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Physica A 239 (1997) 267–275

PHYSICA A

# Pattern formation in size-polydisperse adsorption: fractal properties and transition to order

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**Abstract**

Random sequential adsorption of particles with size polydispersity (PRSA) is investigated. For the PRSA with a power-law small-size distribution, $P(R) \sim R^{\alpha-1}$, we reveal the fractal nature of the arising patterns. The fractal dimension $D_f$ is found to decrease from 2 to $D_A = 1.305\ldots$, the fractal dimension of the Apollonian packing, as $\alpha$ increases from 0 to $\infty$. We examine PRSA by a combination of exact, scaling, mean-field, and numerical approaches. We find that the scaling theory works fairly well for the whole range of $\alpha$, while the mean-field theory (MFT) is applicable only for small $\alpha$. We attribute this failure of the MFT to the increasing regularity of the PRSA patterns with increasing $\alpha$. We confirm this conclusion by the direct measurement of the entropy production rate of the pattern formation process, which demonstrates the transition from an irregular regime of the pattern formation to the regular one.

*PACS*: 81.10.Aj; 02.50.-r; 05.40.+j; 61.43.-j

## 1. Introduction

The adsorption-type processes are very common in nature. One can find corresponding examples in a variety of fields, ranging from ecology to chemistry and physics [1]. In the case of irreversible adsorption, the random sequential adsorption (RSA) models are especially popular. RSA models have been applied to adhesion of proteins and colloidal particles onto surfaces, polymer chain reactions, car parking, etc. [2,3]. In the simplest form, the RSA model may be formulated as a random sequential addition of objects (particles, molecules, cars, etc.) onto a surface under assumptions that objects cannot overlap and once inserted cannot move or leave the structure. At the beginning

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*PII* S0378-4371(96)00485-2

of the process there are no correlations in the positions of particles, while with increasing coverage, the spatial correlations become dominant, demonstrating fairly collective character of the pattern-formation process. In the ordinary RSA of identical objects, the process continues until the the jamming limit is reached, i.e. when no additional object may be placed onto the surface. Geometric and kinetic properties of the RSA processes with identical objects are thoroughly investigated [2,3], while for the RSA of mixtures much less is known [4–7]. The natural generalization of the ordinary RSA is the RSA with polydispersity of particles size (PRSA). In contrast to the ordinary RSA, PRSA models demonstrate a scaling kinetic behavior [6,7], the fractal properties of arising patterns [7], and the transition from the irregular regime of pattern formation to the regular one [7].

The paper is organized as follows. In Section 2 we sketch some results of the RSA model and discuss its generalization to the polydisperse case. In Section 3 the pattern formation kinetics in the PRSA is addressed. We formulate a scaling and a mean-field theory, and present the numerical results for 2D systems. In Section 4 we discuss the spatial properties of the arising patterns and introduce the quantitative measure of their order. With the use of the quantitative criterion we analyze the regularity of the pattern formation process. Finally, Section 5 summarizes our findings.

## 2. Polydisperse random sequential adsorption

Like most statistical mechanical problems, exact solutions for the ordinary RSA exist only for one-dimensional systems [8]. In particular, for the continuum RSA the coverage exhibits the following asymptotic behavior:

$$\theta(t) = \theta_\infty - \frac{\exp(-2\gamma)}{t} + \cdots . \tag{1}$$

Here $\theta_\infty = 0.747597\ldots$ is the jamming coverage, and $\gamma = 0.577215\ldots$ is Euler's constant. In higher dimensions most of the information comes from numerical investigations [2,3]. Many studies have been performed with objects of spherical symmetry (hard discs, hard spheres, etc). It was suggested by Feder [1], and then proven [9,10], that the coverage near the jamming limit behaves as $\theta_d(\infty) - \theta_d(t) \sim t^{-1/d}$ for any dimension $d$. It was believed [10], that such asymptotic behavior is universal for all isotropic RSA systems. In the subsequent studies [4,6], however, it was observed that the asymptotic behavior for mixtures is generally determined by the size distribution near the small-size cutoff. In the present study we also conclude that the long-time behavior of the coverage is sensitive to the particles size distribution. Moreover, we observe that the very regime of the pattern formation qualitatively changes when the parameter of the particles size distribution varies.

Applying the RSA model to real processes in nature, one should take into account that particles are not of the same size. The relevant example is an adsorption of colloidal particles that have a broad radii distribution. It is usually described by the Schulz distribution [11]

$$P(R) = \left[\frac{\alpha}{\langle R\rangle}\right]^{\alpha} \frac{R^{\alpha-1}}{2\Gamma(\alpha)} \exp\left[-\frac{\alpha}{\langle R\rangle}R\right]. \tag{2}$$

Here $R$ is the particle radius, $\Gamma(x)$ is the gamma function, and $\alpha > 0$ due to the normalization requirement. The RSA with the continuous size distribution may be called as (size)polydisperse RSA (PRSA).

Since the most important properties of the PRSA are determined by the size distribution at small size limit, we ignore the large-size tail in (2) and consider a simplified power-law model

$$P(R) = \begin{cases} \alpha R^{\alpha-1} & \text{for } R \leqslant 1\,, \\ 0 & \text{for } R > 1\,, \end{cases} \tag{3}$$

with a cutoff at the dimensionless radius $R = 1$ (one can imagine that we deal with the distribution (3) which is obtained after "filtration", that removes large particles). The distribution (3) exhibits several interesting properties, which are discussed below.

## 3. Scaling and mean-field theories of the PRSA pattern formation

In the following, we assume that the distribution (3) gives the adsorption rates for particles of different sizes, and show how it entails the scaling kinetics and fractal properties of arising structures. It is worth noting that the PRSA does not have the jamming coverage, since smaller and smaller particles can be placed into the holes between the larger ones. This *self-similar process* gives rise to a *self-similar structure*, i.e. fractal. To describe the adsorption kinetics, we introduce the fraction of the uncovered area $\Phi(t)$ at time $t$, and $\Psi(R,t)$ the probability that a disc of radius $R$ can be placed somewhere in the system [7]. From the definition of these functions it follows that $\Psi(0,t) = \Phi(t)$, since the probability of placing a point particle is equal to the free area, and

$$\frac{d\Phi}{dt} = -\int_0^\infty dR\, P(R)\Psi(R,t)\Omega_d R^d\,, \tag{4}$$

since the free area decreases due to adsorption of particles of radii $R$ with probabilities $P(R)\Psi(R,t)$. $\Omega_d$ in Eq. (4) denotes the volume of the $d$-dimensional unit ball. Following the rigorous result of [6] for 1D systems, we assume the scaling behavior of $\Psi(R,t)$ at large $t$:

$$\Psi(R,t) = S^{\theta} F\left(\frac{R}{S(t)}\right). \tag{5}$$

Here $S(t) \sim t^{-\nu}$ is a typical gap between neighboring adsorbed particles, and the scaling description is applied for the scaling regime, $t \gg 1$ and $R \ll 1$ with $R/S(t)$ finite. The scaling assumption for $\Psi(R,t)$ implies $\Phi(t) \sim t^{-z}$ with $z = \theta v$. Using the scaling anzatz (5), one obtains from Eq. (4),

$$v = (\alpha + d)^{-1},$$
$$z \simeq \alpha \Omega_d \int_0^\infty dx\, x^{\alpha+d-1} F(x). \tag{6}$$

For $d=1$ we get $v = (1+\alpha)^{-1}$ in agreement with the exact result [6].

Now we show that the scaling kinetic behavior entails the fractal properties of the arising patterns. Let $n(R)$ be a number of adsorbed particles per unit area, with radii ranging from $R$ to $R + dR$, and $\varepsilon$ be a cutoff size. The structure is a fractal if the number of particles with radii greater than $\varepsilon$ behaves as

$$N(\varepsilon) = \int_\varepsilon^\infty dR\, n(R) \sim \varepsilon^{-D_f} \tag{7}$$

at the small sizes limit (see e.g. [12]). $D_f$ here is a fractal dimension. One can calculate $n(R)$ from the function $\Psi(R,t)$ as

$$n(R) = \int_0^\infty dt\, P(R)\Psi(R,t) \sim R^{\alpha-1+(z-1)/v}. \tag{8}$$

Using (7) and (8), one finds the fractal dimension

$$D_f = d - z(d+\alpha). \tag{9}$$

As follows from Eq. (9), the fractal dimension of the arising patterns is intimately related to the kinetic exponent $z$, similar to the other pattern formation models [13,14].

For the 1D PRSA one has the *exact* result for the exponent $z$ [6]:

$$z = (2-\beta)/(1+\alpha), \tag{10}$$

where $\beta$ is the solution of the equation $2\Gamma(\alpha+2)\Gamma(\beta) = \Gamma(\alpha+\beta+1)$. For $\alpha=1$, i.e. for the flat distribution, one gets $D_f = (\sqrt{17}-3)/2 = 0.561553\ldots$ and for the small $\alpha$ limit the following expansion holds:

$$D_f = 1 - \alpha + \left(\frac{2\pi}{3} + 4\gamma^2 - 2 - 6\gamma\right)\alpha^2 + \cdots. \tag{11}$$

For $\alpha \to \infty$, the trivial limit, $D_f = 0$ is obtained.

In the general case of arbitrary $d$ we are not able to calculate the kinetic exponent, or prove the existence of scaling. For the 2D-systems we perform a Monte Carlo study of the PRSA. For every value of $\alpha$ we generated $10^7$ discs and analyzed the slope of the $N(\varepsilon)$ dependence. From the part of the curve that had a constant slope for several decades we calculated the fractal dimension [12–14]. Typical patterns for

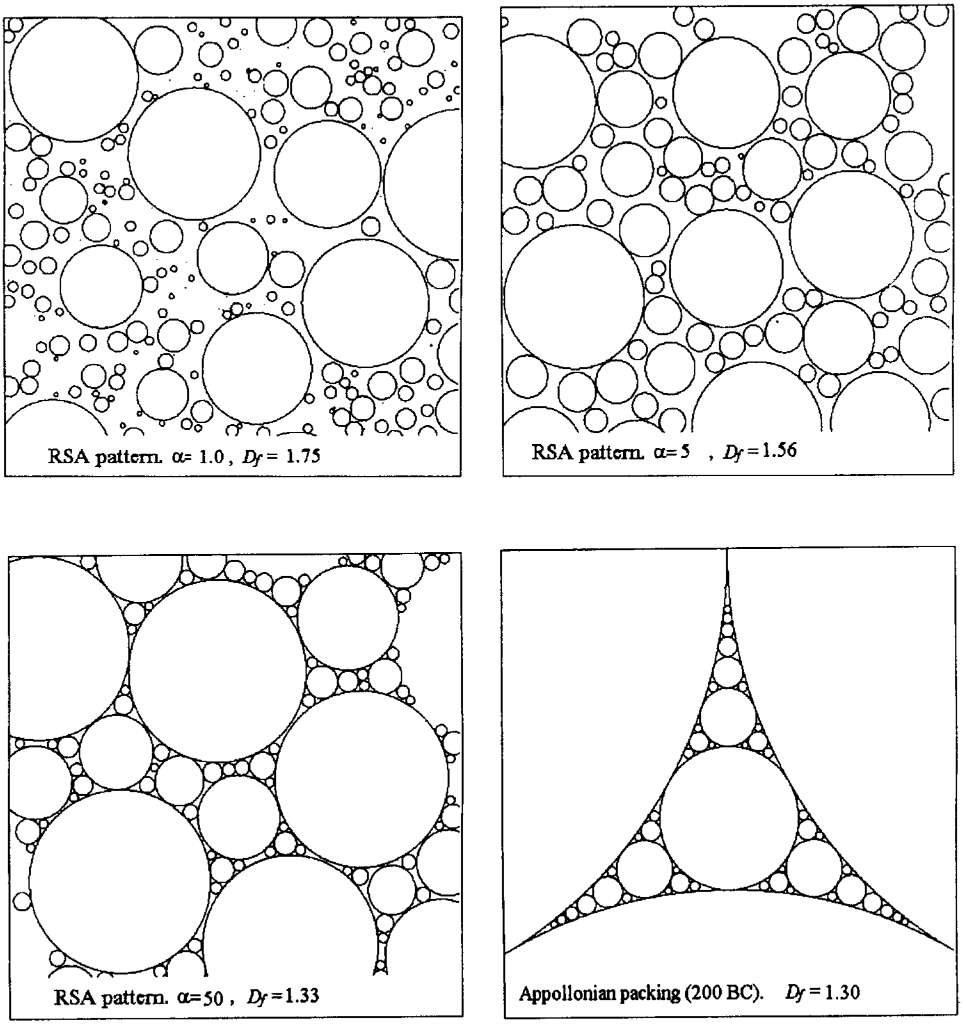


Fig. 1. Typical PRSA patterns for different values of $\alpha$, and the Apollonian packing (right bottom). Only a small part of the total number of generated discs is shown.

different values of parameter $\alpha$ are shown in Fig. 1. The Monte Carlo results for the fractal dimension are presented in Table 1. The fractal dimension, calculated from the scaling theory, with the kinetic exponent $z$, taken from the numerical data is also given. Table I shows that the scaling theory works fairly well for the whole range of $\alpha$.

In the same way as in Refs. [13,14], we developed a mean-field theory (MFT) [7], which becomes exact at $\alpha \to 0$ limit [7]. The MFT expression for the scaling function $F(x)$ reads

$$F(x) = \exp(-A_1 x - \cdots - A_d x^d), \tag{12}$$

Table 1
Kinetic and structural properties of the PRSA model

| Distribution parameter $\alpha$ | Kinetics parameter $z$ | MFT predictions for $z$ | Fractal dimension $D_f$ | Predicted $D_f = D - z(D+\alpha)$ |
|---|---|---|---|---|
| 0.05 | 0.021 ±0.001 | 0.021 | — | — |
| 0.1 | 0.034 ±0.002 | 0.038 | — | — |
| 0.2 | 0.055 ±0.004 | 0.063 | 1.90 ±0.06 | 1.88 |
| 0.5 | 0.078 ±0.003 | 0.109 | 1.83 ±0.04 | 1.81 |
| 1.0 | 0.085 ±0.002 | 0.154 | 1.75 ±0.03 | 1.74 |
| 2.0 | 0.077 ±0.002 | 0.203 | 1.70 ±0.03 | 1.69 |
| 5.0 | 0.060 ±0.002 | 0.261 | 1.56 ±0.02 | 1.58 |
| 10 | 0.038 ±0.002 | 0.295 | 1.51 ±0.02 | 1.54 |
| 20 | 0.024 ±0.001 | — | 1.42 ±0.02 | 1.47 |
| 50 | 0.012 ±0.001 | — | 1.33 ±0.02 | 1.39 |
| Apollonian | — | — | 1.30 | — |
| Packing | — | — | — | — |

where the coefficients $A_1,\dots,A_d$ may be found from the self-consistent equations. In particular, for the 2D system one has the following set:

$$A_{1,2} = c_{1,2}\pi(\alpha+2)\alpha \int_0^\infty x^{d_{1,2}} e^{-A_1 x - A_2 x^2} dx \tag{13}$$

with $c_1 = 2$, $c_2 = \frac{1}{2}$, and $d_1 = \alpha$, $d_2 = \alpha - 1$. Solving Eqs. (13), one can calculate the kinetic exponent $z$ from Eqs. (12) and (6), and finally, the fractal dimension from Eq. (9). The MFT results for $z$ are shown in Table 1. As shown in the table, the MFT is quite accurate for small $\alpha$, but it fails completly at $\alpha > 1$. The failure occurs since the MFT ignores many-particles correlations [13,14], which become dominant for large $\alpha$. The increasing order of the arising patterns is demonstrated in Fig. 1, where the patterns for $\alpha = 1$, $\alpha = 5$, and $\alpha = 50$ are shown. In Fig. 1 we also show the Apollonian packing, which is perhaps the first historically mentioned fractal (200 BC) [15]. Analysing the ordering tendency in Fig. 1 and the $\alpha$ dependence of the fractal dimension, given in Table I, one can guess that the PRSA patterns tend to the Apollonian packing at $\alpha \to \infty$. More detailed analysis confirms this conclusion [7].

The Apollonian packing is obtained as the result of the regular process, when every next disc is placed into a hole between three touching discs. Therefore, one anticipates that the regularity of the pattern formation process increases with increasing $\alpha$, and that it has the maximal regularity at $\alpha \to \infty$. To get a quantitative measure of the regularity of the patterns and of the pattern formation process, we introduce an entropy $S_N$ that characterizes the degree of order of the $N$-particles pattern [7]. If $C_k(N)$ denotes $N$-particle pattern and $p(C_k)$ denotes the probability of that pattern, one can define the Shannon entropy [16]

$$S_N = -\sum_{C_k} p(C_k) \log_2 p(C_k)\,, \tag{14}$$

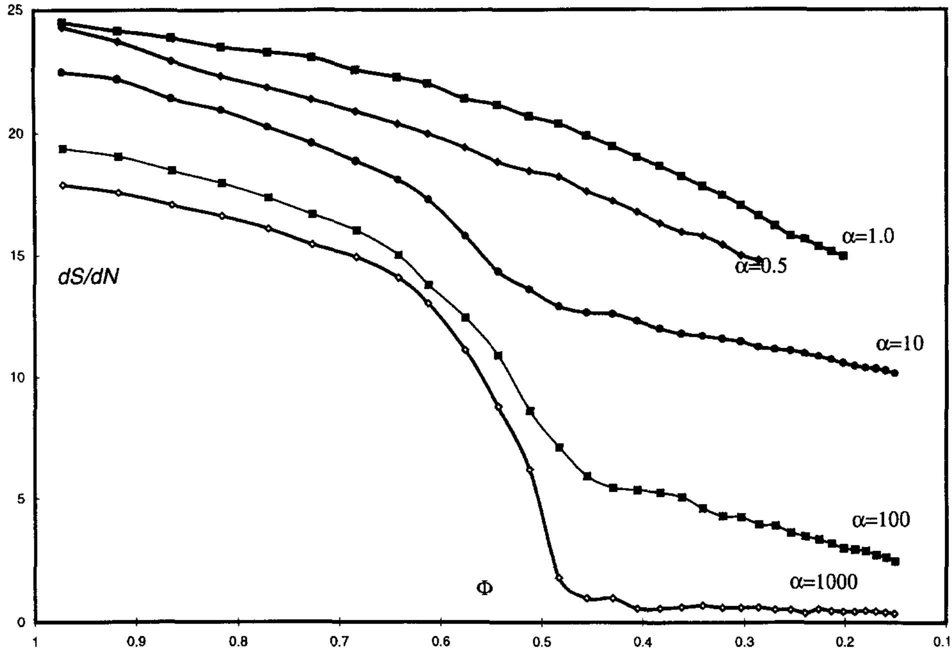


Fig. 2. The dependence of the entropy production rate upon the the uncovered area $\Phi$ for different values of $\alpha$.

where the summation over a continuous set of configurations is implied (obviously, in the numerical studies, only a finite set is used, but we assume that this set is representative). As can be seen from Eq. (14), $S_N = 0$ for a regular pattern, since only one definite configuration with the probability $p = 1$ contributes to the entropy. In contrast, $S_N$ has the maximal value when the number of the allowed configurations is maximal. While $S_N$ characterizes the regularity of the patterns, the closely related value, the entropy production rate, $dS_N/dN \simeq S_{N+1} - S_N$, characterizes the regularity of the pattern formation process. The latter may be computed from the conditional entropy $S_N[C_k(N-1)]$ of the $N$ disc for the given pattern $C_k(N-1)$ of $N-1$ discs [7]. Referring for calculations details to [7], we show the resultant dependence of the entropy production rate upon the uncovered area $\Phi$ (Fig. 2). As one can see from Fig. 2, for small and intermediate values of $\alpha$, $dS_N/dN$ varies smoothly with $\Phi$, while at large $\alpha$, the entropy production rate behavior drastically changes. At the beginning of the PRSA process (at small $\Phi$) $dS_N/dN$ decreases in the same manner as before (for small $\alpha$), but it sharply drops down at $\Phi \approx 0.55$. The latter value of $\Phi$ corresponds to the jamming density $\Phi_\infty = 0.542\ldots$ of the ordinary RSA of identical discs in 2D.

To explain this phenomenon we analyze the adsorption rate distribution, Eq. (3), for $\alpha \gg 1$. In this limit only a disc of the maximal possible size is added to the system at every adsorption event. At the beginning of the PRSA process the maximal radius is equal to 1, and the ordinary RSA takes place. This stage of the process is irregular and there is no qualitative difference between PRSA with different $\alpha$. When the jamming density is reached, the rule "insert the disc of the maximal size" starts to work and a much more regular process with a low entropy production rate is observed. Since the disc of the maximal size should touch the other three ones, as in the Apollonian packing (AP), the fractal dimension of the AP is obtained in the $\alpha \to \infty$ limit (see [7] for details).

## 4. Summary

We studied the random sequential adsorption of particles with size polidispersity (PRSA), modelled by a power-law size distribution. We developed a scaling theory that relates the structural (fractal) properties of the arising patterns with the kinetic exponent and with the power-low exponent of the particle size distribution $\alpha$. The scaling theory was confirmed by numerical studies in 2D and by comparison with exact results for the 1D PRSA. A mean-field theory of the PRSA was also elaborated. We found that the mean-field theory provides a reasonable approximation for small $\alpha$, but completely fails at large $\alpha$, when pronounced spatial correlations were observed. We revealed that the PRSA patterns have a fractal dimension $D_f$ that sensitively depends on $\alpha$. The $D_f(\alpha)$ dependence was analyzed analytically for 1D systems and numerically for 2D systems. For the 2D PRSA we found that $D_f$ decreases from 2 at $\alpha \to 0$ to $D_A = 1.305\ldots$ of the Apollonian packing at $\alpha \to \infty$. We introduced the entropy production rate as a quantitative criterion of the regularity of the pattern-formation process. With the use of this criterion we have found that for large $\alpha$ a transition from the irregular regime of the pattern formation to much more regular occurs at the jamming coverage of the ordinary RSA model.

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