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Random sequential adsorption of oriented superdisks

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In this work we extend recent study of the properties of the dense packing of "superdisks," by Y. Jiao *et al.* [Phys. Rev. Lett. **100**, 245504 (2008)] to the jammed state formed by these objects in random sequential adsorption. The superdisks are two-dimensional shapes bound by the curves of the form $|x|^{2p}+|y|^{2p}=1$, with $p>0$. We use Monte Carlo simulations and theoretical arguments to establish that $p=1/2$ is a special point at which the jamming density, $\rho_J(p)$, has a discontinuous derivative as a function of p. The existence of this point can be also argued for by a phenomenological excluded-area argument.

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There has been recent interest [1–5] in geometrical packing and surface deposition of noncircular objects in two dimensions (2D). This problem is intriguing from the theoretical point of view. In addition, it finds applications in studies of design and control of prepatterned surfaces with special properties. New capabilities to pattern surfaces at the nanoscale, and use nanosize particles, have promise for development of novel biosensors and detectors, applications in electronics [6,7], catalysis [8], and optics [9,10].

Recently, an interesting study was reported [1] of the densest possible packing of (oriented) "superdisks" defined by $|x|^{2p}+|y|^{2p}\leq 1$. These shapes are illustrated in Fig. 1. In particular, numerical evidence for $0\leq p\leq 1$ (where the $p=0$ shapes are defined as a limit which yields crosses) suggests [1] that the point $p=1/2$ separates different closed-packed structures. Note that $p=1/2$ also separates the convex and concave shapes, as shown in Fig. 1.

Particle deposition at surfaces is irreversible in many experimental situations, and for a theoretical description of their adsorption one can use the random sequential adsorption (RSA) model. The RSA model, as well as its various modifications, finds numerous applications and has been extensively studied [11–28].

However, most RSA studies have been carried out for spherical (circular) and other simply shaped objects. The approach to the jamming density, ρ_J, in RSA processes is described by the standard Pomeau [29] and Swendsen [30] conjecture, which gives the asymptotic results for oriented squares and for disks, which are in agreement with Monte Carlo (MC) simulation results [31,32] (oriented squares) and [17,33] (disks). However, for nonoriented squares evidence has been reported [34] that this conjecture might not work. Moreover, the asymptotic behavior of the deposit density for objects with concave shapes on continuum substrates has not been studied. Studies of the RSA of objects with zero area, such as segments and circular arcs, have reported interesting features of the jamming coverage [35,36].

In this work we consider RSA of oriented superdisks in two dimensions. We use a grid-type MC algorithm [31], which is particularly suitable for evaluating the density of the jammed state because it efficiently treats deposition in small remaining vacancy areas close to jamming; see Fig. 2. Similar to the dense-packing results [1], we find that $p=1/2$ is also a special point for the jammed state of RSA. In addition to numerical evidence, this conclusion will also be substantiated by a phenomenological excluded-area argument.

A superdisk is a 2D version of a d-dimensional superball [1], defined as the volume of the Euclidean space bounded by the surface $|x_1|^{2p}+|x_2|^{2p}+\ldots+|x_d|^{2p}=1$, where x_i are the Cartesian coordinates and p is the deformation parameter. Superballs have full rotational symmetry only when $p=1$ (when they became hyperspheres $D=2$).

The reason that we focus on the point $p=1/2$ is that, with the advent of nanotechnology, and with the proliferation of experiments on deposition of proteins [13,37–40], we expect that situations will be realized when the particle shapes on the surface change between concave and convex depending on the physical and chemical conditions of the environment. This might affect the asymptotic approach to the jamming coverage (an issue that requires a separate detailed study). As demonstrated here, the change in the concavity also results in a nonanalytic behavior of the jamming coverage, $\theta_J(p)$, at $p=1/2$.

In RSA, particles are transported to the target surface with a constant, uniform flux (per unit time and per unit surface area). However, an attempt to deposit a superdisk "particle" at the surface succeeds only if this particle does not overlap any previously deposited superdisks. Otherwise, the particle is assumed transported away (discarded). Such adsorption is a nonequilibrium process: It is assumed that no equilibration processes are active at the surface (on the time scale of the deposition experiment). Thus, at large times the deposited

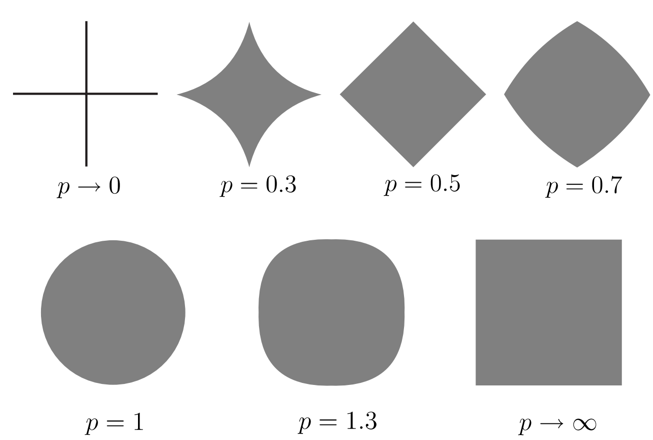

FIG. 1. Superdisk shapes for different values of the deformation parameter p.

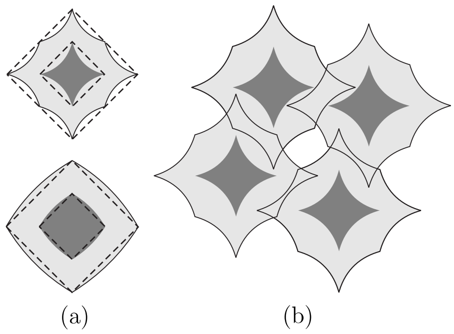

FIG. 2. (a) Superdisks (dark shapes) with their exclusion areas (lighter shapes). Upper panel: a concave superdisk for $p=0.3$. Lower panel: a convex superdisk for $p=0.7$. The dashed lines mark the $p=0.5$ squares and their exclusion areas. (b) A typical configuration of concave superdisks near the jammed state, with at most a single additional superdisk deposition possible with its center landing in the central unshaded area.

particles do not form a regular ordered maximal-density packing. Instead, for large times the deposited layer approaches the jammed-state configuration, with density $\rho_J(p)$. This quantity, the jamming density of the deposited particles per unit area, is related to the jamming coverage $\theta_J(p)$—the fraction of the covered area—via $\theta_J(p)=A(p)\rho_J(p)$, where $A(p)$ is the superdisk area, given by

$$A(p)=\frac{1}{p}\Gamma^2\left(\frac{1}{2p}\right)/\Gamma\left(\frac{1}{p}\right), \qquad (1)$$

where $\Gamma(x)$ is the standard gamma function. Since this function is analytic near $p=1/2$, the behaviors of $\theta_J(p)$ and $\rho_J(p)$ at $p=1/2$ are easily related. We focus on $\rho_J(p)$ because it simplifies some notation below.

The rest of this article is organized as follows. We first describe our MC approach and report simulation results. The phenomenological excluded-area argument for the behavior of the jamming density, including at the special point $p=1/2$, is presented next, followed by summarizing remarks.

In our MC simulations we used an algorithm of the type originally introduced in [31], which allows a particularly efficient simulation of the jammed state and an effective estimation of ρ_J. Specifically, we divided the substrate into small (as compared to the depositing objects) squares of linear size $D/10$. The deposition process was carried out by randomly selecting a fully unblocked or a partially covered square, and generating the position of the center of the next superdisk, the deposition of which is being attempted inside that square. If the square was partially covered by the exclusion areas of the previously deposited superdisc(s), we tested for overlap(s) before allowing the deposition. Finally, after each successful deposition event the coverage configurations of all the squares affected by the newly deposited superdisc were recalculated. The main speed-up of the algorithm [31] is obviously in that for large times, close to jamming, only a very small fraction of all the squares is still "active."

As a substrate we used a square area of size $500D\times 500D$ with periodic boundary conditions, where D is the "diameter" of the superdisks along the x and y axes,

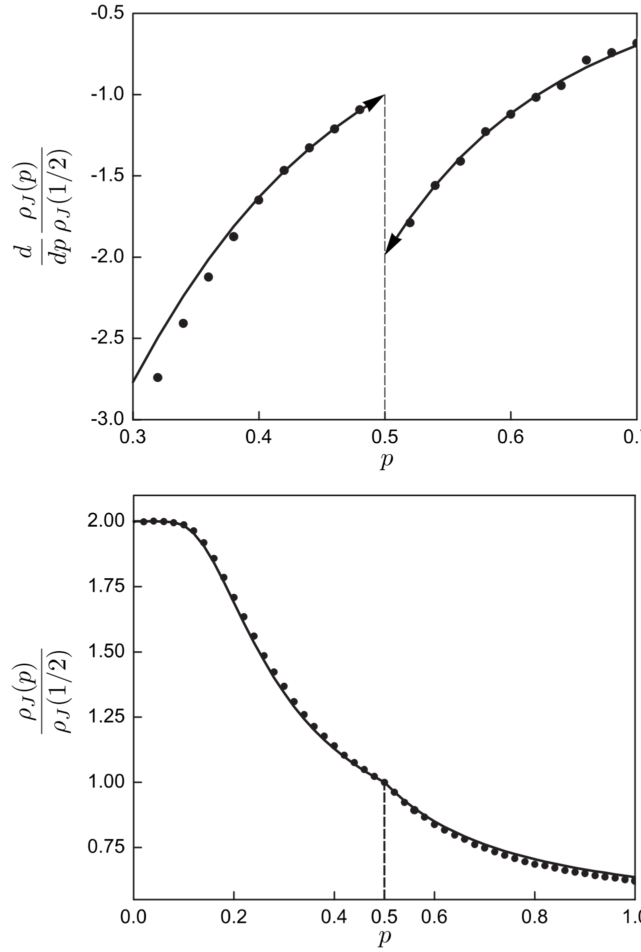

FIG. 3. Lower panel: normalized jamming density of the superdisks, $\rho_J(p)/\rho_J(1/2)$, as a function of the deformation parameter p. Upper panel: the p derivative of the normalized jamming density near the special point $p=1/2$. The symbols are the results of our MC simulations, whereas the solid lines show approximation (2).

equal to 2 in our dimensionless units. Each value of $\rho_J(p)$ was obtained by averaging over 1000 independent runs. The maximum fractional uncertainty in our simulation was estimated as $\Delta\rho_J(p)/\rho_J(p)\simeq 0.002\,23$. Specifically, for the squares ($p=1/2$) and disks ($p=1$) we obtained the estimates $\theta_J(p=1/2)=0.5620\pm 0.0001$ and $\theta_J(p=1)=0.5468\pm 0.0005$, which are consistent with the values reported in [17,31–33].

The behavior of the jamming density as a function of the deformation parameter is shown in Fig. 3. Our data clearly indicate existence of a special point at $p=1/2$. The p derivative of the jamming density $\rho_J(p)$ at this point has a discontinuity, similar to that mentioned in [1] for the densest-packing configuration.

In order to understand the origin of the numerically observed behavior in RSA of superdisks at the special point $p=1/2$, let us consider the exclusion area of a single superdisk, $S(p)$, defined as the area within which it is impossible to deposit another superdisk's center without overlap (Fig. 2). Unlike $A(p)$, the exclusion area $S(p)$ markedly changes its p dependence for p above and below the square-shape value of 1/2; see Fig. 4. It is a continuous function of p, but has a discontinuous derivative at $p=1/2$.

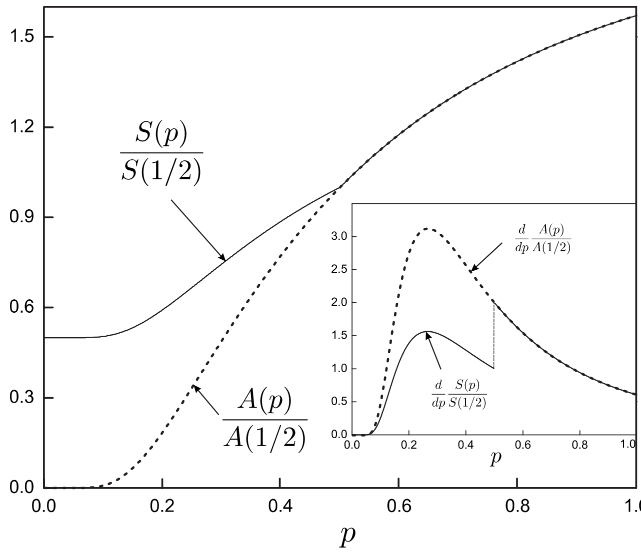

FIG. 4. The dotted line represents the p dependence of the normalized superdisk area, $A(p)/A(1/2)$. The solid line shows the normalized exclusion area of a single superdisk, $S(p)/S(1/2)$, as a function of the deformation parameter p. Inset: The dotted line represents derivative of the normalized superdisk area with respect to the deformation parameter, $\frac{d}{dp}\frac{A(p)}{A(1/2)}$. The solid line shows the derivative of the normalized exclusion area of a single superdisk with respect to the deformation parameter, $\frac{d}{dp}\frac{S(p)}{S(1/2)}$.

We offer that on dimensional grounds it is tempting to conjecture that the following relation should provide a good qualitative *approximation* for the oriented superdisk jamming density ratio,

$$\frac{\rho_J(p)}{\rho_J(1/2)} \simeq \frac{S(1/2)}{S(p)}, \quad (2)$$

at least near $p=1/2$. The expectation is that the product $\rho_J(p)S(p)$ varies much less than the individual factors in it, as a function of p.

It is convenient to define the ratio $s(p) \equiv S(1/2)/S(p)$, given by the following relations:

$$s_+(p) = \frac{A(1/2)}{A(p)} = 2p\Gamma\left(\frac{1}{p}\right)\Gamma^{-2}\left(\frac{1}{2p}\right) \quad \text{for} \quad p \geq \frac{1}{2}, \quad (3)$$

$$s_-(p) = \frac{2A(1/2)}{A(1/2) + A(p)} = \frac{2s_+(p)}{1 + s_+(p)} \quad \text{for} \quad 0 < p \leq \frac{1}{2}. \quad (4)$$

Near $p=1/2$, approximation (2) is a continuous function of p, but has a jump in the p derivative. In fact, the jump in the derivative of $\rho_J(p)/\rho_J(1/2)$, given by our exclusion area approximation, is in a reasonable agreement with the result obtained by MC simulations presented in Fig. 3. The numerical values of the right and left p derivatives of $\rho_J(p)/\rho_J(1/2)$ at $p=1/2$ can be approximated by

$$\lim_{p\to 1/2} \frac{ds_+(p)}{dp} = -2, \quad \lim_{p\to 1/2} \frac{ds_-(p)}{dp} = -1. \quad (5)$$

In summary, in this work we demonstrated by numerical MC simulations, as well as by an approximate excluded-area argument, that the point at which the shape of the superdisks changes from concave to convex is special not only in the geometric closed-packing properties, but also in the jammed-state properties in RSA. Future work will be focused on the dynamical simulations to explore the approach to the jammed state, as well as on studies of unoriented superdisks.

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