Irreversible Multilayer Adsorption

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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 \(-1/1\) power-law preceded, for fast diffusion, by the mean-field crossover regime with the intermediate \(-1/2\) 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 \(-1/2\). In case of RSA-deposition with diffusion of two by two square objects on a 2D square lattice the coverage also approaches 1 according to the power law \(t^{-1/2}\), while on a finite periodic lattice the final state is a frozen random regular grid of domain walls connecting single site defects.
I. Introduction

In monolayer deposition of colloidal particles and macromolecules [2] one can assume that the adhesion process is irreversible. However, recent experiments on protein adhesion at surfaces [3] indicate that in biomolecular systems effects of surface relaxation, due to diffusional rearrangement of particles, are observable on time scales of the deposition process. The resulting large-time coverage is denser than in irreversible RSA and in fact it is experimentally comparable to the fully packed (i.e., locally semi-crystalline) particle arrangement. Experimental studies of multilayer deposition have been reported recently [4] with emphasis on the effects of particle-particle and particle-surface interactions.

II. Random Sequential Adsorption

In this section we survey studies [5] of the deposition of k-mers of length k on the linear periodic 1 D lattice of spacing 1, and the deposition of square-shaped (k x 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 $L^D$ deposition attempts per unit time. We studied systems of sizes up to $L = 10^5$ in 1 D and $L \times L = 1000^2$ in 2D. Various Monte Carlo runs (for k = 2, 3, 4, 5, 10 in 1 D, and k = 2, 4 in 2 D) went up to $t = 150$. Our numerical values are consistent with exact results for layer $n = 1$ in 1 D [6].

We first focus 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 ≥ 1). For small $t$, the coverage (fraction of the total volume covered by depositing particles) increases according to $\theta_n(t) \propto t^\phi$, 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, $\theta_n(t) = \theta_n(\infty) + B_n \exp(-t/t_\tau)$. 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,

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

Within the limits of the numerical accuracy the values of the exponent $\phi$ are universal for $k \geq 2$. Based on numerical data analysis we find the estimates $\phi(1D) = 0.58 \pm 0.08$ and $\phi(2D) = 0.48 \pm 0.06$. These values are most likely exactly 1/2 as suggested by analytical random-walk arguments [7].

Next we consider a model with increasing 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 $k = 2$, 3, 4, 5, 10 studied. We found clear evidence of the power-law behavior (Eq. (1)), with $A < 0$. We found the power $\phi$ 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 $\rho L$ sites thus selected unavailable for deposition for times $0 \leq T \leq T_s$. A “sleeping time” $T_s$ for fraction $\rho$ 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 $\theta(T_{1/2}) = \frac{1}{2} \theta_n(\infty)$, grow according to $T_{1/2} \approx n$\,where the coefficient $n$ 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 $\propto T_s^{-\phi}$, $\phi = 1/3$.

In order to study the continuum limit in RSA [5], consider deposition of objects of size l on a 1 D 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 $\tau$) in continuum can be described as filling up of voids small enough to accommodate only one depositing object. At this time $\tau$, the density of those small gaps (of various sizes) will be $\rho$. For lattice models, a similar picture applies for $k \gg R\tau$. Typical small gaps can be assumed [8] of sizes $k+n$ (n = 0, 1, ... , k-1) with density $\rho/k$ at time $\tau$, and will be filled up at the rate $Rb(n+1)$ per unit time. We will consider $t \gg \tau$ so that no new small gaps are created by the filling up of large gaps. Then the density $\Omega$ of each type of the small gap 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

$$d\theta/dt \approx \sum_{n=0}^{k-1} (Rb l / k)(n+1) \exp(-Rb(n+1)(t-\tau)).$$

After integration we get the asymptotic $(t \gg \tau)$ estimate, generalized to D dimensions [5]:

$$\theta_k(t) - \theta_k(\infty) \approx \frac{b^D}{k^D} \sum_{n=0}^{k-1} \prod_{m=1}^{D} \left( n_m + 1 \right)$$

$$\cdot \prod_{m=1}^{D} \left( n_m + 1 \right)$$

$$\exp\left\{ -\left( \frac{Rb^D t}{k^D} \right) \right\}$$

(2)
We consider some special limits. For $k$ fixed, the “lattice” long time behavior sets in for $R(t) \gg k^D$. In this limit the $n_j = 0$ term in the sums in Eq. (2) dominates: 

$$
\theta(t) \approx \theta(\infty) - (p/D)(1/k^D) \exp(-R(t)/k^D). 
$$

Thus, the time decay constant increases as $k^D$. The continuum limit of Eq. (2) is obtained for $k^D \gg R(t)$. In this limit one can convert the sums to integrals. Recall that all the expressions here apply only for $t \gg 1$ and $k^D \gg R(t)$, where $R(t)$ is a fixed quantity of order 1. Thus, the large-$k$ and large-$t$ conditions are simply $k \gg 1$ and $t \gg 1/(R(t)^D)$. The latter condition allows us to evaluate the integrals asymptotically, to the leading order for large $t$, which yields 

$$
\theta(t) = \theta(\infty) - (p/D)(1/k^D) \exp(-R(t)/k^D). 
$$

The asymptotic $(\ln(R(t)^D))^{-1/n}$ law was derived in [8] 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 $\theta_k(\infty) = \theta_0(\infty) + (A_1/k) + (A_2/k^2) + \ldots$.

By standard manipulations to cancel the leading $1/k$ term, followed by a further extrapolation to $k \rightarrow \infty$, we arrived at the estimate $\theta_0(\infty) = 0.5620 \pm 0.0002$. The errors are small enough to rule out the conjecture of Palásti [9], 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 [6].

III. RSA with Diffusional Relaxation

In this section we survey numerical studies [5] of the effects of diffusion on RSA in 1D and 2D. In the deposition of $k$-mers on a 1 D linear lattice, holes of $k - 1$ sites or less cannot be reached. 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 $k \rightarrow$ inert with partial reaction probability on each encounter of $k$ diffusing particles $\rightarrow$. 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 $1 - \theta(t)$ for $t \gg 1/(k-1)$ in deposition. Consider now the effect of diffusional relaxation in 1 D 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 $\theta(\infty) = 1$, whereas for $p = 1$, $\theta(t) = 1 - \exp[-2(1-\exp(-T))] \approx 1 - e^{-2} < 1$. 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 $t \geq 2$. For fast diffusion there follows a long crossover region from the initially mean-field to the asymptotically fluctuation behavior.

Recently, we studied 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 does deposition occur. 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” $\chi = L^2 \left< m^2 \right> - \left< m \right>^2$, where the average $\left< \right>$ 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, $l(T)$, was defined by $l = 2L \sqrt{\left< m^2 \right>}$.

For $p = 1$, the approach of $\theta(T)$ to the jamming coverage $\theta(\infty) = 0.728 < 1$ 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 $\sim L^2(T)$ and boundary $\sim l(T)$, we anticipate that for large times $1 - \theta(T) \propto l^{-4}(T)$. 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” $\chi$ 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 $T_{\text{peak}} \propto L^2$. Since finite-size effects set in for $l(T) \sim L$, which given the “bulk” power law $l(T) \sim T^{1/2}$ 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.

We also reported recently simulation results [5] for RSA with diffusion on the two-dimensional square lattice with objects occupying two by two squares of four sites. The distinctive feature of this model is the existence of locally frozen single-site defects. RSA with diffusion on a periodic lattice then leads to frozen states with domains of four different phases. The corresponding equilibrium ground states are highly degenerate [10]. With probability $p = 0.1$ here
we try particle deposition at site \((i,j)\) on a periodic square lattice of size \(L \times L\) \((L \text{ is even})\), and with probability \(1 - p\) diffusion. The deposition attempt is successful if the sites \((i,j), (i+1,j), (i,j+1), (i+1,j+1)\) are all empty. Otherwise, we try to diffuse (move) the square in one of the four directions (up, down, left, right) chosen at random, by one lattice spacing. Diffusion is successful if the move is not blocked by other squares. Due to diffusional relaxation the coverage \(\theta\) reaches almost the fully crystalline value 1 for large times, \(t \to \infty\), however, the final configuration on a finite-size lattice typically has frozen defects which are single-site and serve as points of origin of domain walls separating four different sublattice arrangements (“phases”). The defects are locally “gridlocked,” and any state that contains all the empty area in such single-site isolated defects no longer evolves dynamically. The defect lines structure is essentially a random rectangular grid. The single-site defect density \(\rho_d(t)\) decreases at least as \(1/L\), thus \(1 - \theta(\infty) \sim 1/L\), on a periodic lattice. The domain linear size squared grows \(\sim L^{1.6}\). This seems to suggest that the domain size, and possibly shape distributions are non-trivial. \(\rho_d(t)\) has a peak around \(t \approx 10\) and saturates at \(\sim 1/L\). The infinite-\(L\) envelope, obtained for \(t \approx 50\), fits a power law, \(\sim t^{-0.573 \pm 0.004}\). The empty area fraction \(1 - \theta(t)\) is proportional to \(t^{-\alpha}\), where the effective exponent \(\alpha\) decreases from 0.61 to 0.53, as \(t\) increases. Prior to saturation, i.e., asymptotically for infinite lattice, the domain growth is power law with a growth exponent near, or possibly somewhat smaller than, \(1/2\).

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References


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