

# Monomer adsorption on a square lattice with first- and second-neighbor interactions

Alain J. Phares and Francis J. Wunderlich

*Department of Physics, Mendel Hall, Villanova University, Villanova, Pennsylvania 19085-1699*

(Received 2 October 1996)

We obtain the low-temperature phases and phase transitions of monomer adsorption on a semi-infinite square lattice of width  $M$ , with first- and second-neighbor interactions. With first-neighbor interactions assumed to be repulsive, and allowing second-neighbor interactions to be attractive or repulsive, six sets of surface adsorption phases have been identified. Most of the numerical results conducted up to  $M=12$  are found to fit exact closed-form expressions in  $M$ , thus allowing exact analytic extrapolations to the infinite two-dimensional case ( $M=\infty$ ). [S1063-651X(97)03103-6]

PACS number(s): 02.50.-r, 05.50.+q, 05.70.-a, 64.60.Cn

## I. INTRODUCTION

A year ago, we reported a number of crystallization patterns (phases) of monomers with nearest- (first-) neighbor interaction on a multilayered semi-infinite square lattice [1]. This article goes a step further, analyzing the more realistic model of monomer surface adsorption including nearest- and next-nearest- (second-) neighbor interactions. Lattice models have been used for a very long time; a brief summary of lattice calculations done by others can be found in Ref. [1], and the notation used here is very similar to that of Ref. [1].

The surface is a semi-infinite  $M \times N$  square lattice ( $N \rightarrow \infty$ ) in the presence of a gas containing one molecular species and the adsorbed molecules occupy one site. For this reason, we refer to them as monomers. The system is at thermal equilibrium and the chemical potential energy  $\mu$  of a monomer depends on the external gas pressure. The interaction energies of an adsorbed monomer are  $V_0$  with the lattice,  $V$  with any first-neighbor monomer at a distance  $a$ , and  $W$  with any second-neighbor monomer at a distance  $a\sqrt{2}$ . The activities associated with these three interactions are

$$x = \exp\left[\frac{\mu + V_0}{k_B T}\right], \quad y = \exp\left[\frac{V}{k_B T}\right], \quad z = \exp\left[\frac{W}{k_B T}\right], \quad (1)$$

where  $k_B$  is Boltzmann's constant and  $T$  the absolute temperature. Here the transfer matrix  $T_M^1$  for a lattice of width  $M$  is of rank  $D(M) = 2^M$ . It is recursively constructed as in Ref. [1], and we find

$$\begin{aligned} T_M^1 &= \begin{pmatrix} T_{M-1}^1 & xP_{M-1}^1 \\ T_{M-1}^2 & xyP_{M-1}^2 \end{pmatrix}, \\ T_M^2 &= \begin{pmatrix} T_{M-1}^1 & xzP_{M-1}^1 \\ T_{M-1}^2 & xyzP_{M-1}^2 \end{pmatrix} \quad \text{with } T_0^1 = T_0^2 = 1; \\ P_M^1 &= \begin{pmatrix} T_{M-1}^1 & xyP_{M-1}^1 \\ zT_{M-1}^2 & xy^2zP_{M-1}^2 \end{pmatrix}, \\ P_M^2 &= \begin{pmatrix} T_{M-1}^1 & xyzP_{M-1}^1 \\ zT_{M-1}^2 & xy^2z^2P_{M-1}^2 \end{pmatrix} \quad \text{with } P_0^1 = P_0^2 = 1. \end{aligned} \quad (2)$$

The numbers of monomers, first-neighbor monomer-monomer interactions, and second-neighbor monomer-monomer interactions per site are  $\theta_0$ ,  $\theta$ , and  $\beta$ , respectively. In the limit ( $N \rightarrow \infty$ ), these quantities are related to the largest eigenvalue  $R$  of  $T_M^1$  according to

$$\begin{aligned} \theta_0 &= \frac{x}{MR} \frac{\partial R}{\partial x}, \quad \theta = \frac{y}{MR} \frac{\partial R}{\partial y}, \quad \beta = \frac{z}{MR} \frac{\partial R}{\partial z}, \\ S &= \frac{1}{M} \ln R - \theta_0 \ln x - \theta \ln y - \beta \ln z, \end{aligned} \quad (3)$$

where  $S$  is the entropy per site divided by  $k_B$ . For finite length  $N$ , all the eigenvalues contribute to the expressions of  $\theta_0$ ,  $\theta$ ,  $\beta$ , and  $S$  in a manner discussed in Ref. [2]. For given monomer-monomer interactions  $V$  and  $W$  and with the temperature of the system set to be below a certain value as dictated by the relation

$$\frac{V}{k_B T} < -10 \Rightarrow T < \frac{(-V)}{10k_B}, \quad (4)$$

adsorption patterns are observed to occur sequentially with increasing external chemical potential  $\mu$ . The Cray C90 supercomputer of the Pittsburgh Supercomputing Center was used with EISPACK for the numerical computations.

In one dimension ( $M=1$ ), next-nearest-neighbor monomers are at a distance  $2a$  and their interaction is neglected, leaving only first-neighbor interactions. This case has an exact analytic solution and has been fully discussed in Ref. [1]. The case  $M=2$  is the only other case for which an exact analytic solution can be derived including first- and second-neighbor interactions, since the eigenvalues of  $T_M^1$  are the solutions of the secular equation

$$\begin{aligned} \{R - x(y-z)\} \{R^3 - R^2[1 + x(y+z) + x^2y^3z^2] \\ + Rx[(y+z-2)(1 + x^2y^3z^2) + xy(y^2z^2 - 1)] \\ + x^3y(yz-1)((yz+1)(y+z) - 4yz)\} = 0, \end{aligned} \quad (5)$$

where one root is immediately identified as  $x(y-z)$ . The first-neighbor interaction is repulsive ( $V < 0$ ) and, consequently, the second-neighbor interaction  $W$  must be algebraically greater whether it is repulsive or attractive ( $V < W$ ).

TABLE I. Characteristics of the phase adsorptions on square lattices of finite width  $M \geq 3$ . The quantity  $[M/2]$  refers to the integer part of  $M/2$  and the question mark stands for the lack of a closed-form expression for the entropy.

Phases	$\theta_0$	$\theta$	$\beta$	S	
				M odd	M even
$p_0$	0	0	0	0	0
$p_1$	$\frac{M-[M/2]}{2M}$	0	0	0	$(1/2M)\ln[(M+2)/2]$
$p_2$ (M even)	$(M+2)/4M$	0	$1/M$		?
$p_3$ (M even)	$(M+2)/4M$	$(M-2)/2M^2$	$2/M^2$		$(1/2M)\ln(M/2)$
$p_4$ (M even)	$(M+2)/4M$	$1/2M$	0		$(1/2M)\ln(M/2)$
$p_5$	$\frac{1}{2}$	0	$(M-1)/M$	0	0
$p_6$	$(M+2)/2M$	$3/M$	$(M-1)/M$	0	0
$p_7$ (M even)	$\frac{1}{2}$	$2\theta+\beta=(M-1)/M$			?
$p_8$	$\frac{M-[M/2]}{M}$	$\frac{3M-4[M/2]-1}{2M}$	0	0	0
$p_9$ (M even)	$(M+2)/2M$	$(M+3)/2M$	$2/M$		0
$p_{10}$ (M even)	$(M+2)/2M$	$2\theta+\beta=(M+5)/M$			?
$p_{11}$ (M even)	$\frac{3}{4}$	$(M-1)/M$	$(M-1)/M$		?
$p_{12}$ (M even > 4)	$\frac{3}{4}$	$(2M-5)/(2M-4)$	$\frac{M^2-4M+6}{M(M-2)}$		?
$p_{13}$	$\frac{2M-[M/2]}{2M}$	$\frac{3M-2[M/2]-1}{2M}$	$\frac{2M-2[M/2]-2}{M}$	0	$(1/2M)\ln[(M-2)/2]$
$p_{14}$ (M even)	$(3M+2)/4M$	$(M+1)/M$	1		$(1/2M)\ln(M/2)$
$p_{15}$	1	$(2M-1)/M$	$(2M-2)/M$	0	0

Thus  $z > y$  and the root  $x(y-z)$  is negative and cannot be the largest root of Eq. (4). Indeed, according to the Frobenius-Perron theorem, the eigenvalue of the largest modulus of the family of matrices of which the transfer matrices belong must be real and positive.

The energy per site must be continuous across a phase boundary. Thus, with  $\Delta\theta_0$ ,  $\Delta\theta$ , and  $\Delta\beta$  being the corresponding changes of  $\theta_0$ ,  $\theta$ , and  $\beta$  across a given boundary, no change in the energy per site requires

$$(\mu + V_0)\Delta\theta_0 + V\Delta\theta + W\Delta\beta = 0. \quad (6)$$

This equation has been verified to hold in all cases.

Section II provides most of the lattice configurations corresponding to the possible phases encountered for  $M > 2$ . Which phases and phase transitions are observed should depend on the first- and second-neighbor interaction energies. These questions will be answered in Sec. III. Section IV discusses the limit as  $M \rightarrow \infty$  and Sec. V is the summary and conclusion.

## II. LATTICE CONFIGURATIONS OF THE OBSERVED PHASES

With the physical constraints  $V < 0$  and  $V < W$ , numerical calculations were carried out up to and including  $M = 12$ .

The characteristics of all the phases  $p$  encountered for any width  $M$  of the lattice greater than 2 are found in Table I. The phases are ordered by increasing values of the coverage  $\theta_0$  of the lattice, and distinct phases with the same coverage are generally ordered by increasing the number of first neighbors per site. In most cases, the characteristics  $\theta_0$ ,  $\theta$ ,  $\beta$ , and  $S$  of the phases for a lattice of width  $M$  were observed to fit exactly closed-form expressions as reported in Table I. The quantity  $[M/2]$  refers to the integer part of  $M/2$  and the question marks stands for the lack of a closed-form expression for the entropy. For phases  $p_7$  and  $p_{10}$ , we obtain an exact closed-form fit for  $(2\theta + \beta)$ , but not for the separate values of  $\theta$  and  $\beta$ . With these two exceptions, the knowledge in a given phase of  $\theta_0$ ,  $\theta$ , and  $\beta$  analytically in terms of  $M$  should, in principle, allow the construction of all the corresponding lattice configurations. Samples of these configurations are provided in Figs. 1 and 2. They exclude phases  $p_7$  and  $p_{10}$  for the reason mentioned above and the trivial cases of the empty ( $p_0$ ) and the completely filled ( $p_{15}$ ) lattice. In these figures, a diagram represents one possible configuration associated with a given phase whose characteristics  $\theta_0$ ,  $\theta$ , and  $\beta$  have been determined numerically. A diagram only shows the section of the lattice whose configuration repeats throughout the lattice. We were able to enumerate all distinct

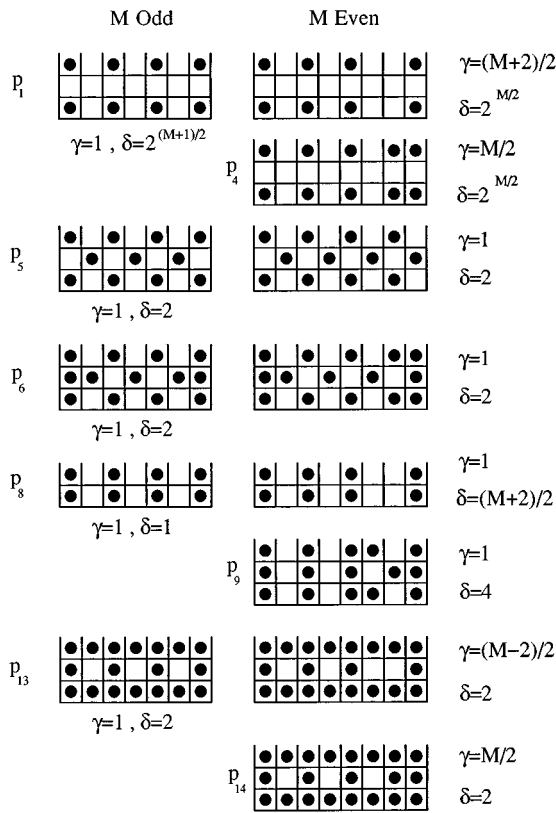


FIG. 1. Lattice configurations for phases  $p_1, p_4, p_5, p_6, p_8, p_9, p_{13}$ , and  $p_{14}$ . A lattice site is represented by a square cell of size  $a$ , which is left blank when unoccupied and has a dot in the middle when occupied.

phase configurations and derive the entropy of all but the two phases mentioned above and four others,  $p_2, p_3, p_{11}$ , and  $p_{12}$ , presented separately in Fig. 2.

As a sample of the manner in which we analytically computed the entropy of the adsorbed system in the phases of Fig. 1, we consider phase  $p_1$ . For  $M$  odd, the configuration shown is the one for which every other column of the lattice of width  $M$  is unoccupied, while the remaining  $(M+1)/2$  columns have every other site occupied. The remaining configurations having the same values of  $\theta_0, \theta$ , and  $\beta$  are obtained from this one by vertically shifting by one lattice site the monomers of one or more of these  $(M+1)/2$  columns. In this manner, we derive that the number  $C$  of all the distinct configurations of the  $p_1$  phase is  $\delta=2^{(M+1)/2}$ . The value of  $S$  follows by dividing the logarithm of  $C$  by the number  $(NM)$  of sites ( $N$  is the length of the lattice) and then taking the limit  $N \rightarrow \infty$ , or

$$S = \lim_{N \rightarrow \infty} \left( \frac{1}{NM} \right) \ln 2^{(M+1)/2} = \lim_{N \rightarrow \infty} \left\{ \left( \frac{M+1}{2NM} \right) \ln 2 \right\} = 0. \quad (7)$$

In the even case, the number of columns having every other site occupied by a monomer is  $(M/2)$ . Thus there is a total of  $\delta=2^{M/2}$  distinct configurations generated by shifting vertically by one site the monomers of one or more of these  $(M/2)$  columns. In addition, any two consecutive lattice rows of each of these  $\delta$  configurations may have their configura-

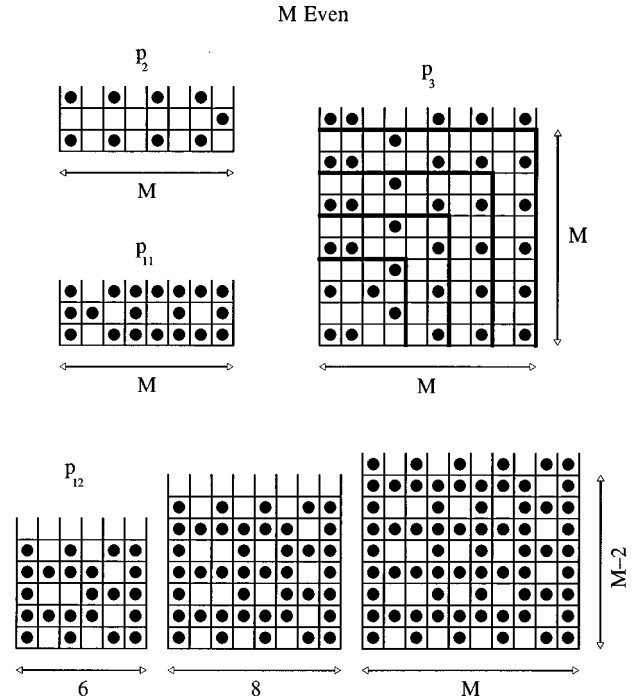


FIG. 2. Lattice configurations for phases  $p_2, p_3, p_{11}$ , and  $p_{12}$  occurring only for lattices of even width. The convention adopted in this figure is the same as in Fig. 1.

tion changed without creating additional first or second neighbors. This is done by shifting horizontally one monomer at a time by one cell, an operation that could not be done for  $M$  odd. For any two consecutive rows, the number of such restricted horizontal shifts is  $(M/2)$ , leading to a total of  $\gamma=(M+2)/2$  distinct configurations. Since there are  $(N/2)$  sections of two consecutive rows, there are  $\gamma^{N/2}$  distinct configurations in each of the previously identified  $\delta$  configurations. Thus the final number  $C$  of all possible configurations in phase  $p_1$  with  $M$  even is

$$C = \delta \gamma^{N/2}. \quad (8)$$

The value of  $S$  follows as

$$S = \lim_{N \rightarrow \infty} \left( \frac{1}{NM} \right) \ln C = \lim_{N \rightarrow \infty} \left\{ \left( \frac{1}{NM} \right) \ln \delta + \left( \frac{1}{2M} \right) \ln \gamma \right\} = \left( \frac{1}{2M} \right) \ln \gamma. \quad (9)$$

Equations (7) and (8) are easily generalized for other phases, and the corresponding values of  $\gamma$  and  $\delta$  are indicated in Fig. 1, accordingly. The theoretical values of  $S$  obtained in this manner are listed in Table I and have been numerically verified to hold within the accuracy of the Cray C90 supercomputer.

For the phases of Fig. 2, a number of configurations can easily be constructed from those presented in this figure. We could not find the total number  $C$  that reproduces the observed numerical values. However, we list in Table I the closed-form expression of the entropy for  $p_3$ ,

$(1/2M)\ln(M/2)$ , which fits exactly the numerical results for even  $M$  up to and including  $M=12$ .

The configurations provided for phases  $p_3$  and  $p_{12}$  require some explanation. Phase  $p_3$  exists for lattices of even width  $M$ . The configuration shown exhibits highlighted sections of the lattice that are  $4\times 4$ ,  $6\times 6$ , etc., up to  $M\times M$ . This indicates that the section of the lattice that repeats throughout the lattice is the highlighted  $4\times 4$  for the lattice of width  $M=4$ ,  $6\times 6$  for the lattice of width 6, and so on. Phase  $p_{12}$  appears only for lattices of even width  $M\geq 6$ . Figure 2 exhibits one possible configuration for each of  $M=6$  and 8, which is then easily generalized for higher even values of  $M$ .

### III. ENERGY REGIONS, SETS OF PHASES, AND PHASE TRANSITIONS

First- and second-neighbor adsorbate-adsorbate interaction energies  $V$  and  $W$  depend on the molecular properties of the monomers and the lattice spacing  $a$ . We were able to identify numerically six interaction energy regions. In each region, only a certain number or set of the phases are observed. In a given set, a phase transition occurs at a certain external gas pressure, or chemical potential  $\mu$ , as required by Eq. (6). For convenience, we introduce the quantities

$$\alpha = -(W/V), \quad f(M) = \frac{1}{2}(M-2)/(M-1), \quad (10)$$

where  $\alpha$  is negative for the repulsive second-neighbor interaction and positive otherwise, with  $\alpha > -1$ . The six sets of phases are ordered by increasing values of  $\alpha$ .

*Set (a).* This set corresponds to  $-1 < \alpha \leq -\frac{1}{2}$  for  $M$  odd and  $-1 < \alpha < -\frac{1}{2}$  for  $M$  even. For odd  $M$ , the order in which the phases appear with increasing  $\mu$  are  $p_0, p_1, p_8, p_{13}$  and  $p_{15}$ . The transitions have been verified to occur exactly as predicted by Eq. (6), namely,

$$\begin{aligned} p_0 \rightarrow p_1, \quad \mu + V_0 &= 0; \\ p_1 \rightarrow p_8, \quad \mu + V_0 &= -2V; \\ p_8 \rightarrow p_{13}, \quad \mu + V_0 &= -2V - 4W; \\ p_{13} \rightarrow p_{15}, \quad \mu + V_0 &= -4V - 4W. \end{aligned}$$

For even  $M$ , the phases encountered sequentially are  $p_0, p_1, p_4, p_8, p_9, p_{13}, p_{14}$ , and  $p_{15}$  and the transitions occur exactly as predicted:

$$\begin{aligned} p_0 \rightarrow p_1, \quad \mu + V_0 &= 0; \\ p_1 \rightarrow p_4, \quad \mu + V_0 &= -V; \\ p_4 \rightarrow p_8, \quad \mu + V_0 &= -2V; \\ p_8 \rightarrow p_9, \quad \mu + V_0 &= -2V - 2W; \\ p_9 \rightarrow p_{13}, \quad \mu + V_0 &= -2V - 4W; \\ p_{13} \rightarrow p_{14}, \quad \mu + V_0 &= -3V - 4W; \\ p_{14} \rightarrow p_{15}, \quad \mu + V_0 &= -4V - 4W. \end{aligned}$$

*Set (b).* This set is observed only for  $M$  odd and corresponds to  $-\frac{1}{2} < \alpha < -f(M)$ . The phases encountered sequentially are  $p_0, p_1, p_5, p_8, p_6, p_{13}$ , and  $p_{15}$  and, as predicted by Eq. (6), the transitions occur exactly at

$$\begin{aligned} p_0 \rightarrow p_1, \quad \mu + V_0 &= 0; \\ p_1 \rightarrow p_5, \quad \mu + V_0 &= -4W; \\ p_5 \rightarrow p_8, \quad \mu + V_0 &= -V(M+1) + 2W(M-1); \\ p_8 \rightarrow p_6, \quad \mu + V_0 &= +V(M-5) - 2W(M-1); \\ p_6 \rightarrow p_{13}, \quad \mu + V_0 &= -4V; \\ p_{13} \rightarrow p_{15}, \quad \mu + V_0 &= -4V - 4W. \end{aligned}$$

*Set (b').* This set is observed only for  $M$  even and corresponds to  $\alpha = -\frac{1}{2}$ . The phases encountered sequentially are  $p_0, p_1, p_3, p_7, p_{10}, p_{12}, p_{14}$ , and  $p_{15}$  and, as predicted by Eq. (6), the transitions occur exactly at

$$\begin{aligned} p_0 \rightarrow p_1, \quad \mu + V_0 &= 0; \\ p_1 \rightarrow p_3, \quad \mu + V_0 &= -V; \\ p_3 \rightarrow p_7, \quad \mu + V_0 &= -2V; \\ p_7 \rightarrow p_{10}, \quad \mu + V_0 &= -3V; \\ p_{10} \rightarrow p_{12}, \quad \mu + V_0 &= -4V; \\ p_{12} \rightarrow p_{14}, \quad \mu + V_0 &= -5V; \\ p_{14} \rightarrow p_{15}, \quad \mu + V_0 &= -6V. \end{aligned}$$

*Set (c).* This set corresponds to  $-f(M) \leq \alpha < 0$  for  $M$  odd and  $-\frac{1}{2} < \alpha < 0$  for  $M$  even. For odd  $M$ , the phases are, sequentially,  $p_0, p_1, p_5, p_6, p_{13}$ , and  $p_{15}$ . As predicted by Eq. (6), the transitions occur exactly at

$$\begin{aligned} p_0 \rightarrow p_1, \quad \mu + V_0 &= 0; \quad p_1 \rightarrow p_5, \quad \mu + V_0 &= -4W; \\ p_5 \rightarrow p_6, \quad \mu + V_0 &= -3V; \quad p_6 \rightarrow p_{13}, \quad \mu + V_0 &= -4W; \\ p_{13} \rightarrow p_{15}, \quad \mu + V_0 &= -4V - 4W. \end{aligned}$$

For even  $M$ , the phases encountered sequentially are  $p_0, p_1, p_2, p_5, p_8, p_{11}, p_{14}$ , and  $p_{15}$  and the transitions occur exactly as predicted

$$\begin{aligned} p_0 \rightarrow p_1, \quad \mu + V_0 &= 0; \\ p_1 \rightarrow p_2, \quad \mu + V_0 &= -2W; \\ p_2 \rightarrow p_5, \quad \mu + V_0 &= -4W; \\ p_5 \rightarrow p_8, \quad \mu + V_0 &= -3V; \\ p_8 \rightarrow p_{11}, \quad \mu + V_0 &= -4V; \\ p_{11} \rightarrow p_{14}, \quad \mu + V_0 &= -4V - 2W; \\ p_{14} \rightarrow p_{15}, \quad \mu + V_0 &= -4V - 4W. \end{aligned}$$

TABLE II. Characteristics of the phase adsorptions on the infinite two-dimensional square lattice.

Phases	$\theta_0$	$\theta$	$\beta$	$S$
$p_0$	0	0	0	0
$\bar{p}_1$	$\frac{1}{4}$	0	0	0
$\bar{p}_2$	$\frac{1}{2}$	0	1	0
$\bar{p}_3$	$\frac{1}{2}$	$\frac{1}{2}$	0	0
$\bar{p}_4$	$\frac{3}{4}$	1	1	0
$\bar{p}_5$	1	2	2	0

Set (d). This set corresponds to  $0 \leq \alpha < f(M)$  and is the same for  $M$  odd and even. The phases encountered sequentially are  $p_0, p_5, p_6$ , and  $p_{15}$  and, as predicted by Eq. (6), the transitions occur exactly at

$$p_0 \rightarrow p_5, \quad \mu + V_0 = -2W(M-1)/M;$$

$$p_5 \rightarrow p_6, \quad \mu + V_0 = -3V;$$

$$p_6 \rightarrow p_{15}, \quad \mu + V_0 = -4V - 2W(M-1)/(M-2).$$

Set (e). This set corresponds to  $f(M) \leq \alpha$  for both  $M$  odd and even. The phases encountered sequentially are  $p_0, p_5$ , and  $p_{15}$  and, as predicted by Eq. (6), the transitions occur exactly at

$$p_0 \rightarrow p_5, \quad \mu + V_0 = -2W(M-1)/M;$$

$$p_5 \rightarrow p_{15}, \quad \mu + V_0 = -2V(2M-1)/M - 2W(M-1)/M.$$

Sets (b), (c), (d), and (e) each have a boundary depending on  $M$ , namely,  $|\alpha| = f(M)$ . Solving this equation for  $M$  gives

$$M_0 = (2 - 2|\alpha|)/(1 - 2|\alpha|). \quad (11)$$

It is therefore possible that, for a given molecular species and a given lattice substrate, a different set of phases may be observed depending on the width of the lattice. For example, the (b) set of phases occurs for  $M$  odd and for  $-\frac{1}{2} < \alpha < -f(M)$ , for as long as  $M < M_0$ . On increasing the odd value of the lattice width, one observes the change from the (b) set to the (c) set. Similarly, the (d) set occurs if  $0 \leq \alpha < f(M) \leq \frac{1}{2}$  and will be observed for  $M \geq M_0 > 2$ ; on decreasing the lattice width, it is possible to observe the change from the (d) set to the (e) set when  $M$  reaches the range  $M_0 > M > 2$ . As expected, the  $\alpha=0$  case with no second-neighbor interaction reproduces the set of phases reported in Ref. [1].

#### IV. THE INFINITE TWO-DIMENSIONAL LATTICE

We gradually increase the lattice width  $M$  to reach the infinite two-dimensional limit. In this limit, one observes the merging of the following phases:  $p_1, p_2, p_3$ , and  $p_4$  into phase  $\bar{p}_1$ ;  $p_5$  and  $p_6$  into phase  $\bar{p}_2$ ;  $p_7, p_8, p_9$ , and  $p_{10}$  into phase  $\bar{p}_3$ ; and, finally,  $p_{11}, p_{12}, p_{13}$ , and  $p_{14}$  into phase  $\bar{p}_4$ . The full coverage  $p_{15}$  phase reaches the limit  $\bar{p}_5$ . With the exception of phases  $p_7$  and  $p_{10}$ , all other mergers are evident from the list of Table I and the lattice configurations of Figs. 1 and 2. The phases predicted to exist on the infinite two-dimensional lattice are listed in Table II.

Sets (a) and (b') merge into a single set ( $\bar{a}$ ) made of phases  $p_0, \bar{p}_1, \bar{p}_3, \bar{p}_4$ , and  $\bar{p}_5$ . We predict set ( $\bar{a}$ ) to occur when  $-1 < \alpha \leq -\frac{1}{2}$ , with phase transitions at

$$p_0 \rightarrow \bar{p}_1, \quad \mu + V_0 = 0;$$

$$\bar{p}_1 \rightarrow \bar{p}_3, \quad \mu + V_0 = -2V;$$

$$\bar{p}_3 \rightarrow \bar{p}_4, \quad \mu + V_0 = -2V - 4W;$$

$$\bar{p}_4 \rightarrow \bar{p}_5, \quad \mu + V_0 = -4V - 4W.$$

As noted in Sec. III, as  $M$  increases, if  $\alpha$  is initially in the range for which the (b) set of phases occurs, then, when  $M$  exceeds the value  $M_0$ ,  $\alpha$  is in the range of the (c) set. Thus, when  $\alpha$  is in the range  $-\frac{1}{2} < \alpha < 0$ , we predict that the (c) set of phases will reach the limit (b), which is made of the phases  $p_0, \bar{p}_1, \bar{p}_2, \bar{p}_4$ , and  $\bar{p}_5$ , with phase transitions at

$$p_0 \rightarrow \bar{p}_1, \quad \mu + V_0 = 0;$$

$$\bar{p}_1 \rightarrow \bar{p}_2, \quad \mu + V_0 = -2W;$$

$$\bar{p}_2 \rightarrow \bar{p}_4, \quad \mu + V_0 = -4V;$$

$$\bar{p}_4 \rightarrow \bar{p}_5, \quad \mu + V_0 = -4V - 4W.$$

The (d) and (e) sets correspond to second-neighbor attraction  $0 \leq \alpha$ . In the infinite limit, they merge into a ( $\bar{c}$ ) set containing phases  $p_0, \bar{p}_2$ , and  $\bar{p}_5$ , with phase transitions at

$$p_0 \rightarrow \bar{p}_2, \quad \mu + V_0 = -2W;$$

$$\bar{p}_2 \rightarrow \bar{p}_5, \quad \mu + V_0 = -4V - 2W.$$

#### V. SUMMARY AND CONCLUSION

All low-temperature adsorption phases of a single species of monomers on a square lattice infinite in length and of finite width  $M$  have been identified. Six sets of possible phases are observed. These sets depend on the relative value of the second- to the first-neighbor interaction energy, while assuming the first-neighbor interaction to be repulsive and allowing the second-neighbor interaction to be either repulsive or attractive, as is often the case experimentally [3]. The absence of a second-neighbor interaction discussed in Ref. [1] is recovered as a special case. Since most numerical results fit exact analytic expressions in terms of  $M$ , it is possible to predict the behavior of monomer adsorption on the infinite two-dimensional lattice by taking the limit as  $M$  goes to infinity. Finite width lattices are a representation of crystal surfaces with terraces having a finite width. A particularly interesting feature of this lattice model is to exhibit different adsorption phases depending on the lattice width. Indeed, it has been observed experimentally that adsorption patterns on terraces vary with the width of the terrace [3]. Another feature of the model is to show that a connection exists between the series of phases observed at different external gas pressures and the relative value of the second- to the first-neighbor interaction energy. Experimentally, from the knowledge of the external gas pressure and the heat of ad-

sorption of a given molecular species on a given crystal surface, one determines the values of the chemical potential  $\mu$  and the lattice interaction energy  $V_0$ . This model shows that the external gas pressure at which a phase transition occurs is simply related to  $V_0$  and to first- and second-neighbor interaction energies  $V$  and  $W$ . Therefore, it suggests that knowledge about short-range adsorbate-adsorbate interaction ener-

gies is possible by identifying adsorption phases and the conditions under which a transition occurs between phases.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the support from the NSF and the Pittsburgh Supercomputing Center, Grant No. PHY910014P.

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- [1] A. J. Phares and F. J. Wunderlich, *Phys. Rev. E* **52**, 2236 (1995).  
[2] A. J. Phares, *J. Math. Phys.* **25**, 1756 (1984).

- [3] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).