October 1992

Collective Effects in Random Sequential Adsorption of Diffusing Hard Squares

Jian–Sheng Wang

Department of Physics, Hong Kong Baptist College, 224 Waterloo Road, Kowloon, Hong Kong

Peter Nielaba*

Institut für Physik, Universität Mainz, Staudingerweg 7, D–6500 Mainz, Germany

Vladimir Privman

Department of Physics, Clarkson University, Potsdam, New York 13699–5820, USA

ABSTRACT

We study by Monte Carlo computer simulations random sequential adsorption (RSA) with diffusional relaxation, of lattice hard squares in two dimensions. While for RSA without diffusion the coverage approaches its maximum jamming value (large-time fractional coverage) exponentially, added diffusion allows the deposition process to proceed to the full coverage. The approach to the full coverage is consistent with the $\sim t^{-1/2}$ power law reminiscent of the equilibrium cluster coarsening in models with nonconserved order-parameter dynamics.

PACS numbers: 68.10.Jy, 02.50.+s, 82.65.-i

Random sequential adsorption (RSA) models have been studied extensively due to their relevance to deposition processes on surfaces [1]. The depositing particles are represented by hard-core extended objects; they are not allowed to overlap. In monolayer deposition of colloidal particles and macromolecules [2] one can further assume that the adhesion process is irreversible. Once a particle is in place its relaxation on the surface proceeds on time scales much larger than the deposition process.

However, recent experiments on protein adhesion at surfaces [3] indicate that in these systems effects of surface relaxation, presumably due to diffusional rearrangement of particles, are observable on time scales of the deposition process. The resulting large-time coverage is denser than in fully irreversible RSA and in fact it is experimentally comparable to the fully packed (i.e., locally semi-crystalline) particle arrangement. Studies of RSA with diffusional relaxation by analytical means encounter several difficulties associated with possible collective effects in hard-core particle systems at high densities (such as, for instance, phase separation), and with the possibility, in certain lattice models, of locally "gridlocked" vacant sites. The latter effect may actually prevent full coverage in some models; this matter remains an open problem at this time.

Both difficulties are not present in $1D$: there are no equilibrium phase transitions, traces of which might manifest themselves as collective effects in $D > 1$ deposition with diffusion, and furthermore diffusional relaxation leads to simple hopping-diffusion interpretation of the motion of vacant sites in $1D$ which recombine to form larger open voids accessible to deposition attempts. Thus, both extensive numerical studies and their analytical interpretation were possible in $1D$ [4]. For higher-D models however, no results were reported in the literature, to our knowledge.

In this work we report extensive numerical simulations of the RSA process with diffusional relaxation, for the lattice hard-square model [5], i.e., the square-lattice hard-core model with nearest-neighbor exclusion. This model is well studied for its equilibrium

phase transition [5] which is second-order with disordered phase at low densities and two coexisting ordered phases, corresponding to two different sublattice particle coverage arrangements, at high densities. Another simplifying feature of the hard-square model is that the only possible gridlocked (locally frozen) vacancies are parts of domain walls (see further below). As a result the coverage reaches the full crystalline limit at large times, by a process of diffusional domain wall motion leading to cluster growth reminiscent of quenched binary alloys and fluids at low temperatures [6].

The approach to the full coverage is numerically consistent with the $\sim t^{-1/2}$ law which in turn can be related to the domain size growth with time as $t^{1/2}$ as expected for order-parameter nonconserving dynamics. In the remainder of this work we first report computational details and numerical results. We then describe the domain-growth interpretation of the dynamics at high densities, as well as discuss some other collective effects observed in our simulations.

In each Monte Carlo trial of our simulation on a $L \times L$ square lattice with periodic boundary conditions, a site is chosen at random. Then with probability r we attempt to deposit a particle and with probability $(1-r)$ we try diffusion. In the case of deposition, we check if the chosen site and its four nearest-neighbor sites are all empty. If indeed they are empty the deposition is performed. The chosen site is marked as occupied. If however any of the five sites are already occupied, then the deposition attempt is rejected and the configuration remains unchanged. In the case of diffusion, which is of course possible only if there is a particle at the selected site, we choose at random with equal probability a direction (up, down, left, or right) and try to move this particle by one lattice spacing. A move is made if the targeted new site and its three nearest neighbors different from the "source" site, are all empty. If the attempted move is not possible, the particle stays at its original position.

A unit Monte Carlo time step is defined such that each lattice site is checked once

on average. This corresponds to L^2 trials as described earlier. This time scale, T, is conveniently related to the physically more interesting time t defined to have fixed deposition attempt rate per site, with varying relative diffusion attempt rate proportional to $(1-r)/r$,

$$t = rT \ . \tag{1}$$

We implement the dynamics in two different ways. The first one is a straightforward simulation of the model. However, it is inefficient at late stages, when most trials are rejected. Thus we have implemented the same dynamics with an event-driven method [7]. We keep a list of all the possible moves, deposition and diffusion. Then we pick a move according to proper probability and always carry it out. The list is then updated if necessary. The Monte Carlo time is incremented according to $\Delta T = -(\ln x)/R$, where x is a uniform random number between 0 and 1, while R is the rate of the system configuration changes in the original dynamics.

Suppose our list contains $N_{\rm depo}$ sites available for deposition and $N_{\rm diff}$ possible diffusional moves. Each occupied lattice site contributes $0, 1, 2, 3$ or 4 possible diffusional moves, while each empty lattice site contributes 0 or 1 deposition counts, all depending on the nearest-neighbor site configuration. Then R is calculated as

$$R = rN_{\rm depo} + \frac{1}{4}(1-r)N_{\rm diff} \ . \tag{2}$$

Numerical estimates were obtained for the following quantities. The coverage, $\theta(T)$, was defined as the total number of sites occupied divided by $L^2/2$. The deposition process always began with empty substrate so that the coverage θ increased from 0 to 1 at full saturation. The "susceptibility" measuring fluctuations of the magnetization, was defined by

$$\chi = L^2\left[\langle m^2\rangle - \langle|m|\rangle^2\right] , \tag{3}$$

where the average $\langle\ \rangle$ is over independent runs. The magnetization or order parameter was defined as usual [5] by assigning "spin" values $+1$ to particles on one of the sublattices and -1 on another sublattice. Empty sites on both sublattices were not counted (effectively having spin values 0). Thus the magnetization magnitude $|m|$ is defined as the difference of the number of particles deposited on two sublattices, normalized by the lattice size L^2. The values of $|m|$ are thus from 0 to $\frac{1}{2}$.

The effective domain size, $\ell(T)$, was defined as in equilibrium-model studies of cluster coarsening [6], by

$$\ell = 2L\sqrt{\langle m^2 \rangle}\ . \tag{4}$$

Here the normalization is such that a uniform state (single-domain) gives the size of the system, L.

Series of snapshots of the coverage buildup are shown in Fig. 1. As is usually done for the equilibrium hard-square system [5], particles are represented by squares of size $\sqrt{2} \times \sqrt{2}$, rotated 45° with respect to the original square lattice on which the particle centers are deposited. Particles on the even and odd sublattices (the sum of the x and y coordinates even or odd) are shown in different shades.

The time-dependence of the coverage is illustrated in Fig. 2. The general features are similar to those found in the $1D$ studies [4]. For fixed deposition rate, corresponding to the time scale t defined in (1), added diffusion [rate $\sim (1-r)/r$] always speeds up coverage growth. For high coverage, the $r < 1$ plots are reminiscent of domain growth in phase-separation models [6].

This similarity with domain growth dynamics can be made more quantitative. Let us first consider the coverage $\theta(T)$ for large times. In the case of deposition rate $r = 1$ (no diffusion), the approach to the jamming coverage $\theta(\infty) \simeq 0.728 < 1$ [8] is generally exponentially fast for lattice models [9]. With diffusion, one can always reach the full

coverage $\theta(\infty) = 1$. However, the approach to the full coverage is slow, power-law, as indicated in Fig. 2. In $1D$, the power-law behavior was related to the coverage growth at large times by the process of hopping and recombination (opening up deposition sites) of small empty regions [4].

The coverage growth mechanism for large times, in the $2D$ hard-square model is instead due to interfacial dynamics. As illustrated in Fig. 1, the void space at late times consists of domain walls separating spin-up and spin-down ordered regions. Since a typical domain has area $\sim \ell^2(T)$ and boundary $\sim \ell(T)$, we anticipate that for large times

$$1 - \theta(T) \propto \ell^{-1}(T) \; . \tag{5}$$

Indeed, $1 - \theta$ is just the void area fraction. The large-time behavior of the domain size in models with nonconserved order-parameter dynamics is typically diffusional $\sim T^{1/2}$. For $\ell(T)$ we report the direct numerical verification later. For the coverage, we found that the data roughly fit the power law,

$$1 - \theta(T) \propto T^{-1/2} \; , \tag{6}$$

for $T > 10^3$ in typical runs such as illustrated in Fig. 2. Thus, the RSA quantity $1-\theta(T)$ behaves analogously to the energy excess in equilibrium domain growth problems.

However, on careful examination we noted that the slopes obtained by least-square fits of the straight-line portions of the curves for large T were not exactly -0.5 but rather ranged from about -0.48 to about -0.52 when the rate parameter r was decreased from 0.8 to 0.01, corresponding to accelerating the relative diffusion rate. These differences could not be fully attributed to statistical errors. Presumably, they represent effects of corrections to the leading power law behavior.

The "susceptibility" χ for a given finite size L has a peak and then decreases to zero, indicating long-range order for large T; see Fig. 3. The peak location seems size-

dependent, at $T_{\rm peak} \propto L^2$; thus, it is difficult to observe for large system sizes. Since finite-size effects set in for $\ell(T) \sim L$, which given the "bulk" power law $\ell(T) \sim T^{1/2}$ leads precisely to the criterion $T \sim L^2$, we expect this maximum in fluctuations to be a manifestation of the ordering process at high densities.

For equilibrium hard squares [5], the critical-point density corresponds to coverage $\theta \simeq 0.742$. However, in all our simulations, even with the fastest relative diffusion rate (the case $r = 0.01$), we found no interesting features in $\chi(T)$ for times for which the coverage was near the critical value. Since numerical effort to reach a given coverage increases with increasing the diffusion rate at the expense of deposition attempts, there still remains a numerical challenge to observe the buildup of rounded critical-point fluctuations in χ or other quantity, for RSA with diffusion. Our present simulations turn out to be sensitive only to those collective effects which are associated with ordering at higher than critical-point coverages.

In Fig. 4, the effective domain size $\ell(T)$ is plotted vs. time for $r = 0.1$. The large-time asymptotic law is well fitted by $T^{1/2}$. As already mentioned, the late-stage dynamics of our model is similar to the kinetics of ordering by quenching an equilibrium system into a two-phase region. In fact, our model can be mapped approximately to the Ising model at zero temperature. Note that the straight-line, diagonal sections of the domain boundaries separating two phases, can not move. Only the corners can evolve due to diffusion, just like corners of interfaces in the Ising models at zero temperature evolve by order-parameter nonconserving dynamics. It has been known that the $t^{1/2}$ law is robust, independent of the number of ordered phases, dimensionality, and details of interactions in domain growth problems [6].

In summary, we found that when diffusion is introduced in random sequential adsorption processes, the system can relax to the full coverage, consistent with experiments on protein adsorption at surfaces. The approach to the full coverage is slow (power law).

The dynamics for large coverages is governed by domain growth.

This research was supported in part by the Hong Kong Baptist College Faculty Research Grant and by the DFG-Sonderforschungsbereich 262/D1 (Germany).

REFERENCES

* DFG Heisenberg Fellow

[1] For recent reviews see M.C. Bartelt and V. Privman, Int. J. Mod. Phys. B**5**, 2883 (1991); J.W. Evans, Rev. Mod. Phys. (1992), in print.

[2] J. Feder and I. Giaever, J. Colloid Interface Sci. **78**, 144 (1980); G.Y. Onoda and E.G. Liniger, Phys. Rev. A**33**, 715 (1986); N. Ryde, N. Kallay and E. Matijević, J. Chem. Soc. Faraday Trans. **87**, 1377 (1991).

[3] J.J. Ramsden, preprint (1992); see also J. Phys. Chem. **96**, 3388 (1992).

[4] V. Privman and P. Nielaba, Europhys. Lett. **18**, 673 (1992); P. Nielaba and V. Privman, Mod. Phys. Lett. B **6**, 533 (1992); V. Privman and M. Barma, J. Chem. Phys. (1992), in print.

[5] L.K. Runnels, in *Phase Transitions and Critical Phenomena*, Vol. 2, p. 305, C. Domb and M.S. Green, eds. (Academic, London, 1972).

[6] J.D. Gunton, M. San Miguel, P.S. Sahni, *Phase Transitions and Critical Phenomena*, Vol. 8, p. 267, C. Domb and J.L. Lebowitz, eds. (Academic, London, 1983); O.G. Mouritsen, in *Kinetics and Ordering and Growth at Surfaces*, p. 1, M.G. Lagally, ed. (Plenum, NY, 1990); A. Sadiq and K. Binder, J. Stat. Phys. **35**, 517 (1984).

[7] K. Binder, in *Monte Carlo Methods in Statistical Physics*, 2nd. ed., p. 1, K. Binder, ed. (Springer-Verleg, Berlin, 1986).

[8] Numerical studies of the RSA process of hard squares without diffusion were reported by P. Meakin, J.L. Cardy, E. Loh and D.J. Scalapino, J. Chem. Phys. **86**, 2380 (1987); R. Dickman, J.–S. Wang and I. Jensen, J. Chem. Phys. **94**, 8252 (1991); see also references quoted therein.

[9] V. Privman, J.–S. Wang and P. Nielaba, Phys. Rev. B**43**, 3366 (1991).

FIGURE CAPTIONS

Fig. 1. Configurations of the hard-square RSA-with-diffusion model obtained with the deposition rate parameter $r = 0.1$, at times $T = 10$, 20, 30, and 100. Particles centered on the even sublattice are shown in grey, while those on the odd sublattice are shown in black. Lattice size was 32×32.

Fig. 2. Void area fraction, $1 - \theta$, plotted against time $t = rT$ on a double-logarithmic scale, for the deposition rate parameter $r = 1$, 0.8, 0.1, 0.01, and system size 521×521. The data were averaged over 800, 600, 800, and 400 runs for $r = 1$, 0.8, 0.1, and 0.01, respectively. The dashed-dotted line has slope of $-\frac{1}{2}$.

Fig. 3. Fluctuation of the magnetization, χ, vs. time T, for system sizes $L =$4, 8, 16, 32, and 64. The deposition rate was $r = 0.1$. The data were averaged over 10^5 to 10^6 runs.

Fig. 4. Effective domain size ℓ, plotted vs. time T on a double-logarithmic scale, with $r = 0.1$ and system size 256×256. The data were averaged over 1500 runs.