Influence of gravity on the jamming-limit coverage for the random deposition of large spheres on one- and two-dimensional collectors

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When colloidal particles are of a density different from the bulk fluid in which they diffuse, prior to their adhesion to an interface, the movement results from the influence of (i) random (Brownian) diffusion, (ii) deterministic vertical displacement due to the gravity, and (iii) hard core repulsion between the particles. It is shown that the mean maximum number of particles that can be deposited either on a line segment or on a surface, or the so-called jamming coverage $\theta(\infty)$, depends on a single parameter (R^*) related to the Péclet number. This parameter contains all the physical characteristics of the process. When suitably normalized, the values of $\theta(\infty,R^*)$ follow a unique function of R^* for one- and two-dimensional collectors.

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The adhesion of colloidal particles (bacteria, cells, synthetic micrometric particles) to solid substrates, either natural or artificial, plays an important role in numerous biological and physical processes. The incidence of adhesion in such processes has stimulated many experimental and theoretical works aimed at a detailed description of the mechanisms ruling them [1–8]. The random sequential adsorption (RSA) model has been widely used to describe this phenomenon, and often serves as a starting point for other models, for particles deposited either on line segments or on surfaces. In the RSA model it is assumed that the particles interact through a hard core potential and that, once adsorbed, they remain permanently fixed in place. Thus the phenomenon is supposed to be fully irreversible. Instead of being rejected at the first collision as in the RSA model, another related model, developed more recently, is the ballistic deposition (BD) model. In the latter, the incoming particle can roll over preadsorbed ones and can eventually reach the line or the surface if a sufficient area is available. The rules are otherwise identical to those of the RSA model.

One particular characteristic of the configurations built up by the particles adsorbed on the collector is the so-called jamming-limit coverage $\theta(\infty)$, which represents the relative length or area occupied by the particles, when no additional particle can be brought to the collector. The theoretical evaluation of $\theta(\infty)$ can only be carried out in (1+1)-dimensional [(1+1)D] systems (i.e., for two-dimensional movement, with adsorption on a line), whereas in (1+2)D systems (i.e., for three-dimensional movement, with adsorption on a surface) simulation is the only means to estimate the value of $\theta(\infty)$ [3,9,10].

However, in experiments, the particles are not infinitely heavy [11]. Therefore both the Brownian diffusion in the bulk liquid [12,13] and the deterministic gravitational force contribute to the resulting trajectory of a particle [14,15]. The model combining diffusion and gravity is hereafter referred to as the diffusion RSA with gravity (DRSAG) model. In the limiting case of zero gravity, it is called the diffusion RSA (DRSA) model [13]. We present a comparative study of the dependence of $\theta(\infty)$ on the relative importance of the deterministic gravitational force compared to the random force responsible for pure Brownian diffusion, in (1+1)D and (1+2)D systems. In both, the final coverage is shown to depend on a single variable (R^*), including all the pertinent characteristics implied in the diffusion process. Therefore we will write $\theta(\infty,R^*)$ from now on. Moreover, a convenient scaling permits the proposition of a "universal" curve for $\theta(\infty,R^*)$.

The movement of spherical particles, of radius R, in the fluid is governed by the Langevin equation that relates the position $\mathbf{r}'(t'+\Delta t')$ of a particle at time $t'+\Delta t'$ to its position $\mathbf{r}'(t')$ at time t':

$$\mathbf{r}'(t'+\Delta t')=\mathbf{r}'(t')+\frac{D\mathbf{F}_g}{kT}\Delta t'+\Delta\mathbf{r}'_B\ , \tag{1}$$

where D is the Einstein-Stockes diffusion coefficient, k the Boltzmann constant, and T the absolute temperature. The vector $\mathbf{F}_g$ represents the gravitational force, i.e., the only deterministic force acting on the particles assumed in the present study; it is given by

$$\mathbf{F}_g=-\tfrac{4}{3}\pi R^3\Delta\rho g\hat{\mathbf{z}}\ , \tag{2}$$

where g represents the acceleration of the gravity, $\Delta\rho$ the difference (supposed to be positive) of specific mass between the particle material and the liquid, and $\hat{\mathbf{z}}$ the unit

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vector on the z axis (ascending vertical axis). The vector $\Delta\mathbf{r}'_B$ represents the random (Brownian) displacement during the time interval $\Delta t'$. As usual, it is assumed that each component of the random movement $(\Delta x'_B, \Delta y'_B, \Delta z'_B)$ is a normal deviate with mean equal to zero and standard deviation equal to $\sqrt{2D\Delta t'}$. These components may therefore be written as

$$\Delta x'_B = \gamma_x \sqrt{2D\Delta t'}, \quad \Delta y'_B = \gamma_y \sqrt{2D\Delta t'}, \quad \Delta z'_B = \gamma_z \sqrt{2D\Delta t'} \,, \tag{3}$$

where γ_x, γ_y, and γ_z are normal deviates, with mean equal to zero and standard deviation equal to 1. Langevin's equation, corresponding to a diffusion in a three-dimensional space, separates into three independent equations:

$$x'(t'+\Delta t') = x'(t') + \Delta x'_B \,, \tag{4a}$$

$$y'(t'+\Delta t') = y'(t') + \Delta y'_B \,, \tag{4b}$$

$$z'(t'+\Delta t') = z'(t') - \frac{DF_g}{kT} + \Delta z'_B \,, \tag{4c}$$

where F_g (equal to $\frac{4}{3}\pi R^3 \Delta\rho g$) appears only in the third component. Applying the transformations $x = x'/R$, $y = y'/R$, $z = z'/R$, $t = Dt'/R^2$, and using the definitions (3), lead to three new equations describing the time evolution of the dimensionless Cartesian coordinates (x,y,z) of the center of a diffusing particle:

$$x(t+\Delta t) = x(t) + \gamma_x \sqrt{2\Delta t} \,, \tag{5a}$$

$$y(t+\Delta t) = y(t) + \gamma_y \sqrt{2\Delta t} \,, \tag{5b}$$

$$z(t+\Delta t) = z(t) - R^{*4}\Delta t + \gamma_z \sqrt{2\Delta t} \,, \tag{5c}$$

where

$$R^{*4} = \frac{4\pi R^4 \Delta\rho g}{3kT} \tag{6}$$

is a dimensionless parameter that contains all relevant physical characteristics of the diffusion. R^{*4} can be interpreted as the work of the gravitational force necessary to change the altitude of the particle by R, expressed in units of the thermal energy kT ($R^{*4} = R|\mathbf{F}_g|/kT$ is proportional to the Péclet number). Equations (5a)–(5c) clearly demonstrate that the diffusion depends on the unique parameter R^*. Therefore, any quadruplet $(R, \Delta\rho, g, T)$ must lead to the same jamming-limit coverage if it corresponds to the same value of R^*. This was already shown in Ref. [15] on the basis of a different argument. Note that, in the case where the particles diffuse in a two-dimensional space, the equation giving either x or y [(5a) or (5b), respectively] is simply eliminated. The above conclusion concerning the jamming-limit coverage remains unaltered.

In the simulation presented here, the adsorbing line (or plane) is at height $z=0$. Each particle starts from a random position at height $z=3$. When adsorbed, its height is $z=1$. If a particle hits another one already adsorbed, it is drawn back to its previous position and a new move is tried. This is fundamentally different from the RSA procedure, where any collision causes the immediate rejection of the particle. The adsorption process was simulated so that the particles adsorb either on square surfaces of side $c=18$ or on line segments of length $L=500$, with periodic conditions applied to the boundaries. The algorithm proceeds up to saturation. Then, if $\langle n_{\text{ads}} \rangle$ particles on average are located on the collector, the jamming-limit coverage is defined by

$$\theta(\infty, R^*) = \begin{cases} \langle n_{\text{ads}} \rangle \dfrac{2R}{L} & \text{for a line segment ,} \quad (7a) \\[2ex] \langle n_{\text{ads}} \rangle \dfrac{\pi R^2}{c^2} & \text{for a surface .} \quad (7b) \end{cases}$$

The estimation of $\theta(\infty, R^*)$ was obtained on the basis of samples whose size was generally of the order of 50 lines or surfaces. For the smallest values of R^*, however, the process became very slow. Then, the size of the corresponding line or surface sample was reduced, with the consequence that the confidence interval (at 95%) increased accordingly. Moreover, when a particle reached an upper line (or plane) at height $z=5$, it was rejected in order to avoid very long diffusion, and hence computer time. We have observed that for $R^* \approx 1.07$ ("light" particles) in a (1+1)D system, when the rejection line is raised from $z=5$ to $z=10$, $\theta(\infty, R^*)$ determined on samples of 50 lines varies from 0.7537 ± 0.0034 to 0.7565 ± 0.0031. Following the Student test, this difference is not significant (risk level $=5\%$). Since the lightest particles are *a priori* the most sensitive to the presence of the rejection line (or plane), we conclude that $z=5$ is a reasonable choice for all values of R^* investigated in this Brief Report, as far as the determination of the jamming coverage is concerned.

For the (1+1)D as well as for the (1+2)D systems, $\theta(\infty, R^*)$ increases with R^* up to the ballistic limit [9,10] (see Table I). For $R^* \to 0$, we previously showed [13] that in (1+2)D the diffusion leads to a jamming-limit coverage not significantly different from its RSA counterpart, i.e., 0.547 [2,3]. In contrast, when the adsorption occurs on a line, the diffusion gives rise to a value of the jamming coverage slightly higher than predicted by the RSA model (0.7529 instead of 0.747 59) [16].

In order to compare more precisely the coverage for the jammed state in (1+1)D and (1+2)D, it is interesting to "normalize" the results by transforming $\theta(\infty, R^*)$ into $\theta_N(\infty, R^*)$ through the relation

$$\theta_N(\infty, R^*) = \frac{\theta(\infty, R^*) - \theta_{\text{DRSA}}(\infty)}{\theta_{\text{BD}}(\infty) - \theta_{\text{DRSA}}(\infty)} \,, \tag{8}$$

where $\theta_{\text{DRSA}}(\infty)$ and $\theta_{\text{BD}}(\infty)$ are the jamming-limit cov-

TABLE I. Values of the jamming-limit coverage corresponding to the DRSA and the ballistic models [$\theta_{\text{DRSA}}(\infty)$ and $\theta_{\text{BD}}(\infty)$, respectively], for diffusion-adsorption in (1+1)D and (1+2)D spaces.

Dimension	$\theta_{\text{DRSA}}(\infty)$	$\theta_{\text{BD}}(\infty)$
1+1	0.7529	0.808 65
1+2	0.547	0.610 56

erages corresponding to the DRSA and the BD models, respectively (see Table I). The two sets of $\theta_N(\infty, R^*)$ resulting from relation (8) are shown in Fig. 1. Within statistical uncertainties, these two groups of $\theta_N(\infty, R^*)$ fall on a common curve with an empirical equation:

$$\theta_N(\infty, R^*) = \exp(-a_0 R^{*-4} - a_1 R^{*-3}) , \quad (9)$$

where $a_0 \approx 1.32$ and $a_1 \approx 3.44$ were determined by means of a least squares method. It may be mentioned that the determination of a_0 and a_1 performed separately on the two sets of data leads to $a_0 \approx 1.16$, $a_1 \approx 3.54$, and $a_0 \approx 1.55$, $a_1 \approx 3.30$ for the (1+1)D and (1+2)D systems, respectively. Although the parameters are slightly different, the resulting fits, if drawn in Fig. 1, are indistinguishable from the fit obtained on the basis of all of the data.

In summary, the jamming-limit coverage for spherical particles deposited randomly on line segments and surfaces has been determined by means of numerical simulations. They were based on a model, taking into account the Brownian diffusion in the liquid and the gravitational force, as well as excluded volume effects (DRSAG model). Somewhat surprisingly, the results obtained in (1+1)D and (1+2)D, though quantitatively different, can be made to form a unique curve by a simple scaling procedure. This set of saturation coverages is accurately fitted by a simple empirical function of R^*. This surprising and unexplained result should stimulate theoretical work. The above study shows that the theoretical jamming limits need only be determined for (1+1)D systems, since a simple scaling law permits conversion to their (1+2)D counterparts.

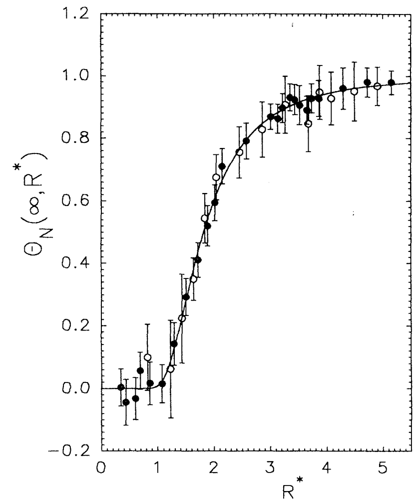

FIG. 1. Normalized jamming-limit coverage $\theta_N(\infty, R^*)$ as a function of the reduced radius R^* [see Eq. (6)] obtained by simulation in (1+1)D (●) and (1+2)D (○) spaces. The error bars represent 95%-confidence intervals. The solid line is a least squares fit of an empirical function [see Eq. (9)] to the data.

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