Irreversible adsorption/deposition kinetics: A generalized approach

Z. Adamczyk, B. Senger, J.-C. Voegel, and P. Schaaf

Articles you may be interested in

Irreversible adsorption of gold nanospheres on fiber optical tapers and microspheres
Appl. Phys. Lett. **100**, 153107 (2012); 10.1063/1.3701730

Nucleation kinetics of Ru on silicon oxide and silicon nitride surfaces deposited by atomic layer deposition
J. Appl. Phys. **103**, 113509 (2008); 10.1063/1.2938052

Adsorption, desorption, and diffusion of nitrogen in a model nanoporous material. I. Surface limited desorption kinetics in amorphous solid water
J. Chem. Phys. **127**, 184707 (2007); 10.1063/1.2790432

Irreversible adsorption of particles at random-site surfaces
J. Chem. Phys. **120**, 11155 (2004); 10.1063/1.1712967

Kinetics of H atom adsorption on Si(100) at 500–650 K
J. Chem. Phys. **119**, 11906 (2003); 10.1063/1.1624827

Irreversible adsorption/deposition kinetics: A generalized approach

Z. Adamczyk[a]

*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek,
30-239 Krakow, Poland*

B. Senger and J.-C. Voegel

*Institut National de la Santé et de la Recherche Médicale, Unité 424, Fédération de Recherche
‘‘Odontologie,’’ ULP, 11, rue Humann, 67085 Strasbourg Cedex, France*

P. Schaaf

*Institut Charles Sadron (CNRS-ULP), 6, rue Boussingault, 67083 Strasbourg Cedex, France
and Ecole Européenne de Chimie, Polymères et Matériaux de Strasbourg, 1, rue Blaise Pascal, Boîte
Postale 296F, 67008 Strasbourg Cedex, France*

A generalized random sequential adsorption (RSA) approach is developed by taking into account diffusion, particle/wall hydrodynamic interactions as well as external forces (e.g., gravity). In analogy to the previous concept of Pagonabarraga and Rubí [Physica A **188**, 553 (1992)] the position dependent available surface function $\Phi(z,\theta)$ is introduced. Using this definition, constitutive expressions for the adsorption flux are formulated which represent the generalization of previous models, including the widely used Langmuirian kinetic approach. It is shown that the overall available surface function $\bar{\Phi}(\Delta,\theta)$ plays the crucial role in these expressions. It represents the net probability of transferring a particle from the arbitrary distance Δ to the interface for a given surface coverage. Explicit expressions in the form of definite integrals are formulated which enable one to calculate the $\bar{\Phi}(\Delta,\theta)$ function in terms of the $\Phi(z,\theta)$ function. In the case of hard spheres, $\Phi(z,\theta)$ is calculated up to the second order of the surface coverage θ using geometrical arguments. The effect of an external force (gravity) is characterized by the dimensionless radius of particles R^*, where $R^*\to\infty$ corresponds to the purely ballistic case, $R^*=0$ to the diffusion RSA, and $R^* \to -\infty$ reflects the case of infinite gravity acting outwards from the surface. Using these expressions, the overall $\bar{\Phi}(\Delta,\theta)$ function is also calculated. It is found that the RSA available surface function is not recovered for $R^*=0$ as expected, but for $R^*\to-\infty$. The transition from the $R^*=0$ to the ballistic case ($R^*=\infty$) is analyzed. Unexpectedly, it is found that for $R^*=1$ the second order term in the coverage expansion of $\bar{\Phi}(\Delta,\theta)$ appears negative which seems an entirely new result. It is also deduced that in the case of an energy barrier, whose extension is much smaller than the particle dimension, the adsorption process can well be characterized for $R^*=0$ in terms of the classical RSA model. This can be explained by the fact that for a high energy barrier the adsorbing particles could randomize over the deposition plane before crossing the barrier and adsorbing irreversibly. © *1999 American Institute of Physics.* [S0021-9606(99)71106-2]

I. INTRODUCTION

The adsorption flux of colloidal particles or large globular molecules such as proteins at solid surfaces is usually written as

$$J = k_a c_b \Phi(\theta) - k_d \rho_a, \tag{1}$$

where c_b represents the particle concentration in the bulk, k_a (resp. k_d) corresponds to the adsorption (resp. desorption) constant, ρ_a is the number density of adsorbed particles, and $\Phi(\theta)$ corresponds to the available surface function (ASF) which depends on the surface coverage $\theta = \pi a^2 \rho_a$ (where a is the particle radius). This equation constitutes the boundary condition for the diffusion/adsorption problem. It assumes that, once the particle concentration in the vicinity of the

adsorption plane and the density of adsorbed particles (or surface coverage) are known, the adsorption rate is fixed. This is only valid if the adsorption rate is slow compared to the characteristic equilibrium time within the adsorption layer.

The use of Eq. (1) requires the knowledge of the ASF. One of the most widely used approaches is the Langmuir model for which the ASF $\Phi(\theta)$ is given by

$$\Phi(\theta) = 1 - \frac{\theta}{\theta_L},$$

where θ_L represents the maximum (saturation) coverage of the surface. The Langmuir equation was originally derived to account for the adsorption of small molecules on sites distributed over the surface, one molecule being able to cover only one site and one site being able to be covered by only one molecule. For the case of large particles this is obviously

---

an oversimplified approach since usually the surface behaves as a continuous plane. Surface exclusion effects become thus much more subtle and complicated. In order to take them properly into account one needs to consider if adsorbed particles can diffuse along the surface or if they keep a fixed position on the surface once adsorbed. One needs also to take the presence of external forces such as gravity into account. The case where particles can diffuse along the surface can be treated by classical statistical mechanics arguments if the adsorption rate is slow compared to the relaxation time of the adsorbed layer. If this condition is not fulfilled, the ASF becomes also a function of the history of the surface.[1] The case where particles, once adsorbed, cannot move along the surface will be called the case of *localized irreversible adsorption*. Indeed, in this case, it is expected that the particles desorb very slowly from the surface and then usually desorption can be neglected. The case of irreversible adsorption has been extensively studied over the last years and two limiting models have been proposed to account for the experimental results (i) in the absence of gravitational effects the random sequential adsorption (RSA) model has been suggested to describe the adsorption process;[2–6] (ii) under strong influence of gravity the ballistic model seems to be well adapted.[7] For the ballistic model the ASF $\Phi(\theta)$ takes, in the low to intermediate coverage regime, the form[8]

$$\Phi(\theta) = 1 - B_3 \theta^3 + O(\theta^4). \tag{2}$$

The fact that the first nonvanishing term in this expansion is of order 3 is due, in this case, to the need of the presence of at least three adsorbed particles in order to prevent a new incoming one to reach the surface. In the RSA case the presence of one adsorbed particle on the surface is already sufficient to prevent a new one from reaching the adsorption plane. The ASF $\Phi(\theta)$ takes then the form[9]

$$\Phi(\theta) = 1 - a_1 \theta + a_2 \theta^2 - a_3 \theta^3 + O(\theta^4). \tag{3}$$

Widom has shown that the coefficients a_1 and a_2 are equal to that corresponding to a system at equilibrium, i.e., in which particles can diffuse along the surface. The differences between $\Phi_{\text{RSA}}(\theta)$ and $\Phi_{\text{eq}}(\theta)$ appear only for terms of order higher or equal to 3.[10] This implies that the RSA adsorption kinetics is almost indistinguishable at low coverages from the equilibrium case. More importantly, Widom has also proposed a general way to determine $\Phi(\theta)$;[11] freeze the system on the surface (in the case of RSA the system is automatically frozen), and let a particle wander randomly over the surface. Each position $\mathbf{r}$ of the particle is characterized by an interaction energy $\Psi(\mathbf{r})$ between the wandering particle and the adsorbed ones. The available surface function $\Phi(\theta)$ is then given by

$$\Phi(\theta) = \left\langle \exp\left(-\frac{\Psi(\mathbf{r})}{kT}\right) \right\rangle,$$

where the average is taken over all the surface, k represents the Boltzmann constant, and T is the absolute temperature. In the case of hard spheres, this simply represents the available surface which justifies its name. In the case of an equilibrium system, the function $\Phi(\theta)$ is directly related to the chemical potential of the adsorbed particles by the relation[11]
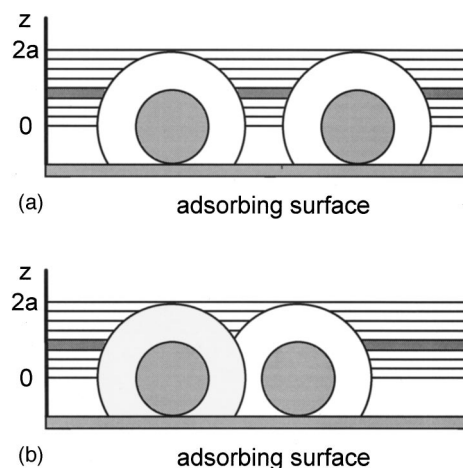

FIG. 1. Schematic representation of the available surface function of a slab at a height z (a) when two particles are deposited on the surface far one from each other; (b) when two particles are deposited close enough one from each other so that their exclusion volumes overlap; the radius of the particles is a.

$$\mu = \mu_0 + kT \ln \theta - kT \ln \Phi(\theta).$$

The use of the available surface function $\Phi(\theta)$, determined on the surface, in Eq. (1) is equivalent to neglecting the transport of particles through the adsorption layer. This layer can be defined as the region in space in which particles from the bulk are interacting with the surface and with adsorbed particles. In the case of hard sphere interactions, the adsorption layer has a thickness of $2a$ (see Fig. 1). When the interparticle interactions are of long range, the thickness of the adsorption layer is of the order of this interaction range. In order to calculate the adsorption rate one has thus to solve the transport equation through the adsorption layer by taking the presence of the adsorbed particles into account. This article is aimed to solve this problem in the case of particles interacting strongly with the surface, this interaction being of short range compared to the size of the particles. We assume additionally that, *once a particle has touched the surface, it is irreversibly bound to it* (see Fig. 2).

This problem has already been analyzed near the jamming limit in the case where adsorbed particles cannot move along the surface.[12] The hydrodynamic interactions were then neglected. It has been shown in this case that the adsorption rate follows the power law $J \propto (\theta_\infty - \theta)^{5/2}$ which is different from that expected from pure RSA, i.e., $J \propto (\theta_\infty - \theta)^3$.

More recently, the group of Rubí has adapted the general approach of ''internal degrees of freedom''[13,14] developed by Prigogine and Mazur[15] to this problem. It can be shown that at low to intermediate coverages both approaches are equivalent. We will follow the same route as the group of Rubí to calculate the adsorption rate in a general way.[15] We will then particularize to the case of hard spheres in the low to intermediate coverage regime by taking hydrodynamic interactions into account.
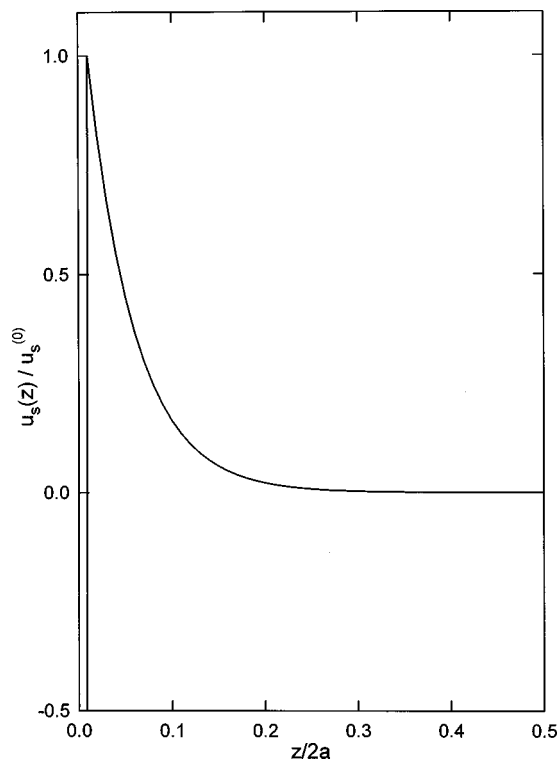
FIG. 2. Schematic representation of the interaction potential of a particle with the surface in the presence of the energy barrier whose maximum is near to the deposition plane.

II. GENERAL CONSIDERATIONS

The aim of this section is to make the connection between the phenomenological kinetic equation (1) and the approach which takes the diffusion of the particles through the adsorbed layer in the vicinity of the adsorption plane into account. To achieve this goal we follow the routes opened by Widom,[11] Prigogine and Mazur,[15] summarized in the book of de Groot and Mazur.[16] In our approach, we discriminate between the particles which are in direct contact with the surface, called adsorbed particles, from the particles which diffuse through the adsorption layer. We only treat the case of a planar adsorption surface and denote the direction perpendicular to this plane by z (see Fig. 1). We can then divide the space above the adsorption surface into layers, parallel to this surface and of infinitesimal thickness δ. Each layer is characterized by the distance z from the adsorption plane and is considered as a thermodynamic system. It is assumed that the densities of particles in the bulk and in the adsorption layer are small so that interactions between moving particles can be neglected. We will assume here that all the particles are spherical, identical and of radius a. A particle is then assigned to a slab at a distance z from the adsorption surface if its center lies inside this slab. The particles in each slab are then characterized by their chemical potential which, following Widom, is given by

$$\mu(z) = \mu_0 + kT \ln \rho(z) - kT \ln \Phi_0(z, \theta), \qquad (4)$$

where $\Phi_0(z, \theta)$ depends on the surface coverage θ and $\rho(z)$ represents the particle concentration at the distance z from the surface. $\Phi_0(z, \theta)$ can be determined by the method of

Widom, the wandering particle being randomly distributed over the slab z. Usually particles interact with the adsorbing surface through a potential $u_s(z)$ which is a function of z. In the absence of spheres on the surface, this constitutes the potential felt by the wandering particle and

$$\Phi_0(z, 0) = \exp\left[-\frac{u_s(z)}{kT}\right].$$

In order to extract from $\Phi_0(z, \theta)$ the contribution of the adsorbed particles, we define the available surface function at a height z, $\Phi(z, \theta)$, as

$$\ln[\Phi(z, \theta)] = \ln[\Phi_0(z, \theta)] + \frac{u_s(z)}{kT}.$$

In the case of hard spheres $\Phi(z, \theta) = 1$ for $z > 2a$ ($z = 0$ is chosen at a distance a above the adsorption plane and corresponds to the plane of location of the centers of the adsorbed particles). For $z < 2a$, the function $\Phi(z, \theta)$ corresponds to the proportion of the volume of the slab z which is accessible to the centers of the particles. We will come back to the estimation of $\Phi(z, \theta)$ for hard spheres in Sec. III.

In the presence of an external potential $u_p(z)$, which depends only on z and is independent of the surface coverage, such as for example the gravitational potential, one has

$$\Phi_0(z, \theta) = \left\langle \exp\left[-\frac{\Psi(\mathbf{r}) + u_s(z) + u_p(z)}{kT}\right]\right\rangle_z$$

$$= \left\langle \exp\left[-\frac{\Psi(\mathbf{r})}{kT}\right]\right\rangle_z \exp\left[-\frac{u_s(z) + u_p(z)}{kT}\right],$$

where $\Psi(\mathbf{r})$ represents the interaction potential between the wandering particle and the adsorbed ones, the external potential being not taken into account. $\langle . \rangle_z$ means the average over the slab z. One thus has

$$\Phi(z, \theta) = \left\langle \exp\left(-\frac{\Psi(\mathbf{r})}{kT}\right)\right\rangle_z$$

so that relation (4) becomes

$$\mu(z) = \mu_0 + kT \ln \rho(z) - kT \ln \Phi(z, \theta) + u(z),$$

where $u(z) = u_s(z) + u_p(z)$.

Following de Groot and Mazur,[16] one can then, starting from the principles of irreversible thermodynamics, derive the diffusion equation governing the transport of the particles through the diffusion layer,

$$J(z) = -D(z)\left\{\frac{\partial \rho}{\partial z} + \frac{\rho}{kT}\frac{\partial C}{\partial z}\right\}, \qquad (5)$$

where $D(z)$ represents the diffusion coefficient which is assumed to be a function of z only and where $C(z) = -kT \ln \Phi(z, \theta) + u(z)$. This equation can be rewritten in the form

$$J(z) = -D(z)\exp\left(-\frac{C(z)}{kT}\right)\frac{\partial}{\partial z}\left\{\exp\left(\frac{C(z)}{kT} + \ln \rho\right)\right\}.$$

The adsorption flux J through a portion of space bounded by the planes $z = \delta$ and $z = \Delta$ can then be calculated under steady state conditions. It is given by

$$J = - \frac{\exp\left\{\frac{\mu'(z=\Delta)}{kT}\right\} - \exp\left\{\frac{\mu'(z=\delta)}{kT}\right\}}{\int_{z=\delta}^{z=\Delta} \frac{1}{D(z)} \exp\left\{\frac{C(z)}{kT}\right\} dz},$$ (6)

where $\mu'(z) = \mu(z) - \mu_0$. The denominator can be identified with a static diffusion resistance $R(\delta, \Delta)$ originally introduced by Ruckenstein and Prieve[17]

$$R(\delta, \Delta) = \int_{z=\delta}^{z=\Delta} \frac{1}{D(z)} \exp\left(\frac{C(z)}{kT}\right) dz.$$ (7)

If one makes the analogy between $\exp-[\mu'(z)/kT]$ and the electrostatic potential in the case of the electrical current, one realizes that Eq. (6) is the analog of Ohm's Law. The same rules for the resistances of systems in series then exist. It can thus easily be shown that the resistance of two adjacent portions of space, one extending from $z=\delta_1$ to $z=\delta_2$ and the second from $z=\delta_2$ to $z=\delta_3$ is simply given by the sum of the two resistances

$$R(\delta_1, \delta_3) = R(\delta_1, \delta_2) + R(\delta_2, \delta_3).$$

One can thus characterize an interface by its diffusional resistance. This latter will be a function of the thickness of the diffusion boundary layer Δ. One can make use of the fact that particles deposited on the surface introduce an additional resistance to the diffusion and thus define an excess resistance due to their presence

$$R^{exc}(\theta) = \lim_{\Delta \to \infty} (R(\delta, \Delta, \theta) - R(\delta, \Delta, \theta=0)).$$

Using expression (7) for the resistance one gets

$$R^{exc}(\theta) = \int_{\delta}^{\infty} \left(\frac{1}{\Phi(z, \theta)} - 1\right) \frac{1}{D(z)} \exp\left(\frac{u(z)}{kT}\right) dz.$$ (8)

From relation (8) it is clear that $R^{exc}(\theta)$ describes only the contribution of the adsorbed particles to the resistance and not the excess due to the modification of the potential felt by the particles due to the presence of the adsorption wall. This excess resistance is thus not exactly equal to the Gibbsian excess quantities[18] generalized by Bedeaux and Vlieger to optical problems.[19] Due to the fact that $\Phi(z, \theta) \to 1$ when $z \to \infty$, the integral appearing in Eq. (8) converges. The adsorption rate J_a which is equal to the opposite of the flux given by relation (6) then takes the form

$$J_a = \frac{\bar{\Phi}(\Delta, \theta)}{R(\delta, \Delta)} \left\{ \rho(\Delta) \exp\left(\frac{C(\Delta)}{kT}\right) - \rho(\delta) \exp\left(\frac{C(\delta)}{kT}\right) \right\}.$$ (9)

This expression is valid for Δ large enough so that $\Phi(z=\Delta, \theta)=1$, but also small enough so that steady state conditions are established over a time scale which is small compared to the characteristic time over which the surface coverage changes appreciably.

The function $\bar{\Phi}(\Delta, \theta)$ can be treated as the overall available surface function defined as

$$\bar{\Phi}(\Delta, \theta) = \frac{R(\delta, \Delta)}{R(\delta, \Delta) + R^{exc}(\theta)}.$$ (10)

The quantity $(1 - \bar{\Phi}(\Delta, \theta))$ represents the probability that, when a particle enters the adsorption layer through the plane $z=\Delta$, it will not adsorb on the adsorption plane due to the presence of already adsorbed particles.

The adsorption rate given by Eq. (9) can be rewritten in a form similar to the generalized Langmuir equation (1),

$$J_a = k_a \rho(\Delta) \bar{\Phi}(\Delta, \theta) - k_d' \frac{\bar{\Phi}(\Delta, \theta)}{\Phi(\delta, \theta)} \rho(\delta),$$ (11)

with

$$k_a = \frac{\exp\left(\frac{u(\Delta)}{kT}\right)}{R(\delta, \Delta)} \quad \text{and} \quad k_d' = \frac{\exp\left(\frac{u(\delta)}{kT}\right)}{R(\delta, \Delta)}.$$

The case where the particles, once adsorbed, are irreversibly fixed to the surface corresponds to the case where $u(\delta^-) = -\infty$ so that $k_d'=0$. From Eq. (11) it comes out that the desorption constant k_d, which corresponds to $k_d'[\bar{\Phi}(\Delta, \theta)/\Phi(z=\delta, \theta)]$, is in general a function of the coverage.

If the interaction potential $u_s(z)$ between a particle and the surface exhibits a strong maximum near the surface at a distance z_{max} as represented in Fig. 2, the main contribution to the resistance comes from the region of z around $z=z_{max}$. By expanding $u_s(z)$ around the maximum, and if the energy peak has a width small compared to the radius of the particles, one gets[17]

$$R(\delta, \Delta) \cong \left(\frac{2\pi kT}{\gamma_{max}}\right)^{1/2} \frac{1}{D(z_{max})} \exp\left(\frac{u(z_{max})}{kT}\right)$$

and

$$R(\delta, \Delta) + R^{exc}(\theta)$$
$$\cong \left(\frac{2\pi kT}{\gamma_{max}}\right)^{1/2} \frac{1}{D(z_{max}) \Phi(z_{max}, \theta)} \exp\left(\frac{u(z_{max})}{kT}\right),$$

where

$$\gamma_{max} = - \left.\frac{d^2 u}{dz^2}\right|_{z=z_{max}}.$$

In this case,

$$\bar{\Phi}(\Delta, \theta) \cong \Phi(z_{max}, \theta)$$ (12)

and moreover k_d becomes independent of the coverage θ.

An important conclusion, which can be drawn from relations (10) and (11) is the fact that the value k_a usually measured experimentally depends crucially on the distance Δ over which diffusional quasi stationary conditions are established. If Δ is large compared to the extend of the interaction range between adsorbed and adsorbing particles, then the diffusional resistance is large compared to the resistance of the adsorption layer and $\bar{\Phi}(\Delta, \theta) \cong 1$. In this case the excluded surface effect becomes almost negligible until full coverage where $\bar{\Phi}(\Delta, \theta)$ becomes suddenly very small. In addition, when the bulk concentration at $z=\Delta$ is held fixed experimentally over the whole adsorption experiment, which is often the case, one will get an adsorption kinetics as rep-
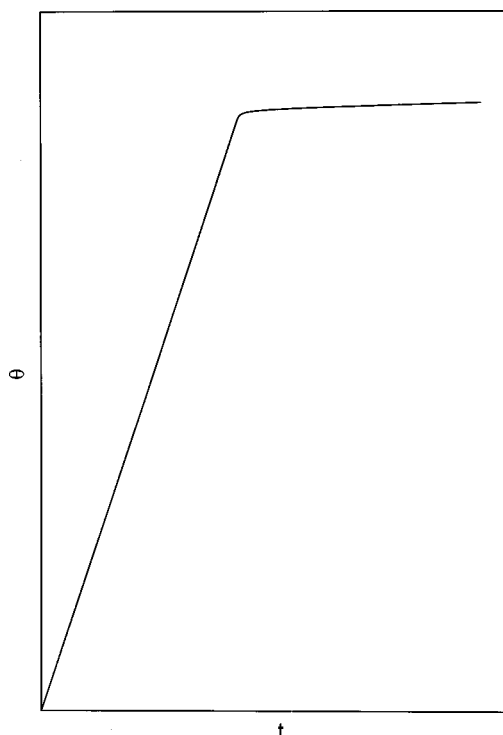
FIG. 3. Schematic representation of the evolution of the surface coverage θ as a function of time t in the case where the length Δ, over which a diffusional steady state is established, is large compared to the size of the particles (see text). The surface exclusion effects play only a role on the deposition kinetics when the surface approaches saturation.

resented schematically in Fig. 3. The adsorption rate is constant until it becomes suddenly very small and finally vanishes. In any case, this analysis shows that the experimental conditions are crucial to determine precisely both the adsorption constant and the surface exclusion effects. One has to know precisely the extend of the diffusion layer in order to estimate correctly these parameters.

III. THE CASE OF HARD SPHERES

In the preceding section we have presented the equations describing the adsorption process in the general case. We will now treat the particular case of hard spheres of radius a. We will, in particular, analyze how the gravitational field influences the deposition kinetics. In the case of hard spheres, the range of interaction between the adsorbed spheres and the spheres from the bulk is equal to $2a$. It is then natural to characterize the surface by the function $\bar{\Phi}(2a,\theta)$ which we will simply denote by $\phi_a(\theta)$. We will further assume that the particles adsorb irreversibly on the surface so that $k_d'=0$. In this case the adsorption flux can be written as

$$J_a(\Delta)=J_0(\Delta)\bar{\Phi}(\Delta,\theta),$$

where J_0 corresponds to the adsorption rate under steady state conditions, for $\theta=0$ (uncovered surface) when the concentration of particles at $z=\Delta$ remains fixed. Using expressions (9) and (10), the adsorption flux can be rewritten by introducing the ASF $\phi_a(\theta)$ in the form,

$$J_a(\Delta)=J_0(\Delta)\,\frac{K_a(\Delta)}{K_a(\Delta)-1+\dfrac{1}{\phi_a(\theta)}},$$

where $K_a(\Delta)=1+[R(2a,\Delta)/R(\delta,2a)]$, and ϕ_a is independent of the thickness of the diffusion boundary layer Δ. If the characteristic equilibration time of the diffuse layer ranging from $z=\delta$ up to $z=\Delta$ is short compared to the characteristic adsorption time over which the coverage varies appreciably, then the kinetic adsorption equation

$$\frac{d\theta}{dt}=J_a(\Delta)$$

is easily integrated and one gets

$$[K_a(\Delta)-1]\theta+\int_0^\theta\frac{d\gamma}{\phi_a(\gamma)}=K_a(\Delta)\tau, \qquad (13)$$

where τ represents the reduced time $J_0(\Delta)t$. In the case where $\Delta=2a$, one has $\bar{\Phi}(\Delta=2a,\theta)=\phi_a(\theta)$ and $K_a(\Delta)=1$ so that Eq. (13) reduces to

$$\tau=\int_0^\theta\frac{d\gamma}{\phi_a(\gamma)}.$$

We know that under a strong influence of gravity, $\phi_a(\theta)$ should become nearly identical to $\Phi_{BD}(\theta)$ which corresponds to the ASF relative to the ballistic deposition model and which is given, in the low to intermediate coverage range, by expression (2). On the other hand, when the gravitational field vanishes, the deposition process should behave more RSA like so that the ASF should take the form (3). The terms of first and second order in the coverage in $\phi_a(\theta)$ should thus gradually vanish by increasing the influence of the gravitational field. It is however not known how these terms evolve with gravity. In order to answer this question we will evaluate $\phi_a(\theta)$ as a function of the gravitational field. This field derives from a potential $u(z)$ which is of the form $[u(z)/kT]=(E/2a)z$. The parameter $(E/2a)$ stands for $\frac{4}{3}(\pi a^4\Delta\rho_d g/kT)$, where $\Delta\rho_d$ corresponds to the density difference between the particles and the surrounding fluid and g represents the acceleration of gravity. The parameter E is thus also equal to $\pm 2R^{*4}$ (the sign is that of $\Delta\rho_d$), where R^* is a dimensionless radius which contains all the physical characteristics of the diffusion under gravity and which has been introduced previously.[20,21]

It should be noted that the expression for $\bar{\Phi}(\Delta,\theta)$ involves the diffusion coefficient $D(z)$. This coefficient is, from a rigorous point of view, a function not only of z but also of the relative position of the diffusing particle with respect to the adsorbed ones. It is, however, interesting to notice that the changes in $D(z)$ in the adsorption layer are mainly caused by the presence of the deposition plane rather than by the adsorbed particles. The problem of calculating the diffusion coefficient of a spherical particle approaching a rigid boundary has been solved in an exact way by Happel and Brenner[22] who also showed that the exact results can be well approximated by the function

$$D(z) = D_0 F(z) = D_0 \frac{z}{z+a}, \tag{14}$$

where $D_0 = (kT/6\pi\eta a)$ is the Stokes diffusion coefficient in the bulk and η is the viscosity of the fluid. The approximate expression (14) of the diffusion coefficient is valid for small distances up to a distance comparable to the particle diameter. For larger separations, due to the appearance of inertial effects, the function $F(z)$ should approach unity much faster than indicated by relation (14) but larger distances do not enter in the evaluation of $\phi_a(\theta)$. By using expressions (7), (8), and (10), the available surface function $\phi_a(\theta)$ takes the form

$$\phi_a(\theta) = \frac{\int_{\bar\delta}^1 \frac{1}{F(\zeta)} \exp(E\zeta) d\zeta}{\int_{\bar\delta}^1 \frac{1}{F(\zeta)} \frac{1}{\Phi(\zeta,\theta)} \exp(E\zeta) d\zeta}, \tag{15}$$

where ζ represents the normalized distance $\zeta = z/2a$ and $\bar\delta = \delta/2a$. The function $F(\zeta)$ is thus equal to $\zeta/(\zeta+1/2)$ and $\Phi(\zeta,\theta)$ stands for $\Phi(z = 2\zeta a, \theta)$. It is assumed here that, once a particle approaches a distance δ from the surface it is irreversibly fixed on it ($u_s(z) \to -\infty$ for $z < \delta$) and that the interaction potential between a particle and the surface $u_s(z)$ is equal to 0 for $z > \delta$.

The determination of $\phi_a(\theta)$ thus requires the knowledge of the function $\Phi(\zeta,\theta)$. This function depends, in the general case, on the average configuration of the adsorbed particles (characterized in terms of the correlation function) which, in turn, is dependent on the transport mechanism. In any case, the general expression for $\Phi(\zeta,\theta)$ should be of the form[9]

$$\Phi(\zeta,\theta) = 1 - A_1(\zeta)\rho_a + \frac{\rho_a^2}{2} \int_0^\infty 2\pi r g_0(r) A_2(\zeta,r) dr$$
$$+ O(\rho_a^3), \tag{16}$$

where ρ_a represents the number density of adsorbed particles which is related to the surface coverage by $\theta = \pi a^2 \rho_a$. $A_1(\zeta)$ corresponds to the area excluded by one particle at a height $\zeta = z/2a$, $A_2(\zeta,r)$ is the overlap of the areas excluded by two particles separated by a center to center distance equal to r and it is given in the Appendix by expression (A3). Finally $g_0(r)$ represents the term of order zero in the density expansion of the radial distribution function $g(r)$. For RSA $g_0(r)$ is equal to 1. It has been shown[23] that this is not the case when the diffusion of the particles in the adsorption layer is taken into account, and the hydrodynamic interactions neglected. However, once the hydrodynamic interactions are taken into account, one recovers a quasi-RSA-like radial distribution function and thus $g_0(r)$ is again approximately equal to 1.[24] In the ballistic case, Thompson and Glandt[8] have shown that the radial distribution function is of the form

$$g_0(r) = 1 + a\delta(r - 2a). $$

The delta contribution comes from the particles which have rolled over the deposited particles during the deposition pro-

cess. This contribution should vanish when $R^* \cong 0$ and it should go to 1 for $R^* > 4$. One can thus expect that $g_0(r)$ takes the approximate form

$$g_0(r) = 1 + f(R^*)a\delta(r - 2a), \tag{17}$$

where $f(R^*)$ is a continuous function whose precise form is not known. Expression (16) can then be rewritten as

$$\Phi(\zeta,\theta) = 1 - C_1(\zeta)\theta + [C_2^{(1)}(\zeta) + C_2^{(2)}(\zeta)]\theta^2 + O(\theta^3) \tag{18}$$

with

$$C_1(\zeta) = A_1(\zeta)/\pi a^2,$$

$$C_2^{(1)}(\zeta) = \frac{1}{2}\left(\frac{1}{\pi a^2}\right)^2 \int_0^\infty 2\pi r A_2(\zeta,r) dr,$$

and

$$C_2^{(2)}(\zeta) = \frac{1}{2}\left(\frac{1}{\pi a^2}\right)^2 f(R^*) 4\pi a^2 A_2(\zeta, 2a).$$

The contribution $C_2^{(1)}(\zeta)$ to the second order term originates from the regular part of the radial distribution function whereas the contribution $C_2^{(2)}(\zeta)$ comes from the delta (i.e., singular) contribution to $g_0(r)$. All these three terms can be determined for hard spheres by using simple geometrical considerations. As it is shown in the Appendix, they are equal to

$$C_1(\zeta) = 4(1-\zeta)^2,$$

$$C_2^{(1)}(\zeta) = \frac{8}{\pi}\left[2\zeta^2(\zeta^2 - 1)\arccos\left(\frac{1}{2\sqrt{1-\zeta^2}}\right) \right.$$
$$\left. + \frac{1}{4}\sqrt{3-4\zeta^2}(3-2\zeta^2) \right], \quad \text{for } 0 \leq \zeta \leq \frac{\sqrt{3}}{2},$$

and

$$C_2^{(1)}(\zeta) = 0, \quad \text{otherwise}.$$

The dependencies of $C_1(\zeta)$ and $C_2^{(1)}(\zeta)$, $C_2^{(2)}(\zeta)$ and $C_2(\zeta) = C_2^{(1)}(\zeta) + C_2^{(2)}(\zeta)$ are plotted in Fig. 4. We have taken for $f(R^*)$ the function

$$f(R^*) = \frac{\theta(\infty, R^*) - \theta_{RSA}(\infty)}{\theta_{BD}(\infty) - \theta_{RSA}(\infty)},$$

where $\theta_{RSA}(\infty)$ (resp. $\theta_{BD}(\infty)$) represents the jamming limit for the RSA (resp. ballistic deposition) model and $\theta(\infty, R^*)$ corresponds to the jamming limit coverage for a system of spheres characterized by R^*, determined in Ref. 25. This function $f(R^*)$ can be adequately approximated by[25]

$$f(R^*) = \exp(-1.32R^{*-4} - 3.44R^{*-3}).$$

Substituting the expression (18) into the general expression (10) of $\phi_a(\theta)$ leads to

$$\phi_a(\theta) = \frac{\int_{\bar\delta}^1 \frac{1}{F(\zeta)} \exp(E\zeta) d\zeta}{\int_{\bar\delta}^1 \frac{1}{F(\zeta)} \frac{\exp(E\zeta)}{[1 - C_1(\zeta)\theta + C_2(\zeta)\theta^2]} d\zeta}. \tag{19}$$
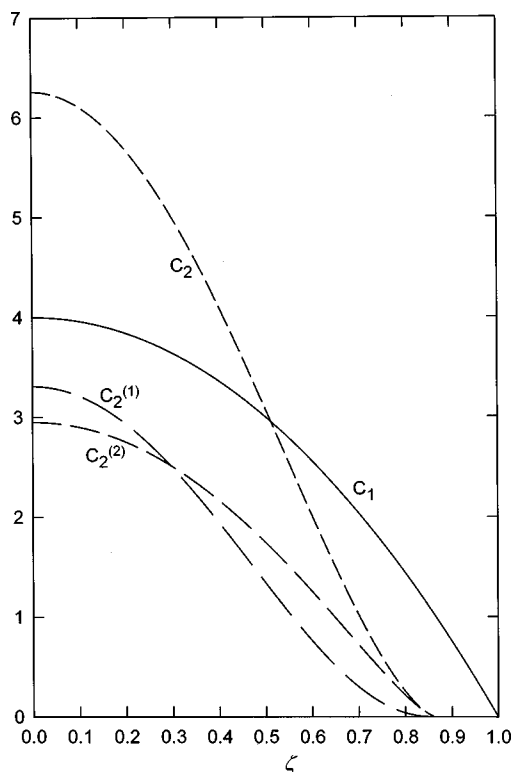
At low coverage ϕ_a may be expressed in the form

FIG. 4. Evolution of the coefficients $C_1(\zeta)$, $C_2^{(1)}(\zeta)$, $C_2^{(2)}(\zeta)$, and $C_2(\zeta)$ $=C_2^{(1)}(\zeta)+C_2^{(2)}(\zeta)$ as a function of the reduced distance $\zeta=z/2a$. The functions $C_1(\zeta)$ and $C_2^{(1)}(\zeta)$ are independent of R^*. The function $C_2^{(2)}(\zeta)$ has been calculated for the case where $R^*=4$.

$$\phi_a(\theta)=\frac{1}{1+f_1\theta}\approx 1-f_1\theta,$$

with

$$f_1=4\,\frac{\int_{\bar{\delta}}^{1}\left(\dfrac{2\zeta+1}{2\zeta}\right)(1-\zeta^2)\exp(E\zeta)d\zeta}{\int_{\bar{\delta}}^{1}\left(\dfrac{2\zeta+1}{2\zeta}\right)\exp(E\zeta)d\zeta}.$$

This coefficient can also be written as

$$f_1=4-2\,\frac{I_1}{I_0}-4\,\frac{I_2}{I_0},$$

with
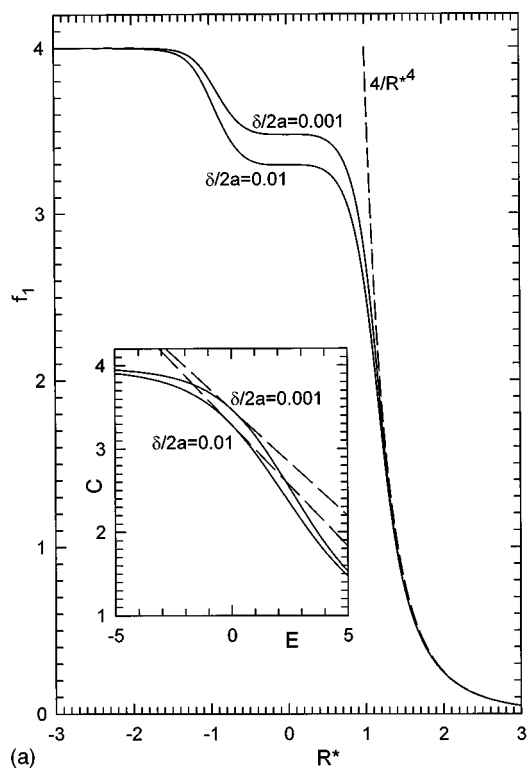
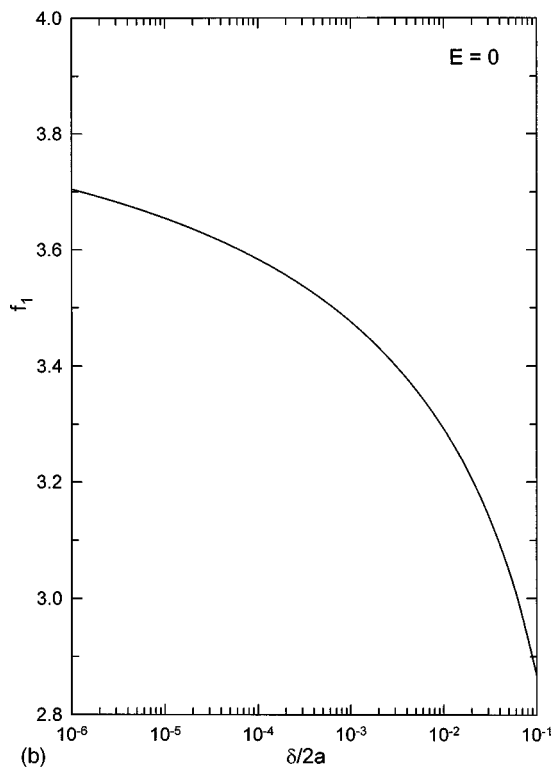$$I_0=e^E-e^{E\bar{\delta}}+\frac{E}{2}\int_{\bar{\delta}}^{1}\frac{\exp(E\zeta)}{\zeta}d\zeta,$$

$$I_1=\exp(E)\left(1-\frac{1}{E}\right)-\exp(E\bar{\delta})\left(\bar{\delta}-\frac{1}{E}\right),$$

$$I_2=\exp(E)\left(\frac{2}{E^2}-\frac{2}{E}+1\right)-\exp(E\bar{\delta})\left(\frac{2}{E^2}-\frac{2\bar{\delta}}{E}+\bar{\delta}^2\right).$$

In the general case, f_1 has to be determined numerically [Fig. 5(a)]. However, in the particular case of $|E|\ll 1$, f_1 can be approximated by a power series of E; $a_0+a_1E+\cdots$, in which a_0 and a_1 are given by

FIG. 5. (a) Evolution of the coefficient f_1 as a function of R^* for two different values of $\delta/2a$. The dashed line ($4/R^{*4}$) represents the asymptotic behavior of f_1 ($E\rightarrow+\infty$). The transition region (E near 0) is plotted in the insert as a function of E. The dashed lines represent the linear approximation $f_1=a_0+a_1E$ for $\delta/2a=0.01$ and 0.001. The expressions of a_0 and a_1 are given by Eqs. (20a) and (20b). (b) Dependence of the coefficient f_1 on $\delta/2a$ in the absence of gravity ($E=0$).

$$a_0 = \frac{(1-\bar{\delta})(5-7\bar{\delta}-4\bar{\delta}^2)-6\ln\bar{\delta}}{3(1-\bar{\delta}-\frac{1}{2}\ln\bar{\delta})} \tag{20a}$$

and

$$a_1 = \frac{(1-\bar{\delta})^2(1+\bar{\delta})(1+2\bar{\delta})(4-\bar{\delta})+(1-\bar{\delta})(5+5\bar{\delta}+5\bar{\delta}^2+3\bar{\delta}^3)\ln\bar{\delta}}{6(1-\bar{\delta}-\frac{1}{2}\ln\bar{\delta})^2}. \tag{20b}$$

The values of $f_1(0)$, i.e., a_0, are represented in Fig. 5(b) as a function of $\bar{\delta}=\delta/2a$. On the other hand, the linear approximation to f_1 is shown (dashed lines) in the insert in Fig. 5(a). It is interesting to note that the coefficient f_1 depends on the parameter $\bar{\delta}$ and thus on the range of interaction between the particles and the surface. However, these changes are of a slow, logarithmic character. This can be illustrated by the fact that the change in $\bar{\delta}$ between 10^{-3} and 10^{-2} (which is a typical range for experimental conditions) will result in the increase of f_1 by 5% only.

Furthermore, when E becomes large, the asymptotic expansion of I_0 is given by

$$I_0(E \gg 1) = \exp(E) - \exp(E\bar{\delta})$$
$$+ \frac{E}{2}\left[\frac{\exp(E)}{E}\sum_{n=0}^{\infty}\frac{n!}{E^n} - \frac{\exp(E\bar{\delta})}{E\bar{\delta}}\sum_{n=0}^{\infty}\frac{n!}{E^n\bar{\delta}^n}\right].$$

Then, using the expressions of I_0, I_1, and I_2 up to their term in $1/E$, and provided that $\exp(E) \gg \exp(E\bar{\delta})$, one obtains

$$f_1(E \gg 1) = \frac{8}{E} + O\left(\frac{1}{E^2}\right) = \frac{4}{R^{*4}} + O\left(\frac{1}{R^{*8}}\right).$$

This asymptotic behavior is also represented in Fig. 5(a), where it is apparent that it constitutes a good approximation of f_1 as soon as $R^* \geqslant 1.5$, i.e., $E \geqslant 10$. As it is expected, in this range of values of R^* the coefficient f_1 is independent of $\bar{\delta}$ and thus also on the precise form of the interaction potential between the particles and the surface.

From expression (19) one can also obtain the development of the available surface function $\phi_a(\theta)$ up to second order in the coverage. One gets

$$\phi_a(\theta) = 1 - f_1\theta + (f_1^2 - f_2)\theta^2 + O(\theta^3),$$

where the coefficient f_2 is given by

$$f_2 = \frac{\displaystyle\int_{\bar{\delta}}^1 \frac{1}{F(\zeta)}(C_1^2(\zeta)-C_2(\zeta))\exp(E\zeta)d\zeta}{\displaystyle\int_{\bar{\delta}}^1 \frac{1}{F(\zeta)}\exp(E\zeta)d\zeta}.$$

In Figs. 6(a) and 6(b), the evolutions of f_1, f_2, and $f_1^2 - f_2$ as a function of R^* are plotted by considering and neglecting hydrodynamic interactions, respectively. It is shown that, in both cases, the coefficient of the second order term in the density expansion of $\phi_a(\theta)$ is not a monotonic function of R^* but exhibits a minimum and becomes even negative for $R^* \cong 1.2$. It was also determined from numerical calculations

(data not shown) that the delta term in expression (17) of the radial distribution function has only a very minor effect on the terms f_2 and $f_1^2 - f_2$ and, on the scale of Fig. 6, one cannot distinguish between the two cases. This comes from the fact that at high R^*, where $f(R^*)$ is different from zero, the system behaves almost ballistically and the two first order terms in the ASF expansion are vanishing. On the other hand, in the small R^* region, where these two first order terms are significantly different from zero, the function $f(R^*)$ vanishes and thus also the delta contribution to f_2 and $f_1^2 - f_2$. The presence of this negative minimum indicates that two adsorbed particles close together have a larger tendency to reduce the deposition rate than do two particles widely separated. This is, at first sight, a surprising result. It is due to the fact that when a particle from the bulk diffuses between two adjacent particles, it is more strongly hindered than for widely separated particles. This is especially the case when there is a slight gravity effect which drives the diffusing particle toward the position between the two adsorbed particles. For zero gravity this effect must be overcompensated by the fact that two deposited particles which are far one from each other exclude a larger area than when they are close and for large gravity the effect becomes negligible because two particles cannot hinder a new one to reach the adsorption plane.

Figure 6 also reveals that the RSA values of the parameters f_1 and $f_1^2 - f_2$ are recovered when $R^* < -1$ (not when $R^*=0$) which can be realized experimentally when gravity is acting opposite to the adsorption plane.[4] This seems to be contradictory with the earlier experimental evidence[26] that the radial distribution function corresponding to small R^* polystyrene particle configurations is very close to its RSA counterpart. It shows that slight changes in the radial distribution function can have quite a significant effect on the ASF. A similar effect on the reduced variance of the number density of adsorbed particles had already been observed. On the other hand, the ballistic behavior is recovered when $R^* \rightarrow +\infty$ and more precisely for $R^* > 2$. This result confirms recent experimental findings where the deposition kinetics of particles characterized by $R^* > 2$ has been measured over a large coverage range.[27] As far as the structure of the deposited layer is concerned, it seems from experiments and computer simulation that values of $R^* > 3$ are required in order to recover the ballistic case.

Experimentally, one also encounters often the case where particles interact with the surface via the potential which is exhibiting a maximum (energy barrier), whose width is small compared to the radius of the particles. Our
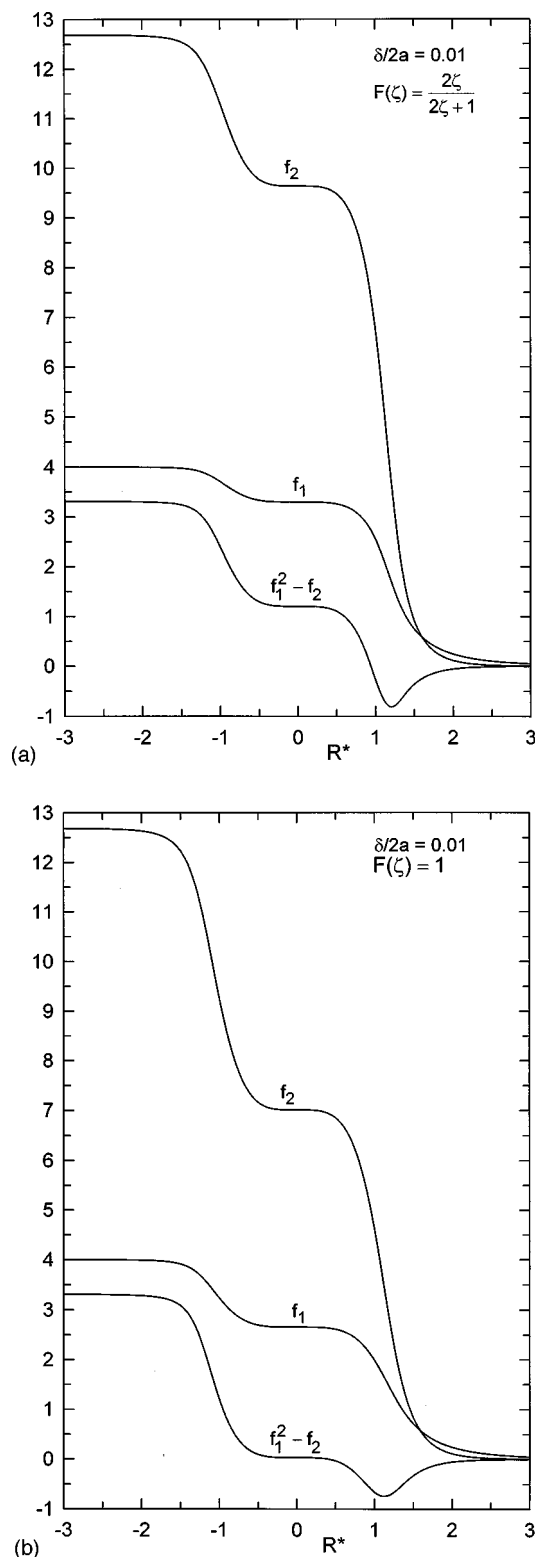
FIG. 6. Evolution of the coefficients f_1, f_2, and $f_1^2-f_2$ as a function of R^*. In (a) the hydrodynamic interactions were taken into account; in (b) the hydrodynamic interactions were neglected. In both cases $\delta/2a$ was taken equal to 0.01.

FIG. 7. Evolution of the coefficients f_1, f_2, and $f_1^2-f_2$ as a function of R^* in the presence of an adsorption energy barrier which is given by expression (20). The value of $\bar{\delta}$ was taken equal to 0.01. The different graphs correspond to different values of the height of the energy barrier $u_s^{(0)}/kT$ (see text).

$$u_s(\zeta)=u_s^0 \exp[-\alpha(\zeta-\bar{\delta})] \text{ for } \zeta \geq \bar{\delta} \tag{20}$$

and

$$u_s(\zeta)=0, \text{ otherwise.}$$

We represent, in Fig. 7, the evolutions of f_1, f_2, and $f_1^2-f_2$ as a function of R^* for different values of u_s^0/kT and α fixed to 20. To determine f_2 we have neglected the delta contribution which seems, according to the preceeding results, a valid approximation. We have also assumed $g_0(\zeta)=1$ for $\zeta>2a$. The value of $\bar{\delta}$ was taken equal to 10^{-2}. The hydrodynamic interactions between the particles and the plane were not taken into account. The general trend that comes out from Fig. 7 is that when the energy barrier becomes high (a few kT), the system exhibits two distinct behaviors. For values of R^* smaller than a critical value which is of the order of 1, but which depends on u_s^0, the system behaves RSA-like. This comes from the fact that, before crossing the energy barrier, the particles have time to randomize in the vicinity of the deposition plane. This behavior has already been suggested in the preceding section by ex-

general scheme allows also to treat this case. In order to capture the general trends for these processes, we have investigated the case where the interaction potential between the particles and the surface varies as
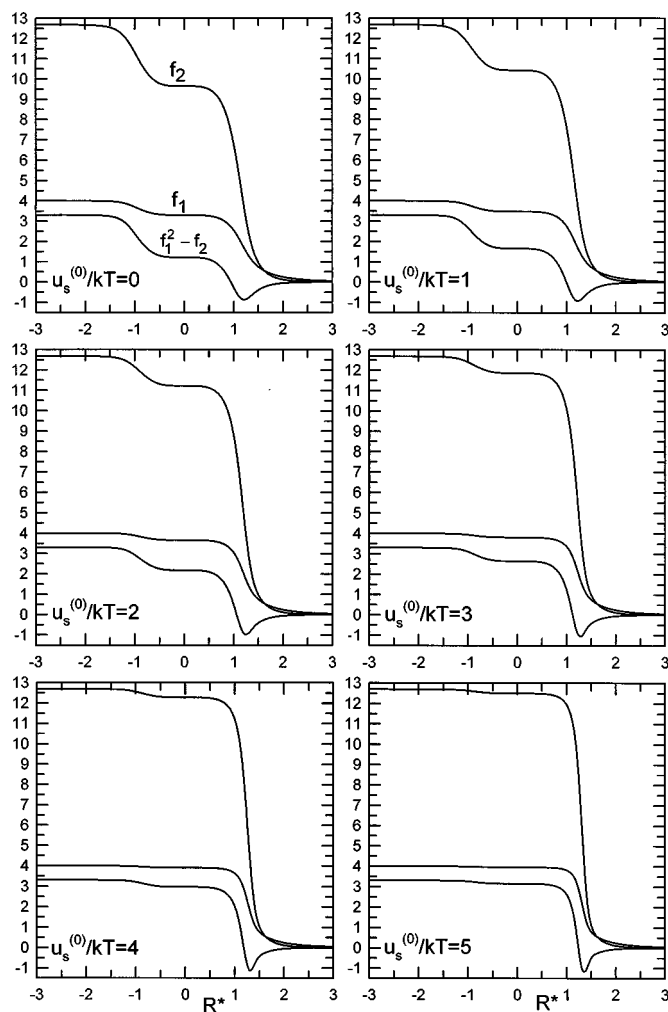
pression (12). For large R^* the system behaves ballistically as far as the first and second order terms in the ASF expansion are concerned. It is however not clear if these conclusions remain valid for the third order term which has an important delta contribution in the ballistic case. Indeed, this delta contribution originates physically from the rolling mechanism of sedimenting particles over already deposited particles. In the case of a high energy barrier, this rolling mechanism should still be present for large R^* until the particle does not feel the presence of the barrier. If the height of the barrier is such that

$$\frac{\zeta_0 R^{*4} - u_s^0}{kT} \gg 1,$$

where ζ_0 represents the spatial extension of the energy barrier, one can expect the ballistic model to remain valid. On the other hand, if

$$\frac{\zeta_0 R^{*4} - u_s^0}{kT} \lesssim 1,$$

then the particles should have time to randomize near the deposition plane before crossing the barrier even if $R^* \gg 1$. The third order term should thus vary with R^* between the RSA and the ballistic value in an unknown way. The prediction of the variations of this coefficient with R^* and u_s^0 constitutes certainly an important objective for future work.

IV. CONCLUSION

The generalized RSA approach developed in our work enables one to analyze the irreversible adsorption of particles and proteins under external and specific force fields. By introducing the concept of the overall available surface function $\bar{\Phi}(\Delta, \theta)$ the connection with the Langmuir model has been made and the correct boundary conditions for the bulk transport equation have been specified.

It has been proven that the usual RSA mechanism should be operating for

(i)   systems with strong external force acting opposite to the adsorption plane,

(ii)   systems characterized by the specific energy barrier appearing at distances much smaller than particle dimensions.

This has been confirmed numerically for the hard sphere problem by using the second order expansion for the available surface function. Additionally, it has been found that the ballistic model is recovered for $R^* > 2$ with the leading term of the expansion vanishing as $4/R^{*4}$.

Our analysis can, in principle, be extended to the third order term in the coverage expansion of the ASF. This seems a complicated task since this term involves the Dirac delta contribution whose dependence on the R^* parameter is not known as yet. Another extension of our work should consist of generalizing the approach of Schaaf *et al.*,[12] valid at the jamming limit, by taking hydrodynamic and gravitational effects into account.

A detailed investigation of this problem is planned in the future.

APPENDIX

In this appendix we calculate the functions $C_1(\zeta)$, $C_2^{(1)}(\zeta)$, and $C_2^{(2)}(\zeta)$ needed for the determination of the first and second order terms in the coverage expansion of the ASF for hard spheres $\phi_a(\theta)$.

The radius of the exclusion disk for a particle located at the distance z over the adsorption plane is

$$R(\zeta) = 2a\sqrt{1 - \zeta^2}, \tag{A1}$$

where $\zeta = (z/2a)$. The function $C_1(\zeta)$ is thus given by

$$C_1(\zeta) = \frac{\pi R^2(\zeta)}{\pi a^2} = 4(1 - \zeta^2)^{1/2}. \tag{A2}$$

The coefficients $C_2^{(1)}(\zeta)$ and $C_2^{(2)}(\zeta)$ depend on the overlap area $A_2(\zeta, r)$ between the exclusion disks at a height z of two spheres having a center to center distance equal to r. This overlap area is given by

$$A_2(\zeta, r) = 2R^2(\zeta)\arccos\left(\frac{r}{2R(\zeta)}\right) - r\sqrt{R^2(\zeta) - \frac{r^2}{4}}. \tag{A3}$$

This relation is valid for $r \leq 4a\sqrt{1 - \zeta^2}$ and varies between 0 and $(\sqrt{3}/2)$. $C_2^{(1)}(\zeta)$ and $C_2^{(2)}(\zeta)$ are given by

$$C_2^{(1)}(\zeta) = \frac{1}{2}\left(\frac{1}{\pi a^2}\right)^2 \int_{2a}^{4a\sqrt{1-\zeta^2}} 2\pi r A_2(\zeta, r) dr, \tag{A4}$$

$$C_2^{(2)}(\zeta) = \frac{1}{2}\left(\frac{1}{\pi a^2}\right)^2 f(R^*) a \int_{2a}^{4a\sqrt{1-\zeta^2}} 2\pi r A_2(\zeta, r)$$
$$\times \delta(r - 2a) dr. \tag{A5}$$

The function $C_2^{(2)}(\zeta)$ is immediately calculated and is expressed by

$$C_2^{(2)}(\zeta) = \frac{1}{2}\left(\frac{1}{\pi a^2}\right)^2 f(R^*) 4a^2 \pi A_2(\zeta, 2a), \tag{A6}$$

which is valid for $\zeta \leq (\sqrt{3}/2)$. For larger values of ζ, one has $C_2^{(2)}(\zeta) = 0$. The calculation of the function $C_2^{(1)}(\zeta)$ is more lengthy but does not present any difficulty. It is given by

$$C_2^{(1)}(\zeta) = \frac{1}{2}\left(\frac{1}{\pi a^2}\right)^2 \int_{2a}^{4a\sqrt{1-\zeta^2}} 2\pi r\left(2R^2(\zeta)\arccos\left(\frac{r}{2R(\zeta)}\right)\right.$$
$$\left. - r\sqrt{R^2(\zeta) - \frac{r^2}{4}}\right) dr. \tag{A7}$$

In this expression all the integrals are tabulated and one gets

3128   J. Chem. Phys., Vol. 110, No. 6, 8 February 1999

Adamczyk *et al.*

$$C_2^{(1)}(\zeta) = \frac{8}{\pi} \left\{ -2\zeta^2(1-\zeta^2)\arccos\left(\frac{1}{2\sqrt{1-\zeta^2}}\right) \right.$$
$$\left. + \frac{1}{4}\sqrt{3-4\zeta^2}(3-2\zeta^2) \right\}. \tag{A8}$$

[1] G. Tarjus, P. Schaaf, and J. Talbot, J. Chem. Phys. **93**, 8352 (1990).

[2] J. Feder and I. Giaever, J. Colloid Interface Sci. **78**, 144 (1980).

[3] G. Y. Onoda and E. G. Liniger, Phys. Rev. A **33**, 715 (1986).

[4] Z. Adamczyk, B. Siwek, M. Zembala, and P. Belouschek, Adv. Colloid Interface Sci. **48**, 151 (1994).

[5] J. J. Ramsden, Phys. Rev. Lett. **71**, 295 (1993).

[6] P. R. Johnson and M. Elimelech, Langmuir **11**, 801 (1995).

[7] P. Wojtaszczyk, P. Schaaf, B. Senger, M. Zembala, and J.-C. Voegel, J. Chem. Phys. **99**, 7198 (1993).

[8] A. P. Thomson and E. D. Glandt, Phys. Rev. A **46**, 4639 (1992).

[9] P. Schaaf and J. Talbot, J. Chem. Phys. **91**, 4401 (1989).

[10] B. Widom, J. Chem. Phys. **44**, 3888 (1966).

[11] B. Widom, J. Chem. Phys. **39**, 2808 (1963).

[12] P. Schaaf, A. Johner, and J. Talbot, Phys. Rev. Lett. **66**, 1603 (1991).

[13] I. Pagonabarraga and M. Rubí, Physica A **188**, 553 (1992).

[14] P. Wojtaszczyk, J. Bonet Avalos, and M. Rubí, Europhys. Lett. **40**, 299 (1997).

[15] I. Prigogine and P. Mazur, Physica (Amsterdam) **19**, 241 (1953).

[16] S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover, New York, 1984), Chap. X, Sec. 6.

[17] E. Ruckenstein and D. C. Prieve, J. Chem. Soc., Faraday Trans. 2 **69**, 1522 (1973).

[18] H. Reiss, *Methods of Thermodynamics* (Dover, Mineola, 1996).

[19] D. Bedeaux and J. Vlieger, Physica (Amsterdam) **67**, 55 (1973).

[20] B. Senger, F. J. Bafaluy, P. Schaaf, A. Schmitt, and J.-C. Voegel, Proc. Natl. Acad. Sci. USA **89**, 9449 (1992).

[21] P. Schaaf, Ph. Carl, J.-C. Voegel, E. K. Mann, and B. Senger, Phys. Rev. E **54**, 6962 (1996).

[22] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Martinus Nijoff, Dordrecht, 1986).

[23] B. Senger, P. Schaaf, J.-C. Voegel, A. Johner, A. Schmitt, and J. Talbot, J. Chem. Phys. **97**, 3813 (1992).

[24] J. Bafaluy, B. Senger, J.-C. Voegel, and P. Schaaf, Phys. Rev. Lett. **70**, 623 (1993).

[25] R. Ezzeddine, P. Schaaf, J.-C. Voegel, and B. Senger, Phys. Rev. E **51**, 6286 (1995).

[26] P. Wojtaszczyk, E. K. Mann, B. Senger, J.-C. Voegel, and P. Schaaf, J. Chem. Phys. **103**, 8285 (1995).

[27] Ph. Carl, P. Schaaf, J.-C. Voegel, J.-F. Stoltz, Z. Adamczyk, and B. Senger, Langmuir (in press).