty$ ; however,  $c_M$  also approaches zero at low temperature, so (A3) gives  $C_v/k_B N_{part} \rightarrow 1$  as  $T \rightarrow 0$  in contradiction to both the third law and experiment. This defect is inherent in the *classical* lattice-gas model, which underlies the equivalences given after (1.1). This classical picture requires that the interparticle spacing be much greater than the thermal wavelength  $\lambda_T$ . Examination of the parameters of the helium-on-Grafoil system near the  $n \approx \frac{1}{3}$  ordering transition reveals that  $\lambda_T$  is already quite comparable to the interparticle spacing (4-5 Å), so the low-temperature side of the transition is certainly *non*classical, and the model appears inapplicable.

One can come to terms with this difficulty at least heuristically by arguing that the dominant quantum effect should be the effective freezing out of the translational kinetic energy. This suppresses the first term in (A3), leaving

$$C_v/k_B N_{\text{part}} = c_M/nk_B$$
 (low temperature), (A4)

which we have used in the text (Sec. III A, Figs. 7-11) in making contact with experiment. The good agreement obtained near and below the ordering transition lends credence to the correspondence (A4) but, of course, leaves moot the question of how the translational term should be reintroduced at higher temperatures.

An additional argument for the validity of (A4) can be constructed along the following lines: At low temperatures and for densities appropriate to the ordering transitions the adatoms are well localized about some set  $\{R_i\}$  of adsorbtion sites. The motion consists in small oscillations about these sites and can be treated in the harmonic phonon approximation, keeping in mind that the normal mode frequencies  $\omega_s(\{R_i\})$  depend on which adsorbtion sites are occupied. The full quantum-

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*mechanical* expression for the energies of the lowlying states of this system is

$$E(\{R_i\}, \{n_s\}) = U_0(\{R_i\}) + \hbar \sum_s \omega_s(\{R_i\})(n_s + \frac{1}{2}).$$
(A5)

 $U_0$  is the rigid lattice energy. Both  $U_0(\{R_i\})$  and  $\omega_s(\{R_i\})$  reflect the substrate potential in addition to the interparticle forces. Because of the substrate potential, the phonon spectrum may be expected to have a gap comparable to the Einstein frequency of the substrate wells. A crude estimate<sup>54</sup> puts this frequency at  $\geq 15$  K, so the excited state  $n_s \geq 0$  may be expected to be frozen out near and below the ordering temperature (~3 K). Under these conditions the canonical partition function for  $N_{part}$  adatoms is

$$Z_{N_{\text{part}}} = \sum_{\{R_i\}} \exp\left[-\beta \left(U_0(\{R_i\}) + \frac{1}{2}\hbar \sum_{s} \omega_s(\{R_i\})\right)\right].$$
(A6)

If the density of phonon states  $g(\omega)$  is not strongly dependent on the adatom positions  $\{R_i\}$ , the zeropoint energy contributes a temperature-independent constant to the free energy. The term involving U leads directly to (A4) via the usual lattice-gas correspondence.

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- <sup>19</sup>M. Nauenberg and B. Nienhuis, Phys. Rev. Lett. <u>33</u>, 944 (1974); <u>33</u>, 1598 (1974).
- <sup>20</sup>B. Nienhuis and M. Nauenberg, Phys. Rev. B <u>11</u>, 4153 (1975).
- <sup>21</sup>B. Nienhuis and M. Nauenberg, Phys. Rev. B <u>13</u>, 2021 (1976), which studies the Ising antiferromagnet on the square lattice.
- <sup>22</sup>Of course, other interactions such as second-neighbor

pair interactions are also introduced. For the transitions we are considering it is expected that these remain small and do not play an important role. See also Ref. 9.

- <sup>23</sup>R. J. Baxter and I. G. Enting, J. Phys. A <u>9</u>, L149 (1976).
- <sup>24</sup>R. J. Baxter and F. Y. Wu, Phys. Rev. Lett. <u>31</u>, 1924 (1973); Aust. J. Phys. 27, 357 (1974).
- <sup>25</sup>D. Imbro and P. C. Hemmer, Phys. Lett. A <u>57</u>, 297 (1976).
- <sup>26</sup>M. P. N. den Nijs, A. M. M. Pruisken, and J. M. J. van Leeuwen, Physica (Utr.) A <u>84</u>, 539 (1976).
- <sup>27</sup>The treatment of Ref. 26 in particular appears to involve 16 couplings and is correspondingly complex.
- $^{28}$  J. M. J. van Leeuwen, Phys. Rev. Lett. <u>16</u>, 1056 (1975).  $^{29}$  We assume the reader to be familiar with the main
- lines of the method, as set out, for example, in Refs. 16 and 17.
- $^{30}$ M. Schick, J. S. Walker, and M. Wortis, Phys. Lett. A <u>58</u>, 479 (1976). This paper reports results for the antiferromagnetic phase boundary at P = 0.
- <sup>31</sup>F. Claro and G. D. Mahan, J. Phys. C<u>10</u>, L73 (1977);
   G. D. Mahan and F. Claro (unpublished).
- <sup>32</sup>Extension of the method to larger cells is quite possible, e.g., M. Schick and J. S. Walker (unpublished) have used three seven -spin asterisk shaped cells.
  However, extension to a larger cell cluster with our spin cell is problematical: Cells must be added in multiples of three to maintain sublattice symmetry. Furthermore, because the coverage of the lattice shown in Fig. 3 is nonuniform, the renormalized couplings will be anisotropic after the first iteration.
- <sup>33</sup>Of course, a cluster containing more than three cells would generate additional interactions. See Refs. 26, 27, and 22.
- <sup>34</sup>A. N. Berker and M. Wortis, Phys. Rev. B <u>14</u>, 4946 (1976).
- <sup>35</sup>We thank Professor M. E. Fisher for pointing out to us that although the analytic expression for the entropy given by G. Wannier, Ref. 11c, is correct, the numerical value given there is not. The correct value is given in our text.
- <sup>36</sup>This was kindly brought to our attention by Dr. Rodney Baxter.
- <sup>37</sup>D. S. Gaunt, J. Chem. Phys. <u>46</u>, 3237 (1967).
- <sup>38</sup>Rather than summing successive contributions to the free energy as in Ref. 19, we iterate recursively the *first derivatives* of the free energy back to their (trivial) fixed-point values This method converges very rapidly and has the additional advantage that only a single numerical derivative is necessary to extract the heat capacity.
- <sup>39</sup>However, M(T, H) = -M(T, -H), so  $T_c(n)$  is symmetric about  $n = \frac{1}{2}$  and one is free to study H > 0.

<sup>40</sup>M. Bretz, Phys. Rev. Lett. 38, 501 (1977).

- <sup>41</sup>The data of Ref. 40 prefers  $\overline{|J|}/K_B = 2.063$  °K, however, the difference is so small we have used (3.2) for all data.
- <sup>42</sup>Direct calculation of *u* using a Lennard-Jones 6-12 potential with  $\sigma$ =2.556 Å,  $\epsilon$ =10.22 °K (Siddon and Schick, in Ref. 9) and a nearest-neighbor distance of *r*=2.451 Å gives *u*=15 °K. However, this number is *exceedingly* sensitive to the choice of both *r* and  $\sigma$ (e.g., *r*=2.49 Å gives *u*=8 °K) because of the steepness of the potential in the core region. In particular motion about the adsorbtion site (neglected in our model) both parallel and perpendicular to the substrate surface might be expected to soften the repulsion substantially in line with our result. See Appendix A and L. M. Sander, M. Bretz, and M. W. Cole, Phys. Rev. B 14, 61 (1976).
- <sup>43</sup>M. Bretz, Ph.D. thesis (University of Washington, 1971) (unpublished).
- <sup>44</sup>M. E. Fisher, Phys. Rev. 176, 257 (1968).
- <sup>45</sup>J. P. Straley and M. E. Fisher, J. Phys. A <u>6</u>, 1310 (1973).
- <sup>46</sup>D. Kim and R. I. Joseph, J. Phys. A 8, 891 (1975).
- <sup>47</sup>T. W. Burkhardt, H. J. F. Knops, and M. den Nijs, J. Phys. A 9, L179 (1976).

<sup>48</sup>As discussed in Sec. I, the +++ "phase" is, in fact, a region of coexistence of three phases, corresponding to a different one of the three sublattices being "down."

- <sup>49</sup>B. Nienhuis and M. Nauenberg, Phys. Rev. Lett. <u>35</u>, 477 (1975).
- <sup>50</sup>This is based on  $y_T = 1.500$  from Ref. 24 plus the conjecture of  $\beta = \frac{1}{2}$  based on series, R. J. Baxter, M. F. Sykes, and M. G. Watts, J. Phys. A 8, 245 (1975).
- <sup>51</sup>The special ambiguities of linear transformations have been discussed by T. L. Bell and K. G. Wilson, Phys. Rev. B 11, 3431 (1975).
- <sup>52</sup>Reference 26 reports two calculations, one with a six-cell cluster and one with a four-cell cluster. We quote six-cell results; four-cell results are qualita-tively the same (three relevant eigenvalues) but generally less accurate. It might be expected that a three-cell calculation would give qualitatively similar results. Such a calculation has been carried out both by K. Subbaswamy and G. D. Mahan [Phys. Rev. Lett. 37, 642 (1976)] and by us. It yields the entirely erroneous conclusion that there is no Baxter-Wu transition at all!
- <sup>53</sup>B. Mihura and D. P. Landau, Ref. 9.
- <sup>54</sup>This is a crude estimate based on the data of Hagen et al., in Ref. 4, Fig. 2, who find a difference of about 20 °K in energy between the center of the adsorbtion site and the cell boundary. Note also in this connection the crucial role played by the interparticle potential in localizing the adatoms. We know that a single helium atom on graphite rides well above the substrate wells.