A solvable model for irreversible adsorption of large particles

1998 J. Phys. A: Math. Gen. 31 73

(http://iopscience.iop.org/0305-4470/31/1/012)

J. Phys. A: Math. Gen. **31** (1998) 73–83. Printed in the UK PII: S0305-4470(98)85914-3

A solvable model for irreversible adsorption of large particles

Jordi Faraudo† and Javier Bafaluy‡
Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain

Received 14 July 1997, in final form 15 September 1997

Abstract. In this paper we propose and solve analytically a class of models generalizing the ballistic deposition (BD) model for irreversible adsorption of hard particles onto a line. In these new models, when an incoming particle interacts with an adsorbed one, it adsorbs next to it leaving between them a small gap of random size with characteristic length λ. The first moments of the gap distribution suffice to describe the lowest-order corrections to the BD model. In particular, for small values of λ we obtain an asymptotic approach to the BD jamming coverage in agreement with previous Brownian simulations which take into account diffusion and gravity.

1. Introduction

Recently, great effort has been devoted to the development of models describing the adsorption of colloidal particles and macromolecules on solid surfaces [1–5]. Often, these particles adsorb irreversibly forming monolayers on which the particles can neither desorb nor diffuse. Realistic models must take into account the transport of the particles from the suspension to the interface and their interaction with the substrate (including the previously adsorbed particles). Several models, accounting for different transport processes, have been introduced to describe these phenomena.

The simplest model is based on a geometric rule for the addition of new particles, the random sequential adsorption (RSA) algorithm: new particles are sequentially added to the surface at random positions, and those overlapping previously adsorbed particles are rejected. This model is simple enough to allow an exact solution on one-dimensional surfaces [6, 7] and approximate solutions and extensive simulations on higher dimensions [8–10]. The RSA model has been shown to reproduce well the spatial distribution of small latex particles adsorbed on solid surfaces [11], although the corresponding kinetic law is not realistic.

Recent experimental results [11] on the adsorption of large colloidal particles show that both the structure of the adsorbed layer and the kinetics of the process are well described by the ballistic deposition (BD) model: the particles approach the surface following randomly chosen vertical trajectories; if they touch an adsorbed particle, then they follow the steepest descent path until they reach the surface and are adsorbed or they are trapped in a stable position over the monolayer of adsorbed particles and are rejected. This mechanism can be reduced to a set of geometric rules for the adsorption or rejection of new particles [12, 13],

† E-mail address:jordi@ulises.uab.es
‡ E-mail address:javier@ulises.uab.es

and can be exactly solved on one-dimensional surfaces [14, 15] and efficiently simulated on higher dimensions.

Models that consider more general transport mechanisms, in particular diffusion [16, 17], diffusion and gravity (DRSAG model) [18–20], hydrodynamic interactions [21, 22] and colloidal forces [23] have also been analysed. In these models the trajectory of each particle needs to be simulated using a Brownian dynamics algorithm [24]. Consequently, the simulations are much more computationally expensive than those corresponding to the geometrical models, and analytic results are difficult to obtain even for one-dimensional models.

It would be useful to have models that, following geometric rules for the positioning of new particles such as the RSA or BD model, could reproduce the main results of the transport models in a much more economical way. Centring our attention on the geometric distribution of the adsorbed particles, the final effect of the transport mechanisms is to modify the adsorption probability at different points of the surface, depending on the vicinity of pre-adsorbed particles. For example, if colloidal forces between particles are important, it has been suggested that new particles adsorb according to a Boltzmann distribution [25]; in this case, each particle alters the adsorption probability in a region of size comparable with the range of the interaction potential. A similar effect is also observed in particles which adsorb after diffusing in a gravitational field (the DRSAG model). If we consider sufficiently large particles for which gravity becomes dominant, they tend to roll over the already adsorbed ones, being adsorbed in their close vicinity. If one defines the dimensionless particle radius R^* (which quantifies the relative relevance of diffusion and gravity) as:

$$R^* \equiv R\left(\frac{4\pi g\Delta\rho}{3k_BT}\right)^{1/4} \tag{1}$$

then the adsorption probability is enhanced in a region with a characteristic length of order $(R^*)^{-8/3}$ [20]. When gravity becomes infinitely strong ($R^* \to \infty$) this region collapses to the point of contact between the particles, recovering the BD limit.

In this paper our aim is to develop a geometrical model similar to the BD model but taking into account in an effective way the deviation which incoming particles suffer after interacting with fixed particles. We assume that, when such an interaction occurs, due to the effect of the different forces and transport mechanisms, the incoming particle adsorbs near the fixed one in a region of size λ around the fixed one. No explicit form for the probability distribution of adsorption at distance h, $\Delta(h)$, is supposed, we only require that it must be zero out of the region of size λ. These assumptions are satisfied in the adsorption of colloid particles with short-range interactions [1], or in the deposition of large particles [20, 22].

The study of the model is carried out in $(1+1)$ dimensions, which allows us to obtain analytic results when λ is smaller than the radius of the particles. As expected, in the limit $\lambda \to 0$ we recover the BD model. When the characteristic distance λ is small we can obtain corrections to the BD kinetics up to any desired order $O(\lambda^n)$. This approximation depends only on the first n moments of $\Delta(h)$. This property makes the results useful, because in models in which transport effects are taken into account the functional form of $\Delta(h)$ is usually unknown, but its first moments can be computed from simulations or approximate methods. The usefulness of this method is illustrated by applying it to the DRSAG model when gravity is strong enough ($R^* \gg 1$). In this case, the mean deviation of an incoming particle after interacting with a fixed one has been computed both from singular perturbation arguments and simulations [20].

This paper is organized as follows. Section 2 is devoted to the description of the model and its basic equations. In section 3 we solve the kinetic equation and corrections to the BD kinetics are obtained and applied to the DRSAG model. The possibility of a universal kinetic curve for all these models, as suggested by experimental results, is discussed. Section 4 is devoted to conclusions.

2. Description of the model

We consider an irreversible deposition model in which disks of unit diameter are sequentially added to an initially empty line. The arrival rate of new disks is supposed to be constant, and can be fixed to one per unit length and unit time by suitably choosing the unit of time. As in the BD model, we assume that when an incoming particle is trapped into a gap of size less than one particle diameter it needs a very large time to escape from it and thus is rejected.

In the BD model it is also assumed that incoming particles which reach the adsorption line after touching on a previously adsorbed one follow the steepest descend path, adsorbing in contact with it. In our model, we generalize this adsorption rule assuming that the transport mechanisms lead to the adsorption of the new particle near the fixed one, provided that enough space is available, leaving between them a gap of size between h and $h + \mathrm{d}h$ with probability $\Delta(h)\,\mathrm{d}h$. The only constraint we impose to the probability density $\Delta(h)$ is that it must be short ranged, namely

$$\Delta(h) = 0 \qquad h > \lambda \tag{2}$$

where λ is a fixed parameter of the model which we restrict to be in the interval $[0, \frac{1}{2}]$ for reasons explained below. This adsorption rule is only valid if there is no superposition between the influence due to an adsorbed particle and its next neighbour; therefore a gap of length $h' \geqslant 1 + 2\lambda$ must exist between these particles. For smaller gaps the adsorption rule has to be modified as shown below.

Thus, the rate of arrival particles $k(h', h)$ per unit time and length at position h into a gap of size h' (see figure 1) is:

$$k(h', h) = 1 + \Delta(h) + \Delta(h' - h - 1) \qquad h' > 1 + 2\lambda. \tag{3}$$

The contribution 1 to this rate comes from the constant raining of particles over the line and $\Delta(h)$ and $\Delta(h' - h - 1)$ are the contributions due to the incoming particles which interact with the particles fixed at both sides of the gap. These particles are eliminated in

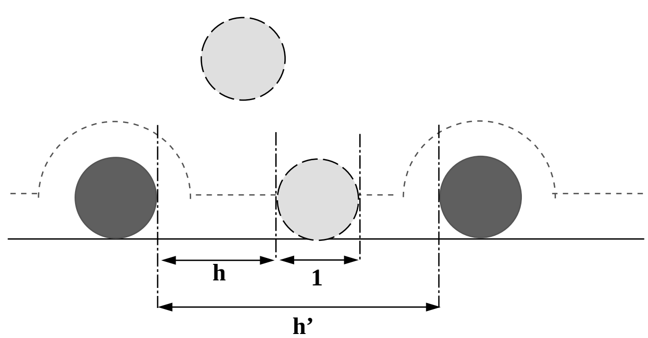

Figure 1. Illustration of the governing equation for the non-uniform deposition.

the RSA model; however, we consider here (as in the BD model) that all of them reach the adsorption line due to the transport mechanisms, therefore we have the normalization

$$\int_0^\lambda \mathrm{d}h\, \Delta(h) = 1. \tag{4}$$

The precise value of λ and the form of $\Delta(h)$ depend on the details of the transport mechanisms present in the problem and need not be specified here. The new gap length h is a random variable with moments

$$\mu_n \equiv \langle h^n \rangle = \int_0^\lambda \mathrm{d}h\, h^n \Delta(h). \tag{5}$$

The BD model is recovered in the limit $\Delta(h) \to \delta(h)$, $\mu_n \to 0$.

If the incoming particle adsorbs into a gap of length $h' \leqslant 1+2\lambda$ there is a superposition between the contributions due to both gap-limiting particles, and the adsorption rate is supposed to adopt the form:

$$k(h', h) = 1 + \Delta_2(h; h') \qquad 1 < h' < 1 + 2\lambda. \tag{6}$$

The only hypothesis we assume about $\Delta_2(h; h')$ is that also in this situation any incoming particle reaching an unstable position will be adsorbed, so that $\Delta_2(h; h')$ is normalized according to

$$\int_0^{h-1} \mathrm{d}h'\, \Delta_2(h; h') = 2. \tag{7}$$

If this normalization is imposed and $\lambda \leqslant \frac{1}{2}$, then the specific form of $\Delta_2(h; h')$ will be irrelevant for the adsorption kinetics, as we will see in section 3.

This adsorption model is local in the sense that the adsorption probability only depends on the gap in which the adsorption attempt takes place. For values of λ larger than $\frac{1}{2}$ one should also consider the possibility of non-local effects; the adsorption rate in a gap could not only depend on the particles limiting the gap but also on further neighbours. Physically this is the case when an incoming particle, after interacting with an adsorbed one, can diffuse over a large distance and interact with several other particles before being adsorbed. In this paper we only consider values of $\lambda \leqslant \frac{1}{2}$ for which non-local effects are not possible.

For one-dimensional adsorption models which satisfy this shielding property, a closed kinetic equation can be written for the density of gaps [17]. Let $G(h, t)$ be the number density of gaps with length h at time t. This quantity evolves according to:

$$\frac{\partial G(h,t)}{\partial t} = -k_0(h) G(h,t) + 2 \int_{h+1}^{\infty} \mathrm{d}h'\, G(h', t) k(h', h) \tag{8}$$

where $k(h', h)$ is the probability per unit length and unit time that the deposition of a disk in a gap of length $h' > h + 1$ produces gaps of length h and $h' - h - 1$, and $k_0(h)$ is the total rate at which gaps of length h are destroyed by the addition of a new particle. The first term on the r.h.s. of equation (8) accounts for the destruction of gaps of size h and the second term accounts for the creation of gaps from larger ones after the adsorption of a new particle.

The total rate at which gaps of length $h' \geqslant 1$ are destroyed is, according to (3), (6) and the normalization (4), (7):

$$k_0(h) = \int_0^{h-1} \mathrm{d}h'\, k(h, h') = h + 1 \qquad h \geqslant 1. \tag{9}$$

Now, we can write explicitly the kinetic equations corresponding to our model. For gaps of size $h \geqslant 1$ (i.e. gaps at which adsorption can take place) we have the integro-differential equation:

$$\frac{\partial G(h,t)}{\partial t} = -(h+1)G(h,t) + 2\int_{h+1}^{\infty} \mathrm{d}h'\, G(h',t)[1+\Delta(h'-h-1)] \qquad h \geqslant 1. \tag{10}$$

Gaps of length $h \leqslant 1$ can only be created, not destroyed. The corresponding kinetic equation is:

$$\frac{\partial G(h,t)}{\partial t} = 2\int_{h+1}^{\infty} \mathrm{d}h'\, G(h',t)k(h',h) \qquad h < 1 \tag{11}$$

where $k(h',h)$ depends on h and h' as given by (3) or (6) depending on the value of h'. Equation (11) is an ordinary differential equation, because in the evaluation of the integral on the r.h.s. one only needs to know $G(h,t)$ for $h \geqslant 1$, which is the solution of (10).

These equations must be supplemented with a normalization condition that, according to the definition of $G(h,t)$, reads [17]

$$\int_0^{\infty} G(h,t)\,\mathrm{d}h + \int_0^{\infty} hG(h,t)\,\mathrm{d}h = 1. \tag{12}$$

Geometrically, the first term is the fraction of the line filled with particles, while the second term is the line fraction occupied by gaps of any length. Note that in equation (10) only the particle adsorption rate given by (3) appears whereas (6) is irrelevant to obtain the distribution of gaps with space available for adsorption. This fact is due to the constraint $\lambda \leqslant \frac{1}{2}$.

Once equation (10) is solved, one can obtain the adsorption rate $\Phi(t)$ by averaging the gap destruction rate $k_0(h)$ given by equation (9) over the number density of gaps $G(h,t)$ for $h \geqslant 1$:

$$\Phi(t) = \int_1^{\infty} (h+1)G(h,t)\,\mathrm{d}h. \tag{13}$$

From the normalization of $G(h,t)$, equation (12), one can see that the value of Φ changes from 1 for an empty line to 0 when all the gaps have a length smaller than 1 (saturation). Equation (13) has another simple interpretation: Φ is the effective fraction of the line available for adsorption of new particles. In order to show this, one should note that a new particle will adsorb in a gap of length $h \geqslant 1$ if it falls directly into the free length of the gap (which is $h-1$) or on an unstable position over the limiting particles of the gap which adds a contribution of 1 for each gap limiting particle. Therefore, the length available for adsorption in a gap of length $h \geqslant 1$ is $h+1$, and the total available surface Φ is the average of this quantity with the distribution of gaps $G(h,t)$.

3. Solution of the model

First, we solve the integro-differential kinetic equation (10). Following the usual ansatz for one-dimensional models [14, 15], we look for a solution of the form

$$G(h,t) = \mathrm{e}^{-(h+1)t}t^2\Gamma(t) \qquad h > 1 \tag{14}$$

where $\Gamma(t)$ is independent of h, and satisfies the first-order differential equation:

$$\frac{\mathrm{d}\ln[\Gamma(t)]}{\mathrm{d}t} = 2\left[\tilde{\Delta}(t)\mathrm{e}^{-t} - \frac{1-\mathrm{e}^{-t}}{t}\right] \tag{15}$$

where $\tilde{\Delta}(t) = \int_0^\infty \mathrm{d}h\, \mathrm{e}^{-ht}\Delta(h)$ is the Laplace transform of $\Delta(h)$. The general solution of equation (15) is:

$$\Gamma(t) = K \exp\left\{ -2\int_0^t \mathrm{d}u \left[\frac{1-\mathrm{e}^{-u}}{u} - \mathrm{e}^{-u}\tilde{\Delta}(u)\right]\right\}. \tag{16}$$

Substituting (14) into (13) one obtains for the available surface function,

$$\Phi(t) = \mathrm{e}^{-2t}(2t+1)\Gamma(t). \tag{17}$$

The constant K can be fixed by imposing the normalization condition (12) at any time, or equivalently $\Phi = 1$ for an empty line ($t = 0$). From equation (17) we obtain $\Phi(t = 0) = K$, so $K = 1$. The coverage $\theta(t)$ (defined as the relative length of the line covered by particles) is obtained by integration of $\Phi(t)$:

$$\theta(t) = \int_0^t \Phi(t')\,\mathrm{d}t' = \int_0^t \mathrm{d}t'\,\mathrm{e}^{-2t'}(2t'+1)\Gamma(t'). \tag{18}$$

The coverage increases monotonically (due to the irreversible nature of the process) until it reaches a model-dependent saturation value, θ_∞, when no available space remains for the adsorption of new particles. Note that in calculating both the coverage and the available surface function, we need $G(h, t)$ only for $h \geqslant 1$, thus none of these quantities depends on $\Delta_2(h'; h)$.

From equation (18) it is easy to obtain the asymptotic approach to saturation following the same procedure as that in the BD case [13]. Subtracting $\theta(t)$ from θ_∞, integrating by parts and retaining the dominant term we have:

$$\theta_\infty - \theta(t) = \frac{\mathrm{e}^{-2t}}{t}\left[\mathrm{e}^{-2\gamma+2\alpha} + \mathrm{O}\left(\frac{1}{t}\right)\right] \tag{19}$$

where γ is the Euler constant and α depends on the specific model considered and is given by

$$\alpha = \int_0^\infty \mathrm{d}u\,\mathrm{e}^{-u}\tilde{\Delta}(u) = \int_0^\infty \mathrm{d}h\,\frac{\Delta(h)}{h+1}. \tag{20}$$

It is easy to show that $\frac{2}{3} \leqslant \alpha \leqslant 1$, thus $\alpha > \gamma$. Therefore, the approach to the jamming limit is exponential, as in the BD model [13] (which is recovered when $\alpha = 1$), the only difference being the value of the proportionality constant. The reason for this is that, as in the BD model [13], the asymptotic behaviour is governed by the filling process of small gaps of length $h \approx 1^+$, and these small gaps are occupied at a rate $h + 1$ independent of the details of the model.

Now we show how the saturation coverage approaches asymptotically the BD value when $\lambda \to 0$ and how to obtain corrections to the BD kinetics up to a desired order in λ. First we use the expansion of $\tilde{\Delta}(u)$ in powers of u, which is related to the moments μ_n by

$$\tilde{\Delta}(u) = \sum_{n=0}^{\infty}(-1)^n \frac{u^n}{n!}\mu_n. \tag{21}$$

When the range λ of the distribution $\Delta(h)$ is small, its moments are quantities of decreasing order of magnitude, $\mu_n = \mathrm{O}(\lambda^n)$. Using (21) in (17) we obtain for the available length:

$$\Phi(t) = \Phi^{\mathrm{BD}}(t)\exp\left\{2\sum_{n=1}^{\infty}(-1)^n\mu_n\left[1 - \mathrm{e}^{-t}\sum_{k=0}^{n}\frac{t^k}{k!}\right]\right\}. \tag{22}$$

This expression can now be expanded in several ways: one can obtain short-time or low-coverage expansions valid for all the allowed values of λ or expansions in powers of λ valid for all time or coverage values.

In the expansion of equation (22) as a power series in t, the term $O(t^k)$ contains contributions from moments μ_n with $n < k$. This fact is also reflected in the low-coverage expansion. For example, up to $O(\theta^3)$ we obtain:

$$\Phi(\theta) = 1 - (5 + 2\mu_1)\frac{\theta^2}{2} + \left(\frac{26}{3} + 2\mu_1 + \mu_2\right)\frac{\theta^3}{3} + O(\theta^4). \tag{23}$$

The term of order $O(\theta)$ is 0 as expected because one particle is not enough to prevent adsorption. The correction of order θ^2 measures the rejecting efficiency (or mean exclusion length) of the two-particle configurations leading to the rejection of new particles. Note that it is exactly linear in μ_1 and does not depend on higher-order moments. The reason for this dependence is that, although the configurations which reject particles are the same in this model as in the BD model, their probability is not the same because our adsorption rule generates traps of characteristic size μ_1.

Now, we expand equation (22) as a power series in λ for all times or coverages. The term $O(\lambda^k)$ depends on the moments μ_n with $n \leqslant k$. This expansion can be integrated in time in order to obtain the coverage $\theta(t)$. For example, up to order $O(\lambda^2)$ we have for the jamming coverage:

$$\theta_\infty = \theta_\infty^{\mathrm{BD}} + c_1\mu_1 + c_{1,2}\mu_1^2 + c_2\mu_2 + O(\lambda^3) \tag{24}$$

where $\theta_\infty^{\mathrm{BD}} = 0.808\,65\ldots$ is the jamming coverage of the BD model and the coefficients c_i, $c_{i,j}$ are given by definite integrals obtained from the integration of (22); the first ones are $c_1 = -0.221\,04\ldots$, $c_{1,2} = 0.070\,10\ldots$, $c_2 = 0.074\,62\ldots$.

As mentioned in the introduction, the moments μ_n can be obtained—at least for small n—from simulations with only one adsorbed particle (or sometimes by approximate methods) taking into account the relevant transport processes. One could try to obtain the kinetic law and the saturation coverage by performing simulations up to the jamming limit, but this requires a large computational effort. Equation (24) provides a simple way to overcome this problem in the case of short-range models. An approximation to the kinetics up to a given order $O(\lambda^n)$ can be obtained if we know the first n moments of $\Delta(h)$. It is not necessary to know the precise form of $\Delta(h)$.

To illustrate the utility of equation (24) we apply it to the $(1+1)$-dimensional DRSAG model in the limit in which the motion of diffusing disks is dominated by gravity ($R^* \gg 1$). In this model, although $\Delta(h)$ does not vanish for finite values of h, it decays exponentially fast, and we expect that a good approximation can be obtained by using equation (24). From a perturbative solution of the transport equation we have obtained up to the lowest order [20]:

$$\mu_1 = \frac{0.6967}{(R^*)^{8/3}} \qquad \mu_2 = \frac{2.0113}{2^{4/3}(R^*)^{16/3}}. \tag{25}$$

Thus, using (25) in (24) we obtain:

$$\theta_\infty = \theta_\infty^{\mathrm{BD}} - 0.1540(R^*)^{-8/3} + 0.0936(R^*)^{-16/3}. \tag{26}$$

This approximate expression is in good agreement with the results obtained in [20] by means of Brownian dynamics simulations which take into account diffusion and sedimentation, as shown in figure 2. Clearly, equation (26) describes fairly well the asymptotic behaviour of θ_∞ when approaching the BD limit ($R^* \gg 1$) and gives good approximations for the jamming coverage for values of R^* larger than $R^* \sim 2.0$ ($\mu_1 \sim 0.11$). At this point, we note that the existence of an universal curve for θ_∞ in the DRSAG model, independent of the dimension of the system, has been proposed based on simulations [19] and on a boundary analysis of the transport equation [20]. Thus, equation (26) could also be useful

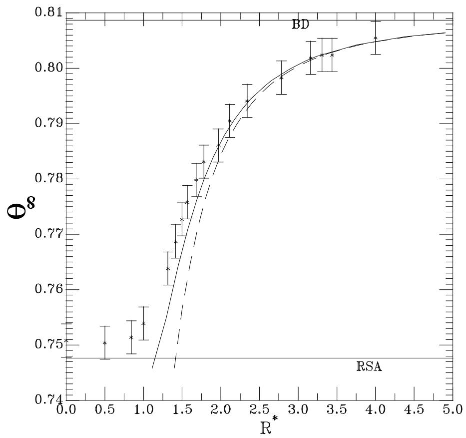

Figure 2. Saturation coverage θ_∞ for the (1 + 1)-dimensional DRSAG model as a function of R^*. Points: simulations data from [20], full curve: equation (26), broken curve: equation (26) truncated to first correction to BD.

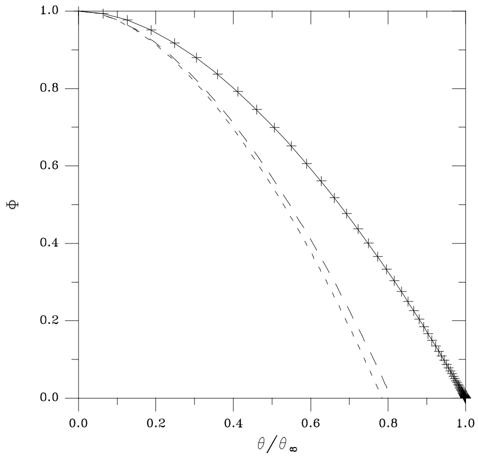

Figure 3. Φ as a function of the coverage for the BD model (broken curves) and using equations (22) and (25) for $R^* = 2.0$ (short broken curves). We also show Φ as a function of θ/θ_∞ for the BD model (full curve) and for $R^* = 2.0$ (crosses).

for the study of large particle adsorption onto bidimensional surfaces. For instance, if we consider polystyrene beads in water at 300 K, $\Delta\rho = 45$ kg m^{-3} from (1) we obtain a radius about 2.45 μm, which is accessible to experimentations [11].

Also, these experiments [11] have shown that some results related to the kinetics of the process (dilution curve, fluctuations in the number of particles), when expressed as a function of θ/θ_∞, seem quite independent of R^* and are close to the BD results. This fact could indicate that Φ is, at least approximately, a function of θ and R^* through the variable $\theta/\theta_\infty(R^*)$ only. This feature is also present in our model, as shown in figure 3 by plotting Φ as a function of θ/θ_∞ for $R^* = 2$ and μ_1, μ_2 given by equation (25). Therefore, the kinetic laws corresponding to models of the class analysed here are very close to the BD kinetics when the coverage (or time) is properly rescaled to take into account the different jamming saturation values reached for each model. One can also easily check that this feature is also present in some other toy models, taking some simple explicit forms for the function $\Delta(h)$ and using equations (17) and (18). We checked this feature taking $\Delta(h)$ linearly increasing or decreasing with distance, and with a step form.

An aspect closely related to the kinetics of the adsorption process, which is also measured in experiments, is the fluctuation observed in the mean number of particles adsorbed on a large, but finite surface. The measured reduced variance $\sigma^2/\langle n\rangle$ shows an horizontal slope for low coverage for all measured R^* [11] and seems to be of the order θ^3 for small θ. Recently [26] a theoretical relationship between $\Phi(\theta)$ and the reduced variance $\sigma^2/\langle n\rangle$ (which is a measurable quantity) has been obtained, and a particularly remarkable result is that if $\Phi(\theta)$ has the form $\Phi(\theta) = 1 - B_k\theta^k + \mathrm{O}(\theta^{k+1})$, i.e. at least k adsorbed particles are required to preclude an adsorption attempt, the reduced variance is:

$$\frac{\sigma^2}{\langle n\rangle} = 1 - \frac{2k}{k+1} B_k\theta^k + \mathrm{O}(\theta^{k+1}). \tag{27}$$

Thus, in these adsorption experiments performed onto bidimensional surfaces, at least three particles are needed to preclude adsorption of an incoming one. In our model of adsorption onto a line we have $k = 2$ and $B_2 = \mu_1 + \frac{5}{2}$ according to (23).

4. Conclusions

In this paper we have analysed a class of geometrical models which generalize the BD model for irreversible adsorption of hard disks onto a line. In the BD model, an incoming disk touching an adsorbed one, rolls over it and adsorbs in contact with it. In our model we assume that, due to transport effects, the incoming particle adsorbs near the fixed one leaving between them a gap of size h with probability density $\Delta(h)$.

The only hypothesis we need is that, after interacting with a fixed particle, an incoming one cannot adsorb at a distance greater than λ from it, i.e. $\Delta(h) = 0$ for $h > \lambda$. To allow an exact description of the model, λ is restricted to be smaller than $\frac{1}{2}$. We do not make any further hypothesis concerning the dependence of Δ with position.

Due to the fact that this one-dimensional model is local (in the sense that the adsorption rate depends only on the gap in which adsorption takes place), an exact balance equation for the free gap distribution can be formulated. This equation has been solved analytically and we have obtained the density of gaps, the available surface function and the coverage as a function of time.

The class of models presented in this work can be used to obtain corrections to the BD kinetics due to transport effects. If the characteristic length λ is small, the moments μ_n of $\Delta(h)$ are quantities of decreasing order in λ ($\mu_n \sim \mathrm{O}(\lambda^n)$). The kinetics of the model can be obtained up to order $\mathrm{O}(\lambda^n)$ if we know up to the moment μ_n although the detailed form of $\Delta(h)$ is not specified. This is a useful feature because when transport effects are included, the transport equation can be solved only in some simplified cases and thus $\Delta(h)$ usually cannot be computed analytically. However, its first moments can be obtained from simulations or approximate methods. We recall that simulations performed in order to obtain the first moments μ_n only require one fixed particle and thus are computationally less expensive than those performed up to saturation.

We have applied these results to large disks diffusing in a gravitational field (the so-called DRSAG model). If gravity becomes dominant, incoming particles tend to roll over adsorbed ones and adsorb at a close distance. The first moments of this deviation, μ_1 and μ_2, were obtained as a function of the scaled particle size R^* ($R^* \gg 1$) in [20] from a boundary layer solution of the transport equation. This result allows one to obtain an approximate expression, equation (26) for the coverage as a function of R^*. The comparison of the saturation coverage obtained from Brownian dynamics simulations with equation (26) shows that the latter gives $\theta_\infty(R^*)$ with good approximation for values of R^* larger than $R^* \sim 2.0$. For smaller values of R^*, incoming particles can diffuse over larger distances after interacting with an adsorbed one, and the general picture of the models outlined in this paper is no longer applicable.

We have also shown that the kinetic laws of the class of models analysed in this paper are close to that of BD if time or coverage is properly normalized to take into account their different jamming coverage values. This is similar to what was observed in adsorption experiments [11] with colloidal particles of different size. In these experiments, several magnitudes intimately related to the kinetic law were well fitted using the ballistic model and they seem independent of the size of the particles when plotted against θ/θ_∞. Of course, this fact does not imply that the structure of the adsorbed layer is similar to BD although the kinetic law is coincident. At this point, we remark that as we showed in [20], for the values of R^* considered here, the δ function singularities present in the radial distribution function $g(r)$ of the BD model are smoothed by diffusion, which diminish strongly the probability of formation of k-mers.

Finally, we should note that the generalization of this class of models for values of

$\lambda > \frac{1}{2}$ is difficult, because in such a case the shielding property is not verified. One must take into account that an adsorbed particle can influence not only the gap which it limits but also other neighbouring gaps. In fact, when diffusion and gravity become comparable, we have showed that the effect of third neighbours affects the structure of the adsorbed layer [20]. After interacting with an adsorbed particle, an incoming one can diffuse far from it and adsorb in another gap. Thus, for these more general cases the kinetic equation for the gap density must be revised consistently with a more detailed description of the particles transport towards the adsorbing surface.

Acknowledgments

The authors wish to thank S Sjöberg for his careful revision of the manuscript. JF was supported by a doctoral scholarship from the Programa de formació d'investigadors of the Generalitat de Catalunya under grant FI/96-2.683. We also acknowledge partial financial support from the Dirección General de Investigación of the Spanish Ministry of Education and Science (grant PB94-0718).

References

[1] Adamczyk Z, Siwek B, Zembala M and Belouschek P 1994 *Adv. Coll. Interface Sci.* **48** 151
[2] Evans J W 1993 *Rev. Mod. Phys.* **65** 1281
[3] Feder J and Giaever I 1980 *J. Coll. Interface Sci.* **78** 144
[4] Ramsden J J 1993 *Phys. Rev. Lett.* **71** 295
[5] Wojtaszczyk P, Schaaf P, Senger B, Zembala M and Voegel J C 1993 *J. Chem. Phys.* **99** 7198
[6] Rènyi A 1963 *Sel. Trans. Math. Stat. Prob.* **4** 205
Cohen E R and Reiss H 1963 *J. Chem. Phys.* **38** 680
Widom B 1966 *J. Chem. Phys.* **44** 2888
Gonzalez J J, Hemmer P C and Høye J S 1974 *J. Chem. Phys.* **3** 288
[7] Bonnier B, Boyer D and Viot P 1994 *J. Phys. A: Math. Gen.* **27** 3671
[8] Pomeau Y 1980 *J. Phys. A: Math. Gen.* **13** L193
Swendsen R H 1981 *Phys. Rev.* A **24** 504
[9] Tarjus G, Schaaf P and Talbot J 1990 *J. Chem. Phys.* **93** 8352
Boyer D, Tarjus G, Viot P and Talbot J 1995 *J. Chem. Phys.* **103** 1607
[10] Hinrichsen E L, Feder J and Jøssang T J 1986 *J. Stat. Phys.* **44** 793
[11] Wojtaszczyk P, Mann E K, Senger B, Voegel J C and Schaaf P 1995 *J. Chem. Phys.* **103** 8285
[12] Jullien R and Meakin P 1992 *J. Phys. A: Math. Gen.* **25** L189
Thompson A P and Glandt E D 1992 *Phys. Rev.* A **46** 4639
[13] Choi H S, Talbot J, Tarjus G and Viot P 1993 *J. Chem. Phys.* **99** 9296
[14] Talbot J and Ricci S M 1992 *Phys. Rev. Lett.* **68** 958
[15] Viot P, Tarjus G and Talbot J 1993 *Phys. Rev.* E **48** 480
[16] Schaaf P, Johner A and Talbot J 1991 *Phys. Rev. Lett.* **66** 1603
Senger B, Voegel J C, Schaaf P, Johner A, Schmitt A and Talbot J 1991 *Phys. Rev.* A **44** 6926
Senger B, Schaaf P, Voegel J C, Johner A, Schmitt A and Talbot J 1992 *J. Chem. Phys.* **97** 3813
Senger B, Talbot J, Schaaf P, Schmitt A and Voegel J C 1993 *Europhys. Lett.* **21** 135
[17] Bafaluy J, Choi H S, Senger B and Talbot J 1995 *Phys. Rev.* E **51** 5985
[18] Senger B, Bafaluy J, Schaaf P, Schmitt A and Voegel J C 1992 *Proc. Natl Acad. Sci., USA* **89** 9449
Senger B, Ezzedine R, Bafaluy J, Schaaf P, Cuisinier F J G and Voegel J C 1993 *J. Theor. Biol.* **163** 457
[19] Ezzeddine R, Schaaf P, Voegel J C and Senger B 1995 *Phys. Rev.* E **51** 6286
[20] Faraudo J and Bafaluy J 1996 *Phys. Rev.* E **54** 3725
[21] Bafaluy J, Senger B, Voegel J C and Schaaf P 1993 *Phys. Rev. Lett.* **70** 623
[22] Pagonabarraga I and Rubí J M 1994 *Phys. Rev. Lett.* **73** 114

[23] Senger B, Schaaf P, Bafaluy J, Cuisinier F J G, Talbot J and Voegel J C 1994 *Proc. Natl Acad. Sci., USA* **91** 3004
[24] Ermak D L and McCammon J A 1978 *J. Chem. Phys.* **69** 1352
[25] Adamczyk Z, Zembala M, Siwek B and Warszyński P 1990 *J. Colloid Interface Sci.* **140** 123
[26] Bafaluy J, Schaaf P, Senger B, Voegel J C and Pagonabarraga I 1997 *J. Chem. Phys.* **107** 2089