Random sequential adsorption of tetramers

Michał Cieśla

M Smoluchowski Institute of Physics, Jagiellonian University, 30-059 Krakow, Reymonta 4, Poland
E-mail: michal.ciesla@uj.edu.pl

Received 14 June 2013
Accepted 27 June 2013
Published 16 July 2013

Online at stacks.iop.org/JSTAT/2013/P07011
doi:10.1088/1742-5468/2013/07/P07011

Abstract. Adsorption of a tetrater built of four identical spheres was studied numerically using the random sequential adsorption (RSA) algorithm. Tetramers were adsorbed on a two-dimensional, flat and homogeneous surface. Two different models of the adsorbate were investigated: a rhomboid and a square one; monomer centres were put on vertices of rhomboids and squares, respectively. Numerical simulations allow us to establish the maximal random coverage ratio as well as the available surface function (ASF), which is crucial for determining kinetics of the adsorption process. These results were compared with data obtained experimentally for KfrA plasmid adsorption. Additionally, the density autocorrelation function was measured.

Keywords: adsorbates and surfactants (theory), colloids, bio-colloids and nano-colloids, jamming and packing

ArXiv ePrint: 1306.2965
1. Introduction

Irreversible adsorption is of major significance for many fields such as medicine and material sciences as well as pharmaceutical and cosmetic industries. For example, adsorption of some proteins is crucial for blood coagulation, inflammatory response, fouling of contact lenses, plaque formation, ultrafiltration and the operation of membrane filtration units. Moreover, controlled adsorption is fundamental for efficient chromatographic separation and purification, gel electrophoresis, and filtration, as well as the performance of bioreactors, biosensing and immunological assays.

Random sequential adsorption (RSA), since its introduction by Feder [1], has become a well established method used in numerical modelling of irreversible adsorption at first of spherical molecules and then of complex ones such as polymers or proteins, e.g. [2]–[6]. Recent studies show that, for the purposes of adsorption modelling, complex molecules can be successfully approximated using coarse-grain models [7]–[10]. For example, a coarse-grain model of fibrinogen can successfully explain the density of adsorbed monolayer for a wide range of experimental conditions [11]–[13].

This study focuses on the RSA of tetramers on a flat and homogeneous two-dimensional collector surface. The interest in this topic was aroused by the work of Adamczyk et al [14], who had experimentally measured adsorption of a KfrA plasmid and shown that it aggregates to a tetramer during adsorption. However, the tetramer structure is common for a number of substrates. Some of the latest theoretical studies in this field investigate Ag tetramer [15] and melanin [16], albeit by using the density-functional approach. On the other hand, in similar works involving RSA modelling, dimer [17, 18] and polymer adsorption [19] has been studied. The primary aim of this paper is to find the maximal random coverage ratio of monolayers built as a result of the irreversible tetramer adsorption. Additionally, I want to calculate parameters needed to estimate the kinetics of the adsorption process.
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2. Model

In this study two independent models of a tetramer are considered. In the first one spheres of radius \( r_0 \), which represent monomers, form a rhomboid (rhomboid model), whereas in the second one these spheres are placed at vertices of a square (square model); see figure figure 1.

Modelled molecules are placed on a flat homogeneous collector surface according to the RSA algorithm [1], which iteratively repeats the following steps.

1. A virtual tetramer is created. Its position and orientation on a collector is chosen randomly according to the uniform probability distribution; however, centres of all the components (see figure 1) are required to be on a collector.
2. An overlapping test is performed for previously adsorbed nearest neighbours of the virtual molecule. The test checks if the surface-to-surface distance between each of the spheres is greater than zero.
3. If there is no overlap the virtual molecule is irreversibly adsorbed and added to an existing covering layer. Its position does not change during further calculations.
4. If there is an overlap, the virtual tetramer is removed and abandoned.

The number of RSA iterations \( N \) is typically expressed in dimensionless time units:

\[ t = N \frac{S_M}{S_C}, \]

where \( S_M = 4\pi r_0^2 \) is an area covered by a single tetramer and \( S_C \) is a collector size. In these simulations, square collectors were used with a side size of \( 1000r_0 \), so \( S_C = 10^6 r_0^2 \), and the algorithm was stopped after \( t = 10^5 \).

Obtained example coverages are presented in figure 2.

The main parameter observed during simulation was a coverage ratio \( \theta \):

\[ \theta(t) = n(t) \frac{S_M}{S_C}, \]

where \( n(t) \) is a number of adsorbed molecules after time \( t \). To decrease statistical error, 100 independent RSA simulations were performed for a single model.

doi:10.1088/1742-5468/2013/07/P07011
3. Results and discussion

The main property of an adsorption layer is its maximal coverage ratio—the area covered by particles adsorbed after a long enough period of time. Moreover, the adsorption kinetics can also be measured; however, it depends not only on the properties of collector and adsorbate particles, but also on the transport process, which brings these particles to surface proximity. On the other hand, due to the finite time of the RSA simulation, the kinetics of the process has to be known to obtain appropriate values of $\theta_{\text{max}} \equiv \theta(t \to \infty)$. Therefore, both the maximal coverage ratio and adsorption kinetics should be analysed together.

3.1. Maximal random coverage ratio

The kinetics of the RSA of spheres obeys the Feder law [20, 21]:

$$\theta_{\text{max}} - \theta(t) \sim t^{-1/d},$$

where $d$ is a collector dimension and $t$ is a dimensionless time (1). The relation (3) has been proved numerically for a one- to six-dimensional space [22] and also for fractal collectors, having $d < 2$ [23], as well as for $2 < d < 3$ [24]. Feder’s law also appeared to be valid for different adsorbates like dimers [17] and polymers [19]; however, for highly anisotropic molecules, parameter $d$ grows with the number of degrees of freedom of the adsorbate particle [19, 25].

For large enough time $t$, the exponent can be measured directly from the $d\theta/dt$ dependence on $t$ using the least squares approximation method (see figure 3). It is interesting that the obtained values of parameter $d$ for both the models are significantly higher than 2, which is the expected value for spherical particles. This suggests that the orientational degree of freedom of the model of the plasmid aggregate cannot be neglected, even though the shape anisotropy in this case is quite small.

Having determined the exponent $d$ let $y = t^{-1/d}$. Then equation (3) follows to $\theta(y) = \theta_{\text{max}} - Ay$, where $A$ is a constant coefficient. Approximation of this linear relation for $y = 0$ reveals the maximal random coverage $\theta_{\text{max}} = 0.5214$ and $\theta_{\text{max}} = 0.4910$ for the rhomboid and square models, respectively. The relative error of both values is approximately 0.5%. The difference is significant but relatively small and therefore it could not be measured experimentally, as the typical error of experimental methods is at the level of 5%.
Figure 3. The dependence of the mean number of adsorbed particles on the dimensionless time. Diamonds and squares are simulation data for the rhomboid and square models, respectively, whereas solid lines correspond to power fits obtained for $t > 1000$: $dn/dt = 5714.4t^{-1.294}$ for the rhomboid model and $dn/dt = 4693.9t^{-1.299}$ for the square model. Corresponding values of exponent $d$ in (3) are $d = 3.40$ and $d = 3.34$ for the rhomboid and square models, respectively.

the cases, the maximal random coverage ratio is smaller than the $\theta_{\text{max}} \approx 0.54$ obtained for spheres [22], dimers [17] or very short polymers [19].

Adsorption of tetramers has been measured experimentally by Adamczyk et al [14]; they studied adsorption of KfrA plasmid on latex particles. KfrA plasmid is a spherical 39.22 kDa particle with a diameter of 4.5 nm [26]. However, the study has shown that KfrA aggregates. The size of the aggregate indicates that it contains four plasmids. AFM observation suggests that the aggregate can be described by the rhomboid model. Obtained values of maximal coverage ratio correspond to a surface density of 2.0–2.1 mg m$^{-2}$ of KfrA, and are almost twice as high as measured experimentally. However, KfrA plasmids have an uncompensated charge of $12e$ [14], which significantly lowers the coverage density due to electrostatic repulsion [18]. Using the effective hard particle concept introduced by Barker et al [27], behaviour of particles interacting according to a short-range potential can be approximated by hard particle behaviour, whose size is uniformly increased by the increment $h$, which is often referred to as the effective interaction range. As the effective size of a particle grows its area is increased, hence the effective coverage ratio should satisfy the following equation [28]:

$$\theta_{\text{eff}} = \frac{\theta_{\text{max}}}{(1 + h/a)^2},$$

where $\theta_{\text{eff}}$ is the measured coverage for interacting particles and $a$ is the original size of the particle. The ratio $H = h/a$ can be treated as the dimensionless effective range of interactions, characterizing the repulsive double-layer interaction, and depends on electrostatic properties of the particles as well as dielectric properties of the solution [28, 29]. To match the experimental values of the saturated random coverage [14], the parameter $H$ should be equal there to 0.39 for the rhomboid model and 0.35 for the square one.
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3.2. Adsorption kinetics

Adsorption kinetics is governed by two factors. The first one is the transport process shifting molecules to surface proximity. As it depends on a given experiment’s conditions, it hardly enters the general theoretical analysis. The second factor is the probability of adsorption; it decreases in time due to the diminishing area of uncovered collector surface. The dependence between adsorption probability and temporary coverage ratio is known as the available surface function (ASF), and it can be easily determined from the RSA simulation. Its dependence on normalized coverage $\bar{\theta} = \theta/\theta_{\text{max}}$ is shown in figure 4. At the limit of low coverage, $\text{ASF}(\theta)$ is commonly approximated by a quadratic fit [6, 4, 28]:

$$\text{ASF}(\theta) = 1 - C_1 \theta + C_2 \theta^2 + o(\theta^3).$$ (5)

The expansion coefficient $C_1$ corresponds to the surface area blocked by a single tetramer, whereas $C_2$ denotes a cross-section of the area blocked by two independent molecules. Both of them have major significance because they are directly related to the second $B_2 = 1/2C_1$ and third $B_3 = 1/3C_1^2 - 2/3C_2$ virial coefficients of the equilibrium tetramer monolayer [4, 28]. For example, the 2D pressure $P$ and the chemical potential of the tetramer $\mu$ can be expressed via the series expansion at a low coverage limit [28]

$$P = \frac{k_B T}{S_F} \left( \ln \theta + B_2 \theta^2 + B_3 \theta^3 + o(\theta^3) \right),$$

$$\mu = \mu_0 + k_B T \left( \ln \theta + 2B_2 \theta + \frac{3}{2} B_3 \theta^3 + o(\theta^3) \right),$$ (6)

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\mu_0$ is the reference potential.

Results presented in figure 4 show that $C_1$ is slightly bigger for the square model, which is expected as the overall size of the particle in this model is slightly bigger than in the rhomboid one. It is also worth noticing that the mean surface blocked by a tetramer is approximately 20% larger than for a spherical particle, for which $C_1 = 4$. On the other hand, in the case of tetramers $C_2 > 5$, whereas for spheres $C_2 \approx 3.308$. Therefore, due
to opposite signs at $C_1$ and $C_2$ in equation (5), the ASF difference between spheres and
tetramers is getting smaller for slightly larger coverages, when the parameter $C_2$ becomes
more important.

Note that in the limit of small coverage $\text{ASF}(\bar{\theta})$ can also be estimated experimentally.
It has been shown that in these conditions $\text{ASF}(\bar{\theta}) = \bar{\sigma}^2(\bar{\theta})$, where $\bar{\sigma}^2(\bar{\theta}) = \sigma^2(\bar{\theta})/\langle n(\bar{\theta}) \rangle$ is
a normalized variance of the number of adsorbed particles [30]. The typical experimental
procedure used for estimation of $\bar{\sigma}^2(\bar{\theta})$, described in [31], can also be used for monolayers
generated by the RSA. Figure 5 shows results of such calculations for tetramer layers in
comparison with the theoretical fit equation (5) obtained above. As expected, agreement
is good only for $\bar{\theta} < 0.2$.

At the jamming limit, the ASF for anisotropic molecules is typically approximated
by [6]

$$\text{ASF}(\bar{\theta}) = (1 + a_1 \bar{\theta} + a_2 \bar{\theta}^2 + a_3 \bar{\theta}^3)(1 - \bar{\theta})^4.$$ (7)

As shown in figure 4 inset, the above relation is also valid for tetramer adsorption. The
fit can be directly used for finding adsorption kinetics when transport is provided by
diffusion or convection. Details of this procedure have been described elsewhere [11, 18].
Note, however, that the repulsive interaction as in the case of KfrA plasmids [14] not
only can lower the coverage ratio, as discussed previously, but also can significantly slow
the adsorption kinetics, which have been observed experimentally [32] as well as in RSA
simulations [18].

3.3. Density autocorrelation

The density autocorrelation function gives additional insight into coverage structure. It is
defined as

$$G(r) = \frac{P(r)}{2\pi \rho},$$ (8)

Figure 5. The ASF approximation by the normalized density variance $\bar{\sigma}^2$. Diamonds and squares are measured values for the rhomboid and square models, respectively; whereas solid lines correspond to the ASF fit in a low coverage limit (5).
Figure 6. Density autocorrelation function $G(r)$ for rhomboid and square models. The inset shows a logarithmic singularity at $r \to r_t^+$. Parameters $r_t = 4.68$ and $t_t = 4.78$ for the rhomboid and square models, respectively.

where $P(r) \, dr$ is the probability of finding two tetramers at a distance between $r$ and $r + dr$. Here, the distance $r$ is measured between the geometric centres of tetramers. Parameter $\rho$ is the mean density of particles inside a covering layer. Such a normalization leads to $G(r \to \infty) = 1$. In the case of spherical particles, $G(r)$ has a logarithmic singularity in the touching limit [20] and superexponential decay at large distances [33]. The density autocorrelation function is shown in figure 6. It can be noticed that the autocorrelation density for the rhomboid model is slightly shifted left compared to the one for the square model. This is due to slightly denser packing of monomers in the rhomboid model and, hence, a somewhat smaller distance possible between the particles. The first maximum is smaller because rhomboid shape anisotropy is greater than the square one, which results in broader dispersion of possible distances. Due to anisotropy of shapes in both models used, there is no singularity at small $r$. However, the $G(r)$ slope past the first maximum resembles logarithmic singularity, especially for the square model, which is shown in the figure 6 inset. For large $r$, autocorrelations approach their limit value very fast, which is similar to the case of spheres' maximal random coverages.

4. Summary

The maximal random coverage ratio of a tetramer monolayer is $\theta_{\text{max}} = 0.5214$ and $\theta_{\text{max}} = 0.4910$ for the rhomboid and square models, respectively. In both cases, the ratio is slightly smaller than for spheres. On the other hand, in the limit of low coverage density, the surface is filled approximately 20% faster by tetramers than by equally sized spheres. At the jamming limit, RSA of tetramers shows behaviour typical of anisotropic molecules, which is rather unexpected considering the small shape anisotropy of both models used. Properties of the density autocorrelation function are similar to those of spheres.

Acknowledgment

This work was supported by grant MNiSW/N N204 439040.

doi:10.1088/1742-5468/2013/07/P07011
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