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, F. H. Stillinger and S. Torquato, 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 geometrical arguments.

There has been recent interest in the problem of 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 particles of nanosizes, have promise for development of novel biosensors and detectors, applications in electronics, catalysis, and optics.

Recently, an interesting study was reported 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 \(0 < p \leq 1\) (where the \(p = 0\) shapes are defined as a limit which yields crosses) suggests 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 typically irreversible, 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 applications and has been extensively studied in RSA processes is described by the standard Fomage and Swendsen conjecture which gives the asymptotic results for oriented squares and for disks, which are in agreement with Monte Carlo (MC) simulation results (oriented squares), and (disks). However, for non-oriented squares evidence has been reported that this conjecture might not work. Moreover, the asymptotic behavior of the deposition density for objects with concave shapes on continuum substrates has not been studied.

Studies of RSA of objects with zero area, such as rods, circular arcs, etc., have reported interesting features of the jamming coverage. In this work we consider RSA of oriented superdisks in two dimensions. We use a grid-type MC algorithm 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, 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 geometrical arguments.

A superdisk is a 2D case of the surface of a \(d\)-dimensional superball. A superball is 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).

For \(0 < p < 1/2\) superdisks are concave and for \(1/2 < p < \infty\) they are convex. The \(p \rightarrow 0\) superdisk is reduced to cross, the \(p = 1/2\) and \(p = \infty\) shapes are squares, and the \(p = 1\) shape is a circle.

The reason that we focus on the point \(p = 1/2\) is that, with the advent of nanotechnology, and with proliferation of experiments on deposition of proteins, 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, \(\theta_J(p)\),

FIG. 1: Superdisks shapes for different values of the deformation parameter \(p\).

\[ \begin{align*} p &< 0.3 \quad \rho_J(p) \quad 0.3 \quad 0.5 \quad 0.7 \quad p \rightarrow \infty \\
\end{align*} \]
at $p = 1/2$.

In RSA, a superdisk can be deposited at a surface if it does not overlap previously deposited particles. Such adsorption is a nonequilibrium process, and therefore the deposited particle density does not reach the maximal dense packing. Instead, it approaches the jamming density, $\rho_J(p)$, at large times. This quantity, the 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. The latter quantity is given by

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

(1)

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

In our MC simulations we used an algorithm originally introduced in [35], which allows to simulate the formation of the jamming state, and to estimate $\rho_J(p)$, using minimal computer resources. We used a square system of size $500D \times 500D$ with periodic boundary conditions, where $D$ is the “diameter” of the superdisks along the $x$ and $y$ axes, equal 2 in our dimensionless units. Each value of $\rho(p)$ was obtained by averaging over 1000 independent runs. The maximum fractional uncertainty in our simulation was estimated as $\Delta \rho_J(p)/\rho_J(p) \simeq 0.00223$. 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 [35], [36], [21], [37].

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 dense-packing density. In order to understand the origin of this behavior in RSA, let us consider the exclusion area of the superdisks, $S(p)$, defined as the area within which it is impossible to deposit another superdisk’s center without overlap, Fig. 2. Unlike $A(p)$, the area $S(p)$ markedly changes its $p$-dependence for $p$ above and below the square-shape value of $1/2$. It is a continuous function of $p$, but has a discontinuous derivative at $p = 1/2$ (we give the expressions shortly). Therefore, on dimensional grounds it is tempting to conjecture that the following relation provides a good qualitative approximation for the superdisk jamming density ratio,

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

(2)

at least near $p = 1/2$.

![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.](image)

![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 the approximation (2).](image)
For superdisks, $s(p) \equiv S(1/2)/S(p)$ is given by following relations,

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

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

Near $p = 1/2$, the 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

\[ \lim_{p \to 1/2} \frac{ds_+}{dp} = -2 \quad \lim_{p \to 1/2} \frac{ds_-}{dp} = -1 \tag{5} \]

In summary, in this work we demonstrated by numerical MC simulations, as well as by approximate exclusion-area arguments, 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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