Generalized model of irreversible multilayer deposition

Shaoxiong Yang,[1] Pascal Viot,[2] and Paul R. Van Tassel[1]
[1]*Department of Chemical Engineering and Materials Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, Michigan 48202*
[2]*Laboratoire Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France*
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The multilayer deposition of macromolecular particles, such as colloids and proteins, is often used to form thin film materials. We present a general model of the irreversible multilayer deposition process that accounts for both surface screening and surface restructuring. Particles are modeled as $(d+1)$-dimensional hard spheres that deposit sequentially at random positions onto a d-dimensional substrate. A particle is considered irreversibly adsorbed if it lands directly on the surface. If the particle instead lands on a previously placed particle, it will do one of three things (depending upon the extent of ''overhang'' with respect to the surface or to the contacting particle): adsorb, desorb, or roll towards the surface. We obtain analytical results for the time evolution of the particle density in the first layer in one dimension when surface overhang rules are employed. We use computer simulation to investigate the other cases. We find that the first-layer saturation density is larger when the deposition rules favor rolling and disfavor higher-layer adsorption. The particle density above the surface exhibits oscillations that also show a strong dependence on the deposition rules.
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I. INTRODUCTION

The deposition of macromolecular building blocks, such as colloids and proteins, from solution onto a solid substrate provides an alternative method (to vapor deposition and self-assembly techniques) of the formation of thin film materials. This route offers several potential advantages such as simpler deposition conditions, structural control over larger length scales, and the possibility of greater yield. Currently, miniature multifunctional biosensors [1–3], high-temperature superconducting thin film ceramic materials [4,5], and high-resolution cathode ray tube coatings [6–8] are all fabricated by particle deposition techniques.

To design, optimize, and control protein and colloid deposition processes, a knowledge of the kinetics of the growth process and their relation to the density and structure of the film is required. Film density and structure clearly affect the physical properties of the resulting material. A predictive knowledge of these properties in terms of the deposition conditions would allow for the rational design of alternative processes for making different materials of specific physical properties.

For this reason, significant effort is being made to develop simple yet realistic models of the multilayer deposition process. Kardar, Parisi, and Zhang neglect the particulate nature of the deposition building blocks and model the growing interface using a nonlinear Langevin equation [9]. This approach, although better suited to describe vapor deposition processes, is successful at predicting computer simulation results of large particle deposition [10]. Lattice models of multilayer deposition have the advantage of accounting for particulate macromolecular building blocks and are often simple enough to treat analytically. Privman and co-workers [11–15] and others [10,16] use exact and mean-field theory along with simulation to determine the kinetics and scaling behavior of k-mers adsorbing onto a linear lattice. In addition to the usual geometrical lattice constraints, a drawback is that overhangs resulting in surface screening are neglected in these works. Continuum descriptions of multilayer particle deposition include irreversible adsorption models (where particles adhere immediately upon contacting the growing interface) and ballistic rolling models (where particles roll to a gravitationally stable position). Simulation and approximate theory are used to understand the structure and kinetics of these deposition processes [17–21].

In this paper we present a general model of irreversible multilayer macromolecular deposition that incorporates all three of the possible events that can occur when a particle contacts an interfacial region: adsorption, desorption, and rolling. The extent of overhang δ of the $(d+1)$-dimensional spherical particle over the d-dimensional surface (surface overhang) or over the contacting particle (particle overhang) determines which of these events will take place. Overhang amounts are compared to an adsorption parameter δ_1 and to a rolling parameter δ_2 $(\delta_1 \leqslant \delta_2)$. If $\delta < \delta_1$, then the particle adsorbs irreversibly. If $\delta_1 < \delta < \delta_2$, then the particle desorbs. If $\delta > \delta_2$, then the particle rolls over the contacting particle and, provided no blockage from previously placed particles occurs, positions itself irreversibly onto the surface. If the path is blocked by at least one other particle, the rolling particle desorbs. These events are depicted in Fig. 1.

The rationale behind letting the extent of overhang determine the subsequent event is as follows. In experimental situations, particles landing directly over other particles will likely have a greater degree of contact and thus are likely to adsorb. Similarly, those with a large overhang will have a lesser degree of contact and since deposition is often induced by gravity or an applied field, the particle is likely to roll and continue descending. The choice of surface or particle overhang rules will depend on whether particle-surface or particle-particle interactions are thought to be more important. Through careful choice of δ_1 and δ_2, one can perhaps

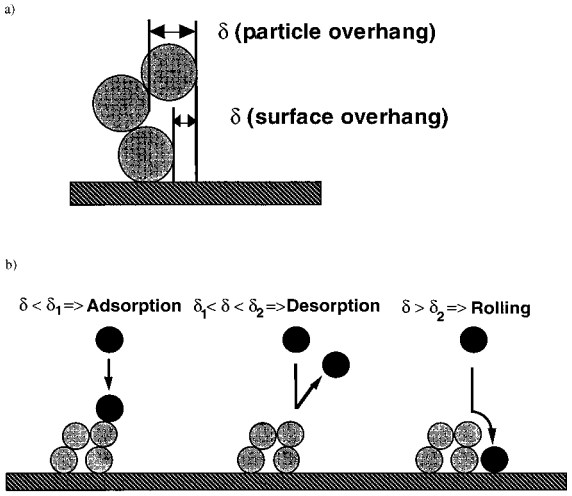

FIG. 1. (a) Depiction of surface and particle overhangs. (b) Schematic of the three possible events that can occur when an incoming particle contacts a previously placed particle.

mimic most experimental situations.

The remainder of this paper is organized as follows. In Sec. II we give a theoretical treatment of one-dimensional (1D) deposition with surface overhang rules. We then describe, in Sec. III, the simulation techniques used to investigate multilayer deposition in higher dimensions and/or deposition when particle overhang rules are used. Results concerning the influence of screening and restructuring on the density and structure of the growing interface are given in Sec. IV and we finish with a discussion and conclusion in Sec. V.

II. THEORY

The time evolution of the surface-contacting layer in this model may be determined analytically in one dimension when overhangs are measured with respect to the surface. This is done by introducing the gap density function $G(h,t)$, defined such that $G(h,t)dh$ is the density of empty, unshielded segments of the surface of length between h and $h+dh$ at time t. For particles of unit diameter depositing at a unit rate, the following integro-differential equation describes the time evolution of the gap function for $h>1$:

$$\frac{\partial G(h,t)}{\partial t} = -[h+1+2(\delta_1-\delta_2)]G(h,t) + 2\int_h^{h+\delta_1} G(h',t)dh' + 2\int_{h+1}^{\infty} G(h',t)dh' + 2(1-\delta_2)G(h+1,t). \quad (1)$$

The corresponding equation for $h<1$ can also be obtained, but is not needed for the analysis presented here. Assuming a solution of the form $G(h,t)=F(t)e^{-[h+1+2(\delta_1-\delta_2)]t}$, Eq. (1) reduces to the ordinary differential equation

$$F'(t)=2F(t)\left[\frac{1+e^{-t}-e^{-\delta_1 t}}{t}+2(1-\delta_2)e^{-t}\right] \quad (2)$$

whose solution is given by

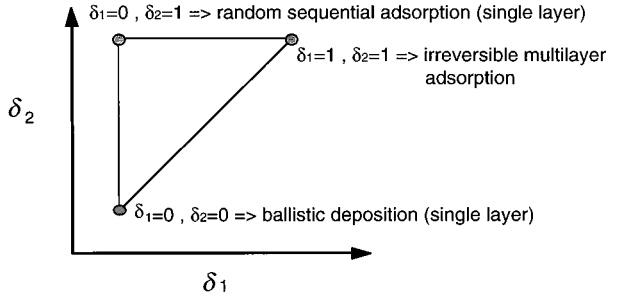

FIG. 2. Region of available parameter space and the positions that correspond to models introduced previously, including random sequential adsorption [22–26], ballistic deposition [27], and irreversible multilayer adsorption [17–19,28].

$$F(t)=t^2\exp\left[2(1-\delta_2)(1-e^{-t})+2\int_0^t \frac{e^{-t'}-e^{-\delta_1 t'}}{t'}\,dt'\right]. \quad (3)$$

The time evolution of the number density of particles in the first layer $\rho(t)$ is related to the gap density function as

$$\frac{\partial \rho(t)}{\partial t}=\int_1^{\infty}(h+1-2\delta_2)G(h,t)dh. \quad (4)$$

The density of particles in the first layer is then

$$\rho(t)=\int_0^t [1+(2-2\delta_2)t'] \times\exp\left[-(2-2\delta_2+2\delta_1)t'+2(1-\delta_2)(1-e^{-t'}) +2\int_0^{t'}\frac{e^{-t''}-e^{-\delta_1 t''}}{t''}\,dt''\right]dt'. \quad (5)$$

We pause for a moment to consider some limiting cases of Eq. (5). When $\delta_1=0$ and $\delta_2=1$, the model reduces to the simple random sequential adsorption model [22–26]. When $\delta_1=\delta_2=0$, we recover the simple ballistic deposition model [27]. When $\delta_1=1$, we recover the irreversible multilayer deposition model (without rolling) [28]. When $\delta_1=0$ and $0<\delta_2<1$, a generalized ballistic deposition process is recovered. Figure 2 shows the occurrence of these limiting cases in parameter space.

III. SIMULATION

The model presented here can be evaluated in all cases by numerical simulation. In one dimension, disk-shaped particles of unit diameter adsorb at a unit rate onto a line of length $L=256$. The line is divided into bins of unit length (there are thus 256 bins). To place a particle, a random position is chosen on the line. The vertical (z) positions are calculated of hypothetically placed particles in contact with each of the previously placed particles that have x positions (i) in the bin containing the chosen position or (ii) in one of the two neighboring bins. The particle is placed in the position that is furthest from the line (i.e., the one with the highest z value). Next, the surface or particle overhang is deter-

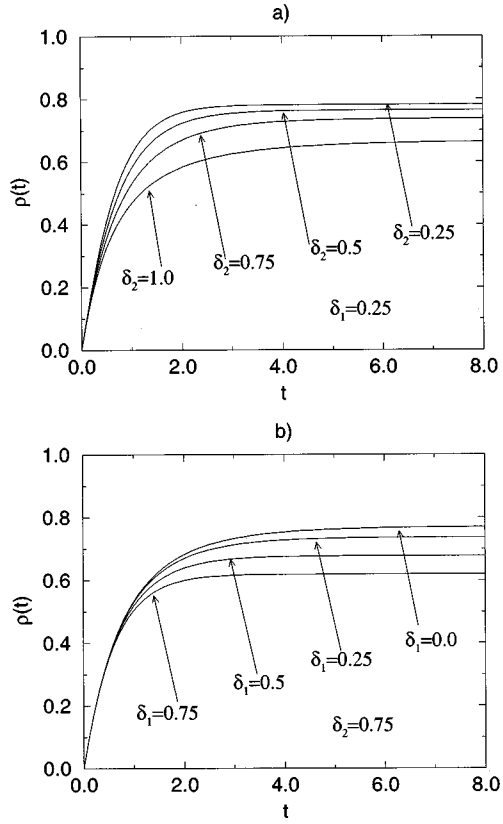

FIG. 3. Density of particles in the lowest layer as a function of time calculated via Eq. (5) at (a) $\delta_1 = 0.25$ and (b) $\delta_2 = 0.75$. Deposition events are dictated by surface overhang rules.

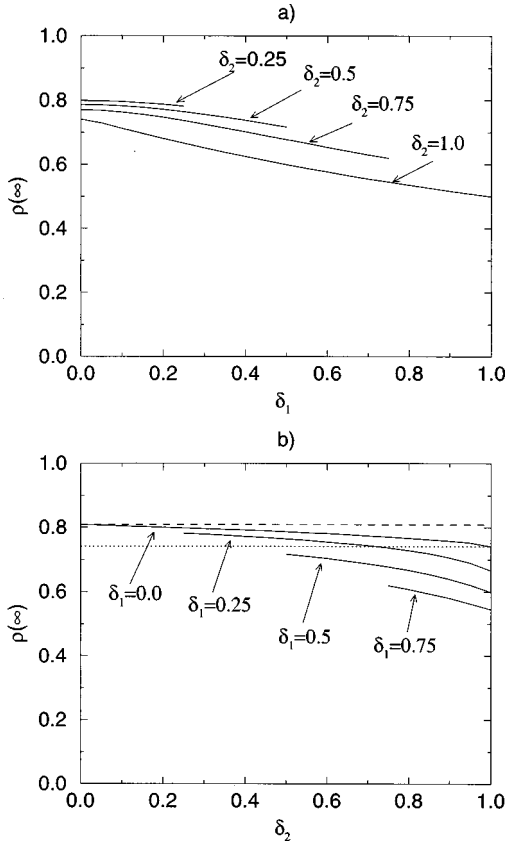

FIG. 4. Saturation density of particles in the lowest layer as a function of (a) δ_1 and (b) δ_2 as calculated by Eq. (5). Deposition events are dictated by surface overhang rules. Also shown in (b) are lines representing the saturation density of random sequential adsorption (dotted line) [22] and ballistic deposition (dashed line) [27].

mined. If this is less than δ_1, then the particle remains in its position for the remainder of the run. If the extent is between δ_1 and δ_2, then the particle is removed. If it exceeds δ_2, all particles in the bin containing the chosen position and the two bins to the rolling side are checked for blocking of a vertical path to the surface. If none block this path, the particle is placed on the line a unit length away from the contacting particle (in the x direction). If the path is blocked, the particle is removed. Note that in this model, rolling over more than one particle is not allowed.

In two dimensions, sphere-shaped particles of unit diameter deposit onto a plane of area 256×256. The simulation proceeds as in the 1D case with all nearest-neighbor bins checked to determine the z position of a depositing particle and all nearest- and next-nearest-neighbor bins checked for the blocking of a rolling particle.

IV. RESULTS

In Fig. 3 we show kinetic curves for the first layer density in one dimension using surface overhang rules as calculated by numerical integration of Eq. (5) for various values of δ_1 and δ_2. We note that saturation is reached quite rapidly, usually in just a few time units. We show the saturation values as functions of these parameters in Fig. 4. We note that the saturation density $\rho(\infty)$ is larger for smaller values of δ_1 and δ_2. A small value of δ_1 causes a reduction in the number of overhanging particles leading to a greater number of particles that can reach the surface. A small value of δ_2 leads to more particles reaching the surface via the ballistic mechanism. This is a very efficient means of covering the surface as it does not result in gaps too small to be occupied by additional particles.

In Fig. 5 we also show the saturation surface densities calculated using numerical simulation of our model with particle overhang rules in one and two dimensions. We note that when either δ_1 or δ_2 is unity, both surface and particle overhang rules lead to the same surface densities. For other values, particle overhang rules yield a higher surface density due to decreased surface screening by upper layer particles. We also note that in two dimensions, the densities (which, in reduced units, are just the projected fractional surface coverages) are lower due to less efficient filling.

We show the density of particles in higher layers as a function of time in two dimensions in Fig. 6. We note the presence of peaks that correspond to particles in distinct layers. When $\delta_1 = \delta_2 = 1$, all particles adsorb irreversibly upon contacting the growing interface. In this case, the density oscillations dampen for distances greater than about four particle diameters. (This special case was previously studied in Ref. [19].) If δ_1 is reduced to 0.75, meaning that overhangs greater than this value will result in desorption, more pronounced oscillations result that persist to distances greater than eight particle diameters. This is due to particles stacking more or less on top of each other. This should also lead to a

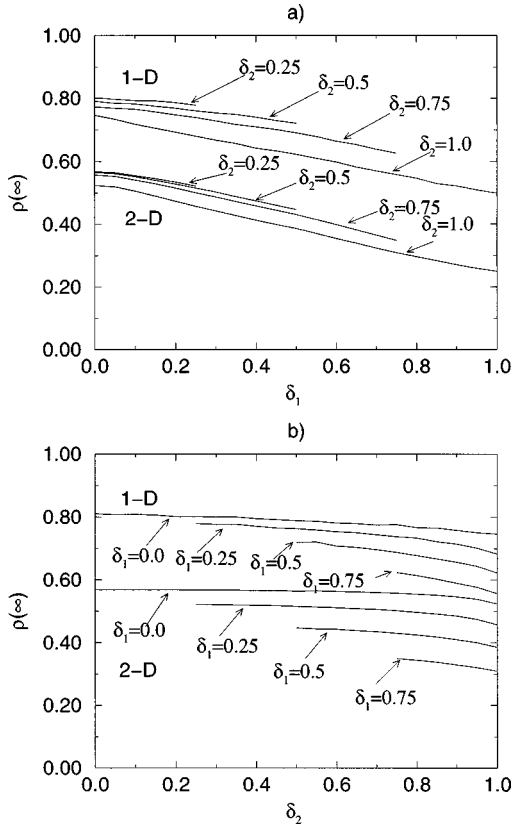

FIG. 5. Saturation density of particles in the lowest layer as a function of (a) δ_1 and (b) δ_2 as calculated by Monte Carlo simulation. Deposition events are dictated by particle overhang rules. One- and two-dimensional results are shown.

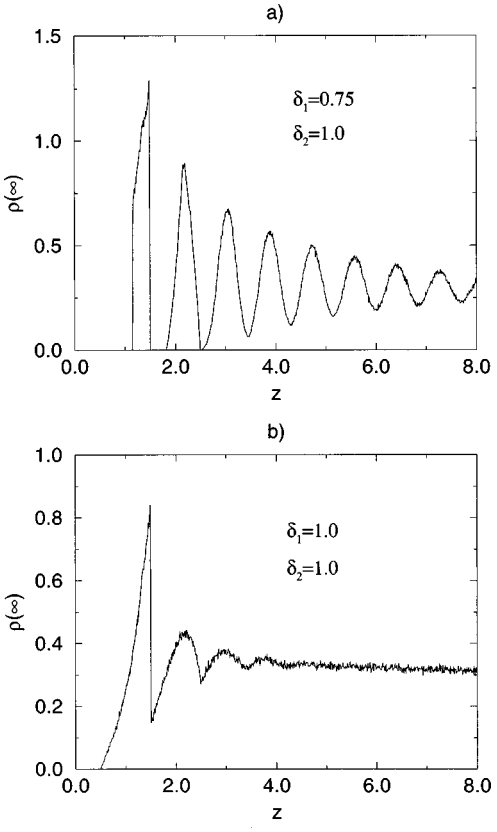

FIG. 6. Density of higher-layer particles as a function of height above the surface in two dimensions for different values of δ_1 and δ_2. Deposition events are dictated by particle overhang rules.

lower asymptotic density. Most importantly, this shows that relatively small changes in the parameters of this model can lead to greatly differing interfacial structures.

V. DISCUSSION

Two important features of any multilayer deposition process are screening and restructuring. Screening is the shielding of empty (available) surface by particles in the upper, nonsurface contacting layers [see Fig. 1(a)]. A high value of the parameter δ_1 in our model promotes screening by increasing the extent to which a particle may overhang another particle; this is seen to decrease the number of particles that reach the surface. Restructuring is the movement of particles following contact with the growing interface. In our model, restructuring is limited to the period of time immediately following contact and occurs only if a vertical path is open for deposition directly onto the surface. A lower value of δ_2 in our model promotes restructuring; this is seen to increase the number of particles that reach the surface.

The generalized multilayer deposition model presented here reduces to previously studied models for certain values of the parameters δ_1 and δ_2. When $\delta_1=\delta_2=0$, all depositing particles either roll to the surface or, if space is unavailable, desorb. This is just the monolayer ballistic deposition model introduced by Talbot and Ricci [27]. When $\delta_1=0$ and $\delta_2=1$, all particles that do not directly contact the surface are removed and the monolayer random sequential adsorption model is recovered [22–26]. By keeping $\delta_1=0$ and letting δ_2 vary between 0 and 1, one obtains a generalized monolayer deposition model that allows for ballistic rolling for superthreshold overhangs.

When $\delta_1>0$, multilayer deposition becomes possible. In the case of $\delta_1=\delta_2=1$, all particles adsorb irreversibly upon contacting the growing interface. This model has been considered previously [17–19] and is especially significant because an analytical solution is available even in higher dimensions [28]. By keeping $\delta_2=1$ and letting δ_1 vary between 0 and 1, one recovers the multilayer deposition model reported recently by Van Tassel and Viot [28]. Finally, when $\delta_1=\delta_2$, one has the generalized model of multilayer adsorption with rolling. These special cases are shown in Fig. 2. We further note that when $t\ll 1/\delta_1$, the density evolves as if the deposition process would be a monolayer process [see Eq. (5)]. Thus it is only after a sufficiently long time that the two processes can be distinguished from one another. Consequently, experiments where multilayer formation is weak may accurately be modeled using a monolayer approach up to a considerable length of time.

In this work we report primarily data on the lowest (surface contacting) layer, for which, in certain cases, an analytical treatment is possible. This layer is especially important because (i) it may be the most strongly adsorbed and therefore survive a subsequent rinsing step and (ii) it surely influences the structure and density of higher layers. For example, when $\delta_1\leqslant\frac{1}{2}$, only one particle may adsorb onto a given previously placed particle. In this case, we find the structure of the interface to be chainlike, with each nonsurface contacting

particle contacting one particle from below and at most one from above. The average density above the surface can be approximated by the average separation in the z (vertical) direction of two contacting particles. One can show that this density is $2\delta_1/[\sin^{-1}\delta_1+\delta_1(1-\delta_1^2)^{1/2}]$ times the surface density in one dimension and $3\delta_1^2/[2-2(1-\delta_1^2)^{3/2}]$ times the surface density in two dimensions (for unit diameter particles). This amounts to an upper bound on the actual density since for a finite height above the surface, some of the chains will have terminated due to crossing by other (longer) chains. Further analysis of the structure of an interface growing via these deposition models will be the subject of a future work.

VI. CONCLUSION

In this paper we present a generalized irreversible multilayer deposition model with two different overhang rules that allow for the possibility of adsorption, desorption, and ballistic rolling. In the case of one dimension and surface overhang rules, the density of particles in the lowest layer is calculated analytically. Numerical simulation is used in other cases and to determine the density of particles above the surface. Previous monolayer deposition models, such as random sequential adsorption, ballistic deposition, and multilayer irreversible adsorption are special cases of this generalized model.

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