Formation of multilayered structures in the layer by layer deposition of colloid particles

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Abstract
Theoretical calculations of particle film formation in the layer by layer (LbL) self-assembling processes have been performed according to the generalized random sequential adsorption (RSA) scheme. The first (precursor) layer was generated using the standard RSA scheme pertinent to homogeneous surface. Formation of the consecutive layers (up to twenty) was simulated for two kinds of particles of equal size. The interaction of two particles of different kind resulted in irreversible and localized adsorption upon contact, whereas particles of the same kind were assumed to interact via the hard potential (no adsorption possible). Using this algorithm particle coverage (2D density) and volume fraction (3D density) were calculated as well as the film thickness as a function of the number of layers. Additionally, the structure of the film was quantitatively characterized in terms of the 2D and 3D pair correlation functions. The simulations revealed that particle concentration distribution in the film was more uniform for low precursor layer density than for higher density, where well-defined layers of closely packed particles appeared. It was also predicted theoretically that the averaged value of particle volume fraction in the uniform film region was $\rho_{LbL} = 0.42$, which is very close to the maximum packing density equal to 0.382 predicted from the 3D RSA model. On the other hand, the roughness of the film was the lowest at the highest precursor layer density. It was shown that for low precursor layer density the film thickness increased with the number of layers in a nonlinear way. However, for high precursor layer density, the film thickness increased linearly with the number of layers and the average layer thickness was close to the hexagonal layer thickness equal to $1.73a_p$. It was concluded that our theoretical results can be effectively exploited for interpretation of the LbL processes involving colloid particles and polyelectrolytes.

Keywords: Colloid deposition; Deposition of particles; Modeling of multilayer deposition of particles; Multilayered colloid films; Random sequential adsorption; Self-assembling of colloid particles

1. Introduction
Adsorption and deposition (irreversible adsorption) of colloids and bioparticles on solid/liquid interfaces has significance for many processes such as protein, bacteria or enzyme immobilization and separation, removal of pathological cells, immunological assays, membrane biofouling, artificial organ implants, etc. Because of important practical aspects, mono- and bilayer deposition of particles has been studied both in theoretical [1–4] and experimental aspects [5–17].

In contrast, the self-assembled colloid particle multilayers have sporadically been studied despite their increasing significance for preparing nano-structured porous materials such as separation membranes and optical elements, e.g., gratings, interferometers, filters, antireflective coatings, etc. Such particle multilayered structures of controlled thickness can most conveniently be produced using the layer by layer (LbL) technique, applied originally by Iller [18]. The essence of this procedure consists in the use of nano-scaled binder, which converts the surface charge of the outermost particle layer. In this way electrostatic attraction between this layer and incoming colloid particles is induced, which allows one to deposit consecutive layers. Iller [18] used for this purpose colloidal fibrils of boehmite alumina of 5–6 nm in diameter, which allowed him to produce saturated multilayers of colloid silica (75 nm in diameter).

An analogous procedure was developed by Bohmer [19] who used a cationic polyelectrolyte, i.e., partially methylated
poly(vinylimidazole) (PVI) to convert the charge of consecutive layers of colloid silica (32 nm in diameter). Particle multilayer formation was observed in situ using optical reflectometry under the forced convection conditions (impinging-jet cell). Multilayer formation of silica particles bind by a cationic polyelectrolyte was also studied by Lvov et al. [20] using the quartz crystal microbalance method.

An alternative LbL technique suitable for producing particle multilayers was developed by Decher et al. [21–23]. It is based on the use of particles (polyelectrolytes) of two kinds, bearing opposite sign of surface charges, to produce consecutive layers. The method has been widely used since then to prepare polyelectrolyte multilayer films on solid substrates of a desired composition and functionality. The simplicity of this procedure, feasibility of embedding various molecules, proteins and colloid particles into the polymeric layer enables one to produce films of targeted architecture [24,25].

A similar LbL procedure was exploited by Fulda et al. [26], who produced multilayers of cationic and anionic latex particles of 200 nm size range on a modified glass substrate. The morphology of particle multilayers was studied by the scanning electron microscopy (SEM) upon drying the sample.

A proper interpretation of these interesting experimental measurements is hindered because of the lack of adequate theoretical models and results. The existing theoretical works were concerned with bilayer formation only [2–4]. On the other hand, multilayer deposition of particles was analyzed theoretically in Refs. [27–29] using various random sequential adsorption models such as the ballistic model involving a rolling over mechanism, or the rain model [30]. However, these approaches do not reflect properly the physics of LbL deposition in the case when particles of different type (surface charge) are involved in the process.

Thus, the goal of this work is to develop an efficient theoretical model enabling a quantitative evaluation of the LbL deposition of particles. In particular, we will be interested in calculating the multilayer thickness as a function of the number of layers and the precursor layer density. The particle density distribution within the multilayer (porosity of the layer) and its structure will also be evaluated. It is to mention that preliminary results obtained by using our theoretical approach have been reported in Ref. [31].

2. The theoretical model

Irreversible, multilayered adsorption of spherical particles on homogeneous surfaces was simulated according to the generalized random sequential adsorption (RSA) model used previously for describing adsorption on heterogeneous surfaces [2,3].

The algorithm consisted of two main stages:

(i) the formation of the first (precursor) layer, where the particles were assumed irreversibly adsorbed upon touching the interface only and were rejected when touching each other,

(ii) the formation of the multilayer, where particles were irreversible adsorbed by touching any particle of a different kind and were rejected when touching the interface or any particle of the same kind.

Physically, the above process corresponds to the situation where the precursor layer is formed by particles having opposite surface charge to the interface. The consecutive layers are formed by adsorbing alternatively particles of two kinds that have surface charge opposite to each other. Hence, our theoretical model can mimic well the situation where multilayer structures are formed by consecutive deposition of positively and negatively charged colloid particles, as done in Ref. [26], or polyelectrolytes.

The substrate surface was pre-covered by sites according to the classical RSA model pertinent to homogeneous surface adsorption [1,4,32,33]. The RSA process consists in placing a spherical particle of the radius \( a_p \) on a homogeneous surface having the geometrical surface area \( \Delta S \). If there is an empty space large enough to accommodate the particle, it is irreversibly adsorbed, otherwise, if particles overlap, i.e., if the distance between the adsorbing particle and any of the previously adsorbed particles is smaller than two particle radii, the adsorption attempt is repeated. The main feature of the RSA process is that the coordinates of the adsorbing particle are chosen at random and that the new adsorption attempt is fully uncorrelated with previous adsorption attempts. In this pre-adsorption process, a prescribed number of spherically shaped sites \( N_{p1} \) was generated. The surface concentration of the sites was then equal to \( N_{p1}/\Delta S \) and the dimensionless coverage (2D density) is defined as \( \Theta_{p1} = \pi a_p^2 N_{p1}/\Delta S \), where \( a_p \) is the particle radius. As proved in the previous numerical simulations [32–34] the distribution of the sites generated in the RSA processes for \( \Theta_{p1} < 0.1 \) remains quasi-random. For higher coverage, however, the distribution of the sites becomes correlated since the number of the particle pairs at closer separations is larger than the average. This can be quantitatively characterized in terms of the pair correlation function as discussed in Refs. [1,4,32].

It is interesting to mention that the maximum (jamming) coverage for hard spheres in two dimensions 2D derived from the RSA process is 0.547 [4,30,32].

Next layer formation at the surface covered by the sites was simulated according to the algorithm being a generalization of the previously used for heterogeneous surfaces [15–17]:

(i) an adsorbing (virtual) particle of the diameter \( 2a_p \) was generated within the simulation area by choosing at random its coordinates \( (x_v, y_v) \)—if it did not touch any of the adsorption sites (particles having the opposite sign of the surface charge), the particle was rejected and another virtual particle was generated;

(ii) otherwise, if the particle touched any of the sites, its \( z_v \) coordinate (perpendicular to the interface) was calculated from the osculation condition with each of the potential
adsorption centers having the coordinates \((x_j, y_j, z_j)\):

\[
z_v = \max\left\{ z_j + \left[ 4a_p^2 - (x_v - x_j)^2 - (y_v - y_j)^2 \right]^{1/2} \right\};
\]

(iii) the overlapping test was performed according to the usual RSA rules, i.e., it was checked if there is any previously adsorbed particle within the exclusion volume—if there was overlapping, the simulation loop was repeated (the number of attempts was increased by one);

(iv) if there was no overlapping, the virtual particle was irreversibly adsorbed at the given position (localized adsorption postulate)—its coordinates were stored and the number of adsorbed particles in the given layer \(N_{pi}\) was increased by one.

At the perimeter of the simulation area, the usual periodic boundary conditions were applied as done previously [1,15–17, 31,32].

It is also interesting to mention that in our simulations the possibility of particle adsorption from the third and other odd layers on the interface was eliminated.

Although the above algorithm allows one to perform simulations of incomplete layers, the results presented in this work concern the limiting situation where each layer was almost completely saturated, i.e., when the dimensionless adsorption time defined as \(\tau = \pi a_p^2 N_{ad,i} / \Delta S\), where \(N_{ad,i}\) is the total number of the adsorption attempts in the layer \(i\), achieved the value of \(10^4\). For sake of simplicity, the size of negative and positive particles was assumed to be equal in the calculations discussed hereafter.

As an outcome from these simulations, the number of particles \(N_{pi}\) adsorbed in each layer \(i\) and a set of coordinates \((x_j, y_j, z_j)\) defining their positions were obtained. In order to attain a sufficient precision of calculations, the number of particles in each layer was larger than \(10^4\). The total number of layers \(l\) generated in our simulations was twenty.

Similarly as in the classical RSA simulation, the two-dimensional (2D) concentration of particles in each layer, which is usually referred to as the coverage, was calculated as

\[
\Theta_{pi} = \pi a_p^2 N_{pi} / \Delta S, \quad i = 1, \ldots, l,
\]

where \(N_{pi}\) is the number of particles forming the layer number \(i\).

The disadvantage of this quantity is that it gives global information only, since the particle distances from the interface in each layer can vary significantly.

Therefore, in order to obtain more precise information on particle distribution in each layer, the particle volume fraction as a function of the distance \(z\) from the interface was also calculated from the dependence

\[
\rho_i(z) = \frac{dv_{pi}(z)}{dv} = \frac{\sum_{j=1}^{N_{pi}} S_{pj}(z)}{\Delta v},
\]

where \(dv_{pi} = dz \sum_{j=1}^{N_{pi}} S_{pj}(z)\) is the infinitesimal fraction of the volume of particles from the layer number \(i\) in the volume element \(dv = dz \Delta S\) (having the infinitesimal thickness \(dz\) and \(S_{pj}(z)\) is the cross-section of the particle \(j\) from the layer number \(i\) at the distance \(z\) from the adsorption surface).

Analogously, the overall particle volume fraction \(\rho(z)\) (3D density) is given by

\[
\rho(z) = \sum_{i=1}^{l} \rho_i(z).
\]

From an experimental point of view one of the quantities of major interest is the particle multilayer (film) thickness \(d\). For the sake of convenience the film thickness is defined in the reduced form, noted by \(\bar{d}(l)\) as the averaged distance of particle centers forming layer number from the interface divided by particle size \(2a_p\). This can be formulated mathematically in the form

\[
\bar{d}(l) = \frac{1}{2a_p N_{pl}} \sum_{i=1}^{N_{pl}} z_j,
\]

where \(N_{pl}\) is the number of particles forming the multilayer and \(z_j\) are the distances of particle centers from the interface.

On the other hand, the structure of the particle multilayer generated in the above RSA process can be quantitatively characterized in terms of the pair correlation function. Because the multilayer adsorption studied in this work is a truly 3D process, one can distinguish two basic types of the pair correlation function (i) the 3D function \(g_{3D}(r)\) where the distance \(r\) between particle centers is measured in space and (ii) the 2D function denoted by \(g_{2D}(r')\) where \(r'\) is the projection of the distance \(r\) on the plane of the interface.

Because there are two types of particles (either positively or negatively charged) one can distinguish in the former case four kinds of the \(g_{3D}\) function, i.e., for positive–negative particles, negative–negative, positive–positive, and the overall function reflecting correlation between all particles. These functions can be calculated from the constitutive dependence [24]

\[
g_{3D}(r) = \frac{v}{N_p \left( \frac{\Delta N_p(r)}{4\pi r^2 \Delta r} \right)},
\]

where \(N_p\) is the total number of particles of a given type adsorbed within the multilayer of the volume \(v\), \(\Delta N_p\) is the number of these particles adsorbed within the volume element \(4\pi r^2 \Delta r\) around a central particle, and the angle brackets mean the ensemble average.

The pair correlation function can be interpreted as the averaged probability of finding a particle of a given type at the distance \(r\) from the center of another particle, normalized to unity at large distances.

In further discussion we consider exclusively the overall \(g_{3D}\) function, representing correlation between particles of arbitrary charge.

Analogously, the 2D pair correlation function for particles belonging to the layer number \(i\) can be calculated from the dependence

\[
g_{2D,i}(r') = \frac{\pi a_p^2}{\Theta_{pi}} \left( \frac{\Delta N_{pi}(r')}{2\pi r' \Delta r'} \right),
\]
where $\Delta N_{pi}$ is the number of particles adsorbed in the layer number $i$, contained in the ring $2\pi r^i \Delta r^i$ drawn around a central particle.

Obviously, all particles located close to the perimeter of the simulation area were discarded from the averaging procedure. In order to obtain a satisfactory accuracy of the correlation functions, particle populations reaching $10^5$ were considered.

3. Results and discussion

Because of equal size of positive and negative particles and the postulate of a saturated coverage of each layer (except the first one) the properties of the multilayer generated in our simulations were dependent on the first (precursor) layer coverage $\Theta_{p1}$ and the number of layers $l$ only. The effect of these parameters on the particle volume fraction, the multilayer thickness and its structure, expressed in terms of the pair correlation functions were systematically studied in our simulations.

Snapshots showing formation of bilayer, i.e., the precursor layer characterized by the coverage $\Theta_{p1} = 0.05$ and 0.3 and the second, particle layer, are shown in Fig. 1. The particles bearing opposite surface charge to the interface (for example positive if the interface is negatively charged) are shown in white, whereas the negatively charged particles (same sign of surface charge as the interface) are shown in black. As can be seen, the number of particles adsorbed in the second layer is much larger than in the precursor layer. This effect appears because every particle in the precursor layer, which can be treated as adsorption center, is able to coordinate a few particles in the second layer. This effect was studied systematically by performing simulations in which the coverage of second layer $\Theta_{p2}$ was determined as a function of $\Theta_{p1}$. The results collected in Fig. 2 indicate that for low $\Theta_{p1}$, the coverage of particles in the second layer $\Theta_{p2}$ increases linearly with the slope equal to 5.5 (dashed line in Fig. 2). As discussed previously [16,17] this slope in the limit of $\Theta_{p1}$ can be treated as the coordination number of the adsorption site, i.e., the averaged number of particles attached to one site (particle in the precursor layer). Because of the multiple site coordination, formation of surface clusters composed on average of 6.5 particles is predicted. It is interesting to mention that such clusters were indeed observed experimentally, as reported in our previous work [17].

It can also be noted in Fig. 2 that with increasing precursor layer coverage, the slope of the dependence of $\Theta_{p2}$ on $\Theta_{p1}$ decreases systematically due to geometrical constrains. It is also interesting to mention that for $\Theta_{p1} = 0.25$ a maximum of the height 0.66 appears on the $\Theta_{p2}$ vs $\Theta_{p1}$ dependence, which exceeds the jamming limit of particles in two dimensions, equal to 0.547 as mentioned above. The maximum appears because particles forming the second layer are adsorbed in a quasi-three-dimensional manner, in various planes. This can be well observed in Fig. 3, where the multilayered (sandwich-like) structures derived from simulations are shown. Hence, the boundaries between consecutive layers are rather diffused, especially for the first layers located close to the interface (see Fig. 3).

Quantitatively, particle distribution in each layer and in the entire film (sandwich) can be characterized, as mentioned above, in terms of the particle volume fraction $\rho_i(z)$ (for each monolayer) and $\rho(z)$ (overall multilayer), defined by Eqs. (2)
Fig. 3. Topology of particle multilayer composed of twenty layers derived from the MC simulations: (a) the first (precursor) layer coverage $\Theta_{p1} = 0.05$, (b) the first layer coverage $\Theta_{p1} = 0.30$.

and (3). Theoretical results derived from simulation are presented in Fig. 4 for $\Theta_{p1} = 0.05$, 0.1 and 0.3. As can be seen, in the case of diluted precursor layer ($\Theta_{p1} = 0.05$) the particle volume fraction profiles in a few first layers are diffused and highly asymmetric. Also the maximum value of $\rho(z)$ for the consecutive layers increases systematically with the layer number $i$. This indicates that a significant penetration of particles from consecutive layers into the film appears. This is so because, for low precursor layer coverage the consecutive particles can attach either vertically, hence the maximum distance from the surface $z/a_p$ could be $2l - 1$, or almost horizontally where $z/a_p \sim 0$. For example, the maximum volume fraction of the layer number five appears at the distance $z/a_p = 7$, having the value of 0.28. For this layer, the particle volume fraction at the distance $z/a_p = 3$ (two nominal layers below) is still about 0.03, i.e., 7% of the maximum value. It is interesting to observe that with the increasing layer number, the asymmetry of the particle density distribution and its spread decreases significantly.

Despite a significant spread of the volume fraction profiles observed in single monolayers, the overall density profile (shown also in Fig. 4) becomes quite uniform outside a transition region having the thickness of one particle diameter. Thus, in the uniform film region, the difference between the maximum and minimum value of the local particle volume fraction equals 0.05, i.e., 8% of the average value. This smoothing-out effect is expected to have profound practical consequences, suggesting that it can be feasible to produce thin films of particles using the LbL technique, which exhibit a uniform density distribution. It is also interesting to mention that the average value of the particle volume fraction in the uniform film region $\rho = 0.42$.

Fig. 4. The dependence of the local volume fraction $\rho_i$ (3D particle density) on the dimensionless distance from the interface $z/a_p$ calculated for single layers (curves 2–20) and for the overall multilayer (curve number 1). The dashed line shows the 3D jamming limit predicted from the RSA model, i.e., 0.425. (a) $\Theta_{p1} = 0.05$, (b) $\Theta_{p1} = 0.10$, (c) $\Theta_{p1} = 0.30$. 
This means that the LbL process carried out according to the above rules can be exploited for producing stable random media (membranes) of high averaged porosity, of about 0.58.

It is interesting to mention that this limiting value of particle density $\rho_{\text{LbL}}$ found in our simulations is slightly above the jamming density $\rho_{\text{RSA}}$, equal to 0.382, predicted theoretically from the 3D random sequential addition (RSA) model [30, 34]. This is understandable because the RSA model is based on the assumption that particles generated at random with uniform probability become permanently fixed in space if there is no overlapping with any previously added sphere. Obviously, the distance between sphere surfaces is always finite, so they never contact each other physically. This is rather artificial assumption because it cannot be imagined how it could be possible to stabilize such sphere configuration in space. On the other hand, our value of $\rho_{\text{LbL}}$ is much smaller than the random close packing of spheres in 3D, equal to 0.629 [35,36], which has an essential significance for determining rheological properties of hard sphere suspension. For comparison, the closest hexagonal packing density of spheres in three dimensions is 0.74.

In the case of the dense precursor layer ($\Theta_{p1} = 0.30$) the particle concentration distribution in each layer is more narrow and very symmetric, see Fig. 4c. Paradoxically, however, variations in the local particle volume fraction are predicted much higher in this case, being about 25% of the average value equal to 0.43, which is close to the RSA jamming limit.

It is interesting to mention that both the single layer distribution profile and the overall profile predicted in our simulations are very similar to what is predicted for the polyelectrolyte multilayer films [23]. Another quantity of a major practical significance is the average multilayer thickness $\bar{d}$ defined by Eq. (4). Values of $\bar{d}$ and $\bar{d}/l$ calculated numerically as a function of the precursor layer coverage and layer number are collected in Tables 1 and 2. The dependence of $\bar{d}$ on layer number is also presented graphically in Fig. 5 for $\Theta_{p1} = 0.05, 0.1$ and 0.30. In this figure not only the average film thickness is plotted but also its maximum and minimum values, which contain information about the roughness of the film.

It was found that for $\Theta_{p1} = 0.05$ the average thickness of the film composed of five layers was $5.57ap$, which gives the average value of the single layer thickness equal to $1.11ap$ (i.e., 0.557 of particle diameter). This value is much smaller than the thickness of the single layer in the hexagonally packed multilayer film, which is equal to $\sqrt{3}ap \equiv 1.73ap$ (0.865 of particle diameter).

However, the average layer thickness grows with the number of layers in the film (see Fig. 5). In consequence, for a film composed of 20 layers, the average value of the single layer thickness derived from simulations is 1.70ap (i.e., 0.850 of the particle diameter). This is very close to the thickness of a packed hexagonal layer. It is interesting to observe that the difference between the maximum and minimum film thickness, which can be treated as a measure of the film roughness, as shown in Fig. 5, for $\Theta_{p1} = 0.05$ and $l = 20$ is $7ap$.

For comparison, the coverage of consecutive layers in the particle film for $\Theta_{p1} = 0.05$ is also plotted in Fig. 5. The coverage attains a maximum of the height of 0.67, for the layer number 5. This is much larger than the jamming coverage for a homogeneous (smooth) surface found to be 0.547 as mentioned above. This difference can be attributed to the fact that particles in every monolayer forming the film are adsorbed in various planes, corresponding to different values of the coordinate $z$, in a quasi-three-dimensional manner. After attaining the maximum, the coverage of the subsequent monolayers decreases gradually to the limiting value of 0.6.
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Fig. 5. The dependence of the multilayer thickness $d/2a_p$ on the number of layers $l$ (full points). Curve 1, the maximum layer thickness (dotted line); curve 2, the average layer thickness; curve 3, the minimum layer thickness (dotted line). The empty points show the coverage of each layer and the solid lines denote interpolations. (a) $\Theta_{p1} = 0.05$, (b) $\Theta_{p1} = 0.10$, (c) $\Theta_{p1} = 0.30$.

Similar results were obtained for $\Theta_{p1} = 0.10$ and $\Theta_{p1} = 0.30$ (see Figs. 5b, 5c). The film composed of 20 layers for $\Theta_{p1} = 0.30$ had the thickness of 17.5 particle diameters, which gives the value of 0.875$d_p$ as the average single layer thickness. The difference between the maximum and minimum film thickness was $5a_p$. This indicates that for the precursor layer density $\Theta_{p1} > 0.10$ the properties of a particle film composed of more than ten layers depend little on the precursor layer density.

The theoretical results shown in Fig. 5c ($\Theta_{p1} = 0.30$) are in agreement with the experimental results concerning the self-assembled multilayer thickness obtained by Fulda et al. [26] using the LbL technique. He demonstrated, using SEM, that the averaged thickness of a film composed of ten layers of latex particles was 1200 nm (for the first layer having the coverage of 0.3 and the averaged particle diameter 200 nm). This gives $\bar{d} = 6$, which is comparable with our theoretical value of 8.4 (see Table 1). The difference stems from the fact that because of limited deposition time, every layer in Fulda et al. experiments was incomplete. Thus the coverage determined by them for two layers was 0.58 (our theoretical prediction for complete layers was 0.95) of three layers 0.8 (our theoretical prediction for complete layers was 1.5).

For sake of convenience, the theoretical results showing the averaged film thickness $\bar{d}$ vs the number of layers $l$ for $\Theta_{p1}$ ranging from 0.02 to 0.30 are presented graphically in Fig. 6.

In addition to particle density profiles and the film thickness $\bar{d}$, it is also interesting to analyze the structure of the adsorbed particle films. As mentioned above, this can be done quantitatively in terms of the 2D pair correlation function $g_{2D}(r')$. In Fig. 7, the pair correlation function determined for various layers is shown (precursor layer density $\Theta_{p1} = 0.1$ and 0.3). As can be observed a significant difference between the first and the second layers appears. For the second layer, the maximum value of $g_{2D}$ appearing at the distance $r' = 2a_p$ was about five, which exceeds several times the maximum for the first layer. This effect, reported previously for heterogeneous bilayer simulations [15–17] is a direct evidence of surface cluster formation, because of the attractive forces between oppositely charged particle in the first and second layers. Note also that the $g_{2D}$ function does not vanish to zero for $r' < 2a_p$ as is the case for the first layer, because the centers of particles forming the second layer are located in various planes. These effects have been confirmed experimentally using direct optical micro-
scope observations [15–17]. As seen in Fig. 7a, the peaks of the pair correlation function for consecutive layers decreased to the limiting value of 3.4. Similarly, the shape of the pair correlation function for the fifth and higher number layers becomes very similar, suggesting that the structure of the particle film became isotropic.

Analogous dependencies were observed for \( \Theta_{p1} = 0.30 \), see Fig. 7b, except that the peak value of the pair correlation function for the second layer was 3.4 and the maximum value for the third and higher number layers was 2.8.

On the other hand, in Fig. 8 the influence of the precursor layer density on the \( g_{2D} \) function for the 20th layer is shown. As can be seen, the precursor layer density, varied between 0.02 and 0.30, exerts a negligible effect on the \( g_{2D} \) function of the 20th layer. The results presented in Figs. 7 and 8 suggest that despite significant variations in particle volume fraction distribution and the roughness of the film, the structure of outermost layers of particle films is little affected by the first layer density. The same conclusion can be drawn when considering the three-dimensional \( g_{3D} \) function, plotted in Fig. 9 for various values of the precursor layer coverage ranging from 0.02 to 0.3.

It is to mention that all results discussed in this work are directly applicable to spherical particles interacting via the short ranged (contact) potential, which is often referred to as hard particle potential. Experimentally this can be realized by performing experiments at high ionic strength of particle suspensions, to compress the range of the electrostatic interactions to a value much smaller than the particle dimensions. However, experiments carried out at high ionic strength can induce particle aggregation in the bulk as well, which decreases the efficiency of the LbL process for colloid particles.

As an alternative one can perform the LbL studies for polyelectrolytes (charged macromolecules), which sign and magni-
tude of the surface charge can be regulated by choosing various polymers. Moreover, at higher ionic strength these polymer molecules assume a compact shape, which can be well approximated by a prolate spheroid or even a sphere [37,38]. One can expect, therefore, that under such conditions the above discussed theoretical results are valid. This prediction was confirmed by the experimental results discussed in Ref. [31], where the LbL technique was used to produce a multilayer film composed of the positively charged polyallylamine (PAH) and the negatively charged poly-4-styrenesulfonate (PSS) molecules adsorbing on an oxidized silicon surface. Both polyelectrolytes had the molecular weight of 70,000. The nonlinear increase in the film thickness with the number of layers was quantitatively accounted for by the theoretically predictions derived from numerical simulations performed according to the algorithm described above. It is interesting to mention that often the nonlinear increase in the film thickness with the number of layers is interpreted in the literature as the exponential growth of the polyelectrolyte film [39,40]. Our theoretical results offer a natural explanation of this phenomenon as due to the penetration of the molecules into the film. These facts suggest that the theoretical results discussed in this work can be efficiently used for interpretation of experimental results not only for colloidal particles but also for the LbL processes involving molecular species.

4. Concluding remarks

The generalized RSA simulation scheme applied in this work proved an efficient tool for modeling formation of self-assembling particle films produced in LbL processes. It was revealed that the particle density (volume fraction) distribution in the film was more uniform for low precursor layer density than for higher density, where well-defined layers of closely packed particles appeared. On the other hand, the roughness of the film was the least for high precursor layer density.

It was also predicted theoretically that the averaged value of particle volume fraction in the uniform film region was \( \rho(z) = 0.42 \), which is very close to the maximum packing density equal to 0.382 predicted theoretically from the 3D RSA model. However, this value is much smaller than the random close packing of spheres in 3D, equal to 0.629, or the closest hexagonal packing in three dimensions, equal to 0.74. This means that the LbL process carried out according to the above rules can be exploited for producing stable random media (membranes) of high average porosity, of about 0.58.

It was also predicted theoretically that the film thickness grows in a nonlinear way with the layer number for low precursor layer density, which can be incorrectly interpreted as an exponential growth regime.

For precursor layer coverage \( \Theta_{p1} > 0.10 \), the film thickness increased linearly with the number of layers for films thicker than five layers. The averaged thickness of a single layer in this linear growth regime was \( 1.7a_p \) (0.87 of particle diameter), which is almost identical to the value predicted for a closely packed hexagonal layer thickness equal to \( \sqrt{3}a_p = 1.73a_p \).

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