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2001 J. Phys. A: Math. Gen. 34 7517

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Competitive random sequential adsorption of point and fixed-sized particles: analytical results

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Received 11 June 2001, in final form 31 July 2001

Published 7 September 2001

Online at stacks.iop.org/JPhysA/34/7517

Abstract

We study the kinetics of competitive random sequential adsorption (RSA) of particles of binary mixture of points and fixed-sized particles within the mean-field approach. The present work is a generalization of the random car parking problem in the sense that it considers the case when either a car of fixed size is parked with probability q or the parking space is partitioned into two smaller spaces with probability $(1-q)$ at each time event. This allows an interesting interplay between the classical RSA problem at one extreme ($q = 1$), and the kinetics of fragmentation processes at the other extreme ($q = 0$). We present exact analytical results for coverage for a whole range of q values, and physical explanations are given for different aspects of the problem. In addition, a comprehensive account of the scaling theory, emphasizing dimensional analysis, is presented, and the exact expression for the scaling function and exponents are obtained.

PACS numbers: 05.20.Dd, 02.50.-r, 05.40-y

The kinetics of adsorption or deposition of particles on a substrate is one of the most common phenomena that occurs in many branches of science and technology including physics, chemistry, biophysics and medicine. Examples include adsorption of macromolecules and microscopic particles such as polymers, colloid, bacteria, protein or latex particles [1–3] on solid surfaces. Due to its importance, it has been studied extensively through all avenues of research comprising experimental, numerical and analytical means. Owing to the complex nature of the process, one can hardly make any progress analytically in more than one dimension (1D) and therefore most of the analytical work remains confined within 1D or quasi-1D [4] only, where it is exactly solvable. The 1D problem is not at all a pedagogical matter; it has been very useful in providing a deep understanding of the underlying mechanism and has offered an insight into more realistic models in higher dimensions. It has also been used as a test model to verify the results obtained from numerical simulations and data achieved through real life experiments (for extensive reviews, see [5]).

The simplest model one can think of that can capture the generic feature of the process is the kinetics of *random sequential adsorption* (RSA) of particles of a fixed size on a clean substrate [6]. This is popularly known as the random car parking problem. It has both an instructional value as well as a long historical significance. The basic rules of the processes are (i) at each time event one particle is adsorbed, (ii) the sites for deposition of adsorbing particles are chosen randomly and (iii), once the site is chosen, the event is successful if the site is empty; otherwise, the particle goes back to the particle reservoir and competes again for further pick up on an equal footing with the rest of the particles in the reservoir. Within this model, no two particles or any of their parts can occupy the same spatial position in the substrate. This means that particle overlapping is forbidden and hence the resulting model describes the kinetics and structure formation of a monolayer. Moreover, once deposited, particles are clamped permanently, making them immobile; therefore, the state of the site at each time step is changed irreversibly from an empty to a filled state. The irreversible nature of the process causes lack of a detailed balance and drives the system out of equilibrium. Therefore, one can no longer use the well-developed standard statistical mechanics approach fit for its equilibrium counterpart. However, there are limited attempt where methods of equilibrium statistical mechanics have been applied, e.g. series and virial expansions [7]. A unique yet fascinating feature of the RSA processes is the existence of a jamming coverage in the arbitrary dimension. This is the state when it is impossible to deposit even one single further particle on the substrate, despite the presence of gaps (voids), which are in fact not large enough to allow any further deposition.

To bring the RSA problem closer to real-life experiment, there exist many interesting variants of this model. Examples include cooperative sequential adsorption (CSA) [5, 8], the accelerated random sequential adsorption (ARSA) model [9], the ballistic deposition (BD) [10] model, the RSA on disordered substrates [11], the RSA of growing objects [12] and many attempts to include transport of depositing particles by diffusion [5]. Recently, there has been an increasing interest in the study of the RSA of a mixture of particles of different degrees, comprising a binary mixture of greatly differing diameters [13, 14], and a continuous mixture of sizes obeying a power-law size distribution [15]. It is important to note that in the former two cases, the ultimate structure in the long time limit is described by the jamming coverage, whereas in the latter, the resulting monolayer is uniquely characterized by an exponent called fractal dimension, since the arising pattern is a fractal [15]. The motivation of our present work comes from Bartelt and Privman [14], who studied the binary mixture of monomers and k -mers on 1D lattice as well as Talbot and Schaaf [14], who studied the RSA of a binary mixture of greatly differing sizes. Bartelt and Privman obtained an approximate expression for the coverage for continuum model by taking $k \rightarrow \infty$.

In the present work, we concentrate on the binary mixture of fixed size and point particles, instead of point-like particles, in a 1D substrate. We give an exact solution for the gap-size distribution function and a continuous spectrum of jamming coverage depending on the probability at which cars are parked. It is noteworthy to mention that within the RSA model only one particle can be adsorbed at each time step. This is the basic principle of the RSA process and it is indispensable if we want to call it sequential adsorption. In our investigation we consider the case when either a car is parked with probability q or the parking space is partitioned with probability $(1 - q)$. That is, points and fixed-sized particles compete for deposition, and at each time step only one of the two events is successful, and hence we call it competitive sequential adsorption. Indeed, we find that both the resulting dynamics and the final coverage differ significantly from previous studies. We find that the RSA of a mixture of point-like and fixed-sized particles, points and fixed-sized particles and the binary mixture of significantly differing sizes behave in a completely different way. This means that one has

to be very careful in making any approximation, since the final results are very prone to the exact ratio of the particle sizes. The beauty of the present work is that the results are exact and obtained analytically.

In addition, we present an explicit scaling description with special emphasis on the dimensional analysis. It is worth mentioning that, despite the long history of the RSA problem, a proper description of the scaling theory has remained untouched, although it has been a potential candidate for this. Dimensional analysis provides an insight into the problem and of course one cannot get things wrong if one remains faithful to the dimensional consistency.

We first give the general rate equation that describes the sequential deposition of particles, whose sizes and positions are determined by the specific choice of the model. Let us denote $P(x, t)$ as the gap size distribution function of size x at time t , consequently $P(x, t)$ obeys the following integro-differential equation

$$\begin{aligned} \frac{\partial P(x, t)}{\partial t} = & -P(x, t) \int_0^x dz p(z) \int_0^{x-z} dy F(x-y-z, y|z) \\ & + 2 \int_x^\infty dy P(y, t) \int_0^{y-x} dz p(z) F(x, y-x-z|z). \end{aligned} \quad (1)$$

Here $p(z)$ is called the parking distribution function, that determines the size of the depositing particle and $F(x-y-z, y|z)$ is the deposition kernel, that determines the rate $a(x, z) = \int_0^x dz p(z) \int_0^{x-z} dy F(x-y-z, y|z)$ at which an interval of size x is destroyed by the deposition of a particle of size z , thus creating two new intervals of sizes $x-y-z$ and y . The first term on the right-hand side of the equation (1) describes the destruction of the interval of size x and the second term their creation from the interval y ($y > x$). Note that if one chooses $F(x, y|z) = 1$ and $p(x) = \delta(x - \sigma)$ (σ is the size of the depositing particle) then the equation (1) simply describes the classical car parking problem [6, 16]. It is further interesting to note that if one chooses $p(z) = \delta(z)$ then the resulting equation describes the random sequential deposition of points, which is equivalent to the standard binary fragmentation of particles [17]. In fact, the car parking problem can be interpreted as placing cuts with finite thickness and fragmenting particles into two pieces at each time step. The connection between the RSA and the binary fragmentation process was first noted by Ziff [18].

In order to gain a detailed insight into the process, we first study the RSA of point-sized particles alone, which in fact describes the kinetics of the binary fragmentation process. Let us consider the simplest case when $F(x, y) = 1$, which is known as the random scission model [17, 19]; the resulting equation is

$$\frac{\partial P(x, t)}{\partial t} = -xP(x, t) + 2 \int_x^\infty P(y, t) dy. \quad (2)$$

First, note that $a(x) = x$ is the quantity that describes the rate and therefore it must bear the dimension inverse of time t . This means that x and t are interlocked and any one of these two variables can be expressed in terms of the other one. On the other hand, since x and t are the only two governing parameters, the quantity $P(x, t)$ can also be expressed in terms of one parameter alone. Therefore, assuming t to be the independent parameter, we can write the following scaling *ansatz*

$$P(x, t) \sim P_0(t)\phi(x/s(t)) \quad (3)$$

where $\phi(\xi)$ is known as the scaling function. The equation (2) will admit scaling if we can choose a time-dependent scale $s(t)$ for the spatial variable, and $P_0(t)$ for the particle-size distribution function so that all plots of $P(x, t)/P_0(t)$ against $x/s(t)$ for any initial distribution collapse onto one single curve. This can only be true if both $P_0(t)$ and $s(t)$ show a power-law

behaviour. This is due to the fact that $P_0(t)$ and $s(t)$ must bear the dimensions of $P(x, t)$ and x , respectively. On the other hand, the dimension of any physical quantity must be of power-monomial nature, i.e. we can write

$$P_0(t) \sim t^\alpha \quad \text{and} \quad s(t) \sim t^z. \quad (4)$$

Simple dimensional analysis of equation (1) immediately reveals $z = 1$ and since it describes the conservation of mass, i.e. $\int_0^\infty x P(x, t) dx$, it is independent of time and yields $\alpha = 2$. The solution of the equation (1) is now well known and reads as

$$P(x, t) \approx t^2 e^{-xt} \quad (5)$$

which gives $\phi(\xi) = e^{-\xi}$. Therefore, both the exact solution and the dimensional analysis confirm that t^2 bears the dimension of $P(x, t)$ and x bears the dimension inverse of time. We shall use this result later.

We now study the random sequential deposition of a mixture of points and of particles of size σ . Considering the rate equation for the classical car parking problem and the binary fragmentation model, we can write the following equations:

$$\begin{aligned} \frac{\partial P(x, t)}{\partial t} = & -(x - q\sigma)P(x, t) \\ & + 2q \int_{x+\sigma}^\infty dy P(y, t) + 2(1 - q) \int_x^\infty P(y, t) dy \quad \text{for } x \geq \sigma \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\partial P(x, t)}{\partial t} = & 2q \int_{x+\sigma}^\infty dy P(y, t) \\ & + (1 - q) \left(-xP(x, t) + 2 \int_x^\infty P(y, t) dy \right) \quad \text{for } x < \sigma. \end{aligned} \quad (7)$$

This is an obvious generalization of the RSA problem, in which at each time event a particle of size σ is deposited with probability q or a point is deposited with probability $(1 - q)$. Another way of interpreting the present model is that at each time event a car is parked with probability q on the one-dimensional parking space or the parking space is divided into smaller spaces with probability $(1 - q)$. Knowing the solution of equation (2) and the solution for the car parking problem alone, we write the following *ansatz*:

$$P(x, t) = A(t)e^{-(x-q\sigma)B(t)} \quad (8)$$

where $A(t)$ and $B(t)$ are yet to be determined. The simplest way of finding $B(t)$ is by appreciating that the argument of an exponential function must be a dimensionless quantity. On the other hand, equation (6) implies that $(x - q\sigma)$ is the rate at which gaps of size x are destroyed, and hence it must bear the dimension inverse of time. Therefore, only $B(t) \sim t$ can make the solution physically acceptable. On the other hand, the factor $A(t)$ must bear the dimension of $P(x, t)$ and hence we must have $A(t) \propto t^2$. In order to obtain exact solutions for $A(t)$ and $B(t)$ one can also substitute the *ansatz* into the equation (6). This gives two differential equations, (i) the differential for $B(t)$, $\frac{dB(t)}{dt} = 1$ and (ii) the differential equation for $A(t)$

$$\frac{d \ln A(t)}{dt} = 2q \frac{e^{-\sigma t}}{t} + \frac{2(1 - q)}{t}. \quad (9)$$

Both the equations should be solved subject to the initial condition $P(x, 0) = 0$ and $\int_0^\infty dy y P(y, 0) = 1$ since initially the line is empty [16]. These two initial conditions imply

$$A(0) = B(0) = 0 \quad \text{and} \quad \lim_{t \rightarrow 0} \frac{A(t)}{B^2(t)} = 1. \quad (10)$$

Solving equations for $A(t)$ and $B(t)$ subject to the initial condition gives

$$A(t) = t^2 F_q(\sigma t) \quad \text{and} \quad B(t) = t \quad (11)$$

where $F_q(\sigma t) = \exp\left(-2q \int_0^{\sigma t} \frac{(1-e^{-u})}{u} du\right)$ and a dimensionless quantity. These explicit solutions for $A(t)$ and $B(t)$ further support our previous observation based on dimensional analysis. The solutions of equations (6) and (7) are, therefore,

$$P(x, t) = t^2 F_q(\sigma t) e^{-(x-q\sigma)t} \quad \text{for } x \geq \sigma \quad (12)$$

and

$$P(x, t) = \int_0^t d\tau \tau F_q(\sigma \tau) e^{-(x-q\sigma)\tau} [2q e^{-\sigma\tau} + (2-\tau)(1-q)] \quad \text{for } x < \sigma. \quad (13)$$

The above solutions imply that we can still recover the solution of the binary fragmentation process by taking $\sigma = 0$. It is important to mention that the solution of equation (6) alone is enough to provide us with all the interesting information we need. In fact, we never use the solution for $P(x, t)$ when $x < \sigma$, which is also true in the case of the classical car parking problem.

To give a scaling analysis and for better clarity we define $P(x, t) \equiv P((x - q\sigma), t)$ for $x \geq \sigma$, then we find that the solution of equation (6) satisfies the following identity:

$$P((x - q\sigma)\lambda, t/\lambda) = \lambda^{-2} P((x - q\sigma), t). \quad (14)$$

This relation is the hallmark for the existence of scale invariance and it is equivalent to a *data-collapse* formalism [20], as we shall show below. It means that if the deposition rate $(x - q\sigma)$ is increased by a factor λ , and the observation time is decreased by the same factor, then the resulting structure would look the same except for a numerical prefactor. In other words, increasing $(x - q\sigma)$ by a factor of λ and decreasing t by the same factor means that the numerical value of the gap-size distribution function is reduced by a factor of λ^2 . Since the equation (13) is true for all positive values of λ , we can choose $\lambda = t$ in equation (13) then

$$P_{\text{scale}} = P(\xi, 1) = \phi(\xi). \quad (15)$$

Here

$$P_{\text{scale}} = \frac{P}{t^2} \quad \text{and} \quad \xi = (x - q\sigma)t \quad (16)$$

and $\phi(\xi)$ is the scaling function. For further clarity we define $\xi = \zeta - q\eta$, where $\zeta = xt$ and $\eta = \sigma t$. Then comparing with the explicit solution we get

$$\phi(\xi) = F_q(\eta) e^{-\xi}. \quad (17)$$

This clearly reveals that ϕ is indeed a dimensionless quantity. Therefore, if P_{scale} is plotted against the scaled size ξ , then the entire family of curves collapses into one single curve described by the function $\phi(\xi)$. This is possible due to the fact that the scaling function depends only on a dimensionless quantity, the numerical value of which must be independent of the choice of units. The method of *data collapse* is a very powerful technique for establishing scaling and it is especially useful to analyse and extract exponents from data obtained from numerical simulations or from real-life experiments.

The most important quantity of interest in the RSA process is the coverage which is defined as

$$\theta(t) = 1 - \int_0^\infty x P(x, t) dx. \quad (18)$$

It tells us the fraction of the substrate covered by the depositing particles. In the case of classical random car parking problem only 74.759% of the total substrate is covered by the

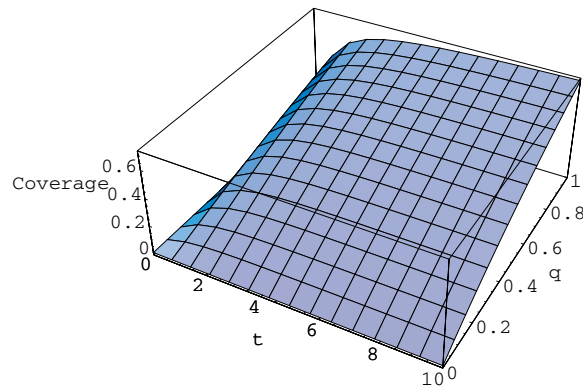


Figure 1. Jamming coverage vs time t and probability q (a 3D view).

depositing particles. It is now interesting to see, how the deposition of points or the division of parking spaces changes the jamming phase. In the present case, of course, there is always space for adsorption of points as the points do not have any width due to their inherent definition. Hence, they do not contribute to the coverage or the jamming phase. Therefore, in this model the jamming coverage is the state when there are no more gaps available for the adsorption of particles of size σ . Once this state is achieved, it is no longer necessary to continue the process as far as the jamming state is concerned. So, it would be interesting to see in what way the coverage changes, if at all.

To find this out, it is more convenient to deal with the rate equation for the coverage than the coverage itself. Combining equations (6), (7) and (17) we get

$$\frac{d\theta}{dt} = q\sigma \int_{\sigma}^{\infty} dx (x - \sigma)P(x, t). \quad (19)$$

Clearly, this states that only fixed-sized particles contribute to the coverage. Note that the right-hand side of equation (18) bears the inverse dimension of time, as it should. Substituting the solution of equation (6) into this and integrating it, we find the final expression for the jamming coverage

$$\theta(\infty) = q \int_0^{\infty} ds F_q(s) e^{-(1-q)s}. \quad (20)$$

This is a dimensionless quantity and hence, upon transition from one unit of measurement to another within a given class, its numerical value must remain unchanged. Therefore, the final coverage or the jamming coverage $\theta(\infty)$ is independent of the size of the depositing particle σ , which is indeed a non-trivial and interesting result. This also reflects the fact that the gap-size distribution function $P((x - q\sigma), t)$ satisfies the exact identity (equation (13)) and the function $F_q(\sigma t)$ is a dimensionless quantity. In fact, all properties of interest are independent of the size of the depositing particle, and the rate at which they are adsorbed is due to the existence of the scaling property. Clearly, if σ is increased by a factor λ , then the time to reach the jamming configuration is reduced by a factor λ . However, this is true only if the substrate is sufficiently large in comparison to the depositing particle. One can now obtain a whole range of values for the jamming coverage by just tuning the q value. Figure 1 shows that the jamming state starts from zero at $q = 0$, since there the problem reduces itself to the random sequential adsorption of points. Note the inherent definition of point that does not occupy space. Therefore, one might apprehend that it does not play any role in achieving the

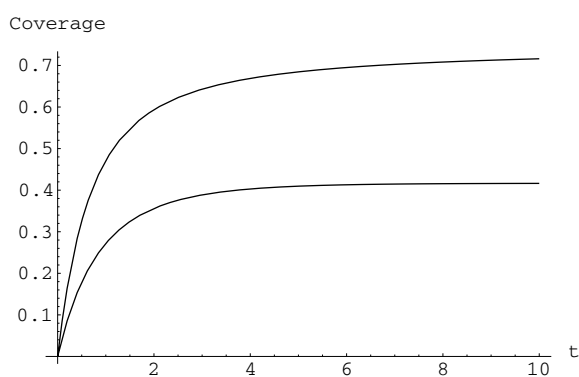


Figure 2. Jamming coverage $\theta(\infty)$ vs time t . The lower curve is for $q = \frac{1}{2}$ and the upper curve for $q = 1$ (the classical car parking).

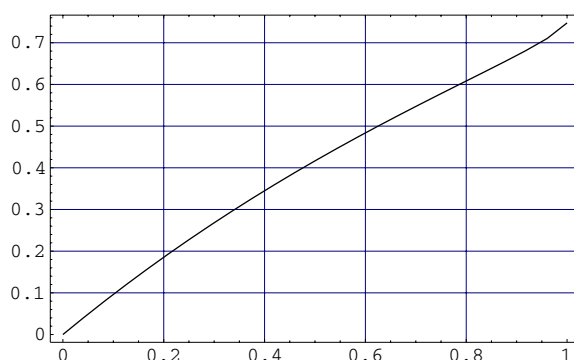


Figure 3. Jamming coverage $\theta(\infty)$ vs q (this is, in fact, the [100] face of figure 1).

jamming coverage if it is adsorbed sequentially with a fixed-sized particle. However, note that once a point is deposited, it excludes fixed-sized particles from landing within around $\sigma/2$, which is the distance between the point where it is chosen to land and the centre of the fixed-sized particle. This exclusion will certainly have effect on the resulting dynamics of the process.

In other words, a point divides the substrate, and hence each successful deposition of points creates two new ends belonging to two different gaps. No particle can be adsorbed on a space which belongs to two different gaps, i.e. overlapping of points is forbidden. We find that for $q > 0$, the jamming coverage changes non-trivially. Figure 1 exhibits a 3D view of the jamming coverage against time and the probability q with which fixed-sized particles are adsorbed. Figure 2 is the cross-section of the coverage–time plane at $q = 1$ and $q = 1/2$ of figure 1. It is generally believed that if a mixture contains a small number of particles of different sizes, then the kinetics and the jamming configurations are primarily determined by the smallest size, which in the present case is a point particle. However, in our study we find that the jamming coverage is primarily determined by the larger particle; yet its dynamics and other aspects are influenced by the size of the smaller particle. For $q > 0$, the jamming coverage is always smaller than its corresponding classical counterpart. Figure 2 is plotted to demonstrate the slower approach to the jamming state as the q value decreases. This is due to the fact that the adsorption of points leads to the crowding of more partition in the parking space than to the adsorption of fixed-sized particles. Figure 3, in fact, is the cross section of

coverage– q plane of figure 1 at the state when the system has achieved the jamming limit. It shows that the jamming coverage increases monotonously as fixed-sized particles win more in the competition with the point particles for adsorption. However, it does not increase linearly with q ; instead one can subdivide the whole curve into a number of regimes of width 0.2 in q values, so that in each regime they can be well approximated to a straight line. The appearance of a nonlinear rise becomes more pronounced if it is plotted on a larger scale.

In conclusion, the present model, though simple, can yet capture some generic features of the RSA of the mixture of particles such as coverage and the scaling behaviour. We find that the coverage of mixture of points with fixed-sized particles stays always lower than its classical counterpart. It would be interesting to see how the results change when both the contents of the binary mixture are of a finite size but differ in length, which we intend to present in a forthcoming paper [21]. In addition, we give an extensive scaling description of the RSA problem which has not been addressed so far. One potential application of the present work could be the simple cyclization reaction process where adjacent pendant groups link randomly along the polymer, or the polymer itself undergoes a possible degradation. This is in fact a natural generalization of the original work by Folry [2]. We believe the present work will shed new light into the underlying mechanism of the problem and will help guiding numerical and experimental works dealing with more realistic situations addressing the adsorption of mixture.

Acknowledgments

We are grateful to P L Krapivsky and Dr G J Rodgers for useful correspondence during the work. MKH is grateful to the Alexander von Humboldt Foundation for awarding the fellowship.

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