An RSA study of dimers

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Abstract. The first theoretical study of a dimer adsorption process at a homogeneous surface is presented. By using the RSA algorithm, we show example monolayers, discuss estimations of random jamming coverages and measure the surface blocking function, which could be used for calculating real systems kinetics. We also find the correlation function for coverages generated and analyse the orientational ordering inside the adsorbed monolayer. The results are compared with theoretical and experimental data.

Keywords: thin film deposition (theory), disordered systems (theory), stochastic processes (theory)

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1. Introduction

Adsorption (in particular irreversible adsorption) of bio-particles at interfaces plays an extremely important role in biotechnology, medicine, chemistry and environmental technology. Some common examples occur in paper production [1], particle deposition control [2] and selective deposition of cells and viruses [3, 4]. Simultaneously, there has been much interest focused on patterned surfaces with regular shape features: circles and dots, squares, stripes and others [4]–[7]. Those works typically have been based on theoretical adsorption models calculated for convex particles like spheres, spheroids [8] and spherocylinders [9]. However, the majority of protein molecules are not convex and, therefore, there has been recent interest in the packing of concave objects [10]–[14]. It appears that particle shape and symmetry can be crucial for fundamental properties of adsorbed monolayers [15]–[18]. In this paper we study the irreversible deposition process of a dimer—the simplest, concave particle that could be used to model many bio-molecules.

Section 2 outlines the model, algorithm and parameters used during the simulation of the dimer deposition process. The next part contains results and discussion. It is focused mainly on the random maximal coverage ratio. The ratio estimation accounts for several theoretical models, including blocking function analysis. This section also describes autocorrelations and orientational ordering inside the covering layer. The paper ends with a short summary.

2. The model and simulation procedure

The adsorption process typically takes place when colloidal particles diffuse close to the surface. Due to adhesion, this process can create a film consisting of randomly adsorbed molecules. Here we focus on irreversible adsorption producing monolayers of adsorbate. The most straightforward approach to numerically simulating these processes is through...
molecular dynamics (MD). The advantages of MD are prediction accuracy and control over most environmental parameters like temperature and the diffusion constant. The main drawback is the performance. For this reason we decided to use another method known as continuum random sequential adsorption (RSA), which had been successfully applied to study colloidal systems [19]. It is based on independent, repeated attempts to add a dimer to film. The features of a single step of the numerical procedure used here are the following.

- A virtual particle was created and its position and orientation on a collector were chosen randomly, according to the uniform probability distribution.
- An test for overlapping with adsorbed earlier nearest neighbors of a virtual particle was performed. This test is based on checking whether the surface-to-surface distance between particles is greater than zero.
- If there was no overlap the virtual particle was adsorbed and added to an existing covering layer. Its position did not change during further calculations, which reflected the irreversibility of the process.
- If there was overlap the virtual particle was removed and abandoned.

Attempts are repeated iteratively. Their number is typically expressed using a dimensionless time unit:

\[ t_0 = N \frac{S_D}{S_C} \]  

where \( N \) is a number of attempts, \( S_D = 2\pi r^2 \) stands for the coverage given by a single dimer (figure 1) and \( S_C \) is a collector area. It is worth noticing that there is at least one RSA algorithm allowing faster saturation of the underlying collector [20]. It is based on tracing the uncovered area and uses this information to decrease the overlapping probability for forthcoming RSA attempts. However, we decided not to use it here, because it complicates analysis of the standard RSA kinetics, which we want to compare with previous works.

In the case of our simulations, the adsorption was stopped after \( T = 10^5 t_0 \). Collector sizes used varied from \( 20r \) to \( 200r \). Simulations were performed using fixed boundary collectors as well as collectors with periodic boundary conditions. In the first case, centres...
of both circles forming a dimer had to be inside a collector area. For each collector we
get at least 100 covering layers. The coverage ratio $\theta$ is calculated as follows:

$$\theta = \frac{n_d S_D}{S_C},$$

where $n_d$ is a number of adsorbed dimers. Typical coverages for three different values
of the coverage ratio $\theta$ are presented in figure 2. Looking at the above drawing for the
jamming coverage ($\theta \approx 0.55$), one can notice that the dimer density seems to be higher
near the collector edges. This is an undesirable effect as we are mainly interested in the
coverage ratio for an infinite collector. In order to control the systematic error caused by
finite size and boundary conditions, the whole process was simulated over different sized
collectors with fixed boundaries as well as with periodic boundary conditions. Results
shown in figure 3 suggest that the bias of a measure (deviation from a pure quadratic
fit) is less than 1% for the largest collector that we used, independently of the specific
boundary conditions used. On the other hand, for small collectors with fixed boundaries,
higher densities near collector edges can be successfully used for producing systems with
interesting optical properties such as microlenses.

Most of the results discussed later in the paper were obtained using the largest
collector ($L = 200r$) with fixed boundaries. We checked that the use of periodic boundary
conditions does not have any significant influence on the conclusions reached.

3. Results and discussion

3.1. The maximal random coverage ratio

The main purpose of this work was to determine the maximal random adsorption ratio for
dimers and compare it with results obtained for hard circles (spheres) [16], [20]–[22]. That
ratio should be specified for an infinite collector area and infinite adsorption time. Despite
controlling the error due to finite collector size, one has to deal with finite simulation times.
In particular, in the case of large collectors, it is not certain whether there is any possibility
of adsorption after the simulation time and therefore approximation of maximal coverage
depends on the RSA kinetics model (see figure 4). There have been plenty of previous
works in this area [19], [21]–[26] and the general conclusion is that asymptotically

$$\theta_{\text{max}} - \theta(t) \sim t^{-1/D}.$$  (3)
Figure 3. Number of adsorbed dimers versus collector side length. Symbols represent values taken from simulations for fixed boundaries (triangles pointing up) and for periodic boundary conditions (triangles pointing down). Lines are quadratic fits: \( n(L) = 0.086L^2 + 0.115L + 2.59 \) (the solid line for fixed boundaries) and \( n(L) = 0.086L^2 - 0.066L + 1.654 \) (the dashed line for periodic boundary conditions).

Figure 4. Coverage versus dimensionless time from (1). The dots come from the simulation. Lines represent example kinetics fits: solid: \( \theta_{\text{max}} - \theta(t) \sim t^{-1/2} \) and dashed: \( \theta_{\text{max}} - \theta(t) \sim \exp(-ct) \).

for irreversible deposition of circles or unoriented squares. \( D \) here denotes the collector dimension. The situation changes when adsorbed particles are ordered [21, 22]. For example, deposition of oriented squares for long enough time obeys the following relation:

\[
\theta_{\text{max}} - \theta(t) \sim \frac{(\ln t)^{D-1}}{t}.
\]
In the case of the present work the planar orientations of particles were chosen randomly with a uniform probability distribution. However this symmetry could be broken, because in close proximity to previously adsorbed particles there is more space for parallel aligned particles than for perpendicular aligned ones. Therefore asymptotic (3) and (4) were compared; see figure 5. Although both relations approximate the experimental data well, the fit of (3) is slightly better in terms of linear correlation coefficient. The values of $\theta_{\text{max}}$ can be obtained by interpolation of $t^{-1/2}$ and $\ln t/t$ to 0. Here they are $\theta_{\text{max}} = 0.5475$ and $\theta_{\text{max}} = 0.5449$ respectively. The difference is located within a 1% systematic margin of error arising from the finite collector size.

In order to compare our result with experiments, we analysed data obtained for the adsorption of insulin. Assuming that the insulin dimer has a mass of 11616 Da and a

![Figure 5](image-url)
size of 875 Å² one can find that \( \theta_{\text{max}} = 0.55 \) corresponds to a monolayer surface density of 1.21 mg m\(^{-2}\). Typical values from experiments are in the range of 1.3–1.6 mg m\(^{-2}\) depending on the concentration and insulin type (human, Zn-free) [27, 28]. The difference is noticeable but not significant. It can be explained by two factors: a more regular shape of the insulin dimer compared to our model (figure 1) and the fact that, depending on the concentration, the insulin particle can also appear as a monomer or hexamer. Both of these cases lead to higher coverages.

3.2. The blocking function and fluctuations in the number of adsorbed particles

In a real experiment, the adsorption kinetics depends typically on two factors: efficiency of the transport process (mainly diffusion or convection, depending on the experimental set-up) that brings the adsorbate from the bulk to the surface; and the probability of catching particles which are in close proximity [8, 23, 25, 26], [29]–[33]. Here we would like to focus on the second factor, which is described by the blocking function, also known as the available surface function (ASF). It can be easily obtained from the simulation as a ratio of successful attempts to all RSA attempts. The ASF obtained is presented in figure 6. The quadratic fit is commonly used to estimate adsorption rates at the limit of small coverages:

\[
\text{ASF}(\theta) = 1 - C_1 \theta + C_2 \theta^2.
\]

In the case of dimers, simulations show that \( C_1 = 4.77 \) and \( C_2 = 5.58 \), whereas those parameters for hard circle adsorption are \( C_1 = 4 \) and \( C_2 = 3.31 \) [25]. This shows that the available surface shrinks faster for dimers. This follows the intuition, because for successful adsorption a particle should have not only appropriate coordinates but also the right orientation.
Moreover, the ASF provides another way to estimate maximal coverage by analysing an adsorption probability. Specifically, the second fit in figure 6 suggests that the maximal coverage is equal to $\theta_{\text{max}} = 0.543$ and also provides additional support for model (3) because

$$\frac{d\theta(t)}{dt} = \text{ASF}(\theta(t)) = \left(1 - \frac{\theta(t)}{\theta_{\text{max}}}\right)^3$$  \hspace{1cm} (6)

yields

$$\theta_{\text{max}} - \theta(t) \sim t^{-1/2}. \hspace{1cm} (7)$$

Although estimating the adsorption kinetics through the ASF is straightforward and commonly adopted, there is a problem with direct measurement of the blocking function during experimentation. Therefore, researchers are likely to count density fluctuations in the number of adsorbed particles for a given coverage. Typically, those fluctuations are expressed in terms of the reduced variance of the particle number $n$ inside a specified area: $\tilde{\sigma}^2 = \sigma^2(n)/\langle n \rangle$. It can be shown that, at least in the limit of small coverages, $\tilde{\sigma}^2(\theta) = \text{ASF}(\theta)$ [34]. This comparison, in the case of our simulations, is presented in figure 7. As expected, $\tilde{\sigma}^2(\theta)$ follows ASF($\theta$) only for small coverages. For $\theta > 0.2$ the difference between them becomes significant.

### 3.3. Autocorrelations

Autocorrelation of particles is another important characteristic of the monolayer. Here we are able to measure at least two different autocorrelations. The first is a standard distribution of distance between two molecules. Results are shown in figure 8. Let us first concentrate on the reference frame given by the autocorrelation inside a monolayer built of spherical particles (plus signs in figure 8). The function has a maximum for $r = 2.0$ (the

![Figure 7. Reduced variance of adsorbed particles as a function of the coverage. Dots correspond to the simulation data, whilst the solid line is a quadratic fit (5) to ASF.](image)

![Figure 8. Autocorrelation of distance between two molecules in a monolayer built of spherical particles.](image)
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Figure 8. Autocorrelation functions. The data were analysed in two different ways. Dots represent results for the dimers themselves, whereas triangles show autocorrelations for circles, regardless of whether they are forming dimers or not. Plus signs show the reference results for circles. The inset shows the asymptotic behaviour for small $r$. The fitted line is $C(r) = -0.481 51 \ln[(r - 2)/2] + 0.356 83$.

nearest possible neighbour), then, due to the excluded volume, it approaches a minimum. Next, there is a much weaker maximum at around $r = 4$. Because of the random character of the coverage, the oscillations vanish superexponentially [20] and the functions stabilize at a value of 1, which is a result of the normalization.

The autocorrelation for dimers (circles) is different. The function rises very slowly with distance, approaching its first maximum at around $r = 3.8$. This suggests for example that there are not many dimers lying side by side, at a distance close to $r \approx 2$. Then, the correlation approaches a wide and shallow minimum at around $r = 5$. This behaviour is mainly an effect of the dimer shape. We expect that for more anisotropic molecules, for example fibrinogens, there could be no minimum at all.

Although at first it seems that autocorrelations for circles and dimers are totally different, they can be easily compared when dimer coverage is treated as if it was built up of independent circles. Here the triangle autocorrelation looks almost the same as that in the case for circles, except that the maxima and minima are sharper. This similarity could explain why maximal random coverages for circles and dimers are so close. The asymptotic behaviours are also similar. At small distances the behaviour has the universal form derived in [21, 22]:

$$C(r) \sim -\ln[(r/2 - 1)] \quad \text{for } r \to 2^+,$$

whereas for large $r$ the decay seems to be even faster than for circles.

3.4. Ordering

The non-uniform shape of a dimer provides the possibility of checking whether any orientational order appears in a monolayer. Such ordering has been widely investigated...
Figure 9. Order $S(\phi_{\text{max}})$ dependence on the collector side size. Triangles represent simulation data for fixed boundaries (triangles pointing up) and periodic boundary conditions (triangles pointing down). The dashed line is a simple analytical fit: $S(\phi_{\text{max}}) = 1.58/L + 2.45/L^2 + 0.5$.

before, but mainly using the lattice topology of the collector surface; see e.g. [35]. As mentioned in section 3.1, it could also have an influence on the kinetics of RSA.

To measure the orientational order in our continuous system, we introduce the following function determined by a dimer configuration:

$$S(\phi) = \frac{1}{N} \sum_{i=1}^{N} (x_i \cos \phi + y_i \sin \phi)^2,$$

where $(x_i, y_i)$ are coordinates of a unit vector along the $i$th molecule in a layer. It can be noted that $S(\phi)$ is an average scalar product between the molecule orientation and the direction given by the angle $\phi$. Thus, for an ideally aligned layer, $S(\phi)$ will oscillate between 0 and 1, where the maximum corresponds to the angle being parallel to the molecules and minima are reached for $\phi$ perpendicular to the direction of alignment. For pure random alignment, $S(\phi)$ will be constant and equal to 0.5. In general, the mean orientation given by the maximum $S(\phi)$ can be estimated from

$$\tan \phi_{\text{ex}} = \frac{\sum_{i=1}^{N} x_i y_i}{\sum_{i=1}^{N} x_i x_i - \sum_{i=1}^{N} y_i y_i}.$$  

The above equation is fulfilled by both the maximum $\phi_{\text{max}}$ and the minimum $\phi_{\text{min}} = \phi_{\text{max}} + \pi/2$. The dependence between the maximal value of $S(\phi)$ and the collector size is shown in figure 9. Global orders, although not very high, are strongest in small collector coverages. There could be at least two reasons for this. Firstly, if the allowed space for placing the following dimer is restricted, it is more probable that one can find enough room for parallel alignment than that one can find enough room for perpendicular alignment. Secondly, our adsorption conditions favour parallel alignment at collector borders, because the dimer is placed down only when the centres of two of the circles are touching the
surface. For small collectors, both of the effects described above are stronger; however the influence of fixed boundaries is irrelevant (figure 9). In order to determine which one of them is the more important, we analysed local ordering in large collectors. This was done by calculating the mean value of the scalar product between two dimers at a given distance. Results are drawn in figure 10. The local ordering and its range are quite small. It practically disappears when the distance exceeds 0.5. This suggests that the ordering visible in tiny collectors is mainly due to their small size.

3.5. RSA for dimers in higher dimensions

RSA for (hyper)spheres shows some universal behaviours regardless of the collector dimension [16], [20]–[22]. The best known are those described by Feder’s law (3) and the asymptotic relation for the autocorrelation function (8). Results described in previous sections show that those relations are also valid for dimers in 2D. Moreover the maximal random coverage ratio agrees with the value obtained for circles. It is of interest to consider whether this is only an accidental coincidence or whether it is a more general feature. To address this question we looked at RSA for dimers in 3D. We used as a collector a cube having side length 35 with periodic boundary conditions and the dimer was modelled by two touching spheres. The results presented were obtained from 50 independent simulation runs.

Figure 11 presents the coverage kinetics versus $t^{-1/3}$. The kinetics (3) fits well to the data. The random coverage for dimers in 3D is 0.37 and, within the margin of error, agrees with the value 0.0381 obtained earlier for spheres [20].

The autocorrelation function is presented in figure 12. Again we observe the same behaviour as in 2D and as for spheres. The decay for larger distances seems to be superexponential. On the other hand, for small $r$ the asymptotic form agrees with (8). The linear coefficients are approximately half the values published for random adsorption for spheres, in both 2D and 3D [20].
Figure 11. Coverage versus $t^{-1/3}$. Bold points are taken from the simulation. Dotted lines represent linear fits: $\theta_{\text{max}} - \theta = 0.36986 - 0.74547t^{-1/3}$.

Figure 12. Autocorrelation function for spheres, regardless of whether they are forming a dimer or not. The inset shows asymptotic behaviour for small $r$. The fitted line is $C(r) = -0.51176\ln[(r-2)/2] + 0.5384$.

4. Conclusions

The maximal random coverage for a dimer monolayer is 0.547 and, within the margin of error, this is not distinguishable from results obtained previously for the adsorption of spherical particles. Also the monolayer density autocorrelations are almost the same. On the other hand, the calculated surface blocking function (ASF) is significantly different (the $C_1$ and $C_2$ coefficients). This suggests another kinetics of adsorption; however, Feder’s law (3) is maintained. Density fluctuations can be used to successfully estimate the ASF only for small coverages. The orientational ordering is imperceptible for macroscopic collectors but could play a significant role on the microscale.

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The results presented for both maximal random coverages and the autocorrelation function suggest that random packing problems for dimers and for spheres are governed by the same rules for $D \geq 2$.

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