MORPHOLOGY OF AMORPHOUS LAYERS BALLISTICALLY DEPOSITED ON A PLANAR SUBSTRATE

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ABSTRACT

We report numerical simulation of the deposition of spherical particles on a planar surface, by ballistic, straight-line trajectory transport, and assuming irreversible adhesion on contact with the surface or previously deposited particles. Our data indicate that the deposit formed has a loosely layered structure within few diameters from the surface. This structure can be explained by a model of growth via chain formation. Away from the surface we found evidence of a monotonic, power-law approach to the bulk density. Both density and contact-statistics results suggest that the deposit formed is sparse: the space-filling fraction is about 15%, and the average number of contacts is 2. The morphology of the deposit both near the surface and in the bulk seems to be a result of competition of screening and branching; nearly half of all the spheres are either single-contact dangling ends, or branching nodes with more than two contacts.

1. INTRODUCTION

Formation of deposits of proteins and monodisperse colloid particles on planar substrates (surfaces) has been a topic of recent theoretical interest [1] due to advances in experimental realizations and characterizations of such systems [2]. Since analytical theories are at best approximate [1], formation of multilayer deposits has been studied mostly by numerical means [1]. However, these numerical studies were limited to lattice models, and many of the detailed results were obtained only for the deposition on linear, one-dimensional "substrates." In this work we report the first detailed numerical investigation of the morphology of off-lattice deposits of spherical particles at a planar, two-dimensional wall. We also introduce a new theoretical model which explains semi-quantitatively the numerical findings.

Our interest is mainly in the morphology of the deposit near the wall (i.e., the structure of the first few layers). Indeed, deposition experiments [1,2] providing motivation for our study typically involve formation of not too many layers. (Note that the concept of "layers" is at best approximate in random, amorphous structures.) As emphasized in earlier studies [1], the transport mechanism of particles to the wall is then not a decisive feature. Here the simplest, ballistic-deposition transport will be assumed: spherical particles are dropped randomly over the substrate. They fall along straight-line trajectories (perpendicular to the substrate) and stick irreversibly, at the first contact, to the substrate or to one of the particles deposited earlier.

We only report results for the final-state structure after many spheres were deposited and the near-wall layers reached saturation. Study of the time-dependent properties is also of interest. However, all such investigations are rather computer-resource (time and memory) demanding. Ballistic deposition modeling of colloid aggregation at surfaces has a long history [3]. Recent studies of ballistic deposition on both linear and planar substrates, mostly limited to lattice models, were largely focussed on the properties of growing surfaces far away from the wall [4-5]. For numerical investigations of amorphous assemblies of spheres produced by means other then irreversible deposition, for modeling experimental "powder" properties, consult, e.g., [6]. Models of epitaxial growth where particles fall on an ordered substrate (e.g., a lattice of spheres) and further relax, for instance by rolling down to the lowest lattice position after the first contact, have been considered in the literature [7] although most numerical simulations were limited to a lower-dimensional case of deposition of circles.

The outline of the later sections is as follows. The model is defined, and the numerical simulation details are given, in Section 2. Section 3 is devoted to the presentation and discussion of our results for the sphere-center density as a function of the distance from the wall. Further discussion of the density properties near the wall, in the framework of the chain-formation model, is the subject of Section 4. Finally, Section 5 contains the presentation of our results on the statistics of sphere contacts and summary.

2. DEFINITIONS AND OUTLINE OF THE NUMERICAL METHOD

Let the ball (sphere) diameter be D. We will measure all quantities in dimensionless units. Thus, the substrate surface was square, of size $\ell D \times \ell D$, with ℓ values of order 200 in our simulations. Periodic boundary conditions were imposed in both directions within the substrate to minimize finite-ℓ effects. Each ball was positioned randomly above the substrate and then "dropped" vertically to stick at its first contact with the substrate or one of the earlier-dropped balls. The number of balls in each run was of order 10^6 and the results were averaged over many runs; specific numbers and computer program details are given later.

We recorded the ball density and the statistics of contacts. The latter will be described in Section 5. The ball-center density was measured by binning the center coordinates in the histogram with bins at

$$\left(\frac{1}{2}+\frac{m}{K}\right) D \leq z < \left(\frac{1}{2}+\frac{m+1}{K}\right) D \,, \tag{2.1}$$

where z is the distance of the ball center from the wall, while $m = 0, 1, 2, \ldots$ labels the bins. Let us denote the count in bin m, averaged over many runs, as mentioned earlier, by C_m.

Note that the ball centers are located at distances $z \geq D/2$ away from the wall. However, we found that the count C_0 is much larger than the counts $C_{m>0}$, due to the formation of a finite surface-coverage density of balls in direct contact with the wall. If we introduce the dimensionless variable

$$h = \frac{z}{D} - \frac{1}{2} \,, \tag{2.2}$$

then the total ball density can be formally written, for $h \geq 0$, as

$$\big[\rho(h) + \theta\delta(h)\big] D^{-3} \ . \tag{2.3}$$

Here the wall-contact density contribution (per unit area) is given by θD^{-2}, where θ can be estimated numerically from the relation

$$\theta = \lim_{K\to\infty} \left(C_0/\ell^2\right) \ . \tag{2.4}$$

The spatial ball-center density for $h > 0$ is ρD^{-3} (per unit volume), where

$$\rho(h) = \lim_{K\to\infty} \left(K C_{Kh}/\ell^2\right) \ . \tag{2.5}$$

Results of our numerical simulations and their analysis will be presented in later sections. In the remainder of this section we outline some of the programming aspects of the simulation. Readers interested in results only can skip now to Section 3.

In the deposition of the $n^{\rm th}$ sphere, we select its planar coordinates (X_n, Y_n) randomly and independently. However, the vertical coordinate $z = Z_n$ must be determined by the first-contact condition. Let (X_m, Y_m, Z_m) denote the coordinates of the centers of spheres deposited earlier, $m = 1, 2, \ldots, n-1$. We examine the numbers z_m defined by

$$z_m = Z_m + \sqrt{D^2 - \left(X_n - X_m\right)^2 - \left(Y_n - Y_m\right)^2} \ . \tag{2.6}$$

Most of these $(n-1)$ numbers will not be real. However, we only keep those for which the argument of the square root is nonnegative so that they are real (for positive arguments the positive root value is taken). The resulting real-z_m values and the number $D/2$ are compared and the *largest* among all these numbers is the required value Z_n.

A straightforward selection by maximization of (2.6), among $(n-1)$ candidates z_m, requires order n computations for particle n and hence order N^2 computations for depositing N particles. Our program actually spent only order N computations for N particles. This was accomplished by splitting the area of the substrate into sectors. For each sector we maintained a list of particles deposited in it. For each new particle, our program checked particles only in a few neighboring sectors, rather than all the previously deposited particles. Moreover, the particles in the sector were ordered according to their z-coordinates, and the checking within each sector was restricted to a few top particles.

3. RESULTS FOR THE DENSITY OF SPHERE CENTERS

Our longest run took about 2 CPU weeks on a SUN SPARC workstation. The substrate size was $\ell = 200$. The number of balls dropped in each run was 10^6, and the results were averaged over 1005 independent runs. The bin size was $1/K = 1/97$. ¿From the data collected in this run as well as in other simulations (see further below), we estimate

$$\theta = 0.318 \pm 0.001 \; . \tag{3.1}$$

Note that if the ball adhesion events were allowed only on the substrate, and not on other balls, then this system would be equivalent to the Random Sequential Adsorption process of depositing disks on a plane [1]. In the latter process, the surface coverage (fraction of area covered) reaches the value ~ 0.547 at large times [8]. This corresponds to the disk-center density ~ 0.430, in units of D^{-2}. The result (3.1) is considerably lower indicating a significant screening of the surface layer by balls deposited in higher layers.

As already mentioned the concept of a "layer" is used here loosely. It turns out, however, that the deposit formed does show some tendency to layering at least for distances up to about $h = 5$. The density of ball centers near the wall, as obtained in our longest run, is shown in Figure 1. The fluctuations observed, suggesting the layered structure, can be attributed to chain formation which will be modeled in detail in the next section. The layering tendency is not due to any ordering of a crystalline type. Examination of few snapshots of the two-dimensional cross-sections parallel to the substrate both near and away from the wall, for a run with the substrate size $\ell = 256$, suggests no crystalline regularity in the ball arrangement.

For distances $h \gtrsim 5$, the density oscillations fade away. Instead, the density decreases monotonically. In earlier numerical studies of ballistic deposit growth from point seeds and on lattice substrates, mainly for low-dimensional, lattice models [4,5,9,10], it was noted that the density away from the seed or surface falls as a power law,

$$\rho(h) \simeq \rho(\infty) + \mathrm{const}/h^p \ , \qquad \text{for} \qquad h \gg 1 \ , \tag{3.2}$$

with the exponent estimates spanning the range $p = 0.80 \pm 0.06$ for two-dimensional substrates; see [4,5,11]. This behavior attracted much interest and it was attributed [11] to the formation of large gaps due to surface roughening which in turn arises from screening effects. As pointed out earlier, the morphology of deposits far away from the substrate is sensitive to the transport mechanism. The ballistic transport yields screening too weak to cause formation of a ramified, fractal structure. The power-law tail is thus the most profound result of screening in ballistic deposits. In particular, the exponent in (3.2) was related to the kinetic roughening exponents; see [11] for further discussion.

Our longest-run data were recorded up to approximately $h \simeq 20$. In order to check that the observed monotonic decrease in density was not due to incomplete saturation, and to make sure that finite-ℓ effects were negligibly small, we made another long run. The number of spheres was increased to $1.6 \cdot 10^6$, while the substrate size was reduced to $\ell = 160$. The bin size was $1/K = 1/41$, and the results were averaged over 236 independent deposition runs. The data were recorded up to approximately $h \simeq 50$. Comparison of the results of the two long runs confirmed the observed monotonic variation. The data from both runs are plotted vs. $h^{-0.8}$ in Figure 2. Despite the statistical noise, it can be claimed that the power-law behavior is consistent with the data and that the exponent in (3.2) is in the range $p = 0.8 \pm 0.2$. The saturation density is

$$\rho(\infty) = 0.280 \pm 0.005 \ . \tag{3.3}$$

We also tried fit to the exponential decay law. However, the power-law is clearly favored.

The asymptotic "bulk" density of sphere centers $\sim 0.28D^{-3}$ corresponds to the packing fraction (fraction of the volume filled up) of $\sim$ 15%. This is considerably smaller than the packing fraction of random assemblies of spheres [6] formed by "bulk" mechanisms with relaxation. Indeed, in the latter processes the filled volume fraction is typically over 60%. Presently, the most accurate estimate of the packing fraction for the ball-deposition ballistic aggregation model in three dimensions is 0.1465 ± 0.0003; see [4]. This range corresponds to

$$\rho(\infty) = 0.2798 \pm 0.0006 \ , \tag{3.4}$$

in excellent agreement with our estimate (3.3).

4. CHAIN MODEL OF THE DENSITY VARIATION NEAR A WALL

Let us assume that the deposit growth can be described in some approximate sense by the following chain-formation model. The incoming balls attach to the end balls of chains of previously deposited balls. Each chain starts with a ball on the substrate and then the later-attached balls can be identified in a linear sequence. Obviously, such a model can be at best approximate. Let us, however, explore its implications.

Within an average, effective-field type prescription, we should be able to assign the probability function $w(x)$ for the $m^{\rm th}$ ball in a given chain to adhere with its center displaced the distance x (measured in units of D) from the center of the ball $(m-1)$. This displacement is in the vertical, h-direction. The function $w(x)$ is normalized,

$$\int_{-\infty}^{\infty} w(x)dx = 1 \; . \tag{4.1}$$

In fact, this function will be strongly localized in $0 \leq x \leq 1$. The value $x = 1$ corresponds to the head-on deposition, while the value $x = 0$ corresponds to the extreme circumferential impact parameter equal the sphere diameter.

The simplest model is of course to assume that both the surrounding-chain spheres and the preceding spheres in the same chain do not interfere in any way with the deposition event. It is then quite easy to check that on geometrical grounds alone a sphere dropped with uniform probability distribution over the cross-section of another sphere, will adhere with probability

$$w(x) = 2x \qquad \text{for} \qquad 0 \leq x \leq 1 \; , \tag{4.2}$$

and $w(x) = 0$ outside this range of the center displacement.

The first balls in the chains, those in direct contact with the wall, contribute the term

$$\rho^{(1)} = \theta\delta(h) \tag{4.3}$$

to the density (measured in units of D^{-3}); see (2.3). The contribution of the balls $m > 1$ can be calculated iteratively,

$$\rho^{(m)}(h) = \int_{-\infty}^{\infty} \rho^{(m-1)}(h-x)w(x)dx \ , \tag{4.4}$$

where the total spatial density in (2.3) is then given by

$$\rho(h) = \sum_{m=2}^{\infty} \rho^{(m)}(h) \ . \tag{4.5}$$

Already the simplest model distribution (4.2), with $\theta = 0.318$ taken from the numerical estimation, see (3.1), gives the density function which has many semi-quantitative similarities with the measured density near the wall. This function was evaluated numerically and plotted in Figure 3. It should be compared with Figure 1; both figures were plotted with the same axes ranges. Note that the resulting density function $\rho(h)$ has a discontinuity at $h = 1$, as well as a discontinuous $(h-1)$-order derivative at each integer value $h > 1$.

The chain-model ideas in deposition, in a somewhat different context, have already been used in the literature; see, e.g., [10] where off-lattice ballistic deposition of circles on a seed was studied. While it is tempting to modify the simplest distribution (4.2) to improve the quantitative consistency with the measured density, the chain model should not, in fact, be taken too seriously. Firstly, at short distances it is not quite clear if the actual density will have true derivative-discontinuities near integer h, or just sharp but rounded anomalies. This is difficult to decide from the numerical data available. Within the chain model, one would then round up the $w(x)$ function near $x = 0$ and $x = 1$.

At large distances, the chain-model prediction for the density is

$$\rho(\infty) = \theta / x_1 \ , \tag{4.6}$$

where x_1 is the first-moment displacement,

$$x_1 = \int_{-\infty}^{\infty} x w(x) dx \ . \tag{4.7}$$

However, our numerical estimates of θ and $\rho(\infty)$ suggest $x_1 \simeq 1.14 > 1$, see (3.1) and (3.3). Thus, the "realistic" distribution $w(x)$ must "protrude" past $x = 1$ to fit the large-h data! (Note that the large-h limiting value in Figure 3 is 0.477.)

Further difficulty is suggested by the power-law tail in the density, (3.2). The Fourier-space considerations not detailed here [note that the convolution (4.4) becomes a product in the Fourier space], suggest that this tail implies long-range tails in the distribution $w(x)$ as well. All these observations make it actually quite difficult to propose a plausible few-parameter form for $w(x)$ to fit all the features of the observed density variation within the chain model.

We therefore adopt the point of view that the chain model can be used (a) to describe the behavior of the saturated-deposit density within few diameters from the wall semi-quantitatively; (b) to suggest some general features of the density to be checked by future numerical simulations such as possible discontinuities in $\rho(h)$ and its derivatives; (c) in time-dependent deposition modeling for short times when the average coverage is within few diameters.

Note that relations (4.3)-(4.5) for the density are recursive <u>along the chains</u> which are anyway approximate objects. In a series of papers [12], Savit and coworkers considered approximate recursive relations in time, for particle adhesion probability distribution within the growing kinetically-roughened interface. Their conclusion was that in many models quasiperiodic irrational-frequency density fluctuations should be present, with density fluctuating on scales larger than the underlying particle-size "clock" length, 1 in our reduced units (2.2). It should be emphasized that fluctuations in density and other quantities (see Section 5) found in our work are not the "bulk" effect described in [12]. In fact, what we are observing is the "clock" particle-size fluctuations with underlying periodicity 1. These fluctuations fade away for distances over 5-6 particle diameters from the wall. Therefore, the irrational-frequency fluctuations [12] cannot be present in the model considered here. Indeed, far from the wall even the basic particle-size periodicity is not preserved; the deposit is truly amorphous. However, "bulk" density fluctuations can be present in lattice ballistic deposition [13], as well as in off-lattice models where the underlying discrete structure is preserved far from the wall. This can be achived by having lattice substrate and relaxation mechanisms for particles to align themselves with the deposit structure on adhesion, or by having particle shapes, e.g., oriented cubes, which force layer structure in the bulk.

5. CONTACT STATISTICS

One of the conclusions of Sections 2-3 was that the deposit formed by ballistic transport and irreversible sticking is quite different from the uniform assembly of randomly packed spheres [6]. We found that the density is much lower, and the structure has a preferred orientation and tendency to layering at least within the first few diameters from the wall. It is well established that the average number of spheres in contact with each given sphere in the randomly packed structure is near 6; see [6].

We collected the statistical data on the number of contacts per ball, binned similarly to the density statistics described in Section 2. We only found contacts with 1, 2, 3, 4, 5, and in very few instances, with 6 balls (the count included wall contacts as well). Let us denote by $f_i(h)$ the fraction of balls with $i = 1, 2, 3, 4, 5, 6$ contacts, at the (dimensionless) distance h from the wall; see (2.2). The average number of contacts is given by

$$\sum_{i=1}^{6} i f_i(h) \ , \qquad \text{where} \qquad \sum_{i=1}^{6} f_i(h) = 1 \ . \tag{5.1}$$

This function, as estimated from our longest run (Section 2), is plotted in Figure 4 for $h > 0$. It shows general pattern of behavior similar to the center density: there are oscillations and (possibly rounded) discontinuities in the function or its derivatives near integer values $h = 1, 2, \ldots$. Although not shown in the figure, the value $\simeq 1.900$ found at $h = 0$ suggests also the discontinuity as $h \to 0$.

The large-h behavior of the average number of contacts can be represented by a power-law relation similar to (3.2). The data from the two long runs are quite straight when plotted vs. $h^{-0.8}$ (cf. Figure 2), suggesting that the same exponent $p \simeq 0.8$ applies here. The limiting value as $h \to \infty$ was estimated as 2.000 ± 0.005. Early numerical studies [3] of ballistic deposition also yielded "bulk" contact numbers near

2. In fact, one can prove that this limiting value is exactly 2, provided the average number of contacts approaches a constant value as $h \to \infty$, i.e., the fluctuations are damped, as is indeed suggested by our data. Note that this "coordination number" is much lower than the typical "powder" values ~ 6 quoted earlier.

The fractions of contacts $f_i(h > 0)$ for $i = 1, 2, 3$ are plotted in Figure 5. The remaining contacts, $i = 4, 5, 6$, amounted to at most 2%, typically less. Thus, Figure 5 summarizes the main contact-statistics properties. Each fraction has (possibly rounded) discontinuities similar to the density and average number of contacts. There is also the discontinuity at $h = 0$ where the values, not shown in the figure, were $\simeq 0.286, 0.541, 0.161$, for $i = 1, 2, 3$, respectively.

Note that the simplest chain model would correspond to $f_2 = 1$ and the number of contacts 2. In actuality, however, far from the wall only about 53% of the balls have two contacts. About 25% of the balls have only one contact which indicates that they were screened from the incoming flux of balls by the surrounding structure, thus becoming "dangling ends." On the other hand, the remaining 22% of the balls have 3 (about 20%) or more (about 2%) contacts thus forming branching points in the structure. Qualitatively, these conclusions were also confirmed by visual examination of a "snapshot" of the ball configuration in the plane perpendicular to the substrate.

The above percentages were far from the wall. Figure 5 suggests that both screening and branching change abruptly near integer h values within the first few diameters from the wall, which correlates with the density fluctuations, although we are not aware of any theoretical modeling of such properties.

In summary, we reported the first detailed investigation of the morphology of ballistic deposits near walls. The observed structure is disordered but an approximate notion of "layers" can be used near the wall. Deposits formed by irreversible sticking are much sparser than the relaxed, powder-type structures. On the average, each particle is in contact with two others particles. The chain model in its simplest form accounted only for the near-wall layering while the more "bulk" properties seem to be governed by competition of screening and branching.

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FIGURE CAPTIONS

Fig. 1. Spatial density of ball centers evaluated numerically in the long run with bin size $1/K = 1/97$, see Section 3. The histogram counts were multiplied by K/ℓ^2 according to (2.5), to yield the density estimates which were plotted at the h values corresponding to the centers of the bins; cf. (2.1)-(2.2). The lines connecting three points near $h = 1$ were drawn to guide the eye.

Fig. 2. Density of ball centers vs. $1/h^{0.8}$. The data shown are from the two long runs as described in Section 3.

Fig. 3. Density of ball centers calculated with the simplest chain-model probability function (4.2).

Fig. 4. Average number of contacts for spheres with centers at $h > 0$; see (5.1).

Fig. 5. The fraction of spheres with 1, 2, and 3 contacts (marked by $f_{i=1,2,3}$), for $h > 0$. The remaining contact fractions, for 4, 5, and 6 contacts, sum up to at most ~ 0.02 and are not shown.

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