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ARTICLES

Effect of transport mechanisms on the irreversible adsorption of large molecules

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We consider one-dimensional models for the irreversible adsorption of large molecules on a solid surface. The study is motivated by recent simulations of the diffusion random sequential adsorption process in which hard spheres diffuse above an adsorbing surface. We first consider a generalized parking process in which the rate of deposition of a particle within a gap formed by two preadsorbed spheres depends on the width of the gap, but is uniform within a gap. We demonstrate simply that all generalized parking processes, including simple random sequential adsorption (RSA), have the same jamming limit coverage. As a by-product of this analysis, we obtain a recursion formula for the saturation coverage in gaps of finite length. In the second part of the paper, we consider a parking process in which the rate of deposition within a gap varies with position as well as the gap width. To apply the model to diffusion random sequential adsorption (DRSA) we solve the steady state diffusion equation to find the probability density function for the creation of a free interval of width h upon adsorption of a particle in a gap of size h'. The resulting jamming limit coverage, $\theta_\infty=0.7506$, is in good agreement with the numerical simulations of the DRSA process (0.7496), but larger than that of simple RSA (0.7476).

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I. INTRODUCTION

When a solid surface is exposed to a suspension of latex spheres, an adsorption process often ensues and the surface becomes coated with at least a monolayer of particles. This example is illustrative of a number of similar phenomena underlying many natural and industrial processes including filtration, water cleansing, biofouling, and chromatography. In developing quantitative descriptions of these adsorption processes, one must account for the transport process of the particles from the bulk to the surface, the interactions between the surface and the adsorbing particles, and the interactions between the adsorbed particles and those in the vicinity of the surface. The latter, which result in a rapidly diminishing rate of adsorption with increasing surface coverage, are difficult to account for theoretically. Furthermore, since the adsorption of large molecules and microparticles is often irreversible, one cannot necessarily use the methods of equilibrium statistical mechanics.

Recently, there has been considerable interest in the random sequential adsorption (RSA) process and its possible application to adsorption phenomena. The idea of this model is very simple: particles are added randomly and sequentially to a surface. No overlap is permitted and no relaxation via surface diffusion or desorption is possible. From various computer simulation studies it is known that the saturation coverage of configurations of hard spheres generated by an RSA process is 54.7% [1,2]. This value agrees rather well with the experimental estimate of Onoda and Liniger [3] for the saturation coverage of latex spheres on a silica surface (55% coverage), suggesting that RSA is at least a reasonable starting point for the development of theoretical descriptions.

However, that the agreement between experiment and simulation is so good is actually rather puzzling, in view of the simplicity of the RSA process. In particular, the algorithm as described above incorporates the transport mechanism of the particles from the bulk to the surface very crudely: if an incoming particle overlaps with an adsorbed particle, the incoming particle is rejected and a new attempt is made in a new position completely uncorrelated with the last. This is an unlikely mechanism, particularly at low densities where an initially rejected particle is still likely to find room on the surface in a nearby location.

A more realistic model, which specifically includes a transport mechanism, has recently been proposed in which the deposition is represented as a diffusion adsorption of hard spheres [4–6]. In simulations of diffusion-random sequential adsorption (DRSA) adsorbed configurations of hard spheres are built up by a number of independent random walks from the bulk to the surface. Each trajectory is initiated by placing the sphere center randomly in a place at a height of $\frac{3}{2}$ diameter above the adsorbing surface. The sphere either eventually adsorbs, or it reaches an upper plane (at $\frac{5}{2}$ particle diameters), in which case it is discarded. Remarkably, the structure, as characterized by the radial distribution function, and coverage of *jammed configurations* generated by this process were found to be indistinguishable from those generated by the simple RSA processes [5,6]. At all lower coverages, however, the structures generated by the two processes are different.

In order to explain this result, Tarjus and Viot [7] considered a generalized parking process in which particles deposit on an infinite line. Like the simple car parking problem [8], the rate of deposition per unit length of the line is uniform within a gap formed by two adsorbed particles. However, in contrast to simple RSA, the rate of deposition per unit length depends on the size of the gaps. This feature is incorporated to reflect the fact that in DRSA a diffusing particle is channeled down a narrow gap. By considering the kinetics of gap formation and destruction, Tarjus and Viot demonstrated that jammed configurations produced by a generalized parking process are independent of the rate of deposition and hence are identical to those of the one-dimensional (1D) RSA process on a line [7]. In the first part of this paper, we present a simpler and more intuitive proof of this equivalence.

Subsequent to the developments described above, a careful simulation study of 1D DRSA [13] revealed that the saturation coverage of this process (0.7529) is slightly, but significantly, larger than that of simple 1D RSA (0.747). The reason for this discrepancy was clearly evident in the simulation results: the diffusion process leads to a nonuniform distribution of particles within the available gaps. In Sec. III of this paper, we extend the generalized parking process to allow for this possibility and compute the saturation coverage which results from an adsorption rate found from an approximate solution of the steady state diffusion equation.

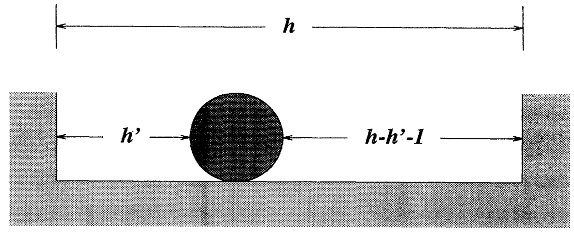

FIG. 1. Illustration of the adsorption process. A disk is inserted in a gap of length h to produce two smaller gaps.

II. GENERALIZATION OF THE RSA MODEL

In the generalized car parking process, disks of diameter 1 are randomly and sequentially deposited onto an infinite line. Unlike the standard parking problem, the rate of deposition per unit length of the surface is not a constant. Rather, it depends on the interval between two preadsorbed disks in which one tries to insert a new disk. If $G(h,t)dh$ is the number of gaps between h and $h+dh$ at time t and $k(h)$ is the rate of adsorption per unit length in an interval of length h, then one may write down a governing kinetic equation for the adsorption process:

$$\frac{\partial G(h,t)}{\partial t} = -k(h)(h-1)G(h,t) + 2\int_{h+1}^{\infty} k(h')G(h',t)dh' \ . \quad (1)$$

It is implicit in this equation that newly arriving disks are distributed uniformly within the gap of length h, i.e., all positions within the gap are equiprobable. In simple RSA, $k(h)=H(h-1)$ where $H(x)$ is the Heaviside unit step function. The introduction of the factor $k(h)$ is merely to account for the fact that, in a diffusion process, small gaps are occupied at a faster rate per unit length than larger ones because the disks colliding with the fixed particles can diffuse down a channel with acts as a funnel as shown by Schaaf, Johner, and Talbot [4] for a two-dimensional model.

Although Tarjus and Viot [7] have already proved that the properties (structure and coverage) of the jammed state are independent of $k(h)$, we present here a simpler explanation of this result. Let us consider the problem of disks adsorbing irreversibly on a line segment of length h (see Fig. 1). Following the usual RSA rule, we wish to determine the average number of disks that are in this gap after an infinite time, $N_\infty(h)$. A key observation is that insertion of one disk into the gap at length h produces two additional gaps of length h' and $h-h'-1$. Therefore, one may write the following recursion formula:

$$N_\infty(h) = 1 + 2\int_0^{h-1} N_\infty(h')P(h,h')dh' \ , \quad (2)$$

where $P(h,h')$ is the probability that insertion of a disk into the gap of length h produces gaps of length h' and $h-h'-1$. Now in the generalized parking problem, of which RSA is a specific case,

$$P(h,h')=1/(h-1)\ , \tag{3}$$

since all positions of the new disk are equiprobable. Thus the final state of the system does not depend on the adsorption rate, $k(h)$, and we conclude that all generalized parking problems, including simple RSA, have the same jamming limit (0.747 in one dimension).

Equation (2) has an interesting by-product. Clearly, we know the initial solutions,

$$N_\infty^{(1)}(h)=0\ ,\quad 0\le h<1\ , \tag{4}$$

$$N_\infty^{(2)}(h)=1\ ,\quad 1\le h<2\ , \tag{5}$$

where $N_\infty^{(i)}(h)$ means $N_\infty(h)$ at $i-1\le h<i$.

Now, representing explicitly the piecewise function,

$$\begin{aligned}N_\infty^{(k)}(h)=1&+\frac{2}{h-1}\int_0^1 N_\infty^{(1)}(h')dh'\\&+\frac{2}{h-1}\int_1^2 N_\infty^{(2)}(h')dh'+\dots\\&+\frac{2}{h-1}\int_{k-2}^{h-1} N_\infty^{(k-1)}(h')dh'\ ,\quad k-1\le h<k\ .\end{aligned} \tag{6}$$

In particular,

$$\begin{aligned}N_\infty^{(k)}(k)=1&+\frac{2}{k-1}\int_0^1 N_\infty^{(1)}(h')dh'+\dots\\&+\frac{2}{k-1}\int_{k-2}^{k-1} N_\infty^{(k-1)}(h')dh'\ .\end{aligned} \tag{7}$$

It follows, therefore, that

$$\begin{aligned}N_\infty^{(k)}(h)=1&+\frac{k-2}{h-1}[N_\infty^{(k-1)}(k-1)-1]\\&+\frac{2}{h-1}\int_{k-2}^{h-1} N_\infty^{(k-1)}(h')dh'\ ,\quad k\ge 2\ .\end{aligned} \tag{8}$$

Using this form, one can find the following analytic expressions:

$$N_\infty^{(3)}(h)=\frac{3h-5}{h-1}\ ,\quad 2\le h<3\ . \tag{9}$$

$$N_\infty^{(4)}(h)=\frac{-17+7h-4\ln(h-2)}{h-1}\ ,\quad 3\le h<4\ . \tag{10}$$

Higher order functions may be conveniently and accurately computed numerically using the recurrence relation. The mean saturation coverage of particles adsorbed in a confined gap of size h is

$$\theta_\infty(h)=\frac{N_\infty(h)}{h}\ . \tag{11}$$

The result is shown in Fig. 2. From Rényi's original work [8], one has the following asymptotic relation:

$$\theta_\infty(\infty)-\theta_\infty(h)\sim\frac{1}{h}\ . \tag{12}$$

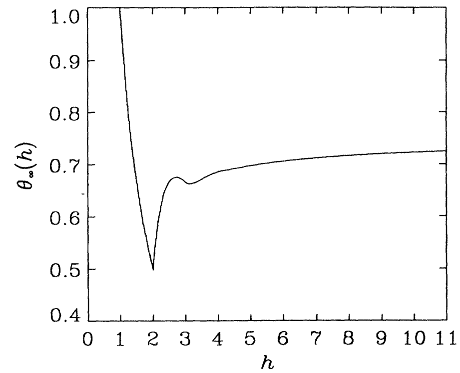

FIG. 2. Saturation coverage of the RSA process in a gap of size h.

Figure 3 shows the complete linear relation between the mean saturation coverage of particles adsorbed on a confined gap of size h, $\theta_\infty(h)$ and the inverse of the size of gap, h when h is greater than about 5. Thus the intersection point of the extrapolation line (represented by dotted line) with the line $1/h=0$ is consistent with the saturation coverage of RSA model, $\theta_\infty(\infty)=0.747\,59\dots$. The recursion formula (12) may find application in the description of adsorption on heterogeneous or step surfaces.

III. NONUNIFORM DEPOSITION OF DRSA

In this section, we describe a general one-dimensional model with nonuniform addition rates. We introduce $k(h',h)$ to denote the probability per unit length and per unit time that deposition of a disk in a gap of length $h'>1$ produces gaps of length h and $h'-h-1$ (the position of the center of the new disk within the gap is thus $x=h+1$ relative to the center of the disk on the left of the gap).

The governing kinetic equation for the adsorption process is (see Fig. 4):

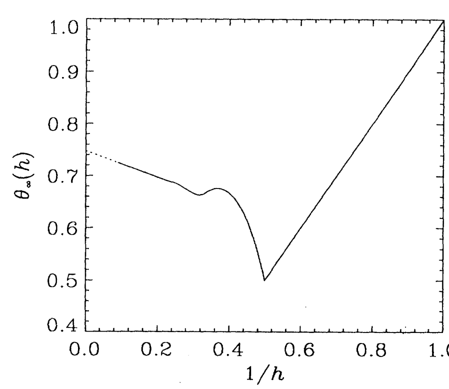

FIG. 3. Asymptotic relation of the mean saturation coverage of particles adsorbed on a confined gap of size h, $\theta_\infty(h)$ with respect to the gap length h (represented by solid line). Extrapolation of the data within the range of $5\le h\le 11$ (represented by dotted line) shows the $\theta_\infty(\infty)=0.747\,603\pm0.000\,013$ when $h\to\infty$.

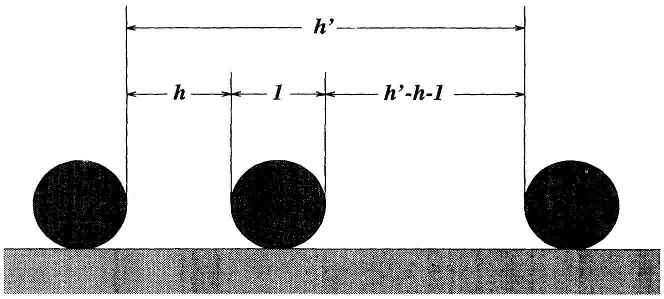

FIG. 4. Illustration of the governing equation for the nonuniform deposition of DRSA.

$$\frac{\partial G(h,t)}{\partial t}=\left[\frac{\partial G(h,t)}{\partial t}\right]_{\text{loss}}+\left[\frac{\partial G(h,t)}{\partial t}\right]_{\text{creation}}$$
$$=-k_0(h)G(h,t)+\int_{h+1}^{\infty}dh'G(h',t)\times[k(h',h)+k(h',h'-h-1)] \;. \quad (13)$$

If the disks are identical, we expect that $k(h',h)$ is a symmetric function, $k(h',h)=k(h',h'-h-1)$. Thus the above equation can be simplified as follows:

$$\frac{\partial G(h,t)}{\partial t}=-k_0(h)G(h,t)+2\int_{h+1}^{\infty}dh'G(h',t)k(h',h) \;. \quad (14)$$

This equation together with the initial condition $G(h,t=0)=0$, and the normalization condition

$$\int_0^{\infty}dh\,(1+h)G(h,t)=1 \quad (15)$$

determines completely $G(h,t)$. The function $k_0(h)$ is the total rate at which gaps of length h are destroyed by the addition of a new particle

$$k_0(h)=\int_0^{h-1}dh'k(h,h') \quad (16)$$

and clearly $k_0(h)=0$ if $h<1$.

The solution of (14) would provide information about the distribution of free gaps along the entire history of the process. However, the distribution in the jammed state can be obtained without knowing the detailed time evolution. This is possible because the final distribution of disks does not depend on the precise time at which a new disk is added to a given gap, but only on the position at which that disk is added. Only the probability of obtaining different small gaps from wider ones is relevant, and not the kinetics of the process. As a consequence, a time independent equation can be derived for the total number of gaps of given length created during the process.

Let $n(h)dh$ be the number of gaps of length between h and $h+dh$ that have been created per unit length at any time along the process. Using the balance equation we have, for $h>0$,

$$n(h)\equiv\int_0^{\infty}dt\left[\frac{\partial G(h,t)}{\partial t}\right]_{\text{creation}}=2\int_{h+1}^{\infty}dh'k(h',h)\int_0^{\infty}dt\,G(h',t) \;. \quad (17)$$

The integration of (17) with respect to h' includes only gaps with $h'>1$. All these gaps are destroyed at the end of the process and therefore one has, for $h'>1$,

$$n(h')=-\int_0^{\infty}dt\left[\frac{\partial G(h,t)}{\partial t}\right]_{\text{loss}}=k_0(h')\int_0^{\infty}dt\,G(h',t) \;. \quad (18)$$

Substituting (18) into (17) gives the integral equation valid for $h>0$,

$$n(h)=2\int_{h+1}^{\infty}dh'P(h',h)n(h') \;. \quad (19)$$

The quantity $P(h',h)$ gives the probability density that the first particle arriving at an interval of length h' creates two new free intervals of length h and $h'-h-1$:

$$P(h',h)=\frac{k(h',h)}{k_0(h')} \;. \quad (20)$$

From the definition of $k_0(h)$, Eq. (16), this function must satisfy the normalization condition

$$\int_0^{h'-1}dh\,P(h',h)=1 \;. \quad (21)$$

Equation (19) is a advanced integral equation from which, in principle, it is possible to obtain $n(h)$ if $P(h',h)$ is known. It expresses the fact that the total number of gaps of length h can be computed from the number of gaps with length $h'>h+1$ and the probability of obtaining an interval on length h from an interval of length h'. That equation must be supplemented by a normalization condition that can be obtained from the normalization of $G(h,t)$. Noting that, for $t\to\infty$, $G(h,t)\to 0$ for $h>1$ and $G(h,t)\to n(h)$ for $h<1$, Eq. (15) reduces in this limit to

$$\int_0^1 dh\,(1+h)n(h)=1 \;. \quad (22)$$

Once $n(h)$ has been determined the final coverage can be obtained as

$$\theta_\infty=\int_0^1 dh\,n(h) \;. \quad (23)$$

In the case of simple RSA, $P(h',h)=1/(h'-1)$. One has then

$$n(h)=2\int_{h+1}^{\infty}dh'\frac{n(h')}{h'-1} \;. \quad (24)$$

This equation can be exactly solved by the Laplace transformation (see the Appendix). The result for $n(h)$,

$$n(h)=2\int_0^{\infty}s\exp\left[-hs-2\int_0^s dt(1-e^{-t})/t\right]ds \;, \quad (25)$$

coincides for $h<1$ with the known expression for the density of gaps at the jamming limit [9]. The expression first found by Rényi is obtained for θ_∞. On the other hand, the limiting case of nonuniform deposition is the ballistic deposition (BD) process in which the depositing particles follow the path of steepest descent by rolling over adsorbed particles [10]. In this case, the probability density function is the sum of two δ functions which have peaks at the two ends of a gap. From this probability density function, it is possible to calculate the saturation coverage of BD and that of the generalized ballistic deposition (GBD) process [11] that interpolates between RSA and BD. Unfortunately, it is not possible to solve analytically more general models, like DRSA. In this case, a numerical solution of Eq. (19) must be envisaged.

An iterative method can be used in order to solve Eq. (19) numerically. Starting from a first approximation of $n(h)$, $n_0(h)$, a sequence of new approximations is generated by the recursion formula

$$n_{k+1}(h)=2\int_{h+1}^{\infty}dh'P(h',h)n_k(h') . \quad (26)$$

Note that, in order to determine the function $n_k(h)$ for $h>0$, it is sufficient to know the values of $n_{k-1}(h)$ for $h>1$; these values can be obtained from the values of $n_{k-2}(h)$ for $h>2$ and, after k steps, one needs the values of $n_0(h)$ for $h>k$ only. Then, a good approximation to $n(h)$ in the interval of interest, $0\le h\le 1$, can be obtained after a sufficient number of iterations from a first approximation valid for large values of h.

To obtain this first approximation, some assumption about the deposition process on large intervals is needed. Then, we assume that the rate of arrival of new particles to points in a gap of length $h'\gg 1$, $k(h',h)$, depends on the arrival point as a consequence of the interaction between the arriving particles and the particles already adsorbed at the ends of the gap. If these interactions decay sufficiently fast with distance, the importance of this inhomogeneity must be very small for large intervals, and one can approximate $P(h',h)$ by a value independent of h that, in view of the normalization (15), must be $P(h',h)\approx 1/(h'-1)\approx 1/h'$. Then, to leading order in h^{-1}, Eq. (19) is satisfied by $n(h)\approx Kh^{-2}$.

The recursion formula (26) can taken be integrated numerically in order to obtain successive approximations to $n(h)$ starting from $n_0(h)=1/h^2$. After k iterations an approximation of order k, $n_k(h)$, will be obtained. This function is not normalized, because the condition (23) has not yet been taken into account. The corresponding approximation to the coverage at the jamming limit can be obtained as

$$\theta_\infty^{(k)}=\frac{\int_0^1 dh\, n_k(h)}{\int_0^1 dh\,(1+h)n_k(h)} . \quad (27)$$

To obtain the rate of arrival of Brownian disks at any point of the line (see Fig. 5), it is necessary to solve the diffusion equation for the probability distribution of the position of the center of the new diffusing particle, $\Psi(r,\theta)$,

$$\nabla^2\Psi=0 , \quad (28)$$

where the assumption of the quasisteady state is applied, with an adsorbing boundary along the line,

$$\Psi=0 \text{ at } z=0 , \quad (29)$$

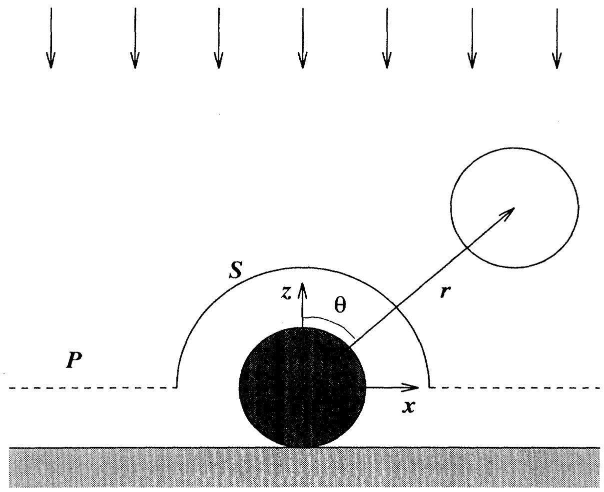

FIG. 5. Illustration of the diffusion of a Brownian disk at the distance r away from a preadsorbed disk. S and P are reflecting and adsorbing boundaries, respectively.

and reflecting boundaries at the exclusion surfaces of the preadsorbed disks:

$$\frac{\partial\Psi}{\partial r}=0 \text{ at } r=1 . \quad (30)$$

Far from the surface, we assume a uniform flux of incoming particles, $\vec{J}=-J_\infty\vec{z}$ in Cartesian coordinates and $J_r=J_\infty\cos\theta$, $J_\theta=J_\infty\sin\theta$ in polar coordinates,

$$J_\infty^2=J_r^2+J_\theta^2=\text{constant as } r\to\infty . \quad (31)$$

Then, the rate of arrival of new disks at a given point depends on the distribution of previously adsorbed disks on the entire line. Nevertheless, it is natural to assume that only the nearest disks, i.e., those located at the ends of the free gap, have a noticeable influence.

If only one disk has been adsorbed, the steady solution of the diffusion equation is, using polar coordinates centered at the center of the fixed disk,

$$\Psi(r,\theta)=J_\infty(r+1/r)\cos\theta , \quad r>1 \quad (32)$$

from which one obtains the rate of arrival of new disks at a point at distance r from the center, $J(r)|_{z=0}=-D(\partial\Psi/\partial z)_{z=0}=J_\infty(1+1/r^2)$. The flux of disks increases in the vicinity of the origin ($r>1$) as a consequence of reflecting from the fixed disk.

Now, in the absence of disks, $J=J_\infty$. If two disks are present, we assume as a first approximation that the deviations from this value produced by each disk are independent and can be added. Therefore, the approximation to $J(r)$ should be $J(r)\approx 1+1/r_1^2+1/r_2^2$, r_1 and r_2 being the distances to the centers of each disk. After normalization one finds

$$P_1(h',h)=\frac{h'}{(h'-1)(h'+2)} \times[1+(h+1)^{-2}+(h'-h)^{-2}] . \quad (33)$$

Then, a first approximation to the DRSA process is obtained using P_1 as valid for any value of h' and h in Eq.

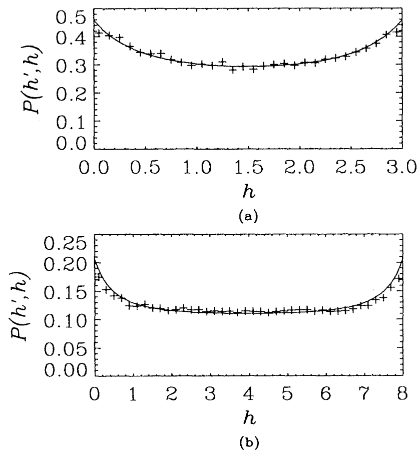

FIG. 6. Comparison of probability density $P(h,h')$ calculated from Eq. (33) with the Monte Carlo simulation result obtained from Senger *et al.* [13]. (a) $h=4$, (b) $h=9$.

(19). This approximation $P_1(h',h)$ is compared with the DRSA results obtained from Senger *et al.* [13] (see Fig. 6). Even though there is a slight discrepancy at each side of gap, this first approximation still shows good agreement with the DRSA results. The numerical computation of using (26), (27), and (33) leads to a value of the final coverage $\theta_\infty \approx 0.750\,65$, slightly greater than the RSA results, 0.747 59. . . . The recursion relation (2) and (11) together with the above first approximation (33) can also give us the saturation coverage of this process. As we did previously in case of RSA, we plot $\theta_\infty(h)$ with respect to the inverse of h: see Fig. 7. From the extrapolation of this curve to $1/h=0$, we obtain $\theta_\infty = 0.750\,621 \pm 0.000\,022$ confirming that both methods give the same coverage values. Once we know the functional form of $P(h',h)$ of any model, we can obtain its saturation coverage with either procedure. Integration and extrapolation with (2), (11), and (12) seems to be rather easier than numerical calculation by using (26) and (27) without loss of accuracy.

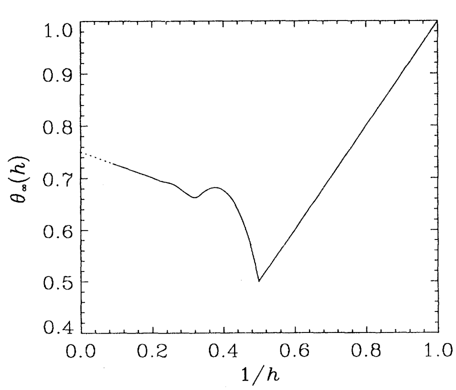

FIG. 7. Asymptotic behavior of the mean saturation coverage of particles adsorbed on a confined gap of size $h, \theta_\infty(h)$ (solid line). Extrapolation of the data within the range of $5 \leq h \leq 11$ (represented by dotted line) yields $\theta_\infty(\infty) = 0.750\,621 \pm 0.000\,022$.

In order to assess the accuracy of the independent disk assumption used alone, we have also constructed the exact solution of the deposition problem in the presence of two disks. We take the x axis as the line passing through the centers of the adsorbed disks, and the y axis as its perpendicular through the center of the gap (Fig. 8). In this coordinate system, the center of the fixed particles is located at $x=\pm L/2$, where $L=h+1$ is the separation. The center of the diffusing particle is excluded from a region of radius unity around these points.

The bipolar coordinates ξ, η are defined through

$$x+iy=ic\cot\left[\frac{\xi+i\eta}{2}\right], \tag{34}$$

where c is a free parameter, to be specified.

The curves $\eta=$ constant are semicircles centered at $x=c\coth\eta$, $y=0$, and radius $r=c/\sinh\eta$. For $\eta=\pm\alpha$, two of these curves coincide with the circumferences of the exclusion disks, of radius unity and located at $x=\pm L/2, y=0$. This happens if $\cosh\alpha = L/2$ and $c=\sinh\alpha=\sqrt{(L/2)^2-1}$.

The diffusion equation now reads as

$$\frac{\partial^2\Psi}{\partial\eta^2}+\frac{\partial^2\Psi}{\partial\xi^2}=0\ . \tag{35}$$

The boundary conditions are

$$\Psi=0 \quad \text{at } \xi=0,\pi\ , \tag{36}$$

and

$$\frac{\partial\Psi}{\partial\eta}=0 \quad \text{at } \eta=\pm\alpha\ . \tag{37}$$

Therefore the problem is separable. The normalized result for the particle flux in the region between the disks is given by the convergent series

$$J=\frac{1}{2c}\left[1+2(1+\cosh\eta)\sum_{n=1}^{\infty}\frac{(-1)^{n+1}ne^{-n\alpha}}{\sinh n\alpha}\cosh\eta\right]\ . \tag{38}$$

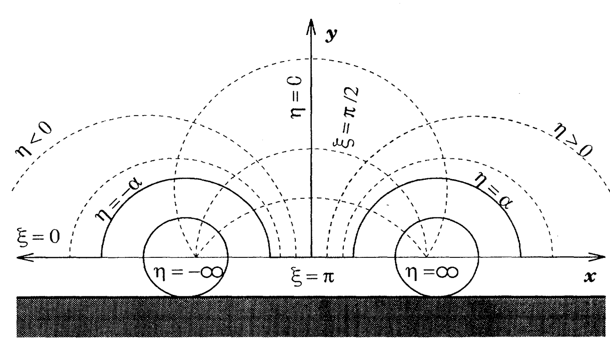

FIG. 8. Two adsorbed particles displayed in the bipolar coordinate system.

This J is exactly the function P_2. It depends on $h'=L-1$ through the coefficients α and c and on h through the coordinate η of the arriving point. ($x=c\tanh\eta/2$ and $h=L/2-x-1$).

Then, one finds that the total rate of deposition in an interval of length h is substantially modified for $h=1\ll 1$, but for such small gaps the relative probability of arrival at different points is nearly uniform. After inserting (28) into (26) and computing numerically, one finds a value of the coverage $\theta_\infty \approx 0.751\,02$, only slightly different from the result obtained with $P_1, \theta_\infty \approx 0.750\,65$. Thus even a first approximation can be enough to estimate the jamming coverage of the DRSA process.

Figure 9 represents the number density $n(h)$ of gaps with size $0<h<1$ at the jamming limit which are obtained from two different methods: the numerical calculation of (26) (solid line) and simulation in a lattice system (triangular points) [13]. The gap density functions obtained from both methods show good agreement over the whole gap sizes. The numerical simulations, which consist of the coverage of 2500 lines of length equal to 50 diameters after diffusion on a lattice with a lattice parameter of 0.005, gave a value of $\theta_\infty = 0.7529 \pm 0.0010$ [13]. The discrepancy with the result of the calculation is probably due to the fact that the theory presented here assumes *continuous* Brownian trajectories of moving particles, whereas the simulations are performed for *discrete* trajectories of particles following lattice spacings. This discrepancy can be corrected by finite-size scaling [Eq. (28) in [14]] of the results for various lattice constants

$$\theta_\infty(l/R,\infty)-\theta_\infty(l/R,R/a)\sim\frac{1}{(R/a)}\,, \qquad (39)$$

where l is the length of the adsorbing segment, R is the radius of a particle, and a is the lattice spacing (see Fig. 10). The jamming coverage at $R/a\to\infty$ is $\theta_\infty(l/R=100,\infty)=0.7496\pm0.0014$, which shows good agreement with the value obtained from the approximations (33) and (38). However, since the simulations per-

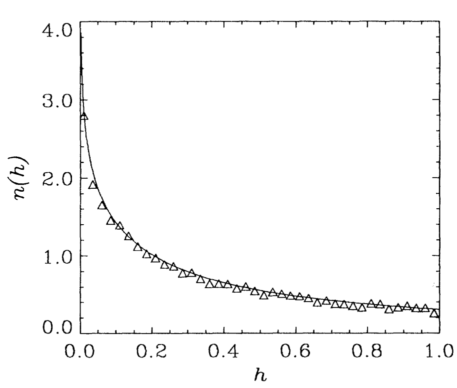

FIG. 9. Gap distribution function at the jamming limit. The solid line was obtained from the second approximation (38) in the bipolar coordinate system, while the triangular points were obtained from the simulation in a lattice system.

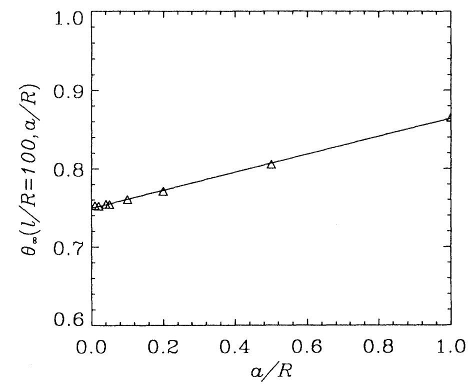

FIG. 10. Finite size scaling of the jamming coverages of the DRSA simulations [13] with the change of the lattice spacings. The solid line shows a least-squares fit of the scaling relation (39).

formed for a *finite* system to which periodic boundary conditions were applied, while the theory presented here assumes an infinite line, the simulation value still shows a small deviation from the theoretical value. We can guess that the coverage of the finite line depends on the system size and approaches the asymptotic limit when increasing the system size.

IV. CONCLUSION

The mechanism by which the particles arrive at the surface in irreversible adsorption processes will, in general, affect the kinetics and the saturation coverage. In this paper, we have attempted to develop some insight into this dependence by studying one-dimensional models of the adsorption process. If the rate of deposition depends only on the size of the gap between two preadsorbed particles, the jamming coverage is the same as in simple RSA (0.747 59. . . in 1D), but if the rate of deposition varies with the position of the adsorbing particle in the gap, the jamming coverage can be considerably different from that of simple RSA. As an extreme case, ballistic deposition (BD) [10] has a singular component of the deposition rate at each end of the available gaps (plus a uniform rate within) which results from the rolling mechanism, and has a saturation coverage of 0.808. . . .

We have developed a general kinetic equation for nonuniform deposition processes (14) and recursion formulas for the saturation coverage, (2) and (26). In DRSA, the nonuniformity is induced by the diffusion of the adsorbing molecules. The deposition probability in the DRSA model has been calculated at two levels of approximation. In the simplest, the influence of the two disks bounding a gap on the diffusing particle is taken as an additive. The saturation coverage obtained from this approach does not differ greatly from that corresponding to the exact analytic solution in the presence of two disks. These results are also consistent with numerical simulations of the DRSA process, if proper allowance (throughout a scaling relation) is taken of the finite lattice of the simulation. Moreover, the position dependent flux of the particles obtained from the simple approximate solution (38) of the diffusion equation is consistent with the data obtained from the numerical simulation of DRSA. The saturation coverage calculated from the theory, Eqs. (26), (27), and (33) is consistent with the value obtained from numerical simulations of the DRSA process if one property accounts for the finite lattices of the simulations.

If hydrodynamic interactions are included in the DRSA process, the distribution is more uniform than with diffusion alone [15] because of the enhanced mobility parallel to the surface. Hence, one would expect the generalized parking process (with a uniform distribution) to be a good description in this case. In a BD process, which takes into account the hydrodynamic interactions [16], it has been shown that while the jamming coverage (0.797) does not change significantly, the local structure is strongly affected by the hydrodynamic interactions and the rate of deposition still shows strong nonuniform behavior. Although in this paper the only nonuniform deposition process studied has been DRSA, our method can be applied to other, more realistic models. The extension of this method is under way.

Since our method has been applied to a $1+1$ dimensional system, a direct comparison with the experimental results is not possible. However, we can make a few comments about some relevant experimental studies. Wojtaszczyk *et al.* [12] used an image analysis technique to examine the structure of particle deposits and showed that the BD model could be considered as an acceptable starting point for the adsorption of rather large particles (radius $>2\ \mu$m). For smaller particles (radius $<0.5\ \mu$m), the RSA model provides a good description of the experimental results (Fig. 53 in [17]). However, we expect that the extension of our model to $2+1$ dimensions will permit an improved description of the structure and kinetics of the deposition process.

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APPENDIX: SOLUTION OF INTEGRAL EQ. (24)

In the case of RSA,

$$n(h)=2\int_{h+1}^{\infty}dh'\frac{n(h')}{h'-1}\ , \tag{A1}$$

differentiating and rearranging yields

$$\frac{d}{dh}[hn(h)]-n(h)=-2n(h+1)\ . \tag{A2}$$

Let

$$n(h)\equiv\int_0^{\infty}ds\,e^{-hs}F(s)\ . \tag{A3}$$

Since, if $F(0)=0$,

$$hn(h)=\int_0^{\infty}ds\,e^{-hs}F'(s)\ , \tag{A4}$$

after substituting (A3) and (A4) into (A2), we obtain

$$\frac{d}{dh}\int_0^{\infty}ds\,e^{-hs}F'(s)-\int_0^{\infty}ds e^{-hs}F(s)=-2\int_0^{\infty}ds e^{-(h+1)s}F(s)\ . \tag{A5}$$

After differentiating the first term of (A5),

$$\int_0^{\infty}ds\,e^{-hs}(-s)F'(s)-\int_0^{\infty}ds\,e^{-hs}F(s)=-2\int_0^{\infty}ds\,e^{-(h+1)s}F(s)\ . \tag{A6}$$

Thus we finally obtain the following differential equation:

$$sF'(s)+F(s)=2e^{-s}F(s)\ . \tag{A7}$$

The general solution of (A7) is

$$F(s)=Ks\exp\left[-2\int_0^{s}dt\frac{1-e^{-t}}{t}\right]\ . \tag{A8}$$

Hence,

$$n(h)\equiv K\int_0^{\infty}ds\,s\exp\left[-hs-2\int_0^{s}dt\frac{1-e^{-t}}{t}\right]\ . \tag{A9}$$

Let

$$G(s)=\int_0^{s}dt\frac{1-e^{-t}}{t}\ . \tag{A10}$$

Then, the normalization condition (22) implies

$$\begin{aligned}K^{-1}&=\int_0^{\infty}ds\,s\,e^{-2G(s)}\int_0^{1}dh\,(1+h)e^{-hs}=\int_0^{\infty}ds\,s\,e^{-2G(s)}\left[1-\frac{d}{ds}\right]\frac{1-e^{-s}}{s}\\&=\int_0^{\infty}ds\,e^{-2G(s)}[(2s+1)G'(s)-1]\\&=\int_0^{\infty}ds\,(s+\tfrac{1}{2})\left[-\frac{d}{ds}e^{-2G(s)}\right]-\int_0^{\infty}ds\,e^{-2G(s)}=-(s+\tfrac{1}{2})e^{-2G(s)}\Big|_0^{\infty}=\tfrac{1}{2}\ .\end{aligned} \tag{A11}$$

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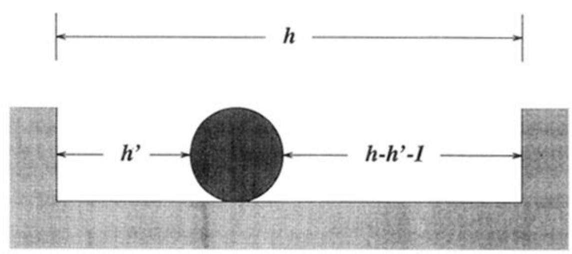

FIG. 1. Illustration of the adsorption process. A disk is inserted in a gap of length h to produce two smaller gaps.

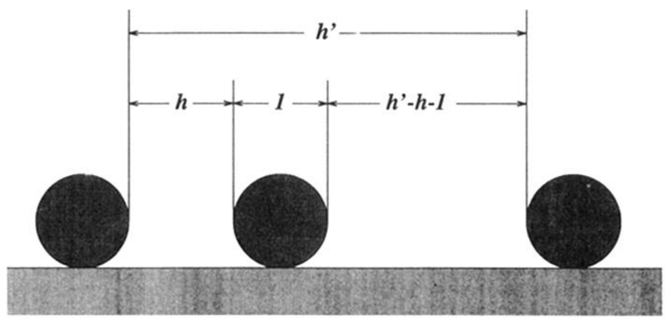

FIG. 4. Illustration of the governing equation for the nonuniform deposition of DRSA.

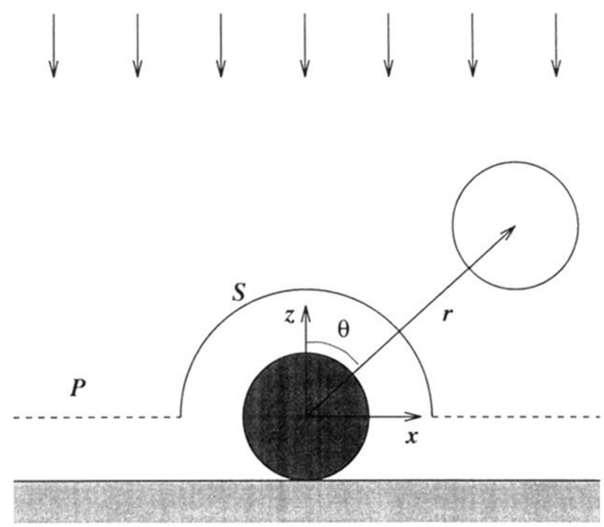

FIG. 5. Illustration of the diffusion of a Brownian disk at the distance r away from a preadsorbed disk. S and P are reflecting and adsorbing boundaries, respectively.

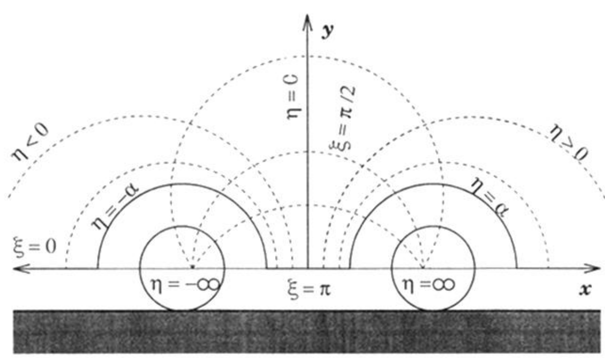

FIG. 8. Two adsorbed particles displayed in the bipolar coordinate system.