Coverage fluctuation and the available line fraction for spheres deposited on a one-dimensional collector after diffusion under the influence of gravity

R. Ezzeddine,[1] P. Schaaf,[2,3] J.-C. Voegel,[1] and B. Senger[1,*]
[1]*Institut National de la Santé et de la Recherche Médicale, Unité 424, Centre de Recherches Odontologiques, Université Louis Pasteur, 1, place de l'Hôpital, 67000 Strasbourg, France*
[2]*Institut Charles Sadron, 6, rue Boussingault, 67083 Strasbourg Cedex, France*
[3]*Ecole Européenne des Hautes Etudes des Industries Chimiques, URA 405 du CNRS, Boîte Postale 296F, 67008 Strasbourg Cedex, France*
(Received 2 May 1995; revised manuscript received 5 July 1995)

It is known experimentally that the diffusion of colloidal particles prior to their adhesion on a solid-liquid interface influences strongly the statistical properties of the assembly of deposited particles. However, in order to perform the simulations taking the diffusion into account, two constraints have been introduced: a maximum number of collisions an adsorbing particle is allowed to make before it is rejected, and/or the height of a rejection plane above the adsorption plane. Their influence on the variance of the number of particles distributed over the subsystems, which is used experimentally to discriminate between different deposition processes, is analyzed in this article. It is shown that great care has to be taken in a comparison between experimental and simulation data.

PACS number(s): 82.70.Dd, 02.50.−r, 68.10.Jy, 82.65.−i

I. INTRODUCTION

Adhesion of colloidal particles to solid surfaces is an important process in many areas of physicochemistry and biology. The deposition process results from the combination of the random motion of the particles in the liquid before adhesion and a number of deterministic forces. These latter may influence greatly the configurations buildup by the adhering particles on the liquid-solid interface. However, in order to simplify the description of the complicated interplay of many interactions, an apparently simple model, called the random sequential adsorption (RSA) model, was proposed at the end of the 1950s and considerably developed since [1–11]. In RSA, particles are deposited sequentially and irreversibly at random positions on a flat surface, with the condition that no particle overlaps any other. If an overlap occurs during an adsorption trial, the trial is rejected and another position is selected at random. In the ballistic deposition (BD) model [8,12,13], in contrast, an incoming particle which hits one already adsorbed is not immediately rejected but rolls over the fixed one and any neighboring particles, adsorbing if it reaches a free area on the surface. It is only discarded if it falls into a trap formed by two fixed spheres (adsorption on a line) or at least three fixed spheres (adsorption on a plane).

Despite the fact that many results have been established both theoretically and from computer simulations performed in the framework of these models, their validity was only poorly established from an experimental point of view [14–16]. Recent irreversible deposition experiments for latex beads of different sizes on flat solid surfaces [17,18] have been performed in order to determine the domain of validity (if it exists) of these models. In these experimental studies, two properties of the assemblies of deposited particles on the surface were measured: the radial distribution function of the adsorbed particles, and the variance $\sigma^2_{\rm expt}$ of the distribution of the number of particles deposited on subsurfaces of small area taken from the whole collector. Four major conclusions could be drawn from this study: (i) the BD model seems in relatively good agreement with the results corresponding to the deposition of large particles where the gravitational field plays a major role during the deposition process. This conclusion had already been obtained in previous studies [16]. (ii) The radial distribution function $g(r)$ determined for small particles is well predicted by the RSA model. On the other hand, even for the smallest size of particles that was investigated (radius of the order of 0.6 μm, density ≈ 1.055 g cm^{-3}) the variance $\sigma^2_{\rm expt}$ of the distribution of particles on small areas of the surface was not in agreement with the value corresponding to the RSA model. (iii) For particles of intermediate radii ($1 \le R \le 3$ μm), neither the RSA nor BD models could accurately predict the radial distribution function $g(r)$. (iv) All experimental results reveal that the diffusion of the particles in the bulk before reaching the adsorbing surface seems to play an important role, and even a prime role for some properties such as the variance $\sigma^2_{\rm expt}$. This seems obvious following the depositon of a particle under a microscope even without analyzing in detail the statistical properties of the assembly of deposited particles.

This latter point had already been recognized for several years and additional simulation models were developed in order to take this diffusion process of the particles in the bulk into account. The first of these

*Author to whom correspondence should be addressed. TEL.: (33) 88 25 66 54. FAX: (33) 88 36 62 37

refined models was the diffusion random sequential adsorption (DRSA) model [19–21]. Since, in the experiments evoked above, the gravity can play an important role, it was introduced in the DRSA model. This model was called the DRSAG model (where G stands for gravity). Another problem arises with the introduction of gravity: particles submitted to large enough gravitational force can become stuck in a "trap" made of at least three adsorbed particles. The adsorption trial of a trapped particle would thus take almost infinite computer time. To get around this problem, a supplementary rule has been added in the DRSA algorithm: if the incoming particle collides k_r times with one or several already adsorbed particles, it is rejected (the adsorption trial has failed).

It is the goal of this paper to analyze the influence of the rejection height and of the maximum number of collisions allowed on the adsorption probability of a particle (usually called the available surface function Φ) and on the variance σ^2 of the distribution of the number of adsorbed particles on surfaces of small area out of the whole collector. This latter parameter is especially important because it can be determined accurately from experiments. The influence of the constraints evoked above will be examined in the framework of a $(1+1)$-dimensional [$(1+1)$D] model (the particles diffuse in a vertical plane and adsorb on a horizontal line), less time-consuming than a $(1+2)$D model (diffusion in a volume, adsorption on a horizontal surface). It will be seen that the conclusions that can be drawn from a $(1+1)$D model, although apparently not realistic from the experimental point of view, apply directly to the natural $(1+2)$D situation as far as the questions raised are concerned.

Section II summarizes the method for simulating the deposition of hard spheres on a line (1D collector) after diffusion in a vertical plane. In Sec. III A, we show the variance of the distribution of adsorbed particles on subsystems of the collector (line). Its behavior is analyzed on the basis of the available line fraction which measures the probability that a particle arriving in the vicinity of the collector will adsorb on it (Sec. III B). This function is related to the variance of the number of particles deposited in the subsystems [17,18], and gives a better insight into the origin of the results discussed in Sec. III A. We perform additional simulations (Sec. III C), similar to those presented in Sec. III A, but changing the simulation conditions according to the analysis of Sec. III B. The conclusion of this study (Sec. IV) is that in a model including diffusion, the diffusion time influences to a large extent the observed final configuration formed by colloidal particles at a solid-liquid interface. This contrasts strongly with the "geometrical models," i.e., with the RSA and the BD models.

II. SIMULATIONS

Spherical hard particles of radius R (or diameter $d=2R$) diffuse in a vertical plane (2D space) and adsorb on a one-dimensional (1D) collector, i.e., a line segment of length L. Periodic conditions are applied at the boundaries of this collector. The particles start sequentially from a point of altitude $z=z_s=3R$, and abscissa $x=x_s$ chosen randomly between 0 and L. The particles are submitted to the random Brownian force due to the molecules of the liquid at absolute temperature T and to the gravitational force $\mathbf{F}_g$ due to the difference $\Delta\rho$ (assumed to be positive) between the particle density and the liquid density. At two successive times t and $t+\Delta t$, the abscissa x and the altitude z are given by

$$x(t+\Delta t)=x(t)+\gamma_x\sqrt{2\Delta t} \ , \qquad (1a)$$

$$z(t+\Delta t)=z(t)-R^{*4}\Delta t+\gamma_z\sqrt{2\Delta t} \ , \qquad (1b)$$

where the length unit is R and the time unit is R^2/D. The time interval Δt is chosen in such a way that the mean displacement at each step represents a small part of the radius. All physical parameters characterizing the process are contained in the unique parameter R^* [22–25] defined by

$$R^*=\left[\frac{RF_g}{kT}\right]^{1/4}=\left[\frac{4\pi\Delta\rho g}{3kT}\right]^{1/4}R \ . \qquad (2)$$

Note that R^{*4} coincides with the Péclet number Pe [26]. In Eq. (2), k represents the Boltzmann constant, g the acceleration of gravity, and D the diffusion coefficient of a sphere in a liquid of viscosity η $(D=kT/6\pi\eta R)$; γ_x and γ_z are normal random deviates of mean equal to 0 and standard deviation equal to 1 [27]. With the numerical values $\Delta\rho=0.055$ g cm^{-3}, $g=9.81$ m s^{-2}, and $T=300$ K kept constant throughout this study, and typical for experiments performed with polystyrene latex particles, the relation between R^* and R (expressed in micrometers) is $R^*\approx0.859R$.

When z becomes equal to R, the particle is adsorbed permanently on the line, and the movement of an additional particle is started. If, during its diffusion, a particle collides with a preadsorbed particle, it is drawn back to the position it had a time Δt before the collision, and a new step is tried. In order to save computer time, a maximum number of collisions k_r (equal to 10000) was allowed for each particle. After this number was reached, the particle was discarded and another one was started. We have verified that increasing this number induces no significant change in the jamming limit coverage $\theta(\infty)$. For instance, for $R=4$ μm (i.e., $R^*=3.438$), we obtained $\theta(\infty)=0.8044\pm0.0027$, 0.8027 ± 0.0027, and 0.8030 ± 0.0026 for $k_r=10\,000$, 20 000 and 30 000, respectively. On the other hand, light particles are not strongly pulled downward by the gravitational force, and may therefore diffuse at high altitude before adsorbing eventually. A rejection height of $5R$ was adopted in order to avoid too large a waste of computer time. It was demonstrated in a previous paper [25] that the latter limitation also did not significantly influence the value of $\theta(\infty)$.

In the framework of the model described above (diffusion RSA with gravity, DRSAG), the coverage of lines $(L/R\approx2700)$ was performed with spherical particles of various radii: R (μm)$=0.6$ (sample size: 250 lines covered), 1.02 (250), 1.2 (250), 1.5 (250), 1.75 (500), 2 (500), 2.5 (1000), 3 (1000), 4 (500), and 6 (1000). In addition, we simulated also the coverage of 2000 lines following the rules of the usual RSA model [3] and of the ballistic deposition (BD) model [8.] These latter run much faster than the DRSAG since the diffusing trajectory is not taken into account. For this reason the results obtained with the DRSAG model were limited to coverages between 0.4 and 0.6, less than the saturation coverage in BD (0.80865. . .) as well as the RSA jamming coverage (0.74759. . .) [8].

Each line was subdivided into ν subsystems, each of length $l=L/\nu$. For a given coverage θ, or a given number N of spheres adsorbed on the whole line, the number n of spheres located in each subsystem is a random variable with mean $\langle n \rangle$ given by

$$\langle n \rangle = N/\nu = \theta l/d \tag{3}$$

and variance σ^2_{sim} where sim stands for simulated. If no rejection occurred during the deposition process, the variance of the number of particles deposited in the ν subsystems would equal the binomial variance σ^2_{bin} defined by

$$\sigma^2_{\text{bin}} = \langle n \rangle \frac{\nu-1}{\nu} \ . \tag{4}$$

The binomial variance depends on the number of subsystems and linearly on their length, at a given coverage [see also Eq. (3)]. We assume that σ^2_{sim} behaves similarly whatever the mechanism involved in the coverage

$$\sigma^2_{\text{sim}} = \frac{\nu-1}{\nu}\left[\frac{l}{d}y_0 + y_1\right] , \tag{5}$$

where y_0 and y_1 are two functions of θ only. The particular case of the binomial variance is recovered if $y_0=\theta$ and $y_1=0$. The additional term y_1 accounts for the fact that, after a collision, a particle during its diffusion may adsorb in some subsystem other than that containing the particle first hit (border effects). Introducing the relation $\nu=L/l$ into Eq. (5) yields an expression for σ^2_{sim} which explicitly displays its dependence on l. The analysis of the variance is, however, rendered much easier if one defines a corrected variance σ^2 by

$$\sigma^2 = \frac{\nu}{\nu-1}\sigma^2_{\text{sim}} = \frac{l}{d}y_0 + y_1 , \tag{6}$$

which is a linear function of l, of slope y_0 and intercept y_1 (see Sec. III A). Furthermore, one can also define a reduced variance y by a simple transformation of Eq. (6):

$$y = \frac{d}{l}\sigma^2 = y_0 + \frac{d}{l}y_1 \ . \tag{7}$$

This equation shows clearly that y_0 represents the contribution to the reduced variance which is independent of l, i.e., independent of the existence of border effects (this y_0 is equivalent to its 2-dimensional counterpart introduced in Ref. [28]). Using Eqs. (3), (6), and (7), we show finally that

$$\frac{y_0}{\theta} = \frac{\sigma^2}{\langle n \rangle} = \frac{\nu}{\nu-1}\frac{\sigma^2_{\text{sim}}}{\langle n \rangle} \tag{8}$$

in the limit $l/d \to \infty$. Equation (8) is important because it constitutes the link between the relative variance $(\sigma^2_{\text{sim}}/\langle n \rangle)$ or the related quantity y_0/θ observed in the simulation, and theoretical expressions of $\sigma^2/\langle n \rangle$ obtained on infinite lines, subdivided into an infinite number of subsystems free of border effects. Note also that if the coverage process follows a binomial law, Eq. (8) leads to the simple relation $y_0/\theta=1$.

III. RESULTS

A. Variance

As indicated above, between 250 and 1000 lines were covered up to a given coverage (between 0.4 and 0.6), depending on the radius of the particle; the length-to-radius ratio was kept fixed ($L/R \approx 2700$). From the position of all adsorbed particles, we derived the corrected variance σ^2 [Eq. (6)] of the number of particles located in the ν subsystems constituting the whole collector (19 values of ν were used, ranging from 16 up to 1024). This variance is represented in Fig. 1 as a function of l/d ($\equiv l/2R$) for $R=2$ μm taken as an example, for a series of values of the coverage (many more values of θ were considered, but not represented, for the sake of clarity). As can be seen, the linearity is very good in all cases. This linearity was also observed for all other particle radii. The hypothesis of linearity expressed by Eq. (6) is thus verified.

From the plots of σ^2 one derives y_0 as a function of θ, for the DRSAG model, as well as for the RSA model and for the BD model (Fig. 2). The curves corresponding to $R=6$, 4, 3, and 2.5μm are identical within the statistical uncertainties, and fall approximately onto the ballistic deposition curve. That particles characterized by a large

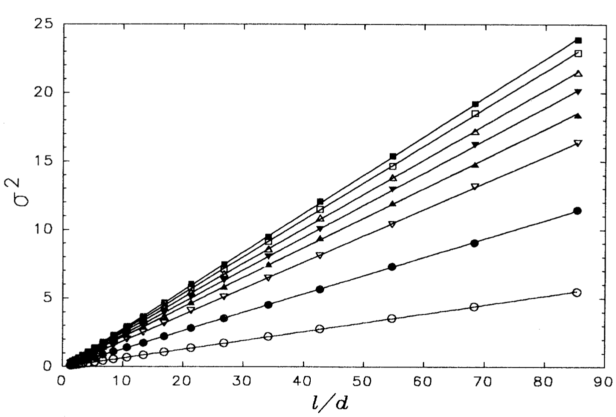

FIG. 1. Corrected variance σ^2 [Eq. (7)] as a function of the ratio of the length l of a subsystem to the diameter d of the spheres. Each set of data points corresponds to a given coverage θ: 0.0659 (○), 0.1392 (●), 0.2124 (▽), 0.2856 (▼), 0.3589 (□), 0.4321 (■), 0.5420 (△), and 0.6006 (▲). The continuous lines are least-squares fits of a linear function to the data derived from the simulations. The linearity of σ^2 vs l/d shown here for particles of radius 2 μm was verified for all particle radii used in this study.

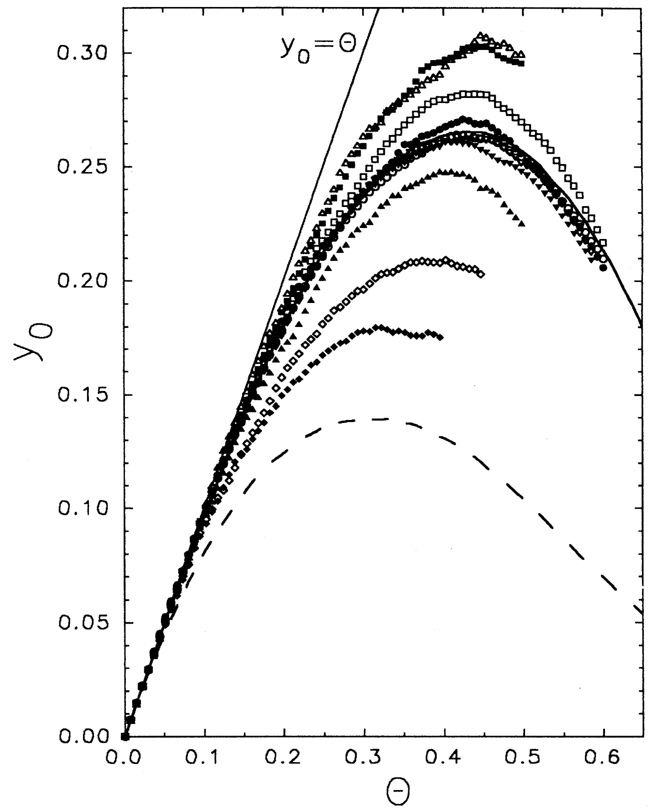

FIG. 2. Asymptotic part y_0 of the reduced variance y [Eq. (8)] as a function of the coverage θ, for a series of particle radii: $R=6$ (○), 4 (●), 3 (▽), 2.5 (▼), 2 (□), 1.75 (■), 1.5 (△), 1.2 (▲), 1.02 (◇), and 0.6 μm (◆). The maximum number of collisions was set to $k_r=10\,000$, and the rejection line at a height $z_r=5R$. The results corresponding to the random sequential adsorption (RSA) model (dashed line) and to the ballistic deposition (BD) model (solid line) are drawn for comparison.

value of R^* behave nearly as ballistic ones is *a priori* not surprising. Indeed, if such a particle collides with a preadsorbed one, it diffuses at the surface of the fixed particle (analogous of the rolling in BD), and adsorbs in its vicinity if enough room is available. If the adsorption is not possible, due to the presence of a second fixed particle which renders the gap too narrow, the diffusing particle stays trapped between the two fixed ones and is finally rejected after it makes a preset number of collisions (10 000 in the simulations leading to the results of Fig. 2). However, this rejection mechanism becomes gradually less efficient when the particle becomes lighter. This greater ease of light particles to escape from a trap is expected to lead to y_0 values representative of the binomial filling of the collector ($y_0=\theta$). Figure 2 clearly shows this tendency for $R=2$ and 1.75 μm. The main problem in the interpretation of Fig. 2 arises from the fact that for $R=1.5$, 1.2, 1.02, and 0.6 μm, y_0 does not follow the trend suggested by the two preceding curves. At this point, the second rejection mechanism must be invoked. If a particle during its diffusion attains an altitude of $5R$, it is rejected, as discussed in Sec. II. This was made to avoid very long diffusion times, hence to save computer time. However, it is now clear that this rule in fact affects the variance of the coverage. If we waited long enough, the particle would eventually adsorb in the subsystem where it was from the beginning of its history. This statement relates to asymptotic subsystems ($l\rightarrow\infty$). But if the particle is rejected (too early) and another one started, the latter will probably start and end (if not also rejected) in another subystem. Therefore, y_0 for the lightest particles deviates again from the binomial law $y_0=\theta$, and approaches the curve obtained in RSA, where the rejection occurs as soon as the first collision is detected.

From this first analysis it can be concluded that if the allowed number of collisions could be unlimited, and if the rejection line at height $5R$ could be removed, each particle would adsorb as long as the collector had not reached its saturated state. In other words, y_0 would equal θ for the whole filling process. Nevertheless, since the computation is very long (several weeks, or even months for the light particles, $R^*\leq 1$), it is not easy to verify this prediction on the basis of variance simulations. We shall therefore first use the available line fraction to test the conclusion drawn above.

B. Available line fraction

The available line fraction $\Phi(\theta)$ is here taken in its probabilistic sense; i.e., $\Phi(\theta)$ measures the probability for a particle starting from the height $z=z_s$ above the collector, characterized by the coverage θ, to adsorb. In DRSAG, the diffusive trajectory of the particle may reach a point located at $z=z_r$. By definition, the particle is thus discarded. This may even occur when the collector is empty, unless $z_r=\infty$. Hence $\Phi(0)$ is generally not equal to 1, whereas it is strictly equal to 1 in the RSA as well as in BD. The observed available line fraction $\Phi'(\theta)$, which can be compared to its RSA and BD counterparts, must therefore be normalized in such a way that $\Phi(0)=1$. Hence the available line fraction must be redefined by $\Phi(\theta)=\Phi'(\theta)/\Phi'(0)$, where $\Phi'(0)=[1+\exp(-2\text{Pe})]^{-1}$ in the present simulation conditions ($z_s=3R, z_r=5R$) [29]. On the other hand, once at least one particle is already adsorbed, the incoming particle may experience k_r collisions before reaching the adsorbing line. It is then also rejected, although it might have adsorbed in a neighboring accessible gap if k_r had been larger. This simple qualitative analysis shows that the two constraints must have a substantial influence on the evaluation of the available line fraction. This problem is discussed in some detail in Secs. III B 1 and III B 2.

1. Influence of the maximum number of collisions allowed

The influence of the maximum number of collisions allowed before rejection of the diffusing particle (k_r) will be illustrated on the basis of two examples ($R=6$ and 1.75 μm) for which the influence of gravity is strong enough to render the rejection line at height $5R$ inoperative [$\Phi'(0)\approx 1$ for $R=1.75$ and 6 μm). Figure 3 shows $\Phi(\theta)$

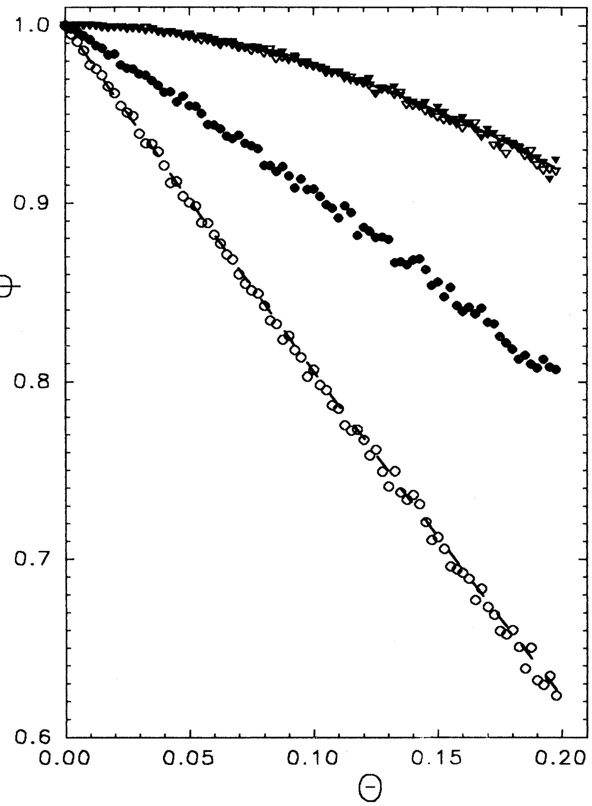

FIG. 3. Available line fraction Φ as a function of the coverage θ for different values of the maximum number k_r of collisions allowed in the DRSAG model [$k_r=1$ (○), 10^3 (●), 10^4 (▽), 10^5 (▼)] before rejection of a diffusing particle of radius $R=6\mu$m ($R^*\approx 5.15$). Sample sizes: 10 000 lines of length $L=800$ R. The theoretical values of Φ for the RSA model (dashed line) coincide with the simulated results for $k_r=1$, whereas the theoretical values of Φ for the BD model (solid line) agree with the simulated results for $k_r=10^4$ and 10^5.

as a function of θ for different values of k_r and $R=6$ μm. For $k_r=1$, i.e., rejection at the first collision, our simulated values of $\Phi(\theta)$ agree with the theoretical series expansion of $\Phi_{\rm RSA}$ [8,9]:

$$\Phi_{\rm RSA}(\theta)=1-2\theta+\frac{1}{2}\theta^2+\frac{2}{9}\theta^3+\frac{7}{48}\theta^4+\frac{17}{150}\theta^5+\frac{1253}{12\,960}\theta^6+\frac{3851}{44\,100}\theta^7+O(\theta^8)\ . \quad (9)$$

When k_r is increased, $\Phi(\theta)$ also increases, since the probability of adsorption depends on the number of collisions that the particle is allowed to make before rejection. Over the coverage investigated in Fig. 3, when k_r reaches 10^4, $\Phi(\theta)$ becomes equal to $\Phi_{\rm BD}$, given by [8]

$$\Phi_{\rm BD}(\theta)=1-\frac{5}{2}\theta^2+\frac{26}{9}\theta^3-\frac{245}{48}\theta^4+\frac{4511}{450}\theta^5-\frac{55\,517}{2592}\theta^6+\frac{253\,9177}{52\,920}\theta^7+O(\theta^8)\ . \quad (10)$$

Further increasing k_r to 10^5 does not lead to any visible difference. This means that 10^4 collisions are sufficient for most particles (if not all) to reach the surface even in the case where collisions occur, if there is sufficient place near the particle hit. In contrast, 10^4 collisions are insufficient for this particle to escape from a trap. The same conclusion remains true when $k_r=10^5$. In order for a "heavy" particle to escape from a trap, the number of collisions would be so large as to render it impossible to simulate such an event. From this example, it may be concluded that DRSAG mimics the BD model if an appropriate maximum number of collisions is chosen. Nevertheless, it also suggests also that the BD model is not a true limit model of the DRSAG because in principle the adsorption probability can be rendered arbitrarily high by simply allowing more and more collisions, even though this is not practical. This conclusion appears also if one determines $\Phi(\theta)$ for particles of radius $R=1.75$ μm, i.e., $R^*\approx 1.5$. Then, even for $k_r=10^4$, $\Phi(\theta)$ lies above $\Phi_{BD}(\theta)$ for all values of θ in the range [0–0.2] explored, and increases further when $k_r\rightarrow\infty$.

2. *Influence of the height of the rejection line*

In order to examine the role of the top rejection line, we use particles of various sizes ($R=1.2$, 1.5, 1.75, 2, and 2.5 μm, corresponding to $R^*\approx 1.03$, 1.29, 1.50, 1.72, and 2.15, respectively), which have a decreasing probability of reaching the rejection altitude, set initially to $5R$. We measured the mean number of trials $\langle n_t\rangle$ necessary to reach the number n_a of adsorbed particles corresponding to a coverage of 0.2, as a function of the rejection height z_r when $k_r=10^4$. This is an integrated quantity, related to the available line fraction, which requires only small samples of lines to provide reliable results. The ratio $n_a/\langle n_t\rangle$ is displayed in Fig. 4, which clearly shows that the value of z_r is a parameter of growing importance when R^* decreases. In particular, it can be seen that for $z_r/R=5$, a non-negligible part of the particles with $R=1.2$ μm are rejected at the upper line, while the adsorption efficiency becomes practically equal to 1 ($n_a/\langle n_t\rangle\approx 1$) when $z_r/R\geq 10$. This is also due to the fact that $k_r=10^4$ is not a strong constraint for $R=1.2$ μm. Conversely, for heavier particles (e.g., $R=2$ μm) a maximum of 10^4 collisions represents an important constraint. The asymptotic value of $n_a/\langle n_t\rangle$ on the one hand is reached already for $z_r/R\approx 4$, but on the other hand does not equal 1. These examples illustrate further that the DRSAG model behaves as a binomial filling procedure as soon as the trajectories of the diffusing particles are not interrupted too quickly.

C. Variance without rejection line

As a consequence of the observations discussed above, the simulations have been repeated removing the top rejection line, i.e., $z_r=\infty$, while keeping k_r fixed at 10 000. Ideally k_r should also be raised to infinity, but this would lead to a prohibitive computation time and, in practice, render the results impossible to obtain for the heaviest particles used in the present study.

For R ranging from 6 to 2.5 μm, the values of y_0 form nearly a single curve within the statistical uncertainties (Fig. 5). For a fixed value of θ, when R decreasing from 2.5 to 1.02 μm, y_0 increases regularly, according to the analysis given in Secs. III A and III B. The case $R = 0.6$ μm was not reanalyzed since the computation time is very long, especially when no limitation is imposed on the height the particles can reach. For R between 1 and 2 μm, the effect of the remaining constraint $k_r = 10\,000$ is still visible. Two facts contribute to the departure from the binomial law $y_0 = \theta$. On the one hand, the heavier the particle, the more collisions are necessary to escape from a trap; on the other hand, when the coverage increases, more and more traps are formed, and in addition they may constitute clusters of traps. Then, even though a particle can escape from a first trap, it may immediately fall into a second one, and so on. In this way, even the lightest particles are liable to be rejected after 10 000 collisions before touching the collector. Obviously, the number of visits to successive traps increases when R^* decreases, provided that the maximum

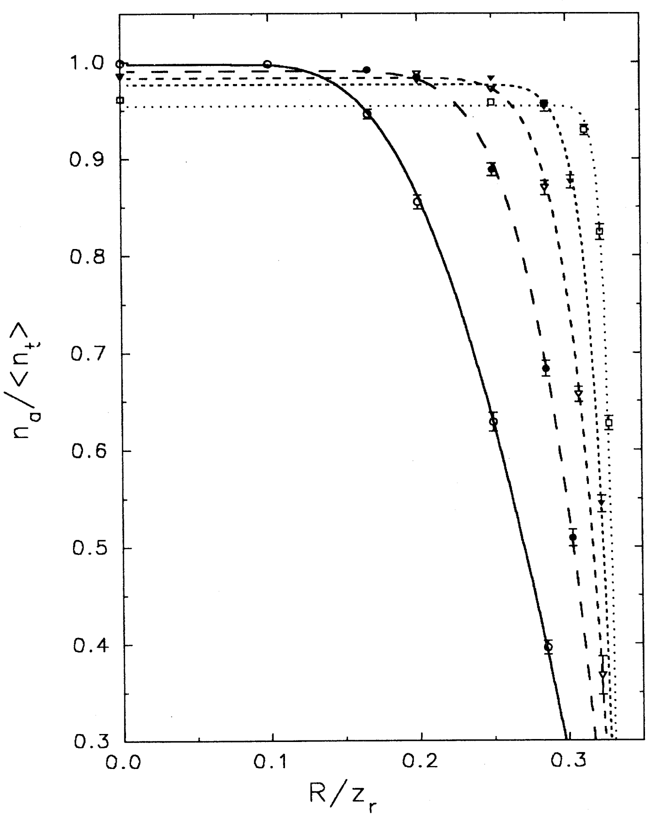

FIG. 4. Ratio $n_a/\langle n_t \rangle$ of the number of adsorbed particles to the corresponding mean number of trial particles for obtaining a coverage of $\theta = 0.2$, as a function of R/z_r, for particle radii $R = 1.2$ (○), 1.5 (●), 1.75 (▽), 2 (▼), and 2.5 μm (□). Sample sizes: 100 lines of length $L = 800$ R. The maximum number of collisions k_r is fixed at 10^4. The error bars correspond to 95%-confidence intervals. The lines represent fits of the empirical function $n_a/\langle n_t \rangle = a\{1-\exp[-b(z_r/R-3)]\}$ to the data, where a and b are free parameters.

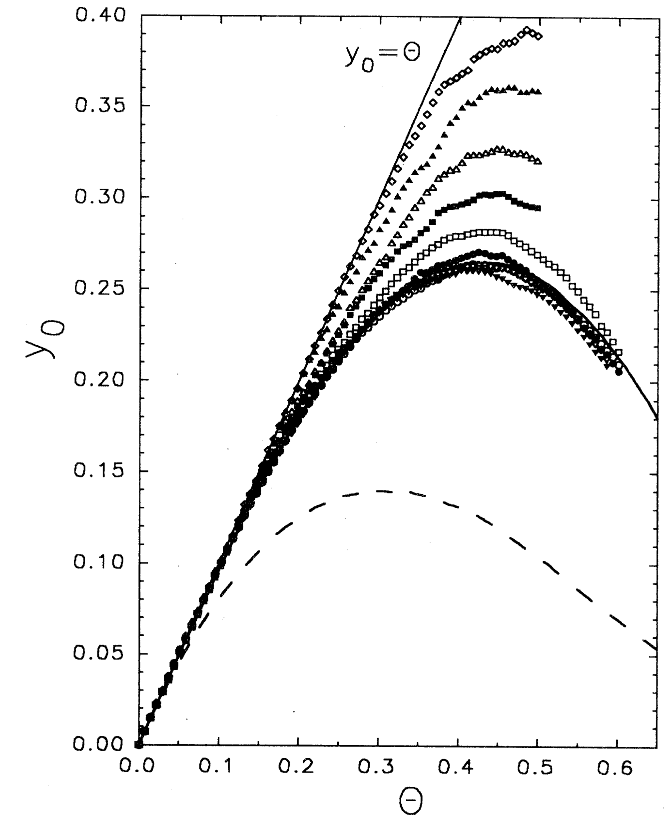

FIG. 5. Asymptotic part y_0 of the reduced variance y [Eq. (8)] as a function of the coverage θ for particle radii $R = 6$ (○), 4 (●), 3 (▽), 2.5 (▼), 2 (□), 1.75 (■), 1.5 (△), 1.2 (▲), and 1.02 μm (◇). The maximum number of collisions was set to $k_r = 10\,000$ and the rejection line at an infinite height. For comparison the results corresponding to the random sequential adsorption (RSA) model (dashed line) and to the ballistic deposition (BD) model (solid line) are also drawn.

number of collisions was the same whatever R^*. This explains why y_0 deviates from the binomial prediction at $\theta \approx 0.32$ for $R = 1.02$ μm, whereas this departure occurs already at $\theta \approx 0.25$ for $R = 1.2$ μm.

It might be interesting in principle to perform further simulations in order to study how y_0 approaches the binomial law when k_r increases. This would, however, require a great deal of computer time, and add little to our understanding of the physical properties of the systems.

IV. DISCUSSION AND CONCLUSION

This article considers the irreversible adsorption of spheres (representing colloidal particles) on a one-dimensional collector, after diffusion in a two-dimensional liquid. In addition to the random force exerted by the liquid molecules onto the particles, the particles were also submitted to a deterministic force, namely their net weight in the liquid, i.e., Archimedean force minus weight (DRSAG model). This study was aimed at the determination of the variance of the number of particles distributed in subsystems constituting the whole collector as it is determined experimentally [16–18]. It was clearly demonstrated that any constraint resulting in the limitation of the diffusion time may substantially modify this variance. In contrast to the familiar random sequential adsorption and ballistic deposition models, the resulting characteristics of the particle configuration buildup with the DRSAG model are no longer dependent on geometrical rules alone, but depend also on time limiting rules. In the absence of such rules, the variance of the number of particles distributed over subsystems is given by the binomial law. This, however, cannot correspond to a real physical case. Indeed, it implies that the diffusion time of an adsorbing particle before it touches the adsorption plane can become infinite, whereas each experiment is characterized by a time scale which is finite. For deposition experiments, one can assume that this characteristic time corresponds roughly to the mean time between the successive deposition of two particles on a surface of area unity if it is totally uncovered. Indeed, in our model, we always assume sequential adsorption and never consider the diffusion of two particles at the same instant. This time will thus be a function of various parameters such as the concentration of the particles in the bulk, the radius of the particles, etc. Due to the influence of these parameters on the final simulation results, great care has to be taken in order to be able to compare the results issued from the simulation with the experimental results. This has not yet been done, and more investigations are needed to better understand these subtle effects.

Finally, it must also be emphasized that our findings, although obtained in the special case of a one-dimensional collector, extend without restriction to the usual experimental case of an adsorbing surface (two-dimensional collector). Furthermore, the results obtained here confirm those presented in previous papers [17,18], namely that the relative variance and the available surface function, or the accessible line fraction, behave in a similar way, at least for low coverage:

$$\frac{\sigma^2}{\langle n \rangle} = \Phi + O(\theta^i) \ , \tag{11}$$

where the exponent i tends to infinity when the diffusion time tends itself to infinity. For an unlimited diffusion time, i.e., in the special case where the binomial law would rigorously apply, both quantities would be exactly equal to one ($\sigma^2/\langle n \rangle = \Phi = 1$), whatever the coverage, as long as saturation is not achieved.

ACKNOWLEDGMENTS

The authors are indebted to E. K. Mann for a critical reading of the manuscript. One of us (R.E.) benefited from financial support from the Faculté de Chirurgie Dentaire of Strasbourg. One of the authors (P.S.) acknowledges the NSF and the CNRS for their support through a NSF/CNRS exchange contract. This work was also partly supported by the Commission of the European Communities through Contract No. SCI/CT/910696 (TSTS).

[1] A. Rényi, Publ. Math. Inst. Hung. Acad. Sci. **3**, 109 (1958).
[2] J. Feder, J. Theor. Biol. **87**, 237 (1980).
[3] E. L. Hinrichsen, J. Feder, and T. Jøssang, J. Stat. Phys. **44**, 793 (1986).
[4] Y. Pomeau, J. Phys. A **13**, L193 (1980).
[5] R. H. Swendsen, Phys. Rev. A **24**, 504 (1981).
[6] P. Schaaf and J. Talbot, Phys. Rev. Lett. **62**, 175 (1989).
[7] P. Schaaf and J. Talbot, J. Chem. Phys. **97**, 4401 (1989).
[8] J. Talbot and S. M. Ricci, Phys. Rev. Lett. **68**, 958 (1992).
[9] G. Tarjus and P. Viot, Phys. Rev. Lett. **68**, 2354 (1992).
[10] B. Bonnier, D. Boyer, and P. Viot, J. Phys. A **27**, 3671 (1994).
[11] J. W. Evans, Rev. Mod. Phys. **65**, 1281 (1993).
[12] R. Jullien and P. Meakin, J. Phys. A **25**, L189 (1992).
[13] A. P. Thompson and E. D. Glandt, Phys. Rev. A **46**, 4639 (1992).
[14] G. Y. Onoda and E. G. Liniger, Phys. Rev. A **33**, 715 (1986).
[15] J. Feder and I. Giaever, J. Colloid Interf. Sci. **78**, 144 (1980).
[16] P. Wojtaszczyk, P. Schaaf, B. Senger, M. Zembala, and J.-C. Voegel, J. Chem. Phys. **99**, 7198 (1993).
[17] E. K. Mann, P. Wojtaszczyk, P. Schaaf, B. Senger, J.-C. Voegel, and D. Bedeaux, J. Chem. Phys. **102**, 5077 (1995).
[18] P. Schaaf, P. Wojtaszczyk, B. Senger, J.-C. Voegel, and H. Reiss, Phys. Rev. E **51**, 4292 (1995).
[19] P. Schaaf, A. Johner, and J. Talbot, Phys. Rev. Lett. **66**, 1603 (1991).
[20] B. Senger, J.-C. Voegel, P. Schaaf, A. Johner, A. Schmitt, and J. Talbot, Phys. Rev. A **44**, 6926 (1991).
[21] B. Senger, P. Schaaf, J.-C. Voegel, A. Johner, A. Schmitt, and J. Talbot, J. Chem. Phys. **97**, 3813 (1992).
[22] B. Senger, F. J. Bafaluy, P. Schaaf, A. Schmitt, and J.-C. Voegel, Proc. Natl. Acad. Sci. USA **89**, 9449 (1992).
[23] B. Senger, R. Ezzeddine, F. J. Bafaluy, P. Schaaf, F. J. G. Cuisinier, and J.-C. Voegel, J. Theor. Biol. **163**, 457 (1993).
[24] B. Senger, J. Talbot, P. Schaaf, A. Schmitt, and J.-C. Voegel, Europhys. Lett. **21**, 135 (1993).
[25] R. Ezzeddine, P. Schaaf, J.-C. Voegel, and B. Senger, Phys. Rev. E **51**, 6286 (1995).
[26] E. Guyon, J.-P. Hulin and L. Petit, *Hydrodynamique Physique* (Editions du CNRS, Paris, 1991).
[27] D. E. Knuth, *The Art of Computer Programming*, (Addison-Wesley, Reading, MA, 1981), Vol 2.
[28] B. Senger, P. Schaaf, J.-C. Voegel, P. Wojtaszcyk, and H. Reiss, Proc. Natl. Acad. Sci. USA **91**, 10029 (1994).
[29] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1990).