Irreversible Multilayer Adsorption

P. Nielaba, V. Privman[1], J.-S. Wang[2]
Institut für Physik, Staudingerweg 7, Universität Mainz, 6500 Mainz, FRG
1) Physics Department, Clarkson University, Potsdam, NY 13699-5820, USA
2) Physics Department, Hong Kong Baptist College, 244 Waterloo Road, Kowloon, Hong Kong

Abstract. Random sequential adsorption (RSA) models have been studied [1] due to their relevance to deposition processes on surfaces. The depositing particles are represented by hard-core extended objects; they are not allowed to overlap. Numerical Monte Carlo studies and analytical considerations are reported for 1D and 2D models of multilayer adsorption processes. Deposition without screening is investigated, in certain models the density may actually increase away from the substrate. Analytical studies of the late stage coverage behavior show the crossover from exponential time dependence for the lattice case to the power law behavior in the continuum deposition. 2D lattice and continuum simulations rule out some "exact" conjectures for the jamming coverage. For the deposition of dimers on a 1D lattice with diffusional relaxation we find that the limiting coverage (100%) is approached according to the $\sim 1/\sqrt{t}$ power-law preceded, for fast diffusion, by the mean-field crossover regime with the intermediate $\sim 1/t$ behavior. In case of k-mer deposition ($k > 3$) with diffusion the void fraction decreases according to the power-law $t^{-1/(k-1)}$. In the case of RSA of lattice hard squares in 2D with diffusional relaxation the approach to the full coverage is $\sim t^{-1/2}$.

1. Kinetics of multilayer adsorption

In this section we study [1] the deposition of k-mers of length k on the linear periodic 1D lattice of spacing 1, and the deposition of square-shaped $(k \times k)$-mers on the periodic square lattice of unit spacing in 2D. The deposition site is chosen at random. The time scale, t, is fixed by having exactly L deposition attempts per unit time. We studied systems of sizes up to $L = 10^5$ in 1D and $L \times L = 1000^2$ in 2D. Various Monte Carlo runs (for $k = 2, 3, 4, 5, 10$ in 1D, and $k = 2, 4$ in 2D) went up to $t = 150$. Our numerical values are consistent with exact results for layer $n = 1$ in 1D [2].

We first report on a model with decreasing layer coverage. Only if *all* the lattice segments in the selected landing site are already covered by exactly $(n-1)$ layers, the arriving k-mer is deposited, increasing the coverage to n

($n \geq 1$). For small t, the coverage (fraction of the total volume covered by depositing particles) increases according to $\theta_n(t) \propto t^n$, as expected from the mean-field theory. Our results suggest that for lattice models the fraction of the occupied area in the nth layer, $\theta_n(t)$, approaches the saturation value exponentially, $\theta_n(t) \approx \theta_n(\infty) + B_n \exp(-t/\tau_n)$. However, the jammed state in the higher layers *in the deposition without overhangs* contains more gaps the larger is the n value. The growth in the higher layers proceeds more and more via uncorrelated "towers". We find that the jamming coverages vary according to a power law, with no length scale, reminiscent of critical phenomena,

$$\theta_n(\infty) - \theta_\infty(\infty) \approx \frac{A}{n^\phi} \tag{1}$$

Within the limits of the numerical accuracy the values of the exponent ϕ are universal for $k \geq 2$. Based on numerical data analysis we find the estimates $\phi(1\mathrm{D}) = 0.58 \pm 0.08$ and $\phi(2\mathrm{D}) = 0.48 \pm 0.06$. These values are most likely exactly $1/2$ as suggested by analytical random-walk arguments [3].

Now we report on a model with decreasing layer coverage. For layers $n > 1$ the deposition is successful only if no gaps of size k or larger are covered. Thus, the deposition is always allowed if all the "supporting" k sites in the $(n-1)$st layer are filled or have only small internal gaps. The coverage *at short times* decreases with layer number. However, for the particular deposition rule considered here the coverage in layer n eventually exceeds that in layer $(n-1)$ at larger times. This unexpected behavior was found numerically for all layers $n \leq 55$ and for all k ($k = 2, 3, 4, 5, 10$) studied. We found clear evidence of the power-law behavior (eq.(1)), with $A < 0$. We found the power ϕ to be universal for all k studied, $\phi = 0.3 \pm 0.15$. When large enough covered (by k-mers or gaps of sizes up to $k-1$) regions have formed in layer $(n-1)$, then the deposition with overhangs beyond those regions will be delayed. Thus, there will be some preference for higher density in layer n especially near the ends of the regions occupied in layer $(n-1)$. To test the above suggestion, we considered the following monolayer dimer-deposition model. We select randomly $\rho L/2$ dimers and make the ρL sites thus selected unavailable for deposition for times $0 \leq T \leq T_s$. A "sleeping time" T_s for fraction ρ of lattice sites (grouped in dimers) in monolayer deposition supposedly will model effect of disallowed overhangs over gaps of size larger than 1 in the lower layer on the multilayer deposition in layer n provided we loosely identify $T_s \propto n$. Indeed, our multilayer data suggest that times needed to build up the nth layer coverage grow linearly with n. For instance times $T_{1/2}$ defined via $\theta\left(T_{1/2}\right) = \frac{1}{2}\theta_n(\infty)$, grow according to $T_{1/2} \simeq \tau n$, where the coefficient τ is of order 1. After time T_s all the blocked sites are released and can be occupied in subsequent deposition attempts. We find that the variation of the jamming coverage $\propto T_s^{-\phi}$, $\phi \simeq 1/3$.

2. Continuum limit in RSA

We consider [1] the deposition of objects of size l on a 1D substrate of size L. R is the rate of random deposition attempts per unit time and volume. The lattice approximation is introduced by choosing the cubic mesh size $b = l/k$. The lattice deposition is defined by requiring that the objects of size l can only deposit in sites consisting of k lattice units. The late stage of the deposition (after time τ) in continuum can be described as filling up of voids small enough to accommodate only one depositing object. At this time τ, the density of those small gaps (of various sizes) will be ρ. For lattice models, a similar picture applies for $k >> Rl\tau$. Typical small gaps can be assumed [4] of sizes $k + n$ ($n = 0, 1, \ldots, k-1$) with density ρ/k at time τ, and will be filled up at the rate $Rb(n+1)$ per unit time. We will consider $t >> \tau$ so that no new small gaps are created by the filling up of large gaps. Then the density Ω of each type of the small gaps will have the time dependence $\Omega(n) = (\rho/k)\exp(-Rb(n+1)(t-\tau))$. In each deposition event with rate $Rb\Omega(n)(n+1)$ per unit time the coverage is increased by (l/L). Thus, we have $d\theta/dt \simeq \sum_{n=0}^{k-1} (Rbl\rho/k)(n+1)\exp\{-Rb(n+1)(t-\tau)\}$. After integration we get the asymptotic ($t >> \tau$) estimate, generalized to D dimensions [1]:

$$\theta_k(t) = \theta_k(\infty) - \frac{\rho l^D}{k^D} \sum_{n_1=0}^{k-1} \cdots \sum_{n_D=0}^{k-1} \exp\left\{ -\left(\frac{Rl^D t}{k^D}\right) \prod_{m=1}^{D} (n_m + 1) \right\} \quad (2)$$

We consider some special limits. For k fixed, the "lattice" long time behavior sets in for $Rl^D t >> k^D$. In this limit the $n_j = 0$ term in the sums in eq.(2) dominates: $\theta(t) \approx \theta(\infty) - (\rho l^D/k^D)\exp(-Rl^D t/k^D)$. Thus, the time decay constant increases as k^D, The continuum limit of eq.(2) is obtained for $k^D >> Rl^D t$. In this limit one can convert the sums to integrals. Recall that all the expressions here apply only for $t >> \tau$ and $k^D >> Rl^D\tau$, where $Rl^D\tau$ is a fixed quantity of order 1. Thus, the large-k and large-t conditions are simply $k >> 1$ and $t >> 1/(Rl^D)$. The latter condition allows us to evaluate the integrals asymptotically, to the leading order for large t, which yields $\theta(t) \approx \theta(\infty) - (\rho/(D-1)!\, Rt)\left[\ln\left(Rl^D t\right)\right]^{D-1}$. The asymptotic $(\ln t)^{D-1} t^{-1}$ law was derived in Ref. [4] for the continuum deposition of cubic objects.

We evaluated $\theta_k(\infty)$ numerically for system sizes $L/k = 200$. Our data suggest a fit of the form $\theta_k(\infty) = \theta_\infty(\infty) + (A_1/k) + (A_2/k^2) + \ldots$. By standard manipulations to cancel the leading $1/k$ term, followed by a further extrapolation to $k \to \infty$, we arrived at the estimate $\theta_\infty(\infty) = 0.5620 \pm 0.0002$. The errors are small enough to rule out the conjecture of Palásti [5], and its generalization for finite k, which state that the jamming coverages for the $2D$ ($k \times k$) oriented squares are equal to the *squared* jamming coverages of the corresponding $1D$ k-mer models. The latter are known exactly [2].

3. Effects of diffusional relaxation

In this section we report numerical studies [1] of the effects of diffusion on RSA in 1D and 2D. In the deposition of k-mers on a 1D linear lattice, holes of $k-1$ sites or less cannot be reached by deposition. Diffusion of the deposited objects can combine small holes to form larger landing sites accessible to further deposition attempts leading to a fully covered lattice at large times. For large times the holes are predominantly single-site vacancies which hop due to k-mer diffusion. They must be brought together in groups of k to be covered by a depositing k-mer. If the deposition rate is small, the k-site holes may be broken again by diffusion before a successful deposition attempt. Thus the process of k-mer deposition with diffusion will reach its asymptotic large-time behavior when most of the empty space is in single-site vacancies. The approach of the coverage to 1 for large times will then be related to the reaction $k\mathcal{A} \to inert$ with partial reaction probability on each encounter of k diffusing particles $\mathcal{A}$. Scaling arguments indicate that the particle density for $k \geq 3$ will follow the mean-field law $\propto t^{-1/(k-1)}$ for large times, with possible logarithmic corrections for $k = 3$ (borderline). This corresponds to $1 - \theta(t\text{-large}) = t^{-1/(k-1)}$ in deposition. Now we study the effect of diffusional relaxation in 1D dimer deposition. At each Monte Carlo step a pair of adjacent sites on a linear lattice ($L = 2000$) is chosen at random. Deposition is attempted with probability p or diffusion otherwise with equal probability to move one lattice spacing to the left or right. The time step $\Delta T = 1$ corresponds to L deposition/diffusion-attempt Monte Carlo steps. We define the time variable $t = pT$. Our Monte Carlo results were obtained for $p = 0.9, 0.8, 0.5, 0.2$. The coverage increases monotonically with $(1-p)/p$ at fixed pT. For $p < 1$ we obtain $\theta(\infty) = 1$, for $p = 1$, $\theta(T) = 1 - \exp\left\{-2\left[1 - \exp(-T)\right]\right\} \to 1 - e^{-2} < 1$. The convergence of $(1-\theta)$ to the limiting value at $t = pT = \infty$ is exponential without diffusion. Small diffusional rates lead to the asymptotically $\sim t^{-1/2}$ convergence to $\theta(p < 1, t = \infty) = 1$. For faster diffusion, the onset of the limiting behavior is preceded by the region of $\sim t^{-1}$ behavior followed by a crossover to $\sim t^{-1/2}$ for larger times. In the cases $k = 3, 4$ the large time results are roughly consistent with the mean-field relation. For all p values studied the void area is dominated by the single vacancies precisely in the regime where the mean-field law sets in. For $k = 2$ the single-site vacancies take over for $t \gtrsim 2$. For fast diffusion there follows a long crossover region from the initially mean-field to the asymptotically fluctuation behavior.

Now we report on collective effects in RSA of diffusing hard squares. In each Monte Carlo trial of our simulation on a $L \times L$ square lattice, a site is chosen at random with deposition probability p. Only if the chosen site and its four nearest-neighbor sites are all empty the deposition is performed. A diffusion move by one lattice spacing is made if the targeted new site and its nearest neighbors are all empty. Numerical estimates were obtained for the coverage and the "susceptibility" $\chi = L^2\left[\langle m^2\rangle - \langle |m|\rangle^2\right]$, where the average $\langle\ \rangle$ is over independent runs. The order parameter was defined by assigning "spin" values $+1$ to particles on one of the sublattices and -1 on another sublattice. The effective domain size, $\ell(T)$, was defined by $\ell = 2L\sqrt{\langle m^2\rangle}$. For $p = 1$, the approach of $\theta(T)$ to the jamming coverage $\theta(\infty) \simeq 0.728 < 1$ is exponentially fast. With diffusion, one can always reach the full coverage $\theta(\infty) = 1$. However, the approach to the full coverage is slow, power-law. Here the coverage growth mechanism for large times is due to interfacial dynamics. 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 $1 - \theta(T) \propto \ell^{-1}(T)$. We found that the data roughly fit the power law, $1-\theta(T) \propto T^{-1/2}$, for $T > 10^3$. Thus, the RSA quantity $1 - \theta(T)$ behaves analogously to the energy excess in equilibrium domain growth problems. The "susceptibility" χ for a given finite size L has a peak and then decreases to zero, indicating long-range order for large T. The peak location seems size-dependent, at $T_{\rm peak} \propto L^2$. 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.

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