Surface Science 612 (2013) 24–30

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Modelling of interacting dimer adsorption

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ARTICLE INFO

Article history:
Received 16 November 2012
Accepted 15 February 2013
Available online 27 February 2013

Keywords:
Dimers
Adsorption
RSA kinetics

ABSTRACT

Adsorption of dimers is modelled using random sequential adsorption algorithm. The interaction between molecules is given by screened electrostatic potential. The paper focuses on the properties of adsorbed monolayers as well as the dependence of adsorption kinetics on interaction range. We designate random maximal coverage ratios, density autocorrelations and orientational ordering inside layers. Moreover the detailed analysis of adsorption kinetics is presented including a discussion of Feder's law validity and new numerical method for modelling diffusion driven adsorption. Results of numerical simulations are compared with experimental data obtained previously for insulin dimers.

1. Introduction

Since its introduction by Feder [1], random sequential adsorption (RSA) became a well established method used for modelling of adsorption properties. Although at the beginning it was used mainly to model adsorption of simple spherical molecules, recent results show that it could be effective also for quite complex structures like proteins [2–4].

Most of the research effort focuses on adsorption of hard objects where geometry is the only factor affecting properties of obtained monolayers. On the other hand, adsorption is often induced by electrostatic interaction between adsorbate and collector (e.g. [5]). In such cases, the hard body interaction can still be a sufficiently good approximation because the electrostatic forces are screened in a solution which makes them negligible. However in the general case, they should be taken into account to find out the level of systematic error provided by such interactionless approximation.

The purpose of presented paper is to extend previous investigations of dimer adsorption [6] to include the case on non-negligible electrostatic repulsion. The paper focuses on fundamental properties of dimer monolayers, such us maximal random coverage ratio, density autocorrelation and orientational ordering, as well as on adsorption kinetics. The additional aim is to develop robust numerical procedure to convert data obtained from RSA to values measured during a typical adsorption experiment.

2. Model

A single dimer particle is assumed to consist of two identical, charged, spherical particles (see Fig. 1).

In RSA studies of soft particles electrostatic interaction potential between particles has been typically an exponentially decaying Yukawa potential, due to the formation of a double layer from solvent particles, which effectively screens the electrostatic charge of an adsorbate. Therefore, such potential is also known as screened electrostatic potential [7,8]. Here, we assumed that the potential given by a single spherical monomer of radius a is equal to $(U_{mbox0}/r)exp[-(r-a)/L_e]$ for $r > a$ and infinite otherwise. Here r denotes distance from a monomer centre. Parameter U_0 characterises electrostatic properties of a monomer and of a solvent. Range of the interaction is controlled by L_e commonly called as the Debye screening length. It is a key parameter for electrostatic interaction in electrolytes and can be calculated as [9,10]:

$$L_e = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2e^2 I}} \tag{1}$$

where ϵ_0 is the permittivity of free space; ϵ_r denotes the dielectric constant of a solvent; k_B is the Boltzmann constant; T denotes temperature; e, elementary charge; and I, the ionic strength of electrolyte solution. Table 1 contains typical values of L_e for the most common solutions.

Electrostatic repulsion was introduced to RSA algorithm by Adamczyk et al. [11] and extended later by Oberholzer et al. [12]. There, the probability of successful adsorption is assumed to depend on the interaction energy U between the new particle and its nearest neighbour through a Boltzmann factor, $exp(-U/kT)$, where U includes interaction with both components of a dimer. Therefore, the adsorption probability of a point-like charged particle on a surface with a single dimer will reflect the dimer effective shape, shown in Fig. 2.

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http://dx.doi.org/10.1016/j.susc.2013.02.013

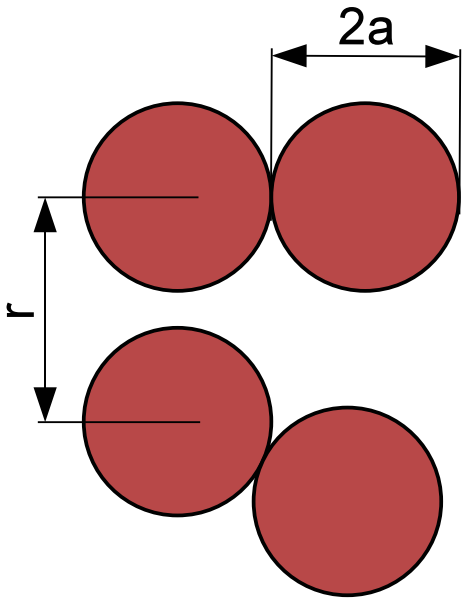

Fig. 1. Two dimers at a distance of r.

When point-like particle is substituted by a sphere, the effective potential changes due to different geometry, which changes double layer interactions. In this case:

$$U_{el} = \begin{cases} \frac{U_0}{r} exp\left[-\frac{r-2a}{L_e}\right] & \text{for } r \geq 2a \\ \infty & \text{for } r < 2a \end{cases}. \quad (2)$$

Note that dimer-to-dimer potential will contain four such terms defining interaction between all pairs of monomers belonging to different particles.

2.1. Simulation details

Adsorbed monolayers were generated using a modified RSA algorithm. The procedure consists of the following steps:

I a new virtual dimer is randomly created. Its centre is set on the collector according to a uniform probability distribution and its orientation (the angle between x-axis and dimer axis) is uniformly chosen from $[0,2\pi)$;

II.a the virtual molecule undergoes overlapping test with its nearest neighbours;

II.b if there is no overlap the total electrostatic potential U between the virtual molecule and previously adsorbed dimers is calculated using Eq. (2)

$$U = \sum_{i=1}^{2} \sum_{j=1}^{2N} U_{el}\left(\left|r_i - r_j\right|\right), \quad (3)$$

where i enumerates the virtual particle monomers, j enumerates monomers belonging to previously adsorbed dimers and r_i is the position of the i-th monomer at the centre; N denotes a number of already adsorbed dimers.

II.c a random number is selected according to uniform probability distribution on the interval [0,1). If it is smaller than $\exp(-U/k_BT)$ the virtual particle is added to the existing layer.

III otherwise the virtual dimer is removed and abandoned.

The whole procedure is repeated for a specified number of times expressed using dimensionless time:

$$t = n\frac{S_m}{S_c} \quad (4)$$

where n is a number of algorithm iterations, $S_m = 2\pi a^2$ is a coverage of a single dimer, and S_c is a collector's surface. The fundamental characteristic of an obtained layer is its coverage ratio defined as follows

$$\theta = N_m\ S_m/S_c \quad (5)$$

where N_m is a number of adsorbed particles.

The adsorption process simulation was performed for a squared collector of $200a$-side size and was stopped at $t = 10^5$. We did not used periodic boundary conditions, as it had been proved earlier, it does not have a significant influence on obtained layers [6]. For each set of parameters, 20 to 100 independent simulations were performed. Parameters of electrostatic potential in Eq. (2) were chosen to describe typical experimental conditions of water solutions. Therefore, relative dielectricity of the solvent was $\epsilon_r = 78$. The parameter $a = 4.65\ nm$ provides a length scale typical to midsized bio-molecules. Value of coefficient $U_0 = (e^2a^2)/(4\pi\epsilon_0\epsilon_r) = 6.78\ k_BT\ nm/e^2$ [10], where ϵ_0 is dielectric constant of vacuum, is fully determined by the above assumptions. The thermal energy k_BT at a room temperature acts as energy unit.

Table 1
L_e in nm for typical electrolytes characterised by different ratios of cations to anions. Values were taken from [10].

Concentration	1:1	1:2 (Na_2SO_4)	2:2	1:3 (Na_3PO_4)
M	(KCl)	2:1 ($CaCl_2$)	($NiSO_4$)	3:1 ($AlCl_3$)
10^{-1}	0.9639	0.5565	0.4820	0.3935
10^{-2}	3.048	1.759	1.524	1.244
10^{-3}	9.639	5.565	4.819	3.935
10^{-4}	30.48	17.59	15.24	12.44
10^{-5}	96.39	55.65	48.19	39.35
10^{-6}	304.8	175.9	152.40	124.4

3. Results and discussion

3.1. Fundamental properties of adsorption monolayer

Example coverages obtained in numerical simulations are shown in Fig. 3. Their main properties, such as maximal random coverage ratio, autocorrelation function and orientational ordering, are analysed in the following sections.

3.1.1. Adsorption ratio

The easiest estimation of maximal random coverage ratio can be done by simply counting the number of adsorbed dimers. Fig. 4 shows raw results taken directly from obtained data.

However, such ratios are underestimated due to the finite time of a simulation; there is no guarantee that all free places on a collector have been filled. To deal with this, the model of RSA kinetics have to be used. The common choice here is the Feder'slaw [13–15], which is valid for a wide range of adsorbate molecule shapes [16] and also proved to be valid for the case of hard-core dimer RSA [6]:

$$\theta_{max}\theta - (t) = At^{-1/d} \quad (6)$$

where t is dimensionless time (Eq. (4)); d is a dimension of a collector and A is a factor of proportionality. Here, $d = 2$. Plots illustrating relation (6) are presented in Fig. 5. They confirm that the numerical data obey the Feder's law. Moreover, at the limit of $t \to \infty$ ($t^{-1/2} \to 0$), the maximal random coverage ratios are higher by about 1–2% than the values obtained directly from data as in Fig. 4 (see Table 2).

It is clear that the maximal random coverage ratio defined using Eq. (5) and Eq. (6) decreases with the growth of the Debye screening length L_e due to the electrostatic repulsion. On the other hand, those results can also be interpreted as an increase in the effective molecule