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Irreversible adsorption of diffusing hard disks: An effective medium approach

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We propose an effective medium theory to analyze the kinetics of nonsequential adsorption of colloidal particles, including transport and blocking effects, valid at all values of surface coverage. The theory is applied to the irreversible adsorption of diffusing hard disks obtaining a kinetic law, which is in excellent agreement with nonsequential computer simulations at all densities of adsorbed particles. [S1063-651X(99)04407-4]

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I. INTRODUCTION

The adsorption of colloidal particles from fluid suspensions to solid surfaces leading to monolayer formation is a complex phenomenon of great practical interest. For many colloidal particles, latexes [1,2], for example, neither surface diffusion nor desorption is observed in the time scale accessible to experiments: the particles remain immobilized after adsorption, and the process can be considered irreversible. Consequently, nonequilibrium configurations are generated and, when the surface coverage attains a given value, a *jamming* configuration is obtained, with no space available on the surface for the adsorption of new particles.

The transport of small colloidal particles in the vicinity of an adsorbing surface is strongly influenced by the interplay between diffusion and the interaction with the adsorbates. In the absence of strong attractive forces, Brownian motion allows diffusing particles to explore large regions and to interact with a possibly large number of adsorbed particles before reaching the surface. Many-body effects are thus essential for the description of the process.

An approach to this problem is based on the introduction of geometric models in which the transport of the particles towards the surface is decoupled from the interaction with the adsorbates; this last one is assumed to lead to certain rules for the addition of new particles to the surface. The simplest of such models is the so-called random sequential adsorption (RSA) model [2,3]. In RSA, it is assumed that diffusing particles explore uniformly the surface; at a given rate (imposed by external conditions) new particles arrive at points randomly and uniformly distributed on the surface; if adsorption at these points is possible, the particles are adsorbed, whereas if the chosen position is not available for adsorption, the particles return to the bulk. RSA and other similar models are exactly soluble in the case of one-dimensional surfaces, and computer simulations can be easily implemented in higher dimensions. Although RSA has succeeded in explaining some experimental observations [4–6], it is not intended to accurately describe the kinetics of the process: its ‘‘kinetic law’’ reflects only the probability of success for each adsorption attempt according to the given filling rules, and it is decoupled from the transport mechanisms present in the suspension.

A more consistent approach should include the interaction with the partially covered surface at the same level than the other mechanisms relevant to the transport of the particles. This means that, near the interface, one has to consider the transport in the presence of a possibly large number of adsorbed particles. In order to take these factors into account properly, several approximate techniques have been proposed recently. The kinetics can be described by an effective transport equation, which includes the blocking effect though a mean-field (MF) approximation [7,8]; it has been shown that this approach is only valid when the surface coverage approaches the saturation value [9]. On the other side, for not too high coverages, an expansion of the adsorption rate in powers of the coverage can be obtained, in which the term of order n is determined from the solution of the transport problem in the presence of n adsorbed particles [9].

However, none of these formalisms allows one to obtain a description of the kinetics at all coverage values, even in the simplest case of adsorption on one-dimensional surfaces. At the core of the problem is the fact that one has to take into account the interaction of diffusing particles with a large number of adsorbates. On the other hand, we note that in a number of situations in physics in which one has to deal with complicated many-body interactions, self-consistent methods based on effective interactions have proven to be very useful. Thus, one can try to describe the detailed interaction with a large number of adsorbates by a certain effective interaction to be determined *a posteriori* in a self-consistent way. The use of an effective medium approach has proven to be very useful in a similar context, namely, the diffusion-controlled ligand binding to a spherical cell partially covered by receptors [10]. The kinetic law obtained within this approach has been shown to be indistinguishable from the results obtained in Brownian dynamics simulations.

Our aim in this paper is to explore the accuracy of such an approximation in nonsequential adsorption processes in which transport is dominated by diffusion. To this end, in Sec. II we introduce a simplified model in which a suspension of hard disks adsorb irreversibly onto a line. In Sec. III the kinetics of the model is analyzed through a generalized car-parking process explicitly coupled to a detailed description of the bulk diffusion process. Also, the validity of the procedure is confirmed by comparison with nonsequential Brownian dynamics simulations. Finally, in Sec. IV we review our main conclusions.

II. DESCRIPTION OF THE MODEL

We want to study a simple model that may allow us to understand the coupled effect of bulk diffusion and surface saturation on the kinetics of monolayer formation. We consider a dilute suspension of disks of radius R that diffuse in a fluid in the bidimensional region $z>0$ with a constant diffusion coefficient D. We are interested in situations in which colloidal adsorption is fully irreversible, so that the interaction potential between the colloidal particles and a clean surface can be replaced by a perfect sink placed very close to the surface [11]. Thus, we consider that when the center of a particle arrives at $z=0$, it is adsorbed irreversibly. The macroscopic state of the adsorbing line is characterized by its coverage, $\theta=2R\rho$, where ρ is the number of adsorbed particles per unit length. As explained in the Introduction, the repulsive interaction between adsorbed and diffusing particles leads to a decrease of the flux of particles when the coverage θ increases (the so-called blocking effect). In our model we assume that the adsorbed particles interact as hard disks with free particles, so the interaction between free and adsorbed particles takes place in the region $0\leqslant z\leqslant 2R$, which we will call the boundary layer from now on. We assume that the thickness $\ell\sim 2R$ of this boundary layer is small compared to the macroscopic length scale L, determined by boundary and initial conditions imposed on the suspension. In addition, we assume that the bulk concentration is diluted, so the interactions between diffusing particles in the bulk are neglected. Out of this boundary layer, the macroscale concentration $c_M(\vec{r},t)$ obeys the diffusion equation:

$$\frac{\partial c_M(\vec{r},t)}{\partial t}+D\nabla^2 c_M(\vec{r},t)=0, \tag{1}$$

and the particles flux towards the adsorbing line entering the boundary layer is $J_S(x,t)=Ddc_M/dz|_{z=2R}$. Equation (1) does not include the details occurring at the ℓ scale, which cannot be distinguished within this spatial resolution. These details will be taken into account by matching the macroscale concentration with an averaged microscale solution obtained from a particle transport problem formulated at the ℓ scale inside the boundary layer region.

We are interested in the microscale concentration c_I near the adsorbing line, which takes into account the local inhomogeneities and the interaction with N adsorbed particles located at $x_1,x_2,\ldots,x_N\equiv\vec{X}_N$. Near the adsorbing surface, after a short transient time of order $\tau\sim\ell^2/D$, the transport process is stationary if the colloidal suspension is diluted enough [9] ($c_B R^2 \ell \ll 1$, where c_B is a characteristic concentration near the boundary layer). From now on, we will use dimensionless units in which lengths are measured in units of $2R$, time in units of $4R^2/D$ and $\theta=\rho=N/A$, A being the length of the adsorbing line. Thus, $c_I(\vec{r};\vec{X}_N)$ is a solution of the stationary diffusion problem:

$$\nabla^2 c_I(\vec{r};\vec{X}_N)=0. \tag{2}$$

By definition, $c_I(\vec{r};\vec{X}_N)$ verifies the boundary condition of zero radial flux at the surfaces of the N adsorbed particles (hard disk interaction) and a perfect sink at the free gaps between the adsorbed particles. The second boundary condition is obtained by realizing that far from the adsorbing surface the particle flux has to match the macroscopic flux, which is homogeneous at the ℓ scale. Thus, we impose a uniform incoming flux of particles J_S far from the adsorbing surface. Due to the linearity of Eq. (2) we can rewrite $c_I(\vec{r};\vec{X}_N)=J_S\Psi(\vec{r};\vec{X}_N)$, where $\Psi(\vec{r};\vec{X}_N)$ is a particular solution of Eq. (2) with unit flux far from the adsorbing surface and verifying the same boundary conditions as $c_I(\vec{r};\vec{X}_N)$ at the surface.

Let us define the average concentration $\langle c_I\rangle(z;\theta)$ as

$$\langle c_I\rangle(z;\theta)\equiv\int p_N(\vec{X}_N)c_I(\vec{r};\vec{X}_N)d\vec{X}_N, \tag{3}$$

where $p_N(\vec{X}_N)$ is the probability that the N adsorbed particles are in the configuration $\vec{X}_N$. Note that $\langle c_I\rangle$ is a function of z and θ only due to the homogeneity of the average. The average $\langle\Psi\rangle(z;\theta)$ is defined analogously and it verifies $\langle c_I\rangle(z;\theta)=J_S\langle\Psi\rangle(z;\theta)$. Out of the boundary layer ($z\geqslant 1$), $\langle c_I\rangle$ must match the macroscopic concentration c_M. From Eqs. (2) and (3) we have, for $z\geqslant 1$:

$$\frac{d^2\langle\Psi\rangle(z;\theta)}{dz^2}=0,\quad z\geqslant 1. \tag{4}$$

The solution of Eq. (4) that verifies the condition of unit flux is

$$\langle\Psi\rangle(z;\theta)=z+k_r^{-1}(\theta),\quad z\geqslant 1 \tag{5}$$

The integration constant $k_r(\theta)$ is a function of θ only which verifies $k_r^{-1}(0)=0$ and $k_r(\theta=\theta_\infty)=0$. Defining $c_B(t)\equiv c_M(z=1;t)$ the continuity of the macroscopic concentration at $z=1$ requires $c_B(t)=J_S\langle\Psi\rangle(z=1;\theta)$. Defining the kinetic coefficient $K^{-1}(\theta)=1+k_r^{-1}(\theta)$ one obtains the following boundary condition for $c_M(\vec{r};t)$:

$$\frac{d\theta}{dt}\equiv J_S(t)=K(\theta)c_B(t). \tag{6}$$

Equation (6) is a generalized Langmuir kinetic equation [9] in which the kinetic coefficient $K(\theta)$ reflects the effect of previously adsorbed particles on the diffusion process near the interface. Once $K(\theta)$ is known, the kinetics of the monolayer formation can be obtained by solving Eq. (1) for the macroscale concentration with the boundary condition (6) at the interface and the appropriate additional initial and boundary conditions in the bulk. The explicit calculation of $k_r(\theta)$ requires a complete solution of the microscale many-particles problem, which is not feasible. Instead we will develop an effective medium approach. This approach is based on the observation that, according to Eq. (5), from the macroscale point of view, the interface acts as a semipermeable medium, which imposes a concentration $k_r^{-1}(\theta)$ at $z=0$. This fact is analogous of that encountered in [10] in the study of adsorption of a spherical cell partially covered by receptors. It suggests that the influence of the adsorbates on diffusing particles can be replaced by the interaction with an effective medium. In the following section, we will develop such an approach.

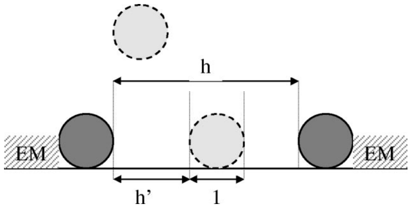

FIG. 1. Illustration of particle adsorption onto a free gap of size h limited by two adsorbed particles (shown in black). A new particle (in gray) has been adsorbed, creating two new gaps of size h and $h'-h-1$. At the same time, another particle (also shown in gray) diffuses near this gap. Region II, at which the effective medium approximation is employed, is denoted by EM.

III. EFFECTIVE MEDIUM APPROACH

We start by obtaining an approximation to $\Psi(\vec{r};\vec{X}_N)$ making use of the effective medium (EM) approach. In this approach, we replace the exact boundary conditions of zero radial flux at the surfaces of the N adsorbed particles (adsorbed at $\vec{X}_N$) and perfect sink at the available space between the adsorbed particles by a simplified boundary condition. An important topological observation is that the line is divided into a set of disjoint gaps between the N adsorbed particles. All adsorption events must take place within any of these gaps. Now, consider an adsorbing gap of size h (see Fig. 1), which we will designate by region I. We will designate the remaining of the line $z=0$ by region II. The concentration at a point $\vec{r}$ of the bulk near region I is strongly influenced by the interaction of the diffusing particles with the two adsorbed particles limiting the gap. The influence of the remaining adsorbed particles is taken into account by assuming a uniform effective medium, that imposes a concentration $k_r^{-1}(\theta)$ at region II. Within this approximation, Ψ_{EM} is a function of $\vec{r}$, the size of the gap h and the coverage θ through the effective medium concentration $k_r^{-1}(\theta)$. $\Psi_{EM}(\vec{r},h;\theta)$ is a particular solution of the stationary diffusion equation (2) that verifies the boundary conditions of uniform unit flux far from the adsorbing surface, perfect sink at region I, and zero radial flux at the surfaces of the two adsorbed particles limiting the gap. At region II, the effective medium approach assumes that $\Psi_{EM}(\vec{r},h;\theta)$ has the uniform value $k_r^{-1}(\theta)$. Thus, the concentration at $z=0$ is $c_I=0$ at region I, and $c_I=J_S k_r^{-1}=(1-K)c_B\equiv c_{EM}$ at region II. This concentration c_{EM} evolves with θ from that of an adsorbing empty line $c_{EM}(\theta=0)=0$ to the bulk concentration at jamming, $c_{EM}(\theta=\theta_\infty)=c_B(\theta_\infty)$.

We can take advantage of the linearity of Eq. (2) by decomposing Ψ_{EM} in the form:

$$\Psi_{EM}(\vec{r},h;\theta)=F_1(\vec{r},h)+k_r^{-1}(\theta)F_2(\vec{r},h), \tag{7}$$

where $F_1(\vec{r},h)$ and $F_2(\vec{r},h)$ are particular solutions of the diffusion equation (2). Both functions verify the boundary conditions of perfect sink in region I and zero radial flux at the surfaces of the two adsorbed particles limiting the gap. $F_1(\vec{r},h)$ is the solution corresponding to the situation in which no more particles than these limiting the gap are present on the line. It therefore verifies the boundary condition of unit flux far from $z=0$ and perfect sink at region II. $F_2(\vec{r},h)$ gives the contribution to Ψ_{EM} due to particles adsorbed on the remaining portion of the line and verifies the boundary condition of constant value 1 in region II and zero flux far from $z=0$. The functions $F_1(\vec{r},h)$ and $F_2(\vec{r},h)$ are obtained in the Appendix and are given by Eqs. (A7) and (A11).

Once $\Psi_{EM}(\vec{r},h;\theta)$ is obtained, we need to describe the evolution of the structure of the adsorbed layer. In the EM approach, we are interested only in the distribution of free gaps of size h at coverage θ. The adsorption of particles onto the adsorbing line continuously destroys existing gaps and creates smaller new gaps. Let $G(h,t)$ be the number density of gaps with length h at time t. The time evolution of $G(h,t)$ due to gap creation and destruction is described by the balance equation:

$$\frac{\partial G(h,t)}{\partial t}=-q_0(h;t)G(h,t)+2\int_{h+1}^{\infty}dh''q(h'',h;t)G(h'',t), \tag{8}$$

which is a generalization of that proposed in [12,13]. The function $q(h,h';t)$ is the rate of destruction of gaps of size h at time t, creating two new gaps of size $h-h'-1$ and h' (see Fig. 1). Destruction of gaps is due to the adsorption of particles, so $q(h,h';t)$ is given by the rate of particles adsorbing at the point $x=h'-(h-1)/2$ at $z=0$, which is

$$q(h,h';t)=\left.\frac{\partial c_I}{\partial z}\right|_{z=0}. \tag{9}$$

In the EM approach, $c_I=J_S\Psi_{EM}$ near the gap, and Eq. (9) can be written as

$$q(h,h';t)\equiv J_S(t)[q^{(1)}(h,h')+k_r^{-1}(\theta(t))q^{(2)}(h,h')], \tag{10}$$

where

$$q^{(j)}(h,h')=\left.\frac{\partial F_j}{\partial z}\right|_{z=0}, \tag{11}$$

for $j=1,2$. The explicit expressions obtained for the functions $q^{(j)}(h,h')$ are given by Eqs. (A8) and (A12) in the Appendix. The function $q_0(h;t)$ is the total rate at which gaps of length h are destroyed at time t, and is given by

$$q_0(h;t)=\int_0^{h-1}dh'q(h,h';t) \equiv J_S(t)[q_0^{(1)}(h)+k_r^{-1}(\theta(t))q_0^{(2)}(h)]. \tag{12}$$

Note that contrary to previous generalized car-parking approaches [12,13], q_0 depends on time. This dependence is due to the contributions coming from the effective medium surrounding the gap, which is in a state characterized by $\theta(t)$. It is a consequence of the fact that the *shielding property*, which allows one to exactly solve other one-dimensional models, is not satisfied here. The flux of par-

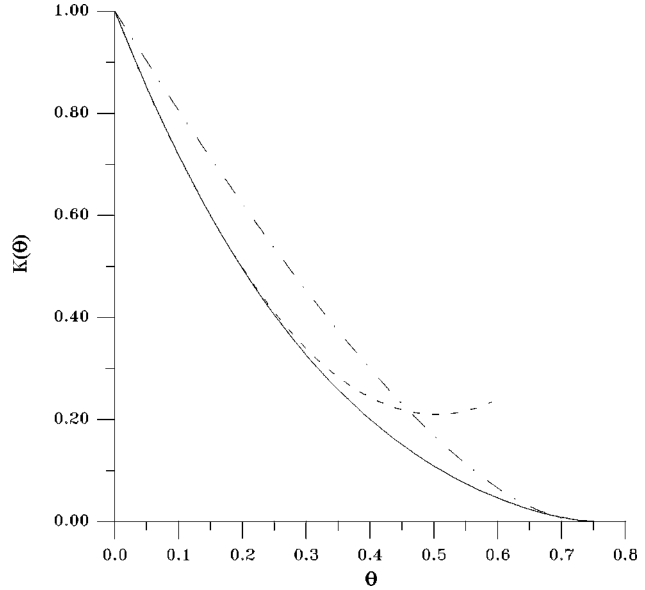

FIG. 2. Dimensionless adsorption rate $K(\theta)$ as a function of the coverage: self-consistent result (solid line), density expansion (short dashed line), and RSA (dotted dashed line).

ticles adsorbing at time t, defined in Eq. (6), must be recovered as the average of $q_0(h;t)$ over all gaps, which can adsorb particles:

$$J_S(t) = \int_1^\infty dh G(h,t) q_0(h;t). \tag{13}$$

Equation (13) gives a consistency condition for the EM calculation. Note that $G(h,t)$ is a function of t only through its dependence on $\theta(t)$. Thus, one can eliminate t in favor of θ noting that the coverage θ is a monotonically increasing function of t. Using Eqs. (10) and (12) in Eq. (8) we obtain for $G(h,\theta)$:

$$\begin{aligned}\frac{\partial G(h,\theta)}{\partial \theta} = {} & -q_0^{(1)}(h) G(h,\theta) - k_r^{-1}(\theta) q_0^{(2)}(h) G(h,\theta) \\ & + 2\int_{h+1}^\infty dh''[q^{(1)}(h'',h) \\ & + k_r^{-1}(\theta) q^{(2)}(h'',h)] G(h'',\theta).\end{aligned} \tag{14}$$

An equation for $k_r(\theta)$ is obtained using Eq. (12) in the consistency relation (13):

$$k_r(\theta) = \frac{\int_1^\infty dh G(h,\theta) q_0^{(2)}(h)}{1 - \int_1^\infty dh G(h,\theta) q_0^{(1)}(h)}. \tag{15}$$

Now, the functions $G(h,\theta)$ and $k_r(\theta)$ are obtained solving numerically the coupled equations (14) and (15). The desired coefficient $K_{EM}^{-1}(\theta) = 1 + k_r^{-1}(\theta)$ is shown in Fig. 2. The effective medium approach does not provide an estimation of the error introduced by the approximations employed, so the only way to check its accuracy is to compare its results with known approximate expressions valid at low or near saturation coverages and with computer simulations.

In [9] an expansion of the exact kinetic coefficient $K(\theta)$ in powers of θ for nonsequential adsorption models was obtained. In the case of diffusing hard disks, the first two terms of the expansion were evaluated giving the result [9]:

$$K(\theta) = 1 - \pi\theta + 3.124\theta^2 + O(\theta^3), \tag{16}$$

which is accurate up to coverages of order $\theta \sim 0.25$. Equation (16) is also shown in Fig. 2 for comparison. As shown in this figure, the EM results agree very well with Eq. (16) in the range of validity of Eq. (16).

Near the jamming limit, the arguments proposed by Schaaf *et al.* [14] adapted to diffusing disks lead to the power-law behavior $K \sim (\theta_\infty - \theta)^{3/2}$. The obtained behavior of $K_{EM}(\theta)$ near the jamming limit reproduces the known power law $K \sim (\theta_\infty - \theta)^{3/2}$, so the effective medium solution is consistent both with low- and near-jamming density known results. From $K_{EM}(\theta)$ we obtain a jamming coverage of $\theta_\infty \simeq 0.751$ that agrees with the value previously obtained by analyzing a sequential model, which includes diffusion random sequential adsorption (DRSA) [13]. As in the three-dimensional case, the jamming coverage is close to the known RSA value [9,15]. In spite of this similarity between diffusing disks and RSA-jamming configurations, the kinetics of both processes are clearly different, as shown in Fig. 2. This comparison shows that the blocking effect of adsorbed particles is larger in our model than in RSA, especially at low and intermediate coverages.

Now, we propose the following simple fitting formula to the EM results:

$$K_{fit}^{-1}(\theta) = 1 + \frac{a_1\theta + a_2\theta^2 + a_3\theta^3}{(1 - \theta/\theta_\infty)^{a_4}}. \tag{17}$$

In order to exactly recover the low density expansion Eq. (16) we fixed the values of a_1 and a_2 to $a_1 = \pi$ and $a_2 = -0.4712$. Also, we have $a_4 = 3/2$ in order to recover the asymptotic behavior of the EM solution. Thus, the only free parameter is a_3, which is obtained by a least-squares fitting, obtaining $a_3 = -0.8509$. Using this value, $K_{fit}(\theta)$ is indistinguishable from $K_{EM}(\theta)$ when plotted in Fig. 2.

In order to check the accuracy of the effective medium result at all coverages, we compare it with computer simulations of nonsequential adsorption of disks. We consider an initial uniform concentration c_0 in a vessel limited by an adsorbing line of length L_x at $z = 0$ and a reflecting line at $z = L_z$. Periodic boundary conditions are applied to the other two walls. Initially, $N_0 = L_x L_z c_0$ particles are placed randomly inside the simulation box. The process is simulated by using a Brownian dynamics algorithm [16] in which all particles diffuse simultaneously in continuous two-dimensional (2D) space. The collision between a diffusing particle and an adsorbed one is modeled as an elastic collision [17] . We are interested in simulations of diluted suspensions, so the interactions between two or more particles in the bulk can be neglected. We only consider the hard disk interaction between adsorbed particles and diffusing ones.

In these simulations, the simultaneous adsorption of two free particles at very close positions, competing to occupy

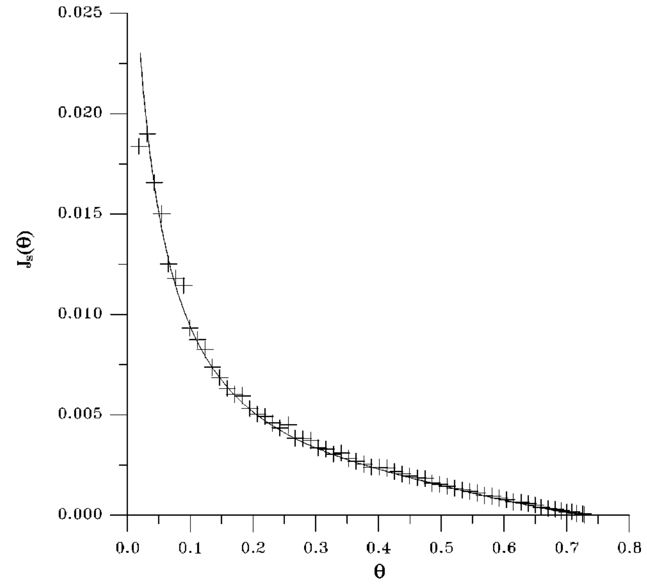

FIG. 3. Dimensionless particle flux $J_s(\theta)$ starting from an initial particle concentration $c_0=0.05$: simulations (crosses) and solution of the time-dependent diffusion equation with boundary condition given by Eq. (6) (solid line).

the same free space on the line is highly improbable due to the low bulk concentration. In fact, this event was not observed in our simulations. Of course, simultaneous adsorptions at different points (at the same or different gaps) or adsorptions separated by very small time intervals were very often observed.

The dimensionless values of the parameters employed in our simulation were $L_x=100$, $L_z=21$, and $c_0=0.05$; the time step was $\Delta t=10^{-4}$ and the simulation results were averaged over 1000 simulation runs.

The flux $J_s(\theta)$ obtained in these simulations is shown in Fig. 3. On the other hand, we have solved numerically the diffusion equation (1) with the boundary condition at $z=1$ given by Eq. (6) using the effective medium $K(\theta)$, a reflecting boundary condition at $z=L_z$ and the initial condition $c_M(t=0)=c_0$. Note that in this situation c_M is a function of z and t only. In Fig. 3 we compare the obtained flux $J_S(\theta)$ with that measured in our simulations, showing an excellent agreement at all coverages except at very short times, before the steady situation is reached in the boundary layer. At this point, we remark that although the time evolution of θ depends on the specified boundary conditions, the jamming coverage θ_∞ defined by $K(\theta=\theta_\infty)=0$ is independent of these. Our simulations give the value $\theta_\infty \simeq 0.7506$, which is consistent with the effective medium calculations.

This simultaneous diffusion of particles is the main difference between our simulations and the sequential simulations of the DRSA [15]. In our algorithm, several particles can adsorb simultaneously (or in a very small time interval) at different points of the adsorbing surface. If one observes the motion of an individual diffusing particle, the mean time needed to reach the adsorbing surface by diffusion can become arbitrarily large (even whether the surface is free of adsorbed particles). However, due to the simultaneous motion of all the particles, the observed time between adsorptions can be arbitrarily small. Due to the competition of the diffusing particles to arrive at the adsorbing line, the observed time between adsorptions is not equal to the mean time, which an individual particle needs to reach the adsorbing line. In contrast, in a DRSA algorithm [18] this competition is not included and the time between consecutive adsorptions is equal to the time which a particle needs to reach the adsorbing line. This time can become very large and, in order to obtain feasible computational times, particles must be rejected when arriving to a given height. In addition, the obtained results depend strongly on the position of this rejection line, so the kinetics of the process is not well defined [18].

Let us note that in order to analyze the effect of synchronous diffusion of several particles in adsorption kinetics, a different simulation model, based on cellular automaton (CA) was proposed in [19]. CA models are interesting because they allow fast simulations, especially in parallel machines. However, the microscopic details of the CA model are different from those of our Brownian dynamics simulations. Unlike our simulations, in the CA model particles perform a random walk on a square lattice. The radius of the particles is fixed to be 1/4 of the mesh size and the probability of jumping to the adjacent site can depend on the direction of the jump. The results obtained in the simulations are observed to depend on the fine microscopic aspects of the jump dynamics. For example, the jamming coverage is found to depend on the diffusion coefficient *D*, whereas in Brownian dynamics the effect of *D* is to change the time scale.

IV. CONCLUSIONS

A simplified (1+1)-dimensional adsorption model has been analyzed in order to investigate the kinetics of nonsequential particles adsorption driven by diffusion. We have analyzed, both theoretically and by nonsequential Brownian simulations, the irreversible adsorption of diffusing hard disks onto a line. The most interesting feature of this model is that the usual hypothesis of sequential adsorption is not valid and a more detailed description of the transport process is required. Thus, this simple model allows us to investigate the coupling between the diffusive transport from the bulk and the blocking effect due to the adsorbed monolayer.

The theoretical analysis was performed by noting that any adsorption event must take place into a free gap limited by two adsorbed particles. However, the diffusive transport towards the interface is influenced not only by the particles limiting the gap, but also by the remaining part of the monolayer. To deal with this many-body effect, we have introduced an effective medium hypothesis: the remaining of the adsorbing line out of a given gap is assumed to be at an uniform concentration $c_{EM}(\theta)$ to be determined in a self-consistent way. Once the diffusion equation near an adsorbing gap surrounded by the effective medium is solved, the adsorption rate is obtained by analyzing the dynamics of gaps creation and destruction. This description leads to an integrodifferential equation for the gap density coupled with a self-consistent condition for the adsorption rate, which we have solved numerically.

The effective medium adsorption rate is in agreement both with known approximate expressions valid at low- and near-saturation coverages as well as with nonsequential computer simulations. Thus, the effective medium approximation gives accurate results at all monolayer densities. We also note that our results show an enhanced blocking effect as compared with an RSA process.

The full analysis of a consistent approach to nonsequential adsorption processes, which includes transport mechanisms and interaction with the interface, is a very complicated problem because it requires us to take into account simultaneous interactions between a large number of particles. The main goal of this paper is to show explicitly, in a simplified case, that the interaction with the adsorbed monolayer can be modeled as an effective medium, to be specified self-consistently *a posteriori*. Such an approach can also be useful for the study of more complex models, including other transport processes [20,21].

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APPENDIX: SOLUTIONS OF THE DIFFUSION EQUATION IN BIPOLAR COORDINATES

In this Appendix, we obtain explicitly the solutions $F_1(\vec{r},h)$ and $F_2(\vec{r},h)$ of the diffusion equation (2) required in Sec. III. To this end, we introduce bipolar coordinates ξ, η centered at the center of region I ($x=0$, $z=0$) defined by [22]:

$$x+iz=i\sinh\alpha\cot\left[\frac{\xi+i\eta}{2}\right], \tag{A1}$$

where the parameter α is related to the gap size h by $2\cosh\alpha=h+1$. The curves $\eta=\text{const}$ are semicircles centered at $x=\sinh\alpha\coth\eta$, $z=0$ with radius $r=\sinh\alpha/\sinh\eta$. The point $\xi=0,\eta=0$ corresponds to $z=\infty$. For $\eta=\pm\alpha$ we obtain two semicircles, which coincide with the circumferences of the exclusion disks of unit radius delimited by the adsorbed particles. In these coordinates, the diffusion equation now reads as

$$\frac{\partial^2 F_j}{\partial\eta^2}+\frac{\partial^2 F_j}{\partial\xi^2}=0. \tag{A2}$$

Both functions $F_1(\vec{r},h)$ and $F_2(\vec{r},h)$ verify Eq. (A2) with the boundary conditions of perfect sink at region I and zero radial flux at the excluded surfaces delimited by the two adsorbed particles. In bipolar coordinates these conditions are given by

$$F_j(\vec{r},h)|_{\xi=\pi}=0, \tag{A3}$$

$$\left.\frac{\partial F_j}{\partial\eta}\right|_{\eta=\pm\alpha}=0. \tag{A4}$$

First, we obtain the function $F_1(\vec{r},h)$. In addition to Eqs. (A2), (A3), and (A4), it also verifies the condition of perfect sink in region II,

$$F_1(\vec{r},h)|_{\xi=0}=0, \tag{A5}$$

and unit flux towards the adsorbing surface at $z\to\infty$, $F_1(z\to\infty,h)\simeq z$. It is useful to rewrite this last condition in bipolar coordinates in the form [22]

$$F_1(z\to\infty,h)\simeq z=2\sinh\alpha\sum_{n=1}^{\infty}e^{-n|\eta|}\sin n\xi. \tag{A6}$$

The solution of Eq. (A2) with the boundary conditions (A3)–(A6) is separable and can be expanded in terms of the elementary orthogonal solutions of Eq. (A2). The elementary solutions, which verifies Eqs. (A3) and (A5), are of the form $\sin n\xi\cosh n\eta$ [22], and applying the boundary conditions (A4) and (A6) one obtains the coefficients of the series expansion. The result is

$$F_1(\vec{r},h)=z+2\sinh\alpha\sum_{n=1}^{\infty}\frac{e^{-n\alpha}}{\sinh n\alpha}\sin n\xi\cosh n\eta. \tag{A7}$$

Using Eq. (A7) in Eq. (11) we obtain the contribution of F_1 to the rate of adsorbing particles:

$$q^{(1)}(h,h')=1-2(1+\cosh\eta)\sum_{n=1}^{\infty}(-1)^n\frac{ne^{-n\alpha}}{\sinh n\alpha}\cosh n\eta. \tag{A8}$$

The function $F_2(\vec{r},h)$ is obtained in a similar way. In addition to Eqs. (A3) and (A4), $F_2(\vec{r},h)$ verifies the boundary conditions of constant value 1 at region II:

$$F_2(\vec{r},h)|_{\xi=0}=1. \tag{A9}$$

It also verifies the condition of no net flux of particles towards region II. This condition is obtained by assuming at $z\to\infty$ the same concentration as in region II:

$$F_2(\vec{r},h)|_{\xi=0,\eta=0}=1. \tag{A10}$$

The solution of Eq. (A2) with boundary conditions (A3), (A4), (A9), and (A10) is a function only of ξ and has the simple form:

$$F_2(\vec{r},h)=1-\frac{\xi}{\pi}. \tag{A11}$$

Using Eq. (A11) in Eq. (11) we obtain the contribution of F_2 to the rate of adsorbing particles:

$$q^{(2)}(h,h')=\frac{1+\cosh\eta}{\pi\sinh\alpha}. \tag{A12}$$

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