Generalized Car-Parking Problem as a Model for Particle Deposition with Entropy-Activated Rate Process

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We study a class of generalized car-parking problems and show analytically that whereas the properties (structure and density) of the configurations generated by the generalized and the standard parking processes are different at most times, they are identical at the jamming limit ($t \to +\infty$). We indicate how such models can be used to describe more realistic particle deposition processes which combine bulk diffusion and irreversible adsorption. This provides a theoretical basis to explain recent simulation results.

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The development of models for the adsorption of large particles (colloids, proteins, latex spheres, etc.) on solid surfaces is an area under active investigation. To describe the physical situations in which the deposition occurs irreversibly, that is, with negligible desorption or surface diffusion, and in monolayers, it has been suggested to use the random sequential addition (RSA) model [1]. In this model, hard objects are deposited randomly and sequentially onto a surface, subject to the condition that once adsorbed they cannot move [1-6]. However, a limitation of the RSA description is that it does not take into account the transport process of the particles from the bulk to the surface nor the interactions between adsorbed particles and particles in solution. A more realistic model has been recently proposed [7,8], which avoids some of the shortcomings of the simple RSA: The deposition is described as a process of diffusion and adsorption of hard spheres; the spheres undergo Brownian dynamics in solution and become irreversibly bound to the surface once they contact it. The long-range hydrodynamic forces are neglected but the short-range interactions between adsorbed spheres and spheres in solution are explicitly accounted for. By means of heuristic arguments, Schaaf, Johner, and Talbot [7] have shown that the asymptotic approach of the coverage towards its saturation value is characterized in this model by a power law in time, the exponent of which is *different* from that obtained in the simple RSA. Interestingly, it has been observed in subsequent computer simulations [8] that the coverage and the structure of the jammed configurations are *indistinguishable* from those of the jammed RSA configurations.

In this Letter, we consider the $(1+1)$-dimensional version of the preceding model: The deposition of hard disks that undergo Brownian motion in solution and are irreversibly adsorbed onto an infinite line. Note that since the disks interact with purely repulsive hard-core potentials, multilayer formation is forbidden. A modification of the present model to allow for multilayered deposits consists of considering the hard disks as "sticky," which would lend to a version of the diffusion-limited aggregation [9].

We show analytically that a class of generalized one-dimensional RSA (or "car parking") processes present the features observed in the above-mentioned studies. At all finite times (except very short ones), the density and the structure of the adsorbed configurations are different from those of the simple parking problem; in particular, the density evolves asymptotically towards its saturation value with an algebraic time dependence which differs in general from the usual t^{-1} behavior. However, the density and the structure of the jammed configurations ($t \to +\infty$) are *identical* to those of the simple car-parking process. This class of generalized parking problems involves a rate of adsorption (per unit length) which, instead of being constant as in the simple case, is a function of the length h of the interval which is locally available for the insertion of a new object. We next show how the diffusion and adsorption of hard disks, which can be viewed as an activated rate process in which the activation free-energy barrier is purely entropic, can be reduced to a generalized car-parking problem. This provides a theoretical basis to explain the recent results [7,8].

We introduce first a new class of generalized car-parking problems. Objects of equal size σ are randomly and sequentially deposited onto an infinite line subject to the constraints that two objects cannot overlap and that once inserted an object is fixed in place. However, contrary to the standard parking problem [1-3], the rate of deposition per unit length is not a constant: It is a function of the length of the interval (between preadsorbed objects) in which one tries to insert a new object. Denoting $G(h,t)$ as the distribution function for intervals of length h and choosing for convenience $\sigma=1$, one derives the following exact rate equation for the kinetics of the process:

$$\frac{\partial G(h,t)}{\partial t} = -k(h)(h-1)G(h,t)+2\int_{h+1}^{+\infty} dh_1\, k(h_1)G(h_1,t)\,, \tag{1}$$

with the additional condition that $G(h,t=0)=0$; $k(h)$ is the rate of adsorption per unit length in an interval of length h and is equal to zero when $h\in[0,1]$. If $k(h)$ is independent of h, $h>1$, the standard car-parking problem is recovered. Note that the preceding model is different from usual cascade processes [10] since it accounts for the exclusion effect due to already adsorbed objects. We choose $k(h)$ as a (positive) monotonously decreasing function in the interval $]1,+\infty[$, with the following properties: (i) $k(h)$ may diverge when $h\to 1^+$, but if so it diverges like $(h-1)^{-\alpha}$ with $0\le\alpha<1$; (ii) $k(h)$ tends to a strictly positive value, $k_\infty>0$, when $h\to+\infty$ and we consider both the case in which $k(h)$ is strictly equal to k_∞ for $h\ge h_c$ and the case in which $k(h)$ approaches k_∞ asymptotically like $Ah^{-\beta}$, $A>0$, $\beta\ge 1$. In the following, the time is expressed in units k_∞^{-1} and we define $K(h)\ge 0$ such that $k(h)=1+K(h)$, and $H(h,t)$, $h>1$, such that $G(h,t)=\exp[-(h-1)t]H(h,t)$, $h>1$.

By introducing the preceding definitions in Eq. (1) and by formally integrating over time, Eq. (1), for $h>1$, can be transformed into

$$H(h,t)=2\int_0^t dt_1 e^{-K(h)(h-1)(t-t_1)}\int_{h+1}^\infty dh_1[1+K(h_1)]e^{-(h_1-h)t_1}H(h_1,t_1)\,. \tag{2}$$

Two noticeable features of the above equation are that the arguments of the exponentials present in the right-hand side are both negative and that the determination of $H(h,t)$ requires only the knowledge of $H(h',t)$ for $h'\ge h+1$. To take further advantage of this latter property, we rewrite Eq. (2) as

$$\begin{aligned}H(h,t)=2^n\int_0^t dt_1 e^{-K(h)(h-1)(t-t_1)}\int_{h+1}^\infty dh_1[1+K(h_1)]e^{-(h_1-h)t_1}\int_0^{t_1}dt_2 e^{-K(h_1)(h_1-1)(t_1-t_2)}\\ \times\int_{h_1+1}^\infty dh_2[1+K(h_2)]e^{-(h_2-h_1)t_1}\cdots\int_0^{t_{n-1}}dt_n e^{-K(h_{n-1})(h_{n-1}-1)(t_{n-1}-t_n)}\\ \times\int_{h_{n-1}+1}^\infty dh_n[1+K(h_n)]e^{-(h_n-h_{n-1})t_n}H(h_n,t_n),\quad h>1\,.\end{aligned} \tag{3}$$

$H(h,t)$ can now be obtained by knowing $H(h',t)$ for $h'\ge h+n$, so that when the procedure is repeated a sufficient number of times, $H(h,t)$ can be expressed in terms of the asymptotic solution $H(h',t)$ for very large h'. Similarly, the interval function $G(h,t)$ for $0<h\le 1$ can be written as

$$\begin{aligned}G(h,t)=-\sum_{p=1}^{n-1}\int_{h+1}^\infty dh_1\frac{2}{h_1-1}\int_{h_1+1}^\infty dh_2\frac{2}{h_2-1}\cdots\int_{h_{p-1}+1}^\infty dh_p\frac{2}{h_p-1}e^{-(h_p-1)t}H(h_p,t)\\ +2\int_{h+1}^\infty dh_1\frac{2}{h_1-1}\int_{h_1+1}^\infty dh_2\frac{2}{h_2-1}\cdots\int_{h_{n-1}+1}^\infty dh_n[1+K(h_n)]\int_0^t dt_1 e^{-(h_n-1)t_1}H(h_n,t_1)\,.\end{aligned} \tag{4}$$

Consider now the case in which $K(h)=0$ for $h\ge h_c$. For all $h\ge h_c$, Eq. (2) reduces then to

$$H(h,t)=2\int_0^t dt_1\int_{h+1}^\infty dh_1 e^{-(h_1-h)t_1}H(h_1,t_1)\,, \tag{5}$$

the solution of which is, as in the standard parking problem [3],

$$H(h,t)=H_0(t)=t^2\exp\left\{-2\int_0^t dt_1\left(\frac{1-e^{-t_1}}{t_1}\right)\right\},\quad h\ge h_c\,. \tag{6}$$

By inserting the above solution in Eq. (3) and choosing n such that $h+n\ge h_c$, we derive that $H(h,t)$, $h>1$, is always bounded and, as a consequence, that $G(h,t)$, $h>1$, vanishes exponentially when $t\to+\infty$: This property is also true for $G_0(h,t)$, the interval distribution in the standard parking process, for $h>1$ [3]. When $h\in]0,1]$, we again choose n in Eq. (4) such that $h+n\ge h_c$ and, using the fact that $G_0(h,t)$ is obtained by setting $K(h)=0$ in Eq. (4), we derive

$$G(h,t)-G_0(h,t)=-\sum_{p=1}^{n-1}\int_{h+1}^\infty dh_1\frac{2}{h_1-1}\cdots\int_{h_{p-1}+1}^\infty dh_p\frac{2}{h_p-1}e^{-(h_p-1)t}[H(h_p,t)-H_0(t)]\,. \tag{7}$$

Since $H(h,t)$ and $H_0(t)$ are bounded, it follows from Eq. (7) that $G(h,t)$ converges uniformly for $h\in]0,1]$ towards $G_0(h,t)$ when $t\to+\infty$.

The procedure can be repeated in the more complicated case for which $K(h)\sim Ah^{-\beta}$, $h\to+\infty$, $\beta\ge 1$, $A>0$. We look for an asymptotic solution of Eq. (2) which has the following form:

$$H(h,t)=H_0(t)\left(1+\frac{R(h,t)}{h^\beta}\right)e^{-K(h)(h-1)t}, \tag{8}$$

where $H_0(t)$ is defined by Eq. (6) and $R(h,t=0)=0$. After some manipulations, it can be shown that $R(h,t)$ is a positive increasing function of time and that the leading term of $R(h,t)$ for very large h goes as $[2A/3(\beta-1)]ht$ when $ht\to 0$, $\beta>1$, as $-(2A/3)ht\ln ht$ when $ht\to 0$, $\beta=1$, and is bounded for all times [11]. Assuming that, for h large enough, $R(h,t)$ is always bounded and inserting Eq. (8) in Eq. (3), we derive that $H(h,t)$, $h>1$, is bounded for all times. This result and the property that

$\int_0^t dt_1 e^{-(h-1)t_1}\{[1+K(h)]H(h,t_1)-H_0(t_1)\}$ converges uniformly towards zero when $h \to +\infty$ can be used to obtain that $G(h,t)$ converges uniformly towards $G_0(h,t)$ when $t \to +\infty$: *The structure of the jammed configurations* (characterized here by the interval distribution function when $t \to +\infty$) is thus *identical for the generalized and for the simple car-parking problems.* The convergence of $G(h,t)$ when $t \to +\infty$ being uniform, we can further conclude that the *saturation coverage* $\rho(\infty) = \lim_{t\to+\infty}\int_0^t dh\, G(h,t)$ *is also identical* to that of the simple parking case [1-3]:

$$\rho(\infty)=\rho_0(\infty)=\int_0^\infty dt \exp\left[-2\int_0^t dt_1\left(\frac{1-e^{-t_1}}{t_1}\right)\right]$$
$$=0.747\ldots \quad (9)$$

If the jammed configurations of the generalized and simple parking processes are identical, it is obvious from Eqs. (2)-(4) and (8) that this is not true for finite times. For instance, it can be easily shown that the coverage $\rho(t)$ asymptotically approaches its saturation value $\rho(\infty)=\rho_0(\infty)$ according to

$$\rho(\infty)-\rho(t) \sim t^{-1/(1-\alpha)}, \quad t\to+\infty, \quad 0\le\alpha<1, \quad (10)$$

if $k(h)$ behaves as $(h-1)^{-\alpha}$ when $h\to 1^+$: The standard case corresponds only to $\alpha=0$. The difference can also be illustrated by considering the short-time behavior. For simplicity, we choose the case for which $K(h)=0$ for $h\ge h_c$ and we then obtain

$$\rho(t)\simeq t-t^2+\left[\frac{5}{6}+\frac{1}{3}\int_1^{h_c} dh\, K(h)(h-1)\right]t^3+\ldots, \quad (11)$$

which reduces to the short-time expansion of $\rho_0(t)$ only when $h_c=1$. Finally, we stress that the configurations produced by the generalized and simple parking processes are also different at the *same given density* [provided $0<\rho<\rho_0(\infty)$]. Using the one-to-one mapping between time, $t\in[0,\infty[$, and density, $\rho\in[0,\rho_0(\infty)[$, one can study, e.g., the fraction of the line which is available for the center of a new object, $\Phi(\rho)=\int_1^\infty dh(h-1)G(h,\rho)$, a quantity that is indicative of the structure of the configurations at a given ρ [5] [note that for a generalized process $d\rho/dt\ne\Phi(\rho(t))$]. For the same model as before, the following low-density expansion can be obtained:

$$\Phi(\rho)=1-2\rho+\frac{\rho^2}{2}+\left[\frac{2}{3}+\left(\int_1^{h_c} dh\, K(h)(h-1)(3-h)+\int_2^{\max(h_c,2)} dh\, K(h)(h-2)^2\right)\right]\frac{\rho^3}{3}+\ldots, \quad (12)$$

which, again, corresponds to the expansion of $\Phi_0(\rho)$ only when $h_c=1$.

We now indicate under what conditions the (1+1)-dimensional deposition process can be reduced to a generalized car-parking problem. The diffusion and adsorption of hard disks represents a particular version of the well-studied activated-rate processes in the Smoluchowski (or Brownian) limit. What is specific here is that the "reaction," which is the adhesion of the disks on the 1D substrate, is irreversible and that the activation free-energy barrier is due to the exclusion effect of the preadsorbed hard disks and is thus purely entropic. If the crossing of the activation entropy barrier is much slower than the characteristic time of diffusion in the bulk, it dominates the kinetics of the whole deposition process. The transient kinetics related to bulk diffusion can then be neglected and the rate of adsorption can be taken as independent of time.

Consider the region of space which is above an interval of length h between two preadsorbed disks [cf. Fig. 1(a)]. If one assumes for simplicity that each time a disk leaves the region another comes to replace it from a neighboring region, the process can be described as the diffusion of points, i.e., centers of hards disks, in a channel of varying cross section with an absorbing boundary segment of length $h-1$. The rate of adsorption can be related to the mean first passage time (from the bulk to the absorbing segment) which in turn can be obtained approximately by using the Fick-Jacobs description [12]. In the latter, the 2D diffusion is replaced by an effective 1D diffusion equation for $P(h,z,t)$, the probability density of finding the center of a hard disk at a height z [measured from the absorbing segment, cf. Fig. 1(a)]:

$$\frac{\partial P(h,z,t)}{\partial t}=D\frac{\partial}{\partial z}x(h,z)\frac{\partial}{\partial z}x(h,z)^{-1}P(h,z,t), \quad (13)$$

$$x(h,z)=\begin{cases} h+1-2(1-z^2)^{1/2}, & 0\le z\le 1,\\ h+1, & z\ge 1,\end{cases} \quad (14)$$

where D is the bulk diffusion constant and $x(h,z)$ is the width of the channel at height z. The Fick-Jacobs equation is a Smoluchowski equation in which the potential energy is replaced by a purely entropic free-energy term [13], $\Delta G(h,z)=-k_BT\ln x(h,z)$, which is illustrated in Fig. 1(b). As recently discussed by Zhou and Zwanzig, the Fick-Jacobs description has no real justification aside from its plausibility, but seems to give a good approximation of the rate constant [13].

The mean first passage time is given by the standard formula:

$$\tau(h)=\left[D\int_0^{z_m} dz\, x(h,z)\right]^{-1}\int_0^{z_m} dz\, x(h,z)\times\int_0^z dz'\, x(h,z')^{-1}\int_{z'}^{z_m} dz''\, x(h,z''), \quad (15)$$

where z_m is the maximum height. The rate of adsorption in the interval of length h can then be written as

$$k(h)(h-1)\propto\left[\int_0^{z_m} dz\, x(h,z)\right]\tau(h)^{-1}, \quad (16)$$

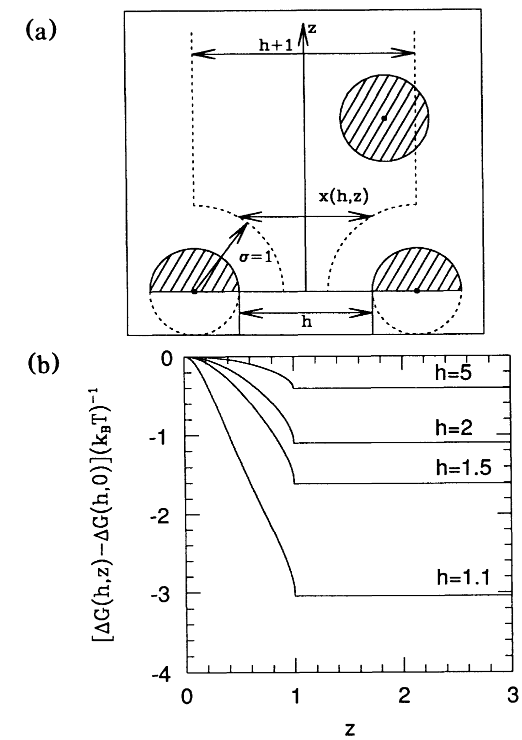

FIG. 1. (a) Diffusion and adsorption of a hard disk onto an interval of length h. The dashed curves indicate the boundaries of the channel in which the center of the disk can diffuse and $x(h,z)$ is the width of the channel at height z ($z=0$ corresponds to the absorbing boundary segment). (b) z-dependent free energy associated with an effective one-dimensional description of the diffusion in the channel illustrated in (a).

where $\int_0^{z_m} dz\, x(h,z)$ is proportional to the relative number of disks that are in the channel under consideration. Note that this treatment assumes implicitly that the adsorption is uniform on the available segment of length $h-1$, which cannot rigorously be true: There is certainly a slight propensity of the disks to adsorb close to the preadsorbed disks rather than in the middle of the segment. In the limit where the deposition process is purely ballistic, this effect has been shown to be non-negligible [14]; however, in the diffusion limit considered here it is expected to be small.

From Eqs. (14)–(16), it can be readily derived that $k(h)$ approaches a strictly positive value, $k(\infty)>0$, when $h\to+\infty$ with an asymptotic h^{-1} dependence and diverges like $(h-1)^{-1/2}$ when $h\to 1^+$; the full h dependence is illustrated in Fig. 2. We can thus conclude that the diffusion-adsorption process can be approximated as a generalized car-parking problem belonging to the above studied class (with $\alpha=\frac{1}{2}$ and $\beta=1$). All the precedently derived properties apply then to the $(1+1)$-dimensional diffusion-adsorption process. As for the simple RSA, there is no known procedure to derive an analytical solution of the diffusion-adsorption model in higher dimensions, but the present comparison between simple and generalized parking problems provides a theoretical basis

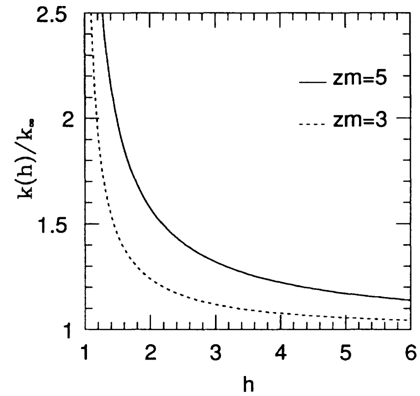

FIG. 2. Variation with the interval length h of the rate of adsorption per unit length as obtained from the Fick-Jacobs approximation, Eqs. (14)–(16), for $z_m=3$ and 5 [$k(h)$ is monotonously decreasing for $z_m \geq 2.53$].

to explain the recent results of Schaaf, Johner, and Talbot [7] and Senger *et al.* [8].

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