Journal of Statistical Physics, Vol. 74, Nos. 1/2, 1994

Computer Simulation of Random Sequential Adsorption of Two Interacting Species on a Lattice

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Received June 24, 1993; final August 25, 1993

A computer-simulation model is introduced to study the variation in the coverage and porosity in a binary system by random sequential adsorption on a periodic square lattice. We study the effects of the range of the repulsive interaction between unlike species and of the probability of deposition of each particle type. For all choices of the interaction range there is a minimum in the total coverage of the lattice which occurs for equal deposition probability of the two species. The saturation coverage decreases on increasing the range of the interaction. For proper choices of the parameters of the model, regimes exist in which either pores or particles of one type form an infinite percolating network.

KEY WORDS: Random sequential adsorption; coverage; percolation.

Many physical, chemical, and biological processes involve the adsorption of objects onto a substrate without subsequent diffusion or desorption.[1-3] These phenomena have been studied using random sequential adsorption (RSA),[4-13] an irreversible process in which objects are adsorbed one at a time subject to the condition that they do not overlap previously deposited objects. RSA in one dimension, also known as the car parking problem,[4] has been used to model the binding of ligands on polymer chains.[1] In two dimensions, RSA is related to the adsorption of small molecules, proteins, and polymers on surface.[2,3] One-dimensional RSA is well understood and exact results are available for some of the adsorption processes, while in

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0022-4715/94/0100-0457$07.00/0

two dimensions the majority of studies are carried out via computer simulations. Of primary interest in these simulations is the coverage[3–13] of the surface as a function of time and its long-time limiting value, i.e., jamming coverage. The effect of the shape of the adsorbant particles on the jamming coverage has been studied extensively. For example, in the RSA of unoriented rectangles with aspect ratio α, the jamming coverage has a maximum at $\alpha \approx 2$ and varies as $\alpha^{-0.22}$ as $\alpha \to \infty$.[7] The saturated coverage of a lattice by adsorption of constrained random chains shows a power-law dependence on the length L_c of the chain as $L_c^{-0.27}$.[14]

The aim of our work is to extend the study of RSA to systems in which two interacting species are allowed to be adsorbed on the same surface. To simplify the simulations and to isolate the effects that are due to the interaction between different species, the particles are treated as point particles which are randomly deposited on the sites of a periodic square lattice. The deposited particle is chosen to be type A with probability p_A and type B with the complementary probability $1 - p_A$. A particle is successfully adsorbed on the surface if the site is both unoccupied and outside the range of interaction of sites occupied by particles of the other type. For example, if we consider the range of interaction to be limited to nearest-neighbor sites, a particle of type A can be adsorbed on an empty site only if none of the adjacent sites are occupied by particles of type B. Similarly, type B particles cannot be adsorbed on sites adjacent to those occupied by type A particles. The repulsive interaction between the two species makes the particles of types A and B immiscible. The surface created by adsorption in this manner consists of isolated clusters of particles of each type separated by clusters of empty sites or voids. The surface is considered to be saturated when t_s consecutive attempts to adsorb a particle are unsuccessful. In our simulations, t_s is typically chosen to be of the order of magnitude of the number of lattice sites. The saturated coverage of the lattice is defined as $\Phi_c = N_{\text{occ}}/N$, where N_{occ} is the number of sites occupied by particles of either type and N is the total number of sites. The porosity[15] of the surface is related to the coverage by $\Phi_p = 1 - \Phi_c$. Fractional coverages of the lattice by each particle type are defined as $\Phi_c(A) = N_{\text{occ}}(A)/N$ and $\Phi_c(B) = N_{\text{occ}}(B)/N$, where $N_{\text{occ}}(A)$ and $N_{\text{occ}}(B)$ are the number of sites occupied by particles of types A and B, respectively.

Simulations were carried out in which both the range of the repulsive interaction between unlike species and the deposition probability for particles of type A were varied. From these simulations it is possible to determine the total and fractional coverages of the lattice and properties of the connectivity of the clusters[16] as a function of these two variables. The interaction range is increased discretely by including additional shells of lattice sites in the repulsive neighborhood of a particle. For example, if we

consider a given site to be located at coordinates (0, 0), the first shell of neighbors includes the sites (1, 0), (0, 1), (−1, 0), and (0, −1), the second shell of neighbors includes the sites (1, 1), (1, −1), (−1, −1), and (−1, 1), etc.

Typical snapshots of the saturated surface are shown in Fig. 1. Figure 1a corresponds to a surface grown with nearest-neighbor interactions and $p_A = 0.5$, Fig. 1b to eighth-neighbor interactions with $p_A = 0.5$,

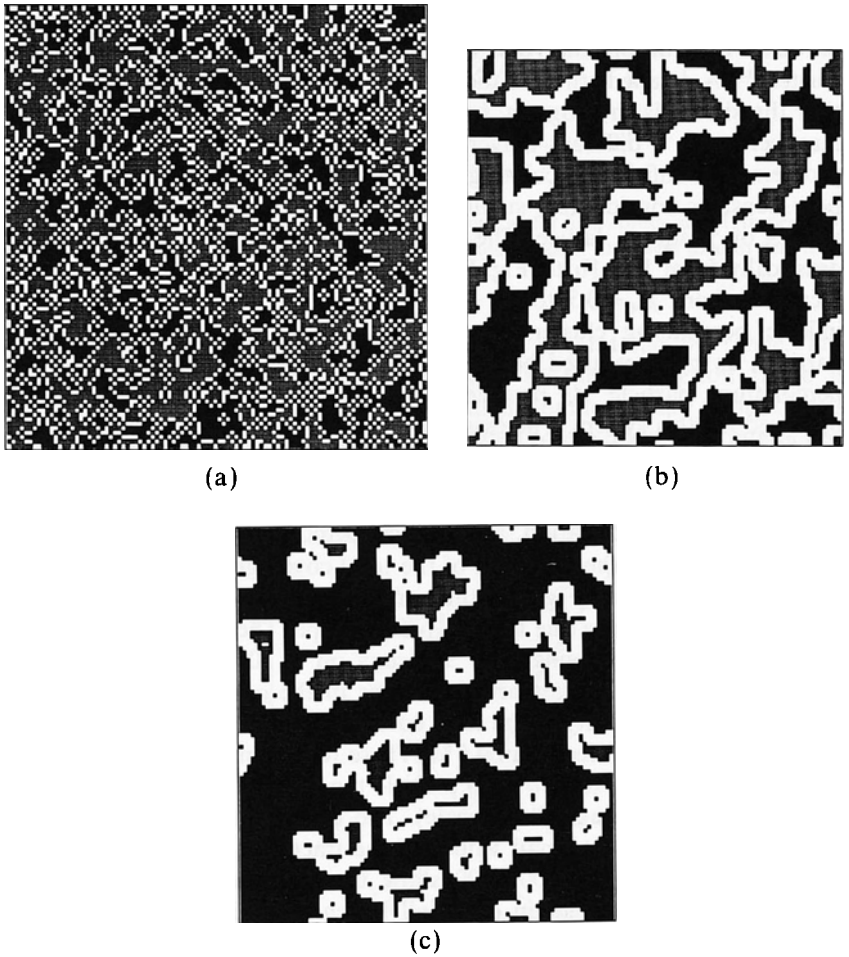

Fig. 1. Snapshots of saturated surface obtained from the binary deposition model on a 100 × 100 square lattice. Particles of type A, type B, and voids are represented by black, gray, and white squares, respectively. (a) $p_A = 0.5$ and nearest-neighbor interactions. (b, c) Interactions up to eighth neighbors and values for p_A of 0.5 and 0.7, respectively.

and Fig. 1c to eighth-neighbor interactions with $p_A = 0.7$. In Fig. 1a the distribution of cluster sizes for both types of particles appears to be rather wide, with clusters of each type interdispersed within each other. Pores, on the other hand, exhibit a narrow size distribution and are distributed homogeneously across the surface. Increasing the range of interaction to include eighth neighbors drastically alters the appearance of the surface. The clusters of each particle type are typically much larger than in the case where only nearest-neighbor interactions are included and exhibit a much larger range in size, with the smallest clusters consisting of single isolated particles. In addition, the voids can be seen to form an infinite percolating cluster.[16] A detailed study of the cluster size distributions and the percolation thresholds is in progress, but it is believed that the pore percolation may belong to a different universality class than the standard percolation problem. The infinite percolating cluster is very ramified and it appears at pore densities considerably smaller than the percolation threshold for one species on a square lattice. The appearance of the surface again changes drastically from Fig. 1b to Fig. 1c as the type A deposition probability is increased from $p_A = 0.5$ to $p_A = 0.7$. The type A particles now form an infinite percolating cluster. Identical behavior is observed for type B particles as p_A is reduced below 0.5. All four percolation regimes, i.e., no percolation, particle A, particle B, and void percolations, have been observed for this system. The existence of a threshold interaction range has been shown for the void percolation, but more extensive studies are required to determine if this system possesses tricritical points between no percolation, pore percolation, and particle percolation.

Figure 2 shows the variation of the total coverage with p_A for various interaction ranges and Fig. 3 is the corresponding plot for the fractional coverages of the surface due to each particle type. The results are obtained for each case by averaging over 100 runs on a 100×100 lattice. Error estimates based on the standard deviations in the coverages indicate that the maximum uncertainty in the total coverage is less than 0.5% and in the fractional coverages is less than 4.5%. These results imply that the fluctuations in the coverages due to each particle type (small scale) are smoothed out in the total coverage (large scale). The uncertainties in the fractional coverages are largest at small values of the fractional coverages. Calculations on lattices of size 200×200 show that for the interaction ranges considered our results remain essentially unchanged, i.e., finite-size effects are not present. The saturation coverage shows a minimum at $p_A = 0.5$ for all interaction ranges and is symmetric about this minimum; $\Phi_c(p_A = 0.5 + x) = \Phi_c(p_A = 0.5 - x)$ with $0 \leqslant x \leqslant 0.5$. Figure 3 shows that the fraction of sites occupied by A and B have a complementary dependence on p_A as expected. The minimum value of the saturation

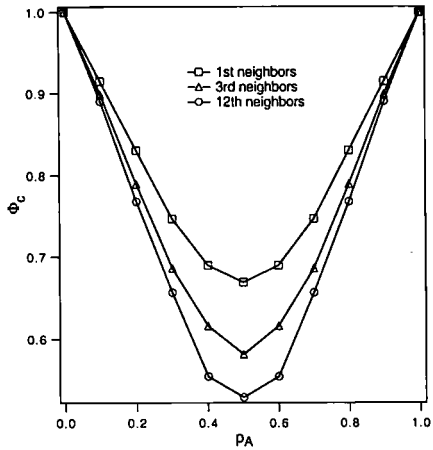

Fig. 2. Variation of the total saturation coverage with p_A for first-, third-, and 12th-neighbor interactions. The substrate size is 100×100, and 100 independent runs were used to determine the average saturation coverage.

coverage is shown in Fig. 4 as a function of the interaction range. The coverage of the lattice generally decreases as the interaction range is increased, but the coverage does show small nonmonotonic variations as particular shells of neighboring sites are added to the domain of interacting sites. We believe that the irregularities in the total coverage at $p_A = 0.5$ are

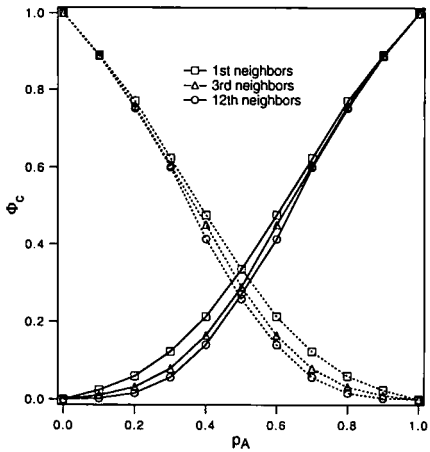

Fig. 3. Fraction of sites occupied by particles A (solid lines) and B (broken lines) at the saturation coverage as a function of p_A for first-, third-, and 12th-neighbor interactions. The statistics are the same as in Fig. 2.

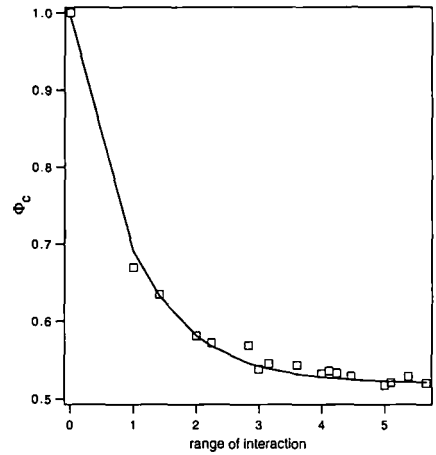

Fig. 4. Minimum value of the saturation coverage versus the range of interaction. Data points correspond to $p_A = 0.5$. Solid line is the best-fit exponential function $\Phi_c = 0.52 + 0.475 \exp(-1.021r)$.

an artifact of the lattice and should vanish in a continuum representation of the model. The total coverage of the lattice asymptotically approaches a value of approximately 0.52 for large interaction lengths. This result implies that the increased distance between clusters of dissimilar types for longer interaction ranges is balanced by an increase in the cluster sizes. For adsorption on a lattice with unit spacing between sites, the total coverage of the lattice as a function of the range of the interaction is described by the exponential function $\Phi_c = 0.52 + 0.475 \exp(-1.021r)$.

ACKNOWLEDGMENTS

R.B.P. acknowledges support from the Navy-ASEE summer research program. R.S.S. was supported by the Office of Naval Technology as an ONT postdoctoral fellow.

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Communicated by D. Stauffer