Fluctuation of the number of particles adsorbed on surfaces under the influence of gravity

P. Schaaf,[1,2,*] P. Wojtaszczyk,[1,3] B. Senger,[3] J.-C. Voegel,[3] and H. Reiss[4]

[1]*Institut Charles Sadron, 6, rue Boussingault, 67083 Strasbourg Cedex, France*

[2]*Ecole Européenne des Hautes Etudes des Industries Chimiques, URA 405 (CNRS), Boîte Postale 296F, 1, rue Blaise Pascal, 67008 Strasbourg Cedex, France*

[3]*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*

[4]*Department of Chemistry and Biochemistry, University of California, 405 Hilgard Avenue, Los Angeles, California 90024-1569*

(Received 28 December 1994)

The fluctuation of the number of particles deposited under a significant gravity field onto systems of finite size is analyzed experimentally and theoretically. In particular, the variance σ^2 varies as $1-\langle\alpha\rangle\theta^3+O(\theta^4)$ with the coverage θ, where $\langle\alpha\rangle$ depends upon the interactions involved in the deposition process. This result is valid for any deposition process in which the gravity is "strong enough," regardless of the radial distribution function corresponding to the process. This conclusion, of interest to a large class of deposition processes, is supported by original experimental results.

PACS number(s): 68.10.Jy, 05.40.+j, 47.15.Gf

The adsorption-adhesion of colloidal particles or proteins on solid surfaces is often an irreversible process in that, once adsorbed, the particles neither diffuse on the surface nor desorb from it. This irreversible character excludes the use of general results derived from equilibrium statistical mechanics [1]. The study of these processes is therefore particularly challenging from a theoretical point of view, and different models have been proposed to describe them. The most popular model is that of random sequential adsorption (RSA), which has been used to account for the adsorption of proteins on solid surfaces [2,3]. However, for large particles (diameter >1 μm) observed under an optical microscope, gravity usually plays an important role and the ballistic model seems more appropriate than RSA [4].

Despite the large number of theoretical results in this field, experimental studies are still rare. This is due, in part, to the difficulty of performing them reproducibly. In addition to the first results of Feder and Giaever [2], Ramsden has attempted to verify the validity of RSA for the adsorption of proteins on surfaces [3,5]. Adamczyk *et al.* have shown, by comparing experimental radial distribution functions $g(r)$ to their simulated counterparts, that the RSA model can also account for the adsorption of colloidal particles on solid surfaces [6].

For large and dense particles, it has been recently verified that the ballistic model correctly describes the statistical properties of the deposition of such particles on surfaces [4]. This conclusion was based on the agreement between the experimental values and the predictions of the model, at different coverages, for both $g(r)$ and the variance σ^2 of the number of deposited particles, on finite areas. This variance corresponds to ν squares of area a constituting a representative part, of area $A=\nu a$, of the whole adsorbing surface. However, small discrepancies were still observed at low or intermediate coverages between the experimental radial distribution functions and those simulated by assuming a ballistic deposition process. These discrepancies were attributed to either the polydispersity of the particles or hydrodynamic interactions, not incorporated in the ballistic model. Recent simulations performed in the (1+1)-dimensional case by Pagonabarraga and Rubi [7] for the ballistic deposition process, taking into account hydrodynamic interactions (HI's) between the adsorbing particles and (i) those already adsorbed, and (ii) the adsorption plane, showed that deviations from the ballistic model are indeed introduced by HI's. More precisely, HI's tend to repel the adsorbing particle from those already adsorbed. The radial distribution function is thus affected by HI's during the deposition process. This appears, however, to contradict the good agreement between the variance found experimentally and that predicted by the ballistic model [4]. Indeed, σ^2 is a function of the mean number of adsorbed particles $\langle n\rangle$ and of the radial distribution function through the relation [8]

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

where ρ represents the density of adsorbed particles on the surfaces, i.e, $\rho=\langle n\rangle/a$. Using this relation and the expression for $g(r)$ given by Thompson and Glandt [9] for the case of ballistic deposition, it can be shown rigorously that for this model

$$\frac{\sigma^2}{\langle n\rangle}=1+k\rho^3+O(\rho^4)\ , \tag{2}$$

where k is a constant. The ballistic model describes the adsorption of spheres that are considered infinitely heavy; an incoming particle is allowed to roll over one or more previously adsorbed ones. Equation (2) assumes that the adsorbing surface is subdivided into an infinitely large number of large subsystems, so that $\nu\to\infty$ and edge

*Corresponding author. FAX: 33 88 41 40 99.

effects are negligible. In this paper we show that as long as the gravitational force acting on the diffusing particle is "strong enough," $\sigma^2/\langle n \rangle$ continues to be given by Eq. (2), independent of the radial distribution function. In particular, no terms in ρ and ρ^2 appear in $\sigma^2/\langle n \rangle$, which should then have a horizontal tangent at $\langle n \rangle = 0$, as observed experimentally [4]. The constant k, on the other hand, should depend upon the deposition mechanism. We compare this theoretical result, which is of general validity, with the results of experiment and explore the dependence of k on both particle size (radius R or diameter $d=2R$) and density.

For the experimental determination of $\sigma^2/\langle n \rangle$, we take a large number of pictures of small sections of a large surface covered with particles. Each picture can be considered a subsystem of the covered surface. The ensemble of these subsystems is the analog of the grand canonical ensemble in equilibrium statistical mechanics. Consider a given subsystem, and let n be the number of particles in this subsystem at time t. Select a given particle (i) out of the n particles of the subsystem. Let $P_i(r,t)2\pi r\,dr$ be the probability of finding, at time t, the center of another adsorbed particle in the circular annulus of radius r, of area $2\pi r\,dr$, centered on particle (i). The integral $\int_0^\Lambda P_i(r,t)2\pi r\,dr$ represents then the mean number of particles adsorbed in a disk C of radius Λ, whose center coincides with the center of particle (i). The dependence of this number on time t satisfies the equation

$$\frac{d}{dt}\int_0^\Lambda P_i(r,t)2\pi r\,dr = \pi\Lambda^2[1-h_i(\Lambda,\rho)] , \quad (3)$$

where $h_i(\Lambda,\rho)$ is the probability that a particle hitting will *not* adsorb on it. When the gravitational effect is "strong enough," a particle moving toward the adsorption plane will eventually adsorb with probability *unity*, unless it is intercepted by a trap out of which it cannot diffuse and which prevents the particle from reaching that plane. Such traps are composed of at least three adsorbed particles (Fig. 1). In disk C of radius Λ one can distinguish two kinds of traps: (a) the first contains the particle (i) and two other particles. This implies that the probability $p_i^{(\mathrm{I})}$ that a particle arriving over disk C will fall within a trap of type I is of the form

$$p_i^{(\mathrm{I})} = \sum_k C_{i,k}\frac{\alpha_{i,k}}{\pi\Lambda^2}\rho^2 + O(\rho^3) , \quad (4)$$

where $C_{i,k}\rho^2$ represents the probability of finding in disk C around particle (i) a configuration k of three particles, whose excluded area is $\alpha_{i,k}$. The coefficient $C_{i,k}$ is independent of Λ for Λ larger than $2d$. (b) Traps of type II consist of at least three particles different from particle (i). The probability $p_i^{(\mathrm{II})}$ that a particle arriving over disk C will fall within a trap of type II is then given by

$$p_i^{(\mathrm{II})} = \sum_k D_{i,k}\frac{\beta_{i,k}}{\pi\Lambda^2}\rho^3 + O(\rho^4) , \quad (5)$$

where $D_{i,k}\rho^3$ represents the probability of finding in disk C around particle (i) a configuration k whose excluded area is $\beta_{i,k}$. In order to use ρ instead of t as the parameter indicating the progress of the adsorption process, one introduces the available surface function Φ through the relation

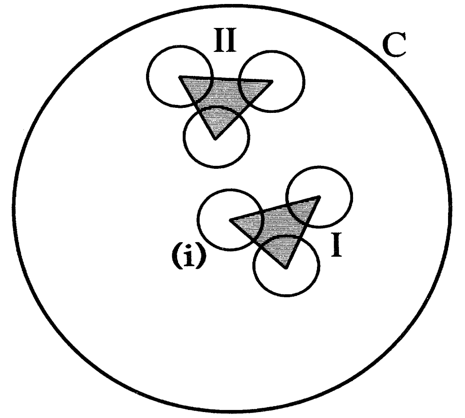

FIG. 1. Excluded areas of types I and II. Type I: the shaded area represents the excluded surface $\alpha_{k,i}$ for the ballistic case, formed by three particles, one of which is particle (i). Type II: the shaded area represents the excluded surface $\beta_{k,i}$ for the ballistic case, formed by at least three particles different from particle (i). The traps are included inside a large circle C of radius Λ and centered on particle (i).

$$\frac{d}{dt} = \frac{d\rho}{dt}\frac{d}{d\rho} = \Phi\frac{d}{d\rho} . \quad (6)$$

Due to the fact that only traps of at least three adsorbed particles can prevent an incoming particle from reaching the surface, the reasoning of Thompson and Glandt for the ballistic model implies that $\Phi = 1 + O(\rho^3)$. To the lowest order in ρ, the relation (3) then takes the form

$$\frac{d}{d\rho}\int_0^\Lambda P_i(r,\rho)2\pi r\,dr = \pi\Lambda^2\left[1-\frac{\langle\alpha_i\rangle}{\pi\Lambda^2}\rho^2 + O(\rho^3)\right] , \quad (7)$$

where $\langle\alpha_i\rangle$ is given by $\sum_k C_{i,k}\alpha_{i,k}$. This relation can be integrated to give

$$\int_0^\Lambda P_i(r,\rho)2\pi r\,dr = \pi\Lambda^2\rho - \frac{\langle\alpha_i\rangle}{3}\rho^3 + O(\rho^4) . \quad (8)$$

Taking the average of both sides of Eq. (8) over all the particles of all the subsystems, leads to

$$\int_0^\Lambda P(r,\rho)2\pi r\,dr = \pi\Lambda^2\rho - \frac{\langle\alpha\rangle}{3}\rho^3 + O(\rho^4) , \quad (9)$$

where $\langle\alpha\rangle$ represents the mean value of the $\langle\alpha_i\rangle$ taken over all particles (i). $P(r,\rho)$ is related to the radial distribution function $g(r,\rho)$ through $P(r,\rho) = \rho g(r,\rho)$. Equation (9) can then be rewritten as

$$\int_0^\Lambda \rho[g(r,\rho)-1]2\pi r\,dr = -\frac{\langle\alpha\rangle}{3}\rho^3 + O(\rho^4) . \quad (10)$$

But only the traps consisting of three particles, one of them being the "center" particle, contribute to the term in ρ^3 in Eq. (10). $\langle\alpha\rangle$ is thus independent of Λ as long as Λ exceeds $2d$. The integral between 0 and Λ can then be extended from 0 to ∞. Thus, the relation (1) giving the variance assumes the form

$$\frac{\sigma^2}{\langle n \rangle}=1-\frac{\langle \alpha \rangle}{3}\rho^3+O(\rho^4)\ . \tag{11}$$

This result is a general law and applies to all deposition processes as long as the gravity is "strong enough." In particular, it applies to ballistic deposition since it can be calculated directly from Eq. (1) using the expressions for the radial distribution function $g(r)$ given by Thompson and Glandt. But it also applies to the *real* deposition mechanism in which hydrodynamic interactions are always present and which do not lead to the function $g(r)$ predicted by the ballistic model.

One might inquire about what sort of particles satisfy the condition that gravity be "strong enough" for the derived law to apply. Qualitatively, it seems that for this result to be valid, the Boltzmann factor must be small: $\exp[-2R(4\pi R^3\Delta\rho_d g/3kT)]\ll 1$, where R is the particle radius and $\Delta\rho_d$ the difference between the specific mass of the particle and that of the solvent. kT has the usual meaning, while $g=9.81$ m s^{-2} is the acceleration of gravity. This criterion can also be written $\exp(-2R^{*4})\ll 1$, where $R^*=R[4\pi\Delta\rho_d g/3kT]^{1/4}$ is a dimensionless reduced particle radius [10]. A series of three experiments has been performed to verify these results. The deposition of three kinds of particles, each having a different value of R^*, has been studied by means of optical microscopy. The variance has been determined for each kind of particle as a function of the number of particles adsorbed on surfaces of finite size. The experimental procedure for determining the variance is similar to that described in Ref. [4]. The particles having $R^*=3.4$ are melamine particles synthesized in the laboratory by the method described in Ref. [4]. These particles have a mean radius R of 2.3 μm, measured by a Coulter counter, and a density ρ_p of 1.5. The two other types of particles are sulfate lattices from Interfacial Dynamics Corp. (Portland, OR). Those with $R^*=2.9$ ($R=3.38$ μm, $\rho_p=1.055$; cat no. 2-234-54) and 1.8 ($R=2.1$ μm, $\rho_p=1.055$; cat no. 2-356-97) had surface charges of -3.80 μC/cm^2 and -5.12 μC/cm^2, respectively (certified by the manufacturer). For the melamine particles, the adsorption procedure was identical to that in Ref. [4]. Due to the negative surface charge of both the latex particles and the silica surface, the same procedure could not be used for the other particles. Their solutions were diluted with deionized super-Q Millipore water containing 10^{-3} M of NaCl, pH around 4, and with 10^{-4} M of NaCl, pH around 5.7 for the particles of radius $R^*=1.8$ and 2.9, respectively. The adsorption substrate consisted of a glass microscope slide precoated with a layer of fibrinogen. The role of this protein was to create a positive charge on the surface in order to bind the particles irreversibly to the substrate. The latex solution was then introduced in the deposition cell as described in Ref. [4]. Using these procedures, the particles could be irreversibly fixed to the surface once they reached it.

For each type of particle, R^* is different, so that the role of Brownian motion during deposition was different. It was thus expected that $g(r)$ should be different, at a

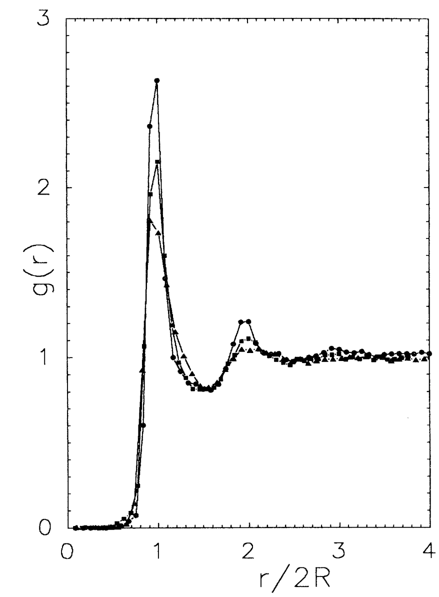

FIG. 2. Experimental radial distribution function $g(r)$ for three types of particles corresponding to $R^*=3.4$ (——●——), 2.9 (——■——), and 1.8 (—— ▲ ——), as a function of the ratio of the center-to-center distance r between two particles to their diameter.

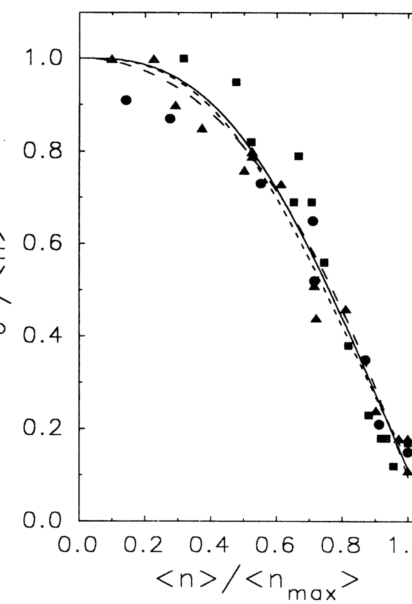

FIG. 3. Evolution of $\sigma^2/\langle n \rangle$ with $\langle n \rangle/\langle n_{\max} \rangle$ on a finite system, σ^2 being the variance the number of particles on finite systems. $\langle n \rangle$ represents the mean number of particles per system, and $\langle n_{\max} \rangle$ the mean maximum number of particles that can be deposited on the systems. Three systems with different renormalized radii R^* are investigated: $R^*=3.4$ (●), 2.9 (■), and 1.8 (▲). The solid line corresponds to the best fit of $f'(x)=1-w_3x^3+w_4x^4$, with $x=\langle n \rangle/\langle n_{\max} \rangle$, $w_3\approx 1.93$, and $w_4\approx 1.04$, to the experimental data. The long-dash line corresponds to the best fit of $f'(x)=1-w_2x^2+w_3x^3$ to the experimental data, obtained with $w_2\approx 0.628$ and $w_3\approx -0.276$. The short-dash line corresponds to the best fit of the ballistic expression $1-2.187\,767x^3+w_4x^4$ to the experimental data, with $w_4\approx 1.32$.

given coverage, for different particles (Fig. 2). Nevertheless, Fig. 3 shows that $\sigma^2/\langle n \rangle$ behaves the same when plotted as a function of $\langle n \rangle / \langle n_{\max} \rangle$ independent of particle type. Moreover, the horizontal tangent to this curve for small $\langle n \rangle / \langle n_{\max} \rangle$ does indeed indicate the absence of the term linear in ρ in relation (10). In addition, the fact that the three curves corresponding to three different radii R^* are identical within the experimental error demonstrates that, in the range of R^* investigated, $\langle \alpha \rangle$ does not vary significantly. The dependence of $\sigma^2/\langle n \rangle$ on $\langle n \rangle / \langle n_{\max} \rangle$ has been fitted to functions of the type $f'(x)=1-w_3x^3+w_4x^4$, where w_3 and w_4 are fitting parameters, as is expected from theoretical grounds. The parameter w_3 in $f'(x)$ is directly proportional to $\langle \alpha \rangle$. The solid line in Fig. 3 is obtained for $w_3 \approx 1.93$ and $w_4 \approx 1.04$. The short-dash line corresponds to the ballistic deposition for which $\sigma^2/\langle n \rangle$ has the same form as $f'(x)$ [11]. Its first nonvanishing term is $2.187\,767x^3$; the second one is obtained by fitting ($w_4 \approx 1.32$). In order to determine how sensitive the fitting function to our measurements is, we have also plotted them with the fitting function $f''(x)=1-w_2x^2+w_3x^3$, where w_2 and w_3 are fitting parameters. The long-dash line is obtained for $w_2 \approx 0.628$ and $w_3 \approx -0.276$. Inspection of Fig. 3 clearly reveals that from our experimental data we cannot demonstrate that w_2 vanishes. However, this figure also shows that the three experimental systems investigated in the present study by no means contradict the hypothesis that their reduced variance may be accounted for by a general law of the type of Eq. (11). In addition, it is shown that our experimental data are fully compatible with the results predicted by the ballistic model. This implies that hydrodynamic interactions play only a minor role in the evolution of the reduced variance with $\langle n \rangle / \langle n_{\max} \rangle$. The question concerning how $\langle \alpha \rangle$, and hence w_3 in $f'(x)$, will change when going from the ballistic model to deposition processes that include HI's is under study and will be reported in a later paper.

This article has presented experimental evidence that three types of colloidal particles of different sizes and densities are indistinguishable within the statistical uncertainties from the point of view of the fluctuation of the number of particles ($\sigma^2/\langle n \rangle$) irreversibly deposited onto subareas of silica slides. In contrast, their respective radial distribution functions $g(r)$ are significantly different. It is also shown that the experimental values of $\sigma^2/\langle n \rangle$ agree with the hypothesis that the deposition process follows the ballistic mechanism for the three types of particles used.

The authors wish to acknowledge the Commission of the European Communities and the Institut National de la Santé et de la Recherche Médicale for their financial support by Contract Nos. SC1-CT-91-0696(TSTS) and CJF 92-04, respectively. P.S. and H.R. acknowledge the NSF and the CNRS for their support of an international program concerned with the present work. The authors are particularly indebted to D. Bedeaux for drawing their attention to the general validity of relation (1), whether the system is at equilibrium or not, and to E. K. Mann for a critical reading of the manuscript.

[1] B. Widom, J. Chem. Phys. **44**, 3888 (1966).
[2] J. Feder and I. Giaever, J. Colloid Interface Sci. **78**, 144 (1980).
[3] J. J. Ramsden, Phys. Rev. Lett. **71**, 295 (1993).
[4] P. Wojtaszczyk, P. Schaaf, B. Senger, M. Zembala, and J.-C. Voegel, J. Chem. Phys. **99**, 7198 (1993).
[5] R. Kurrat, J. J. Ramsden, and J. E. Prenosil, J. Chem. Soc. Faraday Trans. 1 **90**, 587 (1994).
[6] Z. Adamczyk, B. Sywek, M. Zembala, and P. Weronski, Langmuir **8**, 2605 (1992).
[7] I. Pagonabarraga and M. Rubi, Phys. Rev. Lett. **73**, 114 (1994).
[8] L. Landau and E. Lifchitz, *Physique Statistique,* Vol. 5 of *Physique Théorique* (Mir, Moscow, 1984).
[9] A. P. Thompson and E. D. Glandt, Phys. Rev. A **46**, 4639 (1992).
[10] B. Senger, R. Ezzeddine, F. J. Bafaluy, P. Schaaf, F. J. G. Cuisinier, and J.-C. Voegel, J. Theor. Biol. **163**, 457 (1993).
[11] P. Schaaf, P. Wojtaszczyk, E. K. Mann, B. Senger, J. C. Voegel, and D. Bedeaux, J. Chem. Phys. (to be published).