Influence of hydrodynamic interactions on the ballistic deposition of colloidal particles on solid surfaces.

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The ballistic deposition of particles by taking hydrodynamic interactions (HI) into account has been studied by means of computer simulations. The radial distribution function of the assembly of particles deposited on a plane has been determined as a function of the coverage and compared to experimental data. It appears that the introduction of HI in the model when compared to the ballistic model (BM) predictions leads to a better agreement between experiment and simulation in particular for the radial distribution function. HI also modify the value of the first non-vanishing term ($B_3$) in the expansion of the available surface function, $\Phi$, in the coverage. One can estimate the ratio $B_3^{BM}/B_3^{BHM} \approx 0.5$, where $B_3^{BHM}$ (resp. $B_3^{BM}$) corresponds to simulations in which HI have been (resp. have not been) taken into account. The introduction of HI, however, leads to small changes in $\Phi$. Finally, we conclude that, as far as average global quantities are concerned, the BM without HI constitutes a good approximation. It is only for the detailed analysis of the structure of the layer of deposited particles that HI play a significant quantitative role.

I. INTRODUCTION

Irreversible deposition processes of colloidal particles or macromolecules on solid surfaces have received considerable attention during the last years. Both the adsorption (or deposition) kinetics and the structure of the assembly of deposited particles have been analyzed from an experimental and theoretical point of view. By irreversible we mean processes in which, once the particle has interacted with the surface, it can neither desorb from the surface nor diffuse on it. Moreover, we will focus on situations in which, due to the interactions between the spherical particles and the plane, only one adsorbed layer is formed. Despite their apparent simplicity, the deposition processes are determined by the interplay of various processes: the Brownian motion of the adhering particle, the gravitational force, the hydrodynamic interactions (HI) and other kind of interactions between adhering particles and the adsorbed ones. Due to the non additivity of the hydrodynamic interactions, most of the models which have been developed up to now to describe irreversible adhesion processes have neglected these latter, and have focused primarily on the geometric aspects, related to the exclusion surface effects. Among all the models which have been developed, two have captured most of the attention: (i) On the one hand, the Random Sequential Adsorption (RSA) model which has been shown to reproduce some of the properties of the irreversible adsorption of proteins and small colloidal particles on solid surfaces. By small it is meant that the motion of the particles in solution is controlled by Brownian motion, and that therefore the influence of the deterministic forces on their motion can be neglected. In the RSA model particles are placed randomly and sequentially on the surface. If an incoming particle overlaps an already adsorbed one, it is rejected and a new position is chosen randomly over the surface. (ii) The Ballistic Model (BM), on the other

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hand, has been introduced to account for the deposition of large particles on solid surfaces. In this case, the deposition process is dominated by gravity and the diffusion of the particles in the bulk is neglected. In the BM, again the position of each incoming particle is randomly selected, but if it touches an already deposited one, it rolls over this particle according to the deterministic laws of mechanics. It undergoes its motion until it reaches the adhesion plane or is trapped by at least three adsorbed particles.

Both models have been compared to experimental observations and the results can be summarized as follows:

(1) The RSA model has been tested in three different ways:

a) Experimental adsorption kinetics of particles and proteins have been compared to their theoretical expectations. These systems seem to follow an RSA-like adsorption kinetics at low and intermediate coverages. It has also been reported that the jamming limit is reached according to the power law:

$$\theta(\infty) - \theta(t) \sim t^{-1/2}$$

where $\theta(t)$ represents the coverage after a time $t$ of adsorption and $\theta(\infty)$ is the coverage obtained at saturation. However, due to the great experimental difficulties to precisely determine the evolution of the adsorbed amount in the asymptotic regime, one must be cautious with these results and more experimental investigations should be performed to validate them.

b) The statistical properties of surfaces covered by latex particles have been investigated. For small particles depositing under a process widely governed by the diffusion, the radial distribution function $g(r)$ experimentally found is in good agreement with the $g(r)$ determined by computer simulations according to the RSA rules.

c) Finally, the density fluctuations of adsorbed particles have also been determined. Special attention was paid to the reduced variance, $\sigma^2/\langle n \rangle$, where $\sigma^2$ corresponds to the variance of the number of adsorbed particles in sub-systems of a given area out of the adsorption plane, and $\langle n \rangle$ represents the mean number of adsorbed particles on these sub-systems. It can be shown that $\sigma^2/\langle n \rangle$ is directly related to the radial distribution function $g(r)$ through the relation:

$$\frac{\sigma^2}{\langle n \rangle} = 1 + \rho \int_0^{\infty} 2\pi r [g(r) - 1] dr$$

where $\rho = \langle n \rangle / S$, $S$ being the area of the adsorption plane. Surprisingly, it has been found that, for the systems which have been investigated, $\sigma^2/\langle n \rangle$ does not follow the RSA behavior as a function of $\rho$ (or $\theta$) but behaves more closely to the BM predictions. This result can be explained as follows: if one expands $\sigma^2/\langle n \rangle$ as a function of the coverage :

$$\frac{\sigma^2}{\langle n \rangle} = 1 - B_n \theta^n + O(\theta^{n+1})$$

the order $n$ of the first non vanishing term $B_n \theta^n$ represents the smallest number of particles which are required on the surface in order to hinder the adhesion of a new particle. For example, in the RSA case $n = 1$, and in the BM case $n = 3$. Moreover, $B_n$ is related to the mean exclusion area of $n$ deposited particles. In the case experimentally investigated, which led to an RSA-like radial distribution function, the Brownian motion of the particles in the bulk largely dominates over the gravitational effects even if this latter is not totally absent. So, a diffusing particle from the bulk that will touch an already adsorbed particle will diffuse around it at distances which are large compared to the radius of the particles. However, due to the slight gravitational effect, it will finally reach the adsorbing surface. Thus, in this case, $n$ must exceed 1: one deposited particle cannot hinder another particle to adhere on the surface. On the other hand, the presence of HI favors the diffusion of the particle parallel to the plane, implying that the incoming particle can explore much larger distances along the surface than perpendicularly to it before adhering. As a consequence, in first approximation, the incoming particle can be assumed to adsorb randomly on the surface. This implies that the radial distribution function becomes very close to the $g(r)$ predicted by the RSA model. These slight differences between the RSA-like $g(r)$ and the experimental radial distribution function are responsible for the totally different behavior of the experimental $\sigma^2/\langle n \rangle$ as compared to the RSA one. This observation shows how subtle the deposition process can be and the importance of the detailed description of the transport process from the bulk to the interface, in order to account properly for the statistical properties of such assemblies of spheres.
II. HYDRODYNAMIC INTERACTIONS IN THE ADSORPTION PROCESS

The slow motion of a particle suspended in a fluid at rest is governed by the frictional force and torque that the fluid exerts on it. These are linear functions of the center of mass velocity, \( \vec{u} \), and angular velocity, \( \vec{\omega} \) of the particle, the proportionality coefficients being the so-called friction tensors. One can therefore write down:

\[
\vec{F} = - \xi_{tt} \cdot \vec{u} - \xi_{tt} \cdot \vec{\omega} \\
\vec{T} = - \xi_{rt} \cdot \vec{u} - \xi_{rr} \cdot \vec{\omega}
\]

(4)

where \( \vec{F} \) and \( \vec{T} \) account for the total force and total torque acting on the particle. \( \xi_{tt} \) and \( \xi_{rr} \) correspond to the translational and rotational friction tensors respectively, while \( \xi_{rt} \) and \( \xi_{tr} \) are the coupling friction tensors. Due to the reciprocal Onsager relations, they satisfy \( \xi_{rt} = \xi_{tr}^{-1} \), where the superscript \( ^{-1} \) indicates that the transpose of the matrix should be taken.

We are interested in the motion of a free spherical particle in the presence of the gravitational field. Due to the symmetry and homogeneity of the particles, there will be no net external torque acting on them. Therefore \( \vec{T} = 0 \), and from eqs. (4) one can deduce the appropriate expression for the center of mass velocity, which will completely determine the motion of the particles. One then obtains

\[
\vec{F} = - \left( \xi_{tt} - \xi_{tr} \cdot \vec{\mu}_{rr} \cdot \xi_{tr} \right) \cdot \vec{u} = - \xi_{eff} \cdot \vec{u}
\]

(5)

where \( \vec{\mu}_{rr} \) is the rotational mobility matrix, defined as the inverse of the corresponding friction tensor, \( \vec{\mu}_{rr} \cdot \xi_{rr} = \vec{I} \). The coefficient between brackets in eq. (5) can be redefined as an effective friction tensor, \( \xi_{eff} \). The relaxation times for the velocity of colloidal particles are very small, which means that the inertial terms in their motion can be neglected.
This implies that the hydrodynamic force $\vec{F}$ that the fluid exerts on the particle is exactly opposite to the external force, which in our case is the gravity force acting on the suspended particles. Moreover, since we are interested in the deposition of heavy colloidal particles, the effect of Brownian diffusion on their motion can be neglected. Therefore, eq. (5) constitutes the equation of motion of the suspended particles, putting $\Delta \rho = \rho - \rho_{\text{solvent}}$ the density difference between the colloidal particle and the solvent, assumed to be a positive number.

Eq. (5) will describe the motion of a suspended heavy particle both in the case in which it is alone in an unbounded fluid and in the presence of other objects. The HI between the different particles, which are mediated by the host fluid, appear through the specific expressions for the friction coefficients. These depend both on the geometry of the particles and on their relative distribution in the fluid. For example, for an isolated solid sphere, the friction coefficients are constants, and using the standard stick boundary condition for the velocity field on its surface one has, $\vec{\xi}_{tt} = 6\pi \eta a \vec{I} = \vec{\xi}_0$ and $\vec{\xi}_{tr} = 8\pi \eta a^3 \vec{I}$ with $\eta$ being the viscosity of the solvent. In this case, there exists no coupling between translational and rotational motion, $\vec{\xi}_{tr} = 0$.

We will be interested in geometries where one sphere approaches a planar surface covered by preadsorbed spheres. In this case, there exist no general analytic expressions for the friction coefficients since exact solutions for many-body hydrodynamic problems are not available. The difficulty in the derivation of an exact solution lies partially in the non-additive character of the HI, which arises as a consequence of the long-range decay of the Oseen propagator \[16\]. However, in order to get analytic expressions, additivity in the HI will be assumed. There are two natural ways to introduce such an approximation: one can assume additivity of the friction tensors, which is equivalent to assume that the hydrodynamic force acting on one particle due to the presence of the others is equal to the sum of the forces due to each one of them as if the others were not present. One can also assume additivity of the mobilities, according to which the velocity of a given particle is equal to the sum of the velocities induced on it by the other particles independently. Bossis and Brady \[17\] have shown that the additivity of the friction coefficients takes properly into account the lubrication forces, which act when objects are close together. This latter property is not fulfilled under the mobility additivity assumption. Within the friction additivity assumption, the effective friction tensor for a suspended particle at a height $z_o$ from a planar surface in the presence of $N$ previously adsorbed spheres will be written as

$$
\vec{\xi}(\vec{r})_{\text{eff}} = \vec{\xi}_{\text{sp}}(z_o) + \sum_{i=1}^{N} \left( \vec{\xi}_{ss}(\vec{r}_i) - \vec{\xi}_0 \right)
$$

(6)

where $\vec{r}$ represents the position vector of the incoming particle with respect to a given reference frame (we will take the origin of the reference frame at the center of the closest preadsorbed particle), $\vec{r}_i$ is the vector joining the center of the incoming particle and of the $i$th sphere on the plane, $\vec{\xi}_{\text{sp}}$ is the friction tensor of a spherical particle alone in the presence of a plane, $\vec{\xi}_{ss}$ the effective friction tensor of two spheres in an unbounded fluid at relative position $\vec{r}_i$, and $\vec{\xi}_0$ is the Stokes’ tensor, introduced in the preceding paragraph. The previous expression leads to the correct behavior for the friction tensor when the sphere is far from the surface, where one recovers Stokes law. On the other hand, when the adsorbing particle comes into the vicinity of an already adsorbed one, lubrication forces become dominant. Then, only the small region of the fluid between the particles is responsible for the forces which can, thus, be considered as additive. Therefore, eq. (5) also provides the right behavior at short distances. In addition, the advantage of introducing approximation (6) is that the expressions for the friction coefficients appearing in it are known. Indeed, the friction tensor for a sphere at a height $z$ in the presence of a plane, $\vec{\xi}_{sp}$, has been shown to be diagonal and to have one component parallel, $\xi_{||}$, to the plane and one perpendicular to it, $\xi_{\perp}$ \[18,19\]:

$$
\xi_{\perp} = \frac{4}{3} \sinh \alpha \sum_{k=1}^{\infty} \frac{k(k+1)}{(2k-1)(2k+3)} \left( \frac{2 \sinh((2k+1)\alpha) + (2k+1) \sinh 2\alpha}{4 \sinh^2((k+1/2)\alpha) - (2k+1)^2 \sinh^2 \alpha} - 1 \right)
$$

(7)

$$
\xi_{||} = \begin{cases} 
(1 - \frac{\phi_n}{10^2} + \frac{1}{25} \zeta - \frac{4\phi_n}{25} - \frac{\phi_n^2}{10^2} + \ldots)^{-1} & \frac{\phi_n}{\alpha} > 0.1 \nonumber \\
-\frac{1}{5} \ln \left( \frac{\phi_n}{\alpha} - 1 \right) + .95888 + \ldots & \frac{\phi_n}{\alpha} < < 0.1
\end{cases}
$$

(8)

with $\alpha = \arccosh z/a$. It is worth noting that at small particle-plane distances, $\xi_{||}$ diverges much more slowly than $\xi_{\perp}$. Since the diffusion coefficient behaves as the inverse of the friction tensor, this fact is responsible for the “randomization” of the final position of an adhering sphere whose motion is controlled by Brownian motion, as commented in the introduction \[3\]. Regarding the expression for $\xi_{ss}(\vec{r}_i)$, we will use the friction coefficient of two spheres in an
unbounded fluid as worked out at all distances by Jeffrey and Onishi [20]. According to these authors, the effective friction tensor for two spheres at a distance $\vec{r}$ in an unbounded fluid is given by:

$$\vec{\xi}_{ax}(\vec{r}) = X_{11}^A(\vec{r})\hat{e}\hat{e} + \left(Y_{11}^A(\vec{r}) - \frac{(Y_{11}^B(\vec{r}))^2}{3\eta_{11}(\vec{r})}\right)(\vec{r} - \hat{e}\hat{e})$$

(9)

$\hat{e} = \vec{r}/r$ stands for a unit vector along the line of centers of the two spheres, and the expressions for the functions $X_{11}^A$, $Y_{11}^A$, $X_{11}^B$, and $Y_{11}^C$ are given in the appendix for the sake of completeness.

Expression (9), when inserted in (10), provides us with the equation of motion of a suspended particle,

$$\frac{d\vec{r}}{dt} = \vec{\mu}_{eff} \cdot \vec{F}_g$$

(10)

where where the effective mobility $\vec{\mu}_{eff}$ is the inverse of the effective friction tensor given in eq.(9).

The non-linear dependence of the friction tensors as functions of the distance between the particles, together with the fact that the friction tensors associated with the sphere-plane configuration have a spherical symmetry different from the cylindrical one characteristic of the sphere-plane friction tensors, make it impossible to find an analytic solution for eq.(10) even in the simplest case in which a single sphere is adsorbed on the plane. In the general situation of adsorption kinetics, one has to take into account that aside from this problem, the number of particles on the surface increases with time, which implies that only a numerical simulation study of the process can be carried out.

III. SIMULATION MODEL

We have performed numerical studies simulating the trajectories of the colloidal particles from the bulk to the surface, taking into account that as soon as a moving particle touches the surface, it is irreversibly fixed at that position. The model that we will develop constitutes a natural extension of the Ballistic Model. We will study the arrival of particles from the bulk to the surface in a sequential way. This corresponds to the physical situation in which the bulk concentration is low so that the interactions between the particles in the bulk can be neglected. This situation is indeed encountered in the experimental systems to which we will refer later on.

In our simulation algorithm, a position is randomly chosen at a height of 10 particle diameters above the plane. This ensures that initially the effects of the interactions of the incoming sphere and the preadsorbed ones can be neglected. In all the simulation studies, we have rescaled the distances so that the diameter of the spheres is taken as unity, and the time is rescaled by the characteristic sedimentation time $9\eta/2a\Delta \rho g$. With this adimensionalization, when the spheres are far from the plane, their mobility is equal to 1. This scaling, which is possible due to the structure of eq.(10), implies that our results are of general validity and will not depend on the particular system we consider, as soon as both inertial and diffusion effects are negligible.

We have numerically evaluated the trajectories of the incoming particles by numerically integrating eq.(10) with the expression for the friction tensor as given by eq.(9), until they reach either the surface or one or a set of preadsorbed particles. The integration is performed by using a 4th order Runge-Kutta algorithm [21] with variable time step. Since the friction tensor depends on the position of the adsorbing particle relative to the preadsorbed ones, at each time step it is necessary to calculate the appropriate value of the tensor. Moreover, each time a particle adheres, it has to be taken into account in the evaluation of the friction tensor of subsequent adhering spheres. In the numerical integration it is important to take into account that the behavior of the friction changes qualitatively along the trajectory of the particle. When the sphere is far from any other object, the mobility is of order unity, and changes slowly. As the particle comes close to an adsorbed sphere, the mobility becomes anisotropic. Then, while the component associated with the displacement along their line of centers vanishes linearly with the clearance between the spheres (see eq.(A3)), the component related to the displacement at constant separation goes to zero as the inverse of the logarithm of the clearance (see eqs.(A9)-(A7)). Thus, in this region, the mobility changes rapidly, and in a different manner depending on the direction. In fact, the motion will consist basically of angular displacements at practically constant distance between the spheres. Therefore, the variable time step is chosen to ensure that the displacement is never larger than a tenth of the clearance (see fig. 1). Moreover, in order to take the anisotropic behavior of the mobility into account, eq.(10) is solved in spherical coordinates centered on the adsorbed sphere closest to the incoming one.

The fact that the mobility goes to zero when the spheres come into contact, due to the stick boundary conditions, introduces an additional computational difficulty. Indeed, the velocity in that region can become so small that the computer time needed to describe the trajectory becomes exceedingly large. We have decided to stop the trajectory when the clearance between the incoming and an adsorbed sphere becomes smaller than $10^{-4}$ particle diameters.
For particles of diameter $2\mu m$, this corresponds to a minimum clearance of 200 Å. At this point, we impose that the particle will follow the steepest descent path towards the surface. Accordingly, we have implemented the BM algorithm \cite{22} to calculate the final position of the sphere on the plane, if it is not hindered to reach the plane by a group of preadsorbed particles. This assumption seems reasonable because at that point, the trajectory is basically controlled by the geometrical constraint that spheres cannot overlap, while the external force drives the particle to the surface. If the particle cannot reach the plane, it is rejected. We thus neglect multilayer effects.

When the sphere comes close to the plane, the mobility becomes anisotropic and exhibits the same qualitative behavior as explained in the previous paragraph. Again, the mobility tensor goes to zero when the clearance vanishes. Therefore, we also change the time step in order to ensure that the displacement is smaller than a tenth of the clearance between the incoming sphere and the plane. Moreover, in this case we have also to stop the numerical integration of the trajectory. We have considered that when the gap between the sphere and the plane is smaller than $10^{-2}$ diameters, the particle is deposited on the surface at that position. This truncation procedure can be seen as an effective way to account for the attractive short-range particle-surface potential, which binds the sphere to the substrate. The situation would be completely different for trajectories controlled by Brownian motion. The sphere would then have a large tendency to diffuse parallel to the line, leading to a randomization in its final position on the substrate \cite{13}.

A second feature which should be taken into account in the numerical algorithm is the long-range character of HI. In fact, in order to obtain the expression of the effective friction tensor, eq. (6), a sum over all previously adsorbed spheres should be carried out. However, from the computational point of view such a procedure is time consuming. Therefore, a compromise should be reached between the number of preadsorbed particles which will be considered to compute the friction tensor and the computer time needed. We have then used the results obtained from the study of the deposition of particles on a one dimensional substrate in the presence of HI \cite{13}. In this case, it has been shown that if the in-plane initial separation to a preadsorbed sphere is of the order of 10 particle diameters, the effect of HI is negligible on the final location of the incoming sphere. This fact suggests that we can now restrict the interaction of the incoming spheres to all the preadsorbed ones lying in a cylinder of radius 10 diameters centered on the incoming particle (see fig. 2). Moreover, as the particle approaches the surface, the value of the friction tensor will be dominated by the adsorbed particles closest to the adhering one. We have therefore further restricted the range of interaction by considering that the incoming sphere will only be affected by those particles whose distance, $d$, to the projection of the incoming particle on the plane is smaller than the height, $h$, at which this incoming sphere is located. This restriction procedure, however, is only taken into account when the height of the incoming particle is larger than 5. At lower heights, the radius of the interaction cylinder is assumed constant and equal to 5 (see fig. 2). This further conjecture is based on the observation that the deviation from the straight trajectory of the incoming sphere as determined by the gravity field takes place basically at distances of 2 or 3 over the plane \cite{13}. Although this reasoning is based on trajectories obtained with a small number of particles deposited on the surface, it seems reasonable that it also holds in more complex geometries. The advantage of this approximate procedure is that it saves a significant amount of computer time with respect to the initial cylindrical restriction.

We have checked the errors induced by the use of the varying interaction cylinder by covering a surface both using a constant-radius and a varying-radius interaction cylinder, as shown in figure 3. At an intermediate coverage, as shown in figure 3 a, practically all the particles end at the same positions on the plane using both methods, whereas at higher coverages a small fraction of the particles are placed at different positions, as seen in figure 3 b. This is due to the fact that if an incoming sphere arrives close to an ensemble of preadsorbed spheres, a small initial deviation may lead to a completely different final position. Then, due to the infinite memory of the adsorption process, all the particles arriving afterwards will be sensitive to this difference, leading eventually to a different configuration on the surface. Although a\textit{ priori}, from the point of view of average quantities, it is not clear whether this change may lead or not to significantly different statistical properties of the surface, comparison of the data obtained by this procedure with the experimental ones shows a\textit{ posteriori} that this approximation works pretty well, since no significant differences are observed.

We have performed numerical simulations of the adsorption process on a rectangular surface, of sides 23.34 and 27.34, up to a coverage of $\theta = 0.5$. The size of the system has been chosen such that the ratio "size of the system/size of the particles" is the same in the experiments and the simulations (see also next section). We have focused on the study of the radial distribution function, $g(r)$, and of the available surface function, $\Phi(\theta)$, since both represent key quantities for the statistical properties of the adsorbed layer. We have stopped our simulations at a coverage of 0.5, which corresponds to 407 particles deposited on the surface. At this coverage, one can already have an idea of the behavior of the system near jamming, without having to reach it. Indeed, the study of the system in the last 10% until jamming constitutes computationally the most expensive part by far.

We have covered 200 surfaces, and from them, we have constructed the radial distribution function. Simulations of the adsorption process according to BM rules have also been carried out following Ref. \cite{7}, under the same conditions as those exposed in the previous paragraph, in order to compare both models. The model described in this section,
which takes HI into account will be referred to as BHM algorithm hereafter.

IV. RESULTS AND DISCUSSION

All the simulation results were compared with experimental data. The latter correspond to the irreversible deposition of melamine particles of diameter 4.5 μm and density 1.5 g/cm³ on a silica surface. The preparation of the particles, their characterization and the experimental procedure were reported extensively in reference [5] and will only be briefly mentioned here. The experimental system consists of a cell, a flow system that allows the injection of the solution in the cell, an inverted microscope (Axiovert 10, Zeiss, Germany), a CCD video camera (type 4710 CCIR monochrome from Cohn, San Diego, CA) and a computer image analysis system (Visilog, Noesis, France). The experiments were performed in a plane parallel cell whose top and bottom parts are constituted by two silica microscope slides. Once the particle solution was introduced in the cell, it was fixed in its horizontal position to allow the particles to deposit on the lower microscope slide. After the deposition of all the particles present in the cell, a large number of pictures from different regions of the bottom surface were taken. Typically, for coverages of the order of 10-20%, 300 pictures were needed to obtain satisfactory results from the subsequent image analysis. The area that is covered by each picture equals \( s = 105 \times 123 \mu m^2 \). Only the particles that touch the surface were taken into account, the other particles, which can form a second layer were discarded by the image analysis. The geodesic center of all the particles was then determined for each picture. From this set of data, the different statistical properties of the surfaces such as the radial distribution function \( g(r) \) and the reduced variance of the density fluctuations could be determined. The details of the experimental method are given in reference [5]. It must be pointed out that great care had to be taken to determine the \( g(r) \) due to the discrete nature of the positions of the particles determined experimentally because of the finite size of the pixel elements in the camera. The reduced radius \( R^* \) of the particles was equal to 3.4. Let us recall that \( R^* \) is defined by \( R^* = a(4\pi \Delta \rho g/(3kT))^{1/4} \), where \( a \) corresponds to the radius of the colloidal particles, \( \Delta \rho \) to the density difference between the particle material and the solvent and \( kT \) the thermal energy. In the absence of HI, this is the only parameter which is relevant for the description of the deposition process [23]. It has been shown in reference [5] that this system behaves in first approximation in a ballistic way, even if systematic deviations from the model are observed, e.g. in \( g(r) \). However, the experimental data have never been compared to simulations of deposition processes in which the HI are taken into account. This constitutes the main objective of the present work. In order to assess the characteristic features due to the HI we have also compared our results with simulations performed in the framework of the pure BM.

From the previous studies it comes out that the main parameters describing the structure of the assembly of deposited particles are the radial distribution function \( g(r) \) (section IV.B1), the available surface function \( \Phi(\theta) \) (section IV.B1) and the reduced variance of the density fluctuations of the number of adsorbed particles \( \sigma^2/ < n > \). These two quantities do contain the same information at low coverage which is quantified by the third virial coefficient \( B_3 \) in the expansion of \( \Phi \) [1] and to which special attention will be paid in section IV.B2.

A. Radial distribution function

The radial distribution function \( g(r) \) characterizes the correlation between the adsorbed particles, and it can be determined from the positions of the different particles on the surfaces. However, in order to be able to quantitatively compare the \( g(r) \) obtained from the simulation with the experimental ones, it is necessary to treat the simulation data exactly in the same way as the experimental ones. In particular, we have to apply the pixelization procedure (discretization of the positions of the particles) to the coordinates of the particles deposited on a surface by means of the BM or the BHM algorithms. Taking into account that the diameter of the melamine particles used in the experiments is 4.5 μm, the dimensions of the experimental pixel (i.e. 0.48 μm x 0.41 μm) have been scaled to 0.48 / 4.5 and 0.41 / 4.5, along the x- and y-axis, respectively. After performing this rescaling, the unit of distance is the diameter of the particles. The coordinates of the positions of the centers of the particles are then converted into integer numbers of pixels. The center-to-center distances are calculated using these integer coordinates, and the histogram for the relative distribution of particles is evaluated with a width resolution not larger than the smallest side of a pixel (i.e. 0.41 / 4.5) as was done with the experimental data [5]. This is repeated over the 300 to 500 surfaces available (as indicated in the figure captions). The radial distribution function is finally deduced from this cumulated distance frequency histogram.

The results are shown on figure 4 (a-f). For a coverage \( \theta \) of about 0.15, only the first peak can be clearly identified (fig. 4 a,b). The introduction of HI in the description of the deposition process when compared to the BM model results mainly (i) in the lowering of this contact peak, which seems then to be in better agreement with the experimental
data, and (ii) in the broadening of the peak after its maximum, due to the effective repulsion induced by HI between the adsorbing and adsorbed spheres. At intermediate coverages, \( \theta \approx 0.35 \) (fig. 4 c,d), the difference in the height of the peak is less marked; however, the agreement between the simulated data and its experimental counterpart is excellent, and they almost coincide in the broaden region and becomes better in the region around \( r/(2a) = 1.5 \). This observation may also be done in the case of high coverages \( \theta \approx 0.50 \) (fig. 4 e,f). However, for this latter coverage, the simulated data are quite similar, whether or not the HI are taken into account. This is due to the fact that in this regime, the arrival of particles at the surface is almost entirely controlled by geometrical restrictions, since the available area is then only formed by small targets. Therefore, the fraction of rolling particles, which determines the height of the peak, is not so sensitive to HI repulsion because then the arriving particle is forced to enter in one of these target areas and the repulsive friction forces are greatly balanced due to the number of particles surrounding each hole. As a general conclusion, HI do only introduce slight changes in the structure of \( g(r) \). They induce, in particular, an effective repulsion between the particles. The most important change is observed in the first peak, because, at low coverage, it is related with the rolling mechanism over one particle, which is indeed very sensitive to HI [17].

B. Available surface function

1. Analysis over the entire coverage range

In order to further analyze to what extent the introduction of the hydrodynamic forces modifies the structure of the particle configurations on the adsorbing surface, we present in this section the comparison of the available surface function \( \Phi(\theta) \) corresponding to the BM and the BHM, and denote it by \( \Phi_{BM}(\theta) \) and \( \Phi_{BHM}(\theta) \) respectively. For a given coverage \( \theta \), this quantity is equal to the probability that a deposition trial will be successful. For the ballistic deposition, it is theoretically known that \( \Phi_{BM}(\theta) \) behaves as \( 1 - B_3^{BM} \theta^3 + O(\theta^4) \). \( B_3 \) has first been estimated to 9.61205 by Thompson and Glandt [1], and later on corrected to 9.94978 by Choi et al. [22]. It is worth noting that, in fact, \( 1 - B_3^{BM} \theta^3 \) is an acceptable approximation only over a narrow coverage range (up to 10 or 15\%). The absence of the first and second order terms from the series expansion of \( \Phi_{BM}(\theta) \) is due to the fact that the presence of at least three absorbed particles is required for an incoming particle to be rejected. Indeed, a new spherical particle can always roll over one or two fixed spheres and reach eventually the surface. This is also true when HI are involved in the deposition process. Hence, the expansion of \( \Phi \) as a power series of \( \theta \) corresponding to the BHM model must be of the form \( \Phi_{BHM}(\theta) = 1 - B_3^{BHM} \theta^3 + O(\theta^4) \) with \( B_3^{BHM} \) a priori not equal to \( B_3^{BM} \).

The values of \( \Phi(\theta) \) derived from the simulations are shown on figure 5a, where we compare the data obtained in the framework of the BM (400 surfaces) and of the BHM (500 surfaces up to \( \theta = 0.3 \), and 300 surfaces from \( \theta = 0.3 \) up to \( \theta = 0.5 \)). Without any additional computation it is obvious that both data sets are not identical, even though the sample sizes lead to a non negligible noise level. If we fit a polynomial of the fifth degree (without the \( \theta^5 \)-terms) to the simulation data over the whole range (coverage from 0 to 0.5), we obtain \( B_3^{BM} \approx 9.427 \) and \( B_3^{BHM} \approx 4.695 \). Even though the value \( B_3^{BM} \) is not exactly identical to its theoretical prediction (9.94978), it clearly appears that the third-order coefficient is strongly influenced by HI (\( B_3^{BM}/B_3^{BHM} \approx 2 \)). This reduction indicates that the deposition probability falls off less rapidly when HI are introduced in the model. These values must however be taken with great care due to the poor statistics and to the possible mutual influence of the fitting parameters. Moreover, it must be realized that using the values of the fits for the available surface function leads to the values \( \Phi_{BM}(\theta = 0.1) = 0.9906 \) and \( \Phi_{BHM}(\theta = 0.1) = 0.9953 \), which are almost equal. This confirms the observation following from the comparison of the \( g(r) \) (see preceding section) that HI do not deeply alter the deposition process on global average magnitudes in the present conditions. Nonetheless, an additional more precise simulation has been performed, in which 5000 surfaces were covered up to a coverage of 0.1 (fig. 5b). In this regime \( \Phi_{BHM}(\theta) \) should be accurately expressed by \( 1 - B_3^{BHM} \theta^3 \). The value of \( B_3^{BHM} \) deduced from these data is 4.849, which is not far from the former estimate derived from the full data set shown in fig. 5a.

Figure 6 renders clear that the difference between \( \Phi_{BHM} \) and \( \Phi_{BM} \) is almost everywhere positive. This systematic character of the sign of \( \Phi_{BHM} - \Phi_{BM} \) strengthens the opinion that HI play a significant, though weak, role during the deposition process investigated here.

In order to confirm that \( B_3 \) corresponding to deposition with HI is significantly smaller than its ballistic counterpart, we have developed a new simulation method to determine this coefficient, as explained in the next subsection.
In the BM, at least three particles are required to form a trap for a depositing particle. The term $B_3^{BM} \theta^3$ appearing in the series expansion of $\Phi^{BM}(\theta)$ precisely reflects the rejection efficiency of three particle configurations leading to the rejection of a new incoming one. As already discussed by Thompson and Glandt for the BM, an isolated triangle formed by the centers of three adsorbed spheres is a trap if and only if (i) it has no side longer than twice the particle diameter, (ii) all its angles are acute, and (iii) the radius of its circumcircle is not larger than one sphere diameter. For an adsorbing square surface of area $s$, the probability for an incoming particle to be rejected is given by the ratio of the area of the triangle to $s$. When the triangle is not a trap, its exclusion area is evidently equal to zero.

In the BM it is easy to build up a large number of representative traps formed by 3 deposited particles and to evaluate their average exclusion area $< A_{ex} >$. Consider now a large adsorbing surface of area $S$ covered with $N$ particles and virtually subdivided into a large number $\nu$ of sub-surfaces of area $s$ ($\nu = S/s$). The probability $p_1$ that a given sub-system contains effectively three particles is given to a good approximation by

$$ p_1 = \left( \frac{3}{N} \right) \left( \frac{1}{\nu} \right)^3 \left( 1 - \frac{1}{\nu} \right)^{N-3} $$

(11)

In this formula we assume that at low coverage the sub-systems have no mutual influence, which is indeed correct. The probability $p$ for an incoming particle over the surface $S$ to be trapped is then given by the product of the probability $p_3$ that it deposits in a sub-system containing at least 3 particles and the conditional probability $q$ that this particle which ends up over a sub-system which is known to contain at least three adsorbed particles is trapped by them. To lowest order in the coverage, $p_3$ is equal to $p_1$ and the conditional probability $q$ is then given by $< A_{ex} > /s$. Thus one gets:

$$ p \approx \left( \frac{3}{N} \right) \left( \frac{1}{\nu} \right)^3 \left( 1 - \frac{1}{\nu} \right)^{N-3} \frac{< A_{ex} >}{s} $$

(12)

The probability $p$ can be identified with $B_3^{BM} \theta^3$ (where $\theta = \pi N/(4S)$), provided that the diameter of the particles has been taken as unity) in the density expansion of $\Phi$. In the limit when $N \to \infty, \nu \to \infty$, with $N/\nu \to 0$, it follows that:

$$ \Phi = \sum_{N=3}^{\infty} \frac{N!}{3!} \left( \frac{\theta}{4} \right)^3 $$

A simulation consisting in the deposition of $10^8$ independent sets of three particles on a square surface of side length equal to 5,6,...,40 (in units of the diameter), hence of area ranging from $S = 25$ up to 1600, leads to $< A_{ex} > s^2 = 28.89 \pm 0.16$. Inserting this value into eq.(13), one finds the value $B_3^{BM} = 9.939 \pm 0.055$, in good agreement with the theoretical value $9.94978$ given by Choi et al. [22]. Hence, the method provides a convenient means for estimating the first non-vanishing term of the series expansion of the available surface function $\Phi$. It can also be applied to the deposition process which takes HI into account. In this case, a triangle cannot be a trap if it does not constitute a trap for the BM. However, even though a triangle may act as a trap in the presence of HI, its rejection efficiency is no longer proportional to its geometrical area, but it can be significantly smaller. It can never be larger because, as already pointed out, HI introduce an effective repulsion between the adhering particle and the preadsorbed ones. Therefore, each side of the ballistic trapping triangle becomes a concave curved line due to the repulsive hydrodynamic effect of the particle located at the opposite vertex. Also as a result of this effective repulsion, the number of traps formed in the presence of HI should be smaller than the ones formed in a pure ballistic "experiment" for the same coverage. The result of these various effects can only be evaluated by simulation. We have therefore developed a special algorithm aimed at the construction of triangles in the presence of HI.

A large number of sets of three particles were deposited on surfaces of area $s$ in the presence of HI. In order to evaluate $< A_{ex} >$, for each set of three particles the exclusion area $A_{ex}$ should be determined by depositing a fourth particle on the surface $s$ a large number $N_p$ of times. $A_{ex}/s$ is then given by the ratio of the number of successful deposition trials of this fourth particle to the total number of trials $N_p$. $< A_{ex} >$ is then simply the average of these exclusion areas $A_{ex}$ over the great number of independent sets of three initial particles. It can be noticed that many of these sets lead to an exclusion area which is zero. However, this procedure to determine $< A_{ex} >$ is very time consuming from a simulation point of view. We have thus, in a first step, approximated the exclusion area of a triangle by its geometrical area. We have generated $10^8$ triangles taking HI into account, counting which fraction of the generated triangles constitute a trap according to BM. This leads obviously to an upper limit for $B_3^{BHM}$,
estimated to be approximately 7.7. This rough approximation shows that in the presence of HI, $B_3^{BHM}$ is at least 22\% lower than in the ballistic case. This arises from the fact that, on average, the trapping triangles generated by BHM are larger than the ones obtained in the BM due to the effective repulsion of HI.

In order to get a more precise estimate of $B_3^{BHM}$, we should also take into account the change related to the decrease of the excluding area for a given trap. However, the general simulation scheme introduced in the previous paragraph is too time consuming, as already mentioned. We have looked at a simpler procedure by studying first the relative frequencies of the different trapping triangles. We have characterized a triangle by its largest angle and its area, and studied the histogram of trapping triangles. In fig. 7(a-b), we have plotted the histograms of relative frequencies for BM and BHM respectively, constructed using the same procedure which has allowed us to give an upper limit for $B_3$. In both cases, one can see that the equilateral touching triangles are the most probable objects, because the second particle has rolled over the first one, and the third rolls over the two preadsorbed ones. Afterwards, there exists a relatively high curve representing those triangles in which the two latter adhering spheres have rolled only over one preadsorbed particle. One can easily verify that this curve behaves as $\sin(\alpha)/2$, $\alpha$ being the largest angle of the triangle, since this is the area of such triangles. Besides these singular contributions, there exists a plateau, which corresponds to those triangles in which only one adhering sphere has rolled over a preadsorbed particle. Finally, the remaining traps formed without rolling give a negligible contribution to the histogram. Although this general description applies for both models, in the BHM the rolling mechanisms is not as effective, due to the repulsion induced by HI. Nonetheless, we have assumed that by studying only the most probable triangles, one can still improve our first estimate of $B_3$. To this end, we have performed numerical simulations in which we prescribe a rectangle of an area twice a given trapping triangle, and we calculate its excluding area by the general and rigorous method depicted in the previous paragraph. We fix the triangle to have two sides of length 1, and the largest angle to be larger than $60^\circ$, and for each given triangle, we analyze the deposition of $10^5$ particles starting within the prescribed rectangle, counting the fraction of such particles which are able to reach the surface.

As shown in table I, the trapping area remains almost constant with the angle. If one compares the results of the BHM to BM, one can clearly see that for these small triangles, the excluding area is reduced to almost half its BM counterpart due to HI repulsions. If we take into account that the mean geometrical area of the triangles is larger in the presence of HI, which reduces the fraction of traps, and that in addition the excluding area is also reduced by the effective repulsion, we get as a better estimate $B_3^{BHM} \approx 7.7 \times 0.526 = 4.05$, where 0.526 is the ratio of the mean rejection fraction in BHM (0.2634) to the mean rejection fraction obtained by BM (0.5005), according to table I. We can then set bounds to this coefficient, since it should obey, $4.146 \pm 0.003 < B_3^{BHM} < 7.7 \pm 0.003$. It is worth pointing out that the lower bound is close to the one obtained by fitting $\Phi$ with a power series as seen in subsection IV B 1. There, we obtained a value of 4.7. Our new estimate has to be a lower estimate, since we have disregarded the influence of the larger triangles, which also have a larger exclusion area. Nonetheless, the lower estimate is quite close to the value obtained by the fitting procedure, indicating that, indeed, $B_3^{BM}/B_3^{BHM} \approx 2$. This result shows that HI strongly influence the local structure of the deposits, modifying the triplet distribution.

We have finally looked at the fraction of incoming particles ending inside an equilateral triangle as a function of its side. Again, for a given equilateral triangle, we let deposit $10^5$ particles and calculate the fraction which ends within the triangle. As seen in fig. 8, even for triangles of side length 7 diameters, the fraction is smaller than the value 0.5 predicted by BM. This again shows the long-range character of HI, and its tendency to form looser aggregates on the substrate with respect to BM predictions.

It would be interesting to determine the value of $B_3^{BHM}$ more precisely but this requires long computer times. Its study, as well as the evolution of $B_3$ with $R^*$ is currently under way by using the general and rigorous method presented here. It will be the purpose of a future article.

| angle (in degrees) | BM     | BHM     |
|-------------------|--------|---------|
| 60.0              | 0.4987 | 0.2587  |
| 67.5              | 0.4995 | 0.2581  |
| 75.0              | 0.5077 | 0.2694  |
| 82.5              | 0.5003 | 0.2632  |
| 89.9              | 0.4961 | 0.2676  |

**TABLE I.** Fraction of incoming particles which are trapped on an area which is twice the area of the corresponding rectangle triangle both for the BM and BHM. The largest angle characterizing the trapping triangle is given in the first column, and the shortest side is always of one particle diameter.
V. CONCLUSIONS

This article presents a first study in which experimental results concerning the deposition of large particles on a solid surface under the influence of gravity have been compared to both the ballistic deposition model and a simulation model which takes hydrodynamic interactions (HI) into account. We have performed numerical simulations of the deposition of spherical particles on a surface, incorporating the effect of HI, in the case when Brownian motion can be neglected, thus generalizing for a bidimensional surface the previous simulation data for the deposition on a linear substrate [13]. The major effect of HI is the induction of an effective repulsion between the adsorbing sphere and the preadsorbed particles. We have then been able to compare the simulation data with the pair distribution function obtained experimentally for the deposition of melamine particles. We have shown that in the full range of surface coverages, the comparison of the BHM with the experimental results leads to a better agreement than the one obtained when comparing BM to the experimental data. In particular, the height of the first peak of $g(r)$ is improved, especially at low coverages, when the fraction of rolling particles plays an important role. The broadening of the curve after the first peak, which the BM always underestimates, is also in better agreement. These features appear as a result of the effective repulsion induced by HI, although they lead to a quantitative small change in the curve (except in the height of its first peak), because HI does not alter the qualitative features of the adsorption process. As a matter of fact, HI will become more significant the closer we look at the structure of the adsorbed layer. In this sense, we have also studied the third virial coefficient $B_3$ of the available surface function $\Phi$. We have shown that this coefficient drops to half its BM value. This comes from the fact that, due to the effective repulsion, at a given coverage, the fraction of triangles that form a trap is smaller in the BHM, and that the excluding area of a trapping triangle is also smaller than the geometrical area of the triangle. However, the decrease of $B_3$ does not produce a significant change in $\Phi$. As a general remark, we can conclude that HI have only a small effect on global averaged quantities. In this respect, the BM constitutes a good approximation, and this study thus validates the BM which has already been widely studied from a theoretical point of view. On the other hand, for a fine analysis of the local structure, one has to take HI into account. It is not at all obvious, however, whether such conclusions remain valid when the diffusion of the particles in the bulk plays some role i.e. for value of $R^*$ of the order or smaller than 3. In this case HI can again play a major role and this should be investigated in the near future.

NOTATION

BHM : Sequential adsorption model with hydrodynamic interactions at large gravity and BM-like rules

BM : Ballistic model

HI : Hydrodynamic interactions

RSA : Random sequential adsorption model

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APPENDIX: ELEMENTS OF THE SPHERE-SPHERE FRICTION TENSOR

In this appendix we give the explicit expressions for the friction coefficients corresponding to a geometry where two equal-sized spheres are suspended in an infinite fluid. Jeffery and Onishi [20] computed the corresponding friction tensors for any distance separating them. We will follow the notation of eq.(6), considered in the special case of the force acting on one sphere in the presence of another one suspended in an unbounded fluid, and concentrate on the tensor components of interest. The two spheres have a radius unity and are separated a distance $r$. We will call $\hat{e}$ the unit vector of the center-to-center direction. Then, due to the symmetry, the matrices appearing in eq.(6) can be expressed as
(\xi_{ii})_{ij} = X^A_{11} e_i e_j + Y^A_{11} (\delta_{ij} - e_i e_j) \quad (A1)
(\xi_{ir})_{ij} = Y^B_{11} e_ijk e_k \quad (A2)
(\xi_{rr})_{ij} = X^C_{11} e_i e_j + Y^C_{11} (\delta_{ij} - e_i e_j) \quad (A3)

where the different functions correspond to the expressions appearing in eq.(3), and the subindices correspond to the different spatial direction. These new functions are given by

\[
X^A_{11} = \frac{1}{4} \frac{1}{1 - 4r^{-2}} - \frac{9}{40} \ln\left(1 - \frac{4}{r^2}\right) - \frac{3}{112} \left(1 - \frac{4}{r^2}\right) \ln\left(1 - \frac{4}{r^2}\right) \\
+ \frac{3}{4} + \frac{17}{70} \frac{1}{r^2} + \frac{127}{560} \frac{1}{r^4} - \frac{4057}{2240} r^4 + ...
\]

\[
Y^A_{11} = -\frac{1}{6} \ln\left(1 - \frac{4}{r^2}\right) + 1 - \frac{5}{48} \frac{1}{r^2} + \frac{371}{768} \frac{1}{r^4} + \frac{16331}{r^6} + ...
\]

\[
Y^B_{11} = -\frac{1}{4} \left[1 + \frac{1}{2} \left(1 - \frac{4}{r^2}\right)\right] \ln\left(\frac{r + 2}{r - 2}\right) + \frac{3}{2r} - \frac{9}{8r^3} + \frac{1}{1920r^5} + ...
\]

\[
Y^C_{11} = -\frac{1}{5} \left[1 + \frac{47}{50} \left(1 - \frac{4}{r^2}\right)\right] \ln\left(1 - \frac{4}{r^2}\right) + 1 - \frac{194}{125} \frac{1}{r^2} \\
+ \frac{327}{500} \frac{1}{r^4} - \frac{51853}{24000} \frac{1}{r^6} + ...
\]

In these expressions the Stokes value for the friction coefficient is taken as unity.

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Figure captions

Fig. 1 Motion of an adsorbing particle close to a preadsorbed one, when they are at a distance \( r \), with a clearance \( \Delta r \). The time increment in the numerical algorithm is chosen so that \( \Delta r/r \leq 0.1 \). As a result, due to the anisotropic behavior of the mobility, the motion of the sphere is almost parallel to the surface of the adsorbed sphere, i.e. \( \Delta r_p \gg \Delta r \). Therefore, the trajectory of the adsorbing particle will approximately follow the dotted line, which corresponds to the trajectory predicted by BM.

Fig. 2 Interaction cylinder: (—) Constant-radius interaction cylinder, and (- - -) variable-radius interaction cylinder for an adsorbing sphere. The particle is left at an initial height \( h_0 \) and in the second case, the radius of the cylinder diminishes as the height until a height of 5 diameters is reached. At that point the cylinder is kept at a constant radius. In the first case, the adsorbing particle will interact with all the dark adsorbed spheres; in the second, at the end only the black one will influence its motion.

Fig. 3 One surface covered by spheres using a varying-radius (○), and a constant-radius interaction cylinder (●) (see fig. 2), at a coverage of a) \( \theta = 0.25 \), and b) \( \theta = 0.5 \) (the jamming corresponds approximately to 0.6).

Fig. 4 Pair distribution functions: Comparison of the experimental data (●) with the results of a) BM and b) BHM respectively at \( \theta = 0.1489 \). c) and d ) Equivalently at \( \theta = 0.3495 \). e) and f) Correspondingly at \( \theta = 0.4997 \).

Fig. 5 a) Available surface function, \( \Phi(\theta) \), for BM (—) and BHM (○) as a function of the coverage \( \theta \) obtained after covering surfaces of area 23.34x27.34 diameters. The results are obtained after covering 400 surfaces in the BM, and 500 surfaces in BHM until \( \theta = 0.30 \) and 300 from \( \theta = 0.30 \) up to \( \theta = 0.50 \). b) Same as Fig. 5a, except that the sample size is 5000 surfaces for BHM, and the surfaces are covered until \( \theta = 0.1 \).

Fig. 6 Difference between the surface available function of BM and BHM. Note that the average is displaced towards the region of positive numbers.

Fig. 7 Histograms of the relative frequency of the trapping triangles (see definition in the text) as a function of the area and maximum angle of such triangles for a) BM, and b) BHM.

Fig. 8 Fraction of particles adsorbed inside an equilateral triangle of side length \( l \) if initially they are randomly chosen on a rectangle of area twice the corresponding triangle area. (—) BHM, (- - -) BM.