Applied Surface Science 332 (2015) 318–327

Contents lists available at ScienceDirect

Applied Surface Science

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

Structure analysis of layer-by-layer multilayer films of colloidal particles

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ARTICLE INFO

Article history:
Received 1 July 2014
Received in revised form 9 January 2015
Accepted 10 January 2015
Available online 30 January 2015

Keywords:
Multilayer thin-films
Porous material
Computer simulations
Self-assembly
RSA

ABSTRACT

We have mimicked the layer-by-layer self-assembling process of monodisperse colloidal particles at a solid–liquid interface using the extended random sequential adsorption model of hard spheres. We have studied five multilayer structures of similar thickness, each created at a different single-layer surface coverage. For each multilayer, we have determined its particle volume fraction as a function of distance from the interface. Additionally, we have characterized the film structure in terms of 2D and 3D pair-correlation functions. We have found that the coverage of about 0.3 is optimal for producing a uniform, constant-porosity multilayer in a minimum number of adsorption cycles. The single-layer coverage has also a significant effect on the primary maximum of 2D radial distribution function. In the case of multilayer with the coverage lower than 0.30 the 2D pair-correlation functions of even layers exhibit maxima decreasing with the increase in the layer number. We have verified our theoretical predictions experimentally. We have used fluorescence microscopy to determine the 2D pair-correlation functions for the second, third, and fourth layers of multilayer formed of micron-sized spherical latex particles. We have found a good agreement between our theoretical and experimental results, which confirms the validity of the extended RSA model.

1. Introduction

Recent advances in the nanotechnology have made possible the production of highly refined colloidal particles with controlled surface and bulk properties. There have been published novel methods of production of, e.g., surface-activated, magnetic, conductive, biocompatible, fluorescent, hollow, or nanoporous particles [1–11]. Exploiting their ability to self-organize we can synthesize sophisticated functional nanomaterials, which opens a world of novel applications for nanoparticle multilayer structures. Colloidal multilayers are highly porous and exhibit a textured surface, which make them potentially attractive as separation membranes, heterogeneous catalysts, antireflective coatings, and optical elements, e.g., interferometers. Because of major practical importance, the mono- and bi-layer deposition of particles has been extensively studied both theoretically [12–20] and experimentally [18–22]. However, despite their increasing significance for the preparation of nanostructured porous materials, functional multilayers of more than two particle layers are much less discussed in the literature [23–32], and thus less known. In particular, little is known about the effect of formation conditions on the obtained structure.

A common experimental method for fabricating a multilayer with certain characteristics is layer-by-layer (LbL) adsorption of composing particles [33–37]. It is based on the adsorption of consecutive layers by immersing the substrate alternately in suspensions of colloidal particles (or solutions of macromolecules) with positive and negative surface charges. The structure of multilayer obtained in this way depends strongly on the number of adsorption cycles, amount of particles adsorbed in each cycle, and interactions in the system. Therefore, the LbL method allows controlling the various parameters of multilayer, such as the thickness, roughness, porosity, or specific surface area [29,30]. Also, the procedures for the LbL assembly are relatively simple and can be automated. It is worth mentioning that the LbL method is widely used for the preparation of polyelectrolyte multilayer films of desired composition and functionality on solid substrates [38].

A reliable interpretation of experimental measurements requires adequate theoretical models and results. One of our main theoretical tools for a better understanding of the particle deposition mechanism is the computer modeling of the process. Using a numerical approach we can study the kinetics of multilayer formation and then analyze it to also gain insight into its structure. The advantage of such modeling is that in addition to the global

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http://dx.doi.org/10.1016/j.apsusc.2015.01.171
0169-4332/

properties of the multilayer, we can also study its local properties, which play a major role in the mass transport, especially in heterogeneous systems. Thus, computer modeling can be a powerful tool in the study of structural and kinetic aspects of deposition of macromolecules, proteins, and colloidal particles [24,25,29,30,39–42]. There are several advanced algorithms suitable for modeling of colloidal systems [43], especially helpful for understanding the behavior of particles in highly concentrated suspensions. In the dilute regime, however, where the particle–particle interactions can be neglected, the more sophisticated method, such as Brownian dynamics or Molecular Dynamics are in good agreement with statistical–geometric models, such as random sequential adsorption (RSA) and ballistic deposition [44].

The goal of this work is to conduct in-depth analysis of spherical particle multilayers produced using the LbL technique. In what follows we have assumed that particle deposition occurs from dilute suspensions. Therefore, for the sake of simplicity and efficiency, we have simulated our multilayers with the extended RSA model [29]. Then, we have characterized the structure of generated multilayers in terms of the distribution of particle volume fraction in the direction perpendicular to the adsorption surface. We have also calculated the 2D and 3D pair-correlation functions. Additionally, to verify our model experimentally, we have compared the theoretical predictions with experimental results. We have found a good agreement between the theory and experiment.

2. Theoretical model

In this paper we have investigated the five multilayers of hard monodisperse particles, generated as described in detail in Ref. [29]. We have used the extended RSA model mimicking the process of LbL deposition of alternating particles of type 1 (odd layers) and type 2 (even layers) on a homogeneous substrate. Obviously, whether the surface charge of odd layer particles is negative or positive, the resulting multilayer structure is the same, as long as these particles' surface charge is opposite to that of the substrate. According to the model, we have simulated the formation of the first particle layer on the surface $z = 0$ using the classical RSA model [45], i.e., by choosing at random the x and y coordinates of a virtual particle and checking the non-overlapping condition. Creating the second, fourth, and all subsequent even layers is analogous, except the type 2 particles can adsorb onto particles of type 1 only. On the contrary, the particles of the third, fifth, and all subsequent odd layers (type 1 particles) can adsorb both onto the type 2 particles *and* onto the solid/liquid interface at $z = 0$. For each layer, we have continued the sequence of uncorrelated adsorption trials until the desired surface coverage is achieved. At the perimeter of the simulation area we have applied the usual periodic boundary conditions as done previously [24,25,29,30]. Please note that for the sake of notation simplicity, in what follows we have normalized all dimensional parameters and variables by the particle radius a, its square, or cube, to make them dimensionless.

Physically, the algorithm we have used describes a process of successive adsorption cycles in which colloidal particles with alternating positive and negative surface charges are adsorbed from suspensions onto a solid surface to form a multilayer (the LbL technique). The structure of the resulting multilayer depends on a variety of parameters of the adsorption process, such as the adsorption time, ionic strength, or pH, and can be controlled.

In this paper, we have limited our studies to multilayers with a constant number of particles adsorbed per cycle, $N = \text{const.}$, so the corresponding value of arbitrarily chosen single-layer surface coverage:

$$\Theta = \frac{\pi N}{S} \tag{1}$$

is equal 0.10, 0.20, 0.30, 0.40, and 0.50. Here S is the dimensionless adsorption surface area. It is worth to mention that the maximum coverage of the first layer in this process, the so-called jamming limit, is $\Theta_\infty = 0.547$ [45].

From an experimental point of view the quantity of major interest is the mean multilayer thickness:

$$\bar{h} = 1 + \frac{1}{N}\sum_{j=1}^{N} z_{nj} \tag{2}$$

where z_{ij} denotes the coordinate z of the particle j in the layer i, $i = 1, \ldots, n$. Please note that the averaging in Eq. (2) is made over the particles of the outer layer number n only.

The surface coverage and mean thickness give us global information about the multilayer only. To obtain more precise information on particle distribution in each layer, we have also calculated the particle volume fraction as a function of the distance z from the interface using the formula:

$$\phi_i(z) = \frac{dv_i(z)}{dv} = \frac{1}{S}\sum_{j=1}^{N} S_{ij}(z), \tag{3}$$

where $\mathrm{d}v_i = \mathrm{d}z\sum_{j=1}^{N} S_{ij}(z)$ is the infinitesimal volume of particles of the layer i in the volume element $\mathrm{d}v = S\mathrm{d}z$ (having the infinitesimal thickness $\mathrm{d}z$) and $S_{ij}(z)$ is the cross-section area of the particle j of the layer i, at the distance z from the substrate. In the case of a monolayer of monodisperse spherical particles Eq. (3) can be reduced to the simple form

$$\phi_1(z) = \Theta z(2 - z). \tag{4}$$

The overall particle volume fraction $\phi(z)$ is given by the formula

$$\phi(z) = \sum_{i=1}^{n} \phi_i(z). \tag{5}$$

We can also quantitatively characterize the structure of particle multilayer generated in the multilayer RSA process in terms of the 3D pair-correlation function $g_{3D}(r)$, where r is the distance between particle centers. In our system there are two types of particles, therefore we can distinguish several types of correlation function for different pairs of particles. In what follows we present just the pair-correlation function for all particles, calculated from the constitutive dependence:

$$g_{3D}(r) = \lim_{\Delta r \to 0} \frac{v}{N_t} \left\langle \frac{\Delta N_t(r)}{4\pi r^2 \Delta r} \right\rangle, \tag{6}$$

where N_t is the total number of particles adsorbed within the multilayer of the volume v, ΔN_t 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 probability density of finding a pair of particles separated by a distance smaller or equal to r, normalized to unity at large distances. Obviously, we have discarded from the averaging procedure all particles located close to the perimeter of the simulation area, as well as those in the bottom and top parts of the multilayer. As we have demonstrated below, the pair-correlation function can be discontinuous and change rapidly. Therefore, to obtain a good representation of the function, the entire population in each single layer is greater than 10^6 particles. Also, we have used Eq. (6) with the shell thickness $\Delta r \sim 10^{-3}$. Then we have smoothed out the resulting noisy data using quadratic B-splines. For that we have utilized a double-precision version of the subroutine FC [46] by Hanson, which is a part of the open source library SLATEC [47], available on the Internet.