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RANDOM SEQUENTIAL ADSORPTION OF DISCORECTANGLES COVERED WITH REPULSIVE SHELLS

Adsorption of anisometric particles (discorectangles) on a two-dimensional substrate has been studied. The aspect ratio (the length-to-width ratio $\varepsilon = l/d$) was changed within the interval ε = 1–10. A modified random sequential adsorption (RSA) model is studied. In this model, the particles were covered with repulsive shells. The main parameters of the model are the thickness R_c of the permeable shell and the maximum number Z_m of the shells of the nearest particles that can be crossed by the shell of the next deposited particle. The behavior of the degree of surface coverage in the saturated (jammed) state at various values of the parameters R_c, Z_m, and ε is discussed.

Keywords: adsorption, two-dimensional films, jamming, interparticle interactions.

1. Introduction

The model of random sequential adsorption (RSA) is widely used to study the structure of adsorption layers on the surface [1, 2]. In this model, every subsequent attempt to adsorb a new particle is accompanied by a check for the absence of its intersection with previously deposited ones. The particles in the sediment are fixed and do not change their spatial position and orientation. The particles are deposited until reaching the saturation state (jamming).

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The RSA model gained wide popularity, when it was applied to study the adsorption of segments on a one-dimensional line [3]. In this case, the exact value $\varphi_j \approx 0.748$ was obtained for the coverage degree in the jammed state. As a result of computer calculations, the value $\varphi_j \approx 0.547$ was obtained for the model of disc deposition onto a two-dimensional (2D) plane [4]. Currently, the RSA model is widely used to simulate adsorption phenomena during the deposition of macromolecules and colloidal particles [5].

For anisometric particles, the degree of surface coverage in the jammed state, φ_j, depends on the particle aspect ratio ε (this is the ratio between the length of the particle and its width). In particular, for nonoriented discorectangles, the maximum value of $\varphi_j \approx 0.584$ is observed at $\varepsilon \approx 1.84$, and the value of φ_j monotonically decreases as ε grows further [6]. A similar behavior was observed for partially oriented dis-

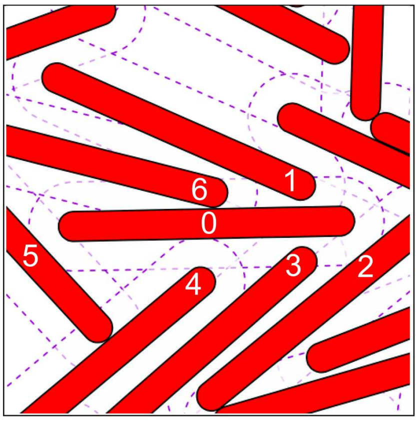


Fig. 1. An example of a packing fragment in the jammed state for discorectangles with the aspect ratio $\varepsilon = 10$. Every particle is surrounded by a permeable shell of thickness $R_c = 1$, which is represented by a dashed curve. The deposited particle is marked with the number 0, and at $Z_m = 6$ it crosses no more than six shells of neighbor particles

corectangles, with the ordering degree substantially affecting the dependencies $\varphi_j(\varepsilon)$ [7].

In the presence of specific interactions between the particle, or between the particles and the surface, the structure of adsorption films can change considerably. Such effects were analyzed in detail for various models of cooperative sequential adsorption (CSA) [8]. For those models, complicated structures, clustering effects, and spatial correlations were observed. In the presence of a specific surface structure, significant changes in the structure of coatings were also observed [9]. The role of electrostatic interactions on the particle adsorption was studied in detail in [10]. The RSA models were also studied in the cases of the particle deposition on partially covered [11] and heterogeneous surfaces [12].

The formation processes for RSA films of discorectangles in thin channels [13], as well as the two-stage RSA models when, for example, the surface is first covered with discs and then with discorectangles [14], were also considered. In the cited works, the kinetics of RSA deposition, the values of the surface coverage degree φ_j in the jammed state, and the structure of adsorption layers were analyzed in detail.

In this paper, a modified RSA model is analyzed for the deposition of discorectangles in which the repulsive interaction between the particles is taken into account. In the modified model, the particles are covered with repulsive shells, which contribute to the loosening of the adsorption layers. The dependences of the surface coverage degree φ_j in the jammed state on the model parameters (the shell thickness R_c and the maximum number of nearest neighbors Z_m) and the particle aspect ratio ε have been analyzed.

2. Computer Model

Discorectangles were randomly and one by one deposited onto a two-dimensional plane. Their aspect ratio was determined as $\varepsilon = l/d$, where l and d sre the length and the thickness, respectively, of the rectangle. All lengths in the model were measured in d units. The total size of the system was $L \times L$, and periodic boundary conditions were imposed.

In the traditional RSA model, the intersection of a deposited particle with pre-deposited particles is forbidden. In the modified model, the intersection of particles is also prohibited. Every particle was surrounded by a permeable repulsive shell of thickness R_c (≥ 0); in Fig. 1, those shells are depicted by dashed curves. When "depositing" every new particle, the number Z of particles that crossed the particle shell at its deposition site (particle 0) was counted. Then the condition $Z \leq Z_m$ was tested, where Z_m (≥ 0) is the maximum allowed number of shell intersections. In the case of a successful deposition attempt, the new particle was put on the list of deposited particles, and an attempt was made to "deposit" another new particle. In effect, the availability of such a repulsive shell corresponds to the modification of the RSA model, in which the adsorption layer is loosened. The value of Z_m determines the intensity of repulsive interactions. In particular, at $Z_m = 0$, they are maximum and gradually decrease, as Z_m increases. If there is no shell ($R_c = 0$) or if $Z_m \to \infty$, this model corresponds to the usual RSA model.

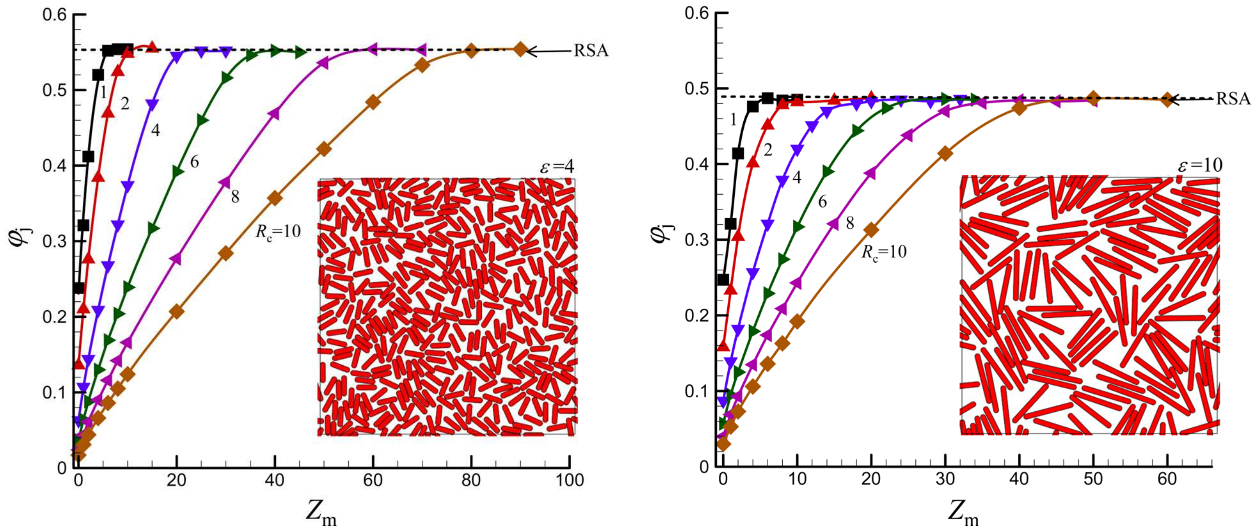
The deposition of particles was continued until the maximum possible degree of surface coverage was achieved,

$$\varphi_j = N\left(\frac{\pi}{4} + \varepsilon - 1\right)\frac{d^2}{L^2},$$

where N is the number of particles in the jammed state.

Figure 1 illustrates an example of a packing fragment in the jammed state for particles with the aspect ratio $\varepsilon = 10$, the shell thickness $R_c = 1$, and $Z_m = 6$.

In this work, all calculations were performed for the fixed value $L = 256$, which substantially exceeds the



a *b*

Fig. 2. Dependences of the coverage degree in the jammed state, φ_j, on the parameter Z_m for various shell thicknesses R_c and various aspect ratios $\varepsilon = 4$ (*a*) and 10 (*b*). The horizontal dashed lines correspond to the corresponding coverage degree in the jammed state for the usual RSA model without particle repulsion. Examples of packing for the usual RSA model are shown in the insets

particle length l. The value of ε was varied within an interval of $1 \le \varepsilon \le 10$. For every set of parameters (ε, R_c, Z_m), 10 to 100 different spatial distributions of particles were generated. The φ_j-values presented in the paper were averaged over different spatial distributions of particles. The calculation errors in the plots correspond to the standard error of the sample mean.

3. Results and Their Discussion

In Fig. 2, examples of the dependences of the coverage degree in the jammed state, φ_j, on the quantity Z_m are shown for various shell thicknesses $R_c = 1 \div 10$ and two values of the aspect ratio $\varepsilon = 4$ (*a*) and 10 (*b*). The values of φ_j increase with the growth of Z_m and gradually approach the values corresponding to the coverage degree for the usual RSA model in the absence of repulsive shells (the horizontal dashed lines). The presence of repulsive shells manifests itself most strongly at large R_c-values and $Z_m = 0$. In this case, the saturation regime is observed at rather low φ_j-values. For a fixed R_c and increasing Z_m, the repulsion between the particles weakens, and this leads to the packing compaction, i.e., to the growth of φ_j. At sufficiently large $Z_m > Z_m^{\mathrm{RSA}}$, a transition is observed to the adsorption regime in the conventional RSA model.

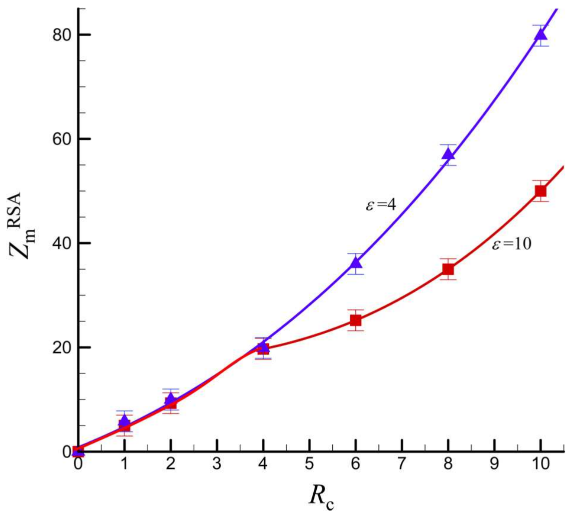


Fig. 3. Dependences of the threshold value Z_m^{RSA} on the shell thickness R_c for two fixed values of the aspect ratio $\varepsilon = 4$ and 10

Figure 3 demonstrates examples of the dependences of the quantity Z_m^{RSA} on the repulsive shell thickness R_c for two values of the aspect ratio: $\varepsilon = 4$ and 10. The magnitude of the threshold Z_m^{RSA}-value at which the transition to the regime of the usual RSA model takes place increases with the growth of R_c. For rather small values $R_c \le 4$, the behav-

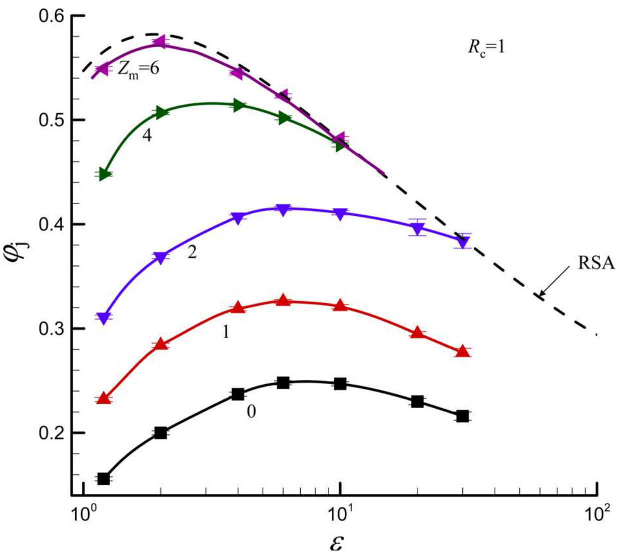


Fig. 4. Examples of the dependence of the coverage degree in the jammed state, φ_j, on the aspect ratio ε for various values of the maximum number of nearest neighbors, Z_m, and the fixed shell thickness $R_c = 1$. The dashed curve corresponds to the dependence $\varphi_j\,(\varepsilon)$ in the usual RSA model

ior of $Z_m^{\mathrm{RSA}}(R_c)$ for $\varepsilon = 4$ and 10 are practically identical, but this behavior is substantially different at larger R_c's. To some extent, the presented dependences $Z_m^{\mathrm{RSA}}(R_c)$ can be considered as two-dimensional phase diagrams for particles with various ε-values. In particular, the structure of jammed packings is loose at $Z_m < Z_m^{\mathrm{RSA}}$, but it coincides with the structure characteristic of the usual RSA model at $Z_m \geq Z_m^{\mathrm{RSA}}$.

In Fig. 4, examples of the dependences of the coverage degree in the jammed state, φ_j, on the aspect ratio ε are exhibited for a fixed shell thickness $R_c = 1$ and various values of the maximum number of nearest neighbors, Z_m. An interesting feature of the presented dependences $\varphi_j(\varepsilon)$ is the presence of a maximum whose position depends on Z_m. Note that for usual RSA (the dashed curve), the maximum value $\varphi_j \approx 0.584$ is observed at $\varepsilon \approx 1.84$ [6]. As Z_m decreases to zero, i.e., if the repulsion between the particles increases, the maximum value of φ_j decreases, and it is observed at larger ε-values.

4. Conclusions

The adsorption of anisometric particles (discorectangles) on a surface is studied. The aspect ratio (the particle length-to-width ratio $\varepsilon = l/d$) was changed within the interval $\varepsilon = 1 \div 10$. A modified model of random sequential adsorption (RSA) is used. In this model, the particles are covered with repulsive shells. The main parameters of the model are the thickness of the permeable shell R_c and the maximum number Z_m of the shells in the nearest particles that can be crossed by the shell of the next deposited particle. The behavior of the surface coverage degree in the jammed state at various values of the parameters R_c, Z_m, and ε is discussed. In further research, it is planned to study the unified RSA model, where attractive and repulsive interactions will be taken into account and to study, in detail, the porous structure of packings in this model.

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ВИПАДКОВА ПОСЛІДОВНА АДСОРБЦІЯ ДИСКОПРЯМОКУТНИКІВ, ПОКРИТИХ ВІДШТОВХУЮЧИМИ ОБОЛОНКАМИ

Проведено дослідження адсорбції анізометричних частинок (дископрямокутників) на двовимірній площині. Співвідношення сторін (відношення довжини до ширини $\varepsilon = l/d$) змінювали в інтервалі ε = 1–10. Було вивчено модифіковану модель випадкової послідовної адсорбції (RSA). У цій моделі частинки були покриті оболонками, що відштовхуються. Основними параметрами моделі є товщина проникної оболонки R_c і максимальна кількість Z_m оболонок найближчих частинок, яку може перетнути оболонка наступної осадженої частинки. Обговорено поведінку ступеня покриття поверхні в насиченому стані при різних значеннях параметрів R_c, Z_m, ε.

Ключові слова: адсорбція, двовимірні плівки, стан насичення, міжчастинкові взаємодії.