Universal behavior of the structure of assemblies of particles irreversibly deposited on solid surfaces

P. Schaaf,[1,2,*] Ph. Carl,[3] J.-C. Voegel,[3] E. K. Mann,[1] and B. Senger[3]

[1]*Institut Charles Sadron, Unité de Recherches Associée n° 405 du Centre National de la Recherche Scientifique, 6, rue Boussingault, 67083 Strasbourg Cedex, France*

[2]*Ecole Européenne de Chimie, Polymères et Matériaux de Strasbourg, 1, rue Blaise Pascal, Boîte Postale 296F, 67008 Strasbourg Cedex, France*

[3]*Institut National de la Santé et de la Recherche Médicale, Unité 424, Fédération de Recherche Odontologique, Université Louis Pasteur, 11, rue Humann, 67085 Strasbourg Cedex, France*

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The diffusion of Brownian particles in a gravitational field and their adhesion to a horizontal plane is analyzed, from the point of view of both the Langevin and Smolukowski equations. It is shown that even when hydrodynamic interactions of the diffusing particles with the collector and the preadsorbed particles are taken into account, the structure built up by the irreversibly fixed particles and the jamming coverage are uniquely determined by one parameter R^*. This latter depends solely on the radius of the particles, their density relative to the density of the fluid, the temperature, and the acceleration of gravity. The viscosity of the fluid does not enter into this parameter. [S1063-651X(96)08312-2]

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The irreversible deposition of particles on solid surfaces has received considerable attention both from experimental and theoretical points of view. Such processes are common in sedimentation and adsorption phenomena. Due to their irreversible character, the properties of the assemblies of deposited particles cannot be described by the general laws of statistical mechanics; their description requires a different approach. In the present paper we will only be interested in adsorption/deposition processes in the absence of flow in the liquid in contact with the adsorbing surface (the collector).

By irreversible we denote processes in which, once the particle has ''touched'' (closely interacted with) the surface, it is irreversibly fixed on it, and can thus no longer be desorbed from the surface nor diffuse along the surface. To describe both the deposition/adsorption kinetics and the structure of an assembly of spheres formed in this way, different models have been developed. The first and most popular one is the random sequential adsorption (RSA) model which was suggested to describe the adsorption of proteins on solid surfaces [1,2]. It is defined by the following rules: (i) Particles are adsorbed randomly and sequentially on the surface. (ii) In an adsorption trial, the position of the particle is chosen randomly and uniformly over the surface. (iii) If this particle overlaps with already deposited ones, the trial is rejected and an independent one is started. Otherwise, the particle is irreversibly fixed on the surface. While this model captures the irreversible nature of the deposition process, as well as the excluded surface effects due to the deposited particles, it does not take the diffusion of the particles in the vicinity of the collector into account during the deposition process. To account for this effect, the Diffusion RSA (DRSA) model has been introduced [3,4]. In this model the particles diffuse in the solution before reaching the surface. Once they have interacted with the surface they are, as in the RSA model, irreversibly bound on the surface. It must be noted that this model neglects hydrodynamic interactions between the diffusing particles, the deposition plane, and the already deposited spheres. It has been shown that, for all coverages different from the jamming limit, this model leads to a structure of the assembly of deposited particles which is different from its RSA counterpart. It is only in the jammed state that both models lead to a similar structure and also to the same coverage, within the statistical uncertainty attained in the numerical simulations [4].

However, experimentally, it is often the case that the particles are large and heavy enough that gravitational effects also play a role. The gravitational force was therefore introduced in the DRSA model [5–7]. Analysis of the problem of the irreversible deposition of particles under the influence of gravity, taking into account the diffusion process during the sedimentation, showed that, at a given coverage, the only parameter characterizing the structure of the assembly of deposited particles is the reduced radius R^* given by

$$R^*=R\left(\frac{4\pi\Delta\rho g}{3kT}\right)^{1/4}, \qquad (1)$$

where R represents the radius of the particles; $\Delta\rho$ the relative density, i.e., the difference in density between the particles and the surrounding liquid medium; g the acceleration of gravity; and kT the thermal energy. This parameter also characterizes the jamming limit of this system. Physically, 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. It should be noted that the viscosity of the surrounding medium does not enter into this dimensionless parameter. However, this result was found for the DRSA model with gravity, in which hydrody-

*Author to whom correspondence should be addressed. Fax: (33) (0)3 88414099. Electronic address: schaaf@ics-crm.u-strasbg.fr

namic interactions are neglected, and might be supposed to apply only to this particular case.

The aim of this Brief Report is to give a strong argument which indicates that R^* is also the *only* parameter needed to describe both the structure at a given coverage and the jamming limit for real systems in which hydrodynamic interactions are present, with the restriction that the particles interact, aside from the hydrodynamic interactions, as hard spheres; i.e., in the equilibrium case, the system would be described by an ensemble of hard spheres. This result is of great importance because hydrodynamic interactions, are always present and, as has been demonstrated, they play an important role in the structure of the deposited particles. In fact, the DRSA model predicts that, for particles, in the absence of any gravitational force, the structure is different from its RSA counterpart. However, introducing the hydrodynamic interactions, one recovers a deposition probability, as a function of the adhesion position, which follows the RSA laws [8]. This comes from the fact that, due to the hydrodynamic interactions, the diffusion coefficient related to the movement parallel to the deposition plane decreases more slowly with the plane-particle distance than the diffusion coefficient related to the movement perpendicular to the plane. The particle can thus ''randomize'' its position along the plane before touching it. This is equivalent to the RSA deposition rule in which the deposition probability is uniform all over the available space.

Let us now develop the argument showing that the dimensionless radius R^* given by relation (1) also describes a system in which hydrodynamic interactions are present. To this end, consider a monodisperse system of hard spheres deposited irreversibly on a plane. This system is characterized by a given structure and by its coverage. In order to determine the deposition probability for a new incoming particle as a function of the adhesion probability, two routes can be followed: the first is based on Langevin's equation, the second on Smolukowski's equation. Both are discussed below.

(1) We can choose a random initial position for the depositing particles in a plane parallel to the deposition plane at a large distance above this plane. We can then follow the trajectory of this particle by solving, step by step, a Langevin equation with a diffusion tensor which varies with the relative position of the depositing particle with respect to the deposition plane and to the already deposited particles. Once the particle has touched the surface it is removed from it, and a new deposition trial is started independently. If such a procedure is repeated a great number of times, one obtains the deposition probability. The Langevin equation must be solved with the constraints that the particles behave like hard spheres. This is the route which has been followed in the DRSA case with gravity, taking the hydrodynamic tensor as a constant scalar given by the usual Stokes-Einstein formula:

$$D_s=\frac{kT}{6\pi\eta R}, \tag{2}$$

where η represents the viscosity of the medium.

When the diffusion tensor depends upon the position of the particle, the Langevin equation takes the form [9]

$$\Delta\mathbf{r}=\frac{\bar{\bar{D}}\mathbf{F}}{kT}\,\Delta t+\boldsymbol{\nabla}\cdot\bar{\bar{D}}\Delta t+\Delta\mathbf{r}_B. \tag{3}$$

This vectorial equation gives the displacement of the particle during the time interval Δt. The three terms on the right hand side represent, respectively, the drift term, the gradient term, and the stochastic term. $\bar{\bar{D}}$ represents the diffusion tensor, which reduces to the scalar Stokes-Einstein diffusion coefficient D_s, when the particle diffuses far from walls or other particles. In that case, obviously, the gradient term vanishes. The first term on the right hand side contains the sum of all external forces acting on the particle; in the present study, this force is simply the gravitational force which is parallel and opposite to the unit vector of the z axis.

In the particular case of constant diffusion coefficient, Ezzeddine *et al.* [7] have shown that the diffusion of a spherical particle in a gravitational field is entirely determined by the reduced radius R^*, defined by Eq. (1). The same observation holds for the coverage at the jamming limit. We shall now show that this conclusion stays true even when the diffusion is a tensor instead of a scalar, i.e., in the presence of hydrodynamic variable drag forces.

Consider first the simplest case of a particle sedimenting in a liquid and approaching a free horizontal collector [10]. We have only to consider the modification of the mobility of the particle due to the presence of the plane. Following Clark, Lal, and Watson [9] (see also [11]), the diffusion tensor is written as

$$\bar{\bar{D}}=D_s\begin{pmatrix}\lambda_\parallel^{-1} & 0 & 0\\ 0 & \lambda_\parallel^{-1} & 0\\ 0 & 0 & \lambda_\perp^{-1}\end{pmatrix}, \tag{4}$$

where $\lambda_\parallel$ and $\lambda_\perp$ account for the effect of the wall on the diffusion of the particle parallel to it and perpendicular to it, respectively. These components are functions of the unique dimensionless variable z/R.

If we split the vectorial equation (3) into three scalar equations corresponding to the three components of the displacement vector $\Delta\mathbf{r}$, we obtain

$$\Delta x=\gamma_x\sqrt{2D_s\lambda_\parallel^{-1}\Delta t}, \tag{5a}$$

$$\Delta y=\gamma_y\sqrt{2D_s\lambda_\parallel^{-1}\Delta t}, \tag{5b}$$

$$\Delta z=D_s\,\frac{F_z\lambda_\perp^{-1}}{kT}\,\Delta t+D_s\,\frac{\partial\lambda_\perp^{-1}}{\partial z}\,\Delta t+\gamma_z\sqrt{2D_s\lambda_\perp^{-1}\Delta t}. \tag{5c}$$

The gradient term does not contribute to the x and y displacements, i.e., the displacements parallel to the adsorbing plane, since $\lambda_\parallel$ depends only on $z[(\partial\lambda_\parallel^{-1}/\partial x)=(\partial\lambda_\parallel^{-1}/\partial y)=0]$. The three components of the stochastic term $\Delta\mathbf{r}_B$ are still assumed to be normal (Gaussian) deviates, with means equal to zero [9]. They are obtained by multiplying normal deviates of zero mean and unit standard deviation, γ_x, γ_y, and γ_z, by the appropriate standard deviations, that depend on D_s and the component $\lambda_\parallel$ or $\lambda_\perp$. Finally, the drift term appears only in Eq. (5c), since the z axis coincides with the vertical (ascending) direction. The vertical projection of the gravitational force is $F_z=-(4/3)\pi R^3\Delta\rho g$. The minus sign accounts simply for the fact that the gravitational force pulls the particle downward, i.e., tends to reduce its altitude z. Using R as the unit of length and R^2/D_s as the unit of time, Eqs. (5a)–(5c) may be recast in the following form:

$$\Delta x' = \gamma_x \sqrt{2\lambda_\parallel^{-1}\Delta t'}, \tag{6a}$$

$$\Delta y' = \gamma_y \sqrt{2\lambda_\parallel^{-1}\Delta t'}, \tag{6b}$$

$$\Delta z' = -R^{*4}\lambda_\perp^{-1}\Delta t' + \frac{\partial \lambda_\perp^{-1}}{\partial z'}\,\Delta t' + \gamma_z \sqrt{2\lambda_\perp^{-1}\Delta t'}, \tag{6c}$$

where a primed symbol represents a dimensionless spatial or time step. These equations show that, once the time step $\Delta t'$ is chosen, the evolution of the system is completely determined by R^*, exactly as in the case where the drag force was considered as independent of the particle position, since the tensor components $\lambda_\parallel$ and $\lambda_\perp$ depend only on z'.

It may be noted that if one considers the sphere-sphere interaction from the hydrodynamic point of view [12], the diffusion tensor again can be written as the product of Stokes-Einstein diffusion coefficient and a tensor whose elements depend solely on the center-to-center distance of the two spheres. Here also, the movement can be rescaled using R as the unit of length, and R^2/D_s as the unit of time.

Finally, in order to face the more complicated problem of a particle diffusing in the vicinity of a collector already partially covered by irreversibly fixed spheres, one may assume the additivity of the friction tensors [8,13]. Since the separate tensors depend only on distances that can be expressed as multiples of R, their combination is a tensor depending only on the geometry of the system, provided that D_s has been factorized everywhere. Then the resulting movement and the resulting structure of the assembly of particles will display a universal behavior determined by R^* and only R^*. This depends only on the assumption of additivity for the friction tensors.

(2) The second route which can be followed is to solve the Smoluchowski equation corresponding to the diffusion sedimentation process. One takes the concentration of the particles constant at a plane parallel to the deposition surface far above it. The boundary conditions at the interface are the following: the flux is zero perpendicularly to the deposited particles (reflecting boundary conditions), and the concentration of the particles is zero at the surface (perfectly adsorbing boundary condition). By solving the steady state problem, one can calculate the adsorption flux toward the surface as a function of the adsorption position and thus evaluate the deposition probability. The Smoluchowski equation takes the form

$$\frac{\partial P}{\partial t} = \boldsymbol{\nabla}\cdot\left[\bar{\bar{D}}\cdot\left(\boldsymbol{\nabla}P - P\,\frac{4\pi R^3\Delta\rho g}{3kT}\,\mathbf{u_z}\right)\right], \tag{7}$$

where P is proportional to the concentration of particles at the position $\mathbf{r}$, and $\bar{\bar{D}}$ represents the diffusion tensor which depends also upon the position. $\mathbf{u_z}$ represents the unit vector parallel to the gravitational field. The diffusion tensor is related to the inverse of the friction tensor by the Einstein relation

$$\bar{\bar{D}} = kT(\bar{\bar{\xi}})^{-1}. \tag{8}$$

Again, using the approximation of the additivity of the friction tensors, approximate formulas can be obtained for the friction tensor for the whole distance range between the diffusing particle, the fixed particles on the surface, and the deposition plane. These formulas lead to the Stokes expression when the diffusing particle is far from the surface, and include the lubrication theory for diffusing particles near the deposition plane. The interesting feature that appears out of these expressions is that the diffusion tensor can be written in the simple form

$$\bar{\bar{D}} = D_s\bar{\bar{F}}(\{(\mathbf{r}_i - \mathbf{r})/R\}), \tag{9}$$

where $\mathbf{r}_i - \mathbf{r}$ represents the vector joining the position $\mathbf{r}_i$ of the center of the particle i to the position $\mathbf{r}$. The tensor $\bar{\bar{F}}$ thus represents a dimensionless diffusion tensor. It can be noted that the only characteristic length entering into this problem is the particle radius R. One can then rewrite the diffusion equation (7) in a dimensionless form,

$$\frac{\partial P}{\partial t'} = \boldsymbol{\nabla}'\cdot\left[\bar{\bar{F}}\left(\frac{\mathbf{r_i}}{R},\frac{\mathbf{r}}{R}\right)\cdot\left(\boldsymbol{\nabla}'P - P\,\frac{4\pi R^4\Delta\rho g}{3kT}\,\mathbf{u_z}\right)\right], \tag{10}$$

where ∇' represents the derivative with respect to the rescaled variable $\mathbf{r}/R$, and $t' = D_s t/R^2$ is the dimensionless rescaled time. The same rescaling can be done on the boundary conditions, which can be exclusively expressed in terms of the rescaled lengths due to the fact that no additional length enters the problem. Since the change in the structure due to a change in coverage can be obtained by solving Eq. (10) in steady state conditions with the appropriate boundary conditions expressed exclusively in rescaled dimensions, the only parameter that enters into the problem is the dimensionless radius R^* given by Eq. (1). Moreover, the kinetics of the process is obtained by solving Eq. (10) with the boundary conditions discussed previously. These boundary conditions thus only depend on the coverage and the structure of the interface. This latter, however, is only dependent upon the coverage and the parameter R^*, as just discussed. The deposition kinetics is then obtained by the equation

$$\frac{\partial P}{\partial t'} = \mathbf{J}'_{z'}(z'=0), \tag{11}$$

where $\mathbf{J}'_{z'}(z'=0)$ corresponds to the rescaled flux to the surface at $z'=0$. This rescaled flux is given by

$$\mathbf{J}'_{z'}(z'=0) = \left\langle \left\{ \bar{\bar{F}}\left(\frac{\mathbf{r_i}}{R},\frac{\mathbf{r}}{R}\right)\cdot(\boldsymbol{\nabla}'P - PR^{*4}\mathbf{u_z}) \right\}_{z,z'=0} \right\rangle, \tag{12}$$

where the average is taken over the entire surface, and the symbol $\{\}_{z,z'}=0$ means that only the z component of this vector, i.e., the component of the flux perpendicular to the surface, is taken at $z'=0$. The fact that the flux toward the surface can be rescaled in this way implies that the deposition kinetics is governed by two parameters: the rescaled radius R^* and the dimensionless time R^2/D_s.

The two main conclusions that arise from the above analysis of sedimentation of Brownian particles and of their adhesion to an horizontal plane, taking into account hydrodynamic interactions with this plane and with preadsorbed particles, are (i) that the structure of the adsorbed layer, as for instance quantified by the radial distribution function, depends only on the reduced radius R^* which contains all pertinent physical parameters; and (ii) that the kinetics of the coverage process depends on R^* and also on the ratio R^2/D_s. In other words, the viscosity of the solvent changes the time necessary to obtain a given coverage, but not the relative position of the particles at the interface between the solid and the particle suspension.

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