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Universality of the power-law approach to the jamming limit in random sequential adsorption dynamics

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Random sequential adsorption (RSA), on a two-dimensional continuum substrate, of different types of zero area objects that disallow domain formation and hence lead to jamming, is examined by simulation. In all the cases, in the asymptotic time regime, the approach of the number density $\rho(t)$ at instant t to jamming density $\rho(\infty)$ is found to exhibit power law $\rho(\infty)-\rho(t)\sim t^{-p}$ as that for RSA of finite area objects. These results suggest the possibility of the power law being universal for all jamming systems in RSA on a continuum substrate. A generalized analytical treatment is also proposed.

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Over the past two decades considerable scientific effort has been devoted to the understanding of the random sequential adsorption (RSA) process in view of its known significance in the context of a wide variety of deposition processes involving species ranging from pointlike particles to proteinlike complex structures in physical, chemical, and biological systems [1]. In this model, objects are added one by one onto a substrate without overlapping with others. Any event resulting in an overlap causes the object to be rejected while the nonoverlapping objects are rigidly fixed to the substrate. The RSA models are broadly classified into continuum and lattice models on the basis of the substrate and are also characterized by the object type, either of nonzero (finite) area or zero area [2]. The main focus of this research is the nature of approach to the jammed state, it being a matter of significance and interest to both science and applications. It can be easily appreciated that objects with finite area must eventually lead to a jammed state and a large number of studies about RSA of such objects with different shapes have been reported. However, it is equally interesting to point out that even objects with zero area can lead to jamming under certain circumstances even on a continuum substrate; an issue that appears to have been completely overlooked in the literature. In this work we not only address this issue computationally but also provide analytical insights implying a universal behavior in the form of power law approach to the jammed state.

For RSA of objects with nonzero (finite) area on a continuum substrate, the already adsorbed objects occupy an area on the substrate and cause blocking of some of the area available for new additions, and this leads to a jammed state. The approach of $\Theta(t)$, the fraction of the total substrate area covered by the adsorbed objects at instant t, to the jamming coverage $\Theta(\infty)$ is a matter of considerable interest. Previous studies by various researchers show that for any type of object this approach follows a power law $\Theta(\infty)-\Theta(t)\sim t^{-p}$, although object shape has significant influence on the $\Theta(\infty)$ and p values [3,4].

In the case of zero area objects, the RSA of the line segments (hard rods or needles) is the only system studied quite extensively. Sherwood [5] has studied the RSA of needles on a two-dimensional (2D) continuum substrate analytically as well as by simulation and found that the number density $\rho(t)$ increases indefinitely with time and follows the kinetics $\rho(t)\sim t^{p}$ with $p=1/3$ in the late time regime. Later, Tarjus and Viot [6] gave more rigorous analytical treatment to obtain $p=\sqrt{2}-1$. The analysis in both the works is based on the fact that there is formation of domains where the needles are arranged almost parallel to each other. In the asymptotic time regime, although the kinetics get slower, there is always a chance that an object can get accepted if its position lies within a domain and the orientation matches with that of the domain. Later, Khandkar *et al.* [7] studied RSA of yet another zero area object, namely, symmetric angled objects on a continuum substrate for the full range (0°–180°) of values of the arm angle ϕ. The value of the exponent was found to be significantly lower in the case of angled objects than that for needles, with a crossover near $\phi=0°$ or 180°. The results highlighted the important role of the intradomain spaces. Since these are the only systems studied so far, there is an impression that in RSA of zero area objects there is no jamming. However, even for zero area objects there are object types, which can disallow domain formation and lead to jamming. We address RSA of such unique objects in this work. To our knowledge, this problem has not been previously addressed. The different objects studied are (1) star-shaped object with n congruent (of equal length l) arms with uniform angular separation, (2) bracket-shaped object with end arms of length l' making an angle θ ($\theta\leq 90°$) with the central arm of length l, and (3) circular arc object of radius l and arc angle θ ($\theta\geq 180°$) as shown in the insets of Fig. 1. These objects are specifically chosen to represent different categories: The star-shaped object is a branched one and cannot be generated by self-avoiding random walk (SARW) while the bracket-shaped object can be generated by SARW. The circular arc object is an unbranched smooth curve.

In each simulation a 2D continuum substrate of size $L\times L$ is taken. The objects are dropped one by one per unit

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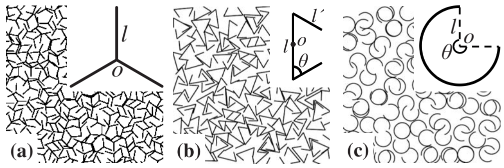

FIG. 1. Snapshot of typical configurations of RSA of (a) 3-star-shaped, (b) bracket-shaped, and (c) circular arc objects on a 2D continuum substrate. The inset in each case shows the details of the object.

time on the substrate. The orientation of the objects and the position of point O, referred to as the center of the object, are chosen randomly on the substrate so that the object lies wholly on the substrate. If any part of the newly arriving object intersects with any of the parts of the previously adsorbed objects, it is discarded, otherwise it is accepted. In either case, the time is incremented by one unit before the next adsorption attempt. For all three types of objects, l was taken to be $l=L/100$ in order to minimize the finite size effects. Runs were also carried for $l=L/50$ to check for the size dependence but no significant dependence was observed. Each simulation is carried out up to $t=3\times10^8$ time steps and the results presented below are the average of 50 simulation runs.

In the case of a star-shaped object, n was taken to be $n=3$. The bracket-shaped object considered was with $l'=l/2$ and $\theta=60°$. The circular arc object had the arc angle $\theta=270°$.

Figure 1 shows snapshots of typical late time regime configurations of RSA of the three object types. It can be clearly seen that for all types of objects there is no domain formation.

In Fig. 2 the number density $\rho(t)$ is plotted against time t. In the initial time regime, $\rho(t)$ increases rapidly with time since the substrate area available for adsorption is substantially higher than that blocked by the adsorbed objects. The depletion of the available area with every new addition eventually leads to the jammed state.

The plots of $d\rho/dt$ versus t on a log-log scale are shown as insets of Fig. 2 for the three types of objects. Extremely good linear fits to the simulation data over four to five orders of magnitude on both the scales confirms beyond any doubt

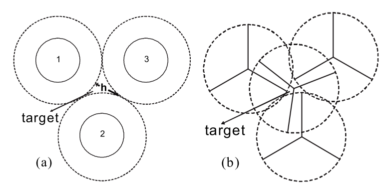

FIG. 3. Representative target for (a) circular disks and (b) 3-star-shaped objects. From (b) it is clear that only certain orientations are allowed for the object with its center in the target area.

that the number density $\rho(t)$, in the asymptotic time regime, reaches the jamming density $\rho(\infty)$ as a power law $\rho(\infty)-\rho(t)\sim t^{-p}$ in all the cases similar to that for RSA of finite area objects of different shapes. The average values of exponent p were found to be 0.27 ± 0.02, 0.13 ± 0.02, and 0.19 ± 0.02 for star-shaped, bracket-shaped, and circular arc objects, respectively. Investigations were also carried out with wide variations in object parameter values in all three types of objects. It was found that the power law behavior is always followed, though the value of the exponent is parameter dependent. Hence, all of these results make one wonder about the possibility of power law behavior being universal. In the following analysis we establish that this indeed is the case.

In the case of hard circular disks it was first conjectured by Feder [8] and later proved by Pomeau [9] and Swendsen [3] that the coverage follows the law $\Theta(\infty)-\Theta(t)\sim t^{-p}$ with $p=1/2$. Their analysis is based on the exclusion of area of radius $2r$ around each disc of radius r for selecting the center of the newly arriving disc. After a certain time t_c characterizing the beginning of the asymptotic regime, the area that is available to the center of a new disc consists of isolated targets: small disconnected areas that can be occupied by only one additional disc [Fig. 3(a)].

For a typical target, having linear dimension h, the area available for the disc getting newly added goes as h^2. Thus the rate of disappearance of such a target is proportional to h^2 and as a consequence the number density $n(h,t)$ of targets characterized by linear size h at instant t decays exponentially in time according to $n(h,t)=n(h,t_c)e^{-kAh^2(t-t_c)}$, k being the rate of deposition and A is a mean shape factor. It has been further assumed that the density of targets $n(h,t_c)$ goes to a nonzero constant $n(0,t_c)$, when h goes to zero.

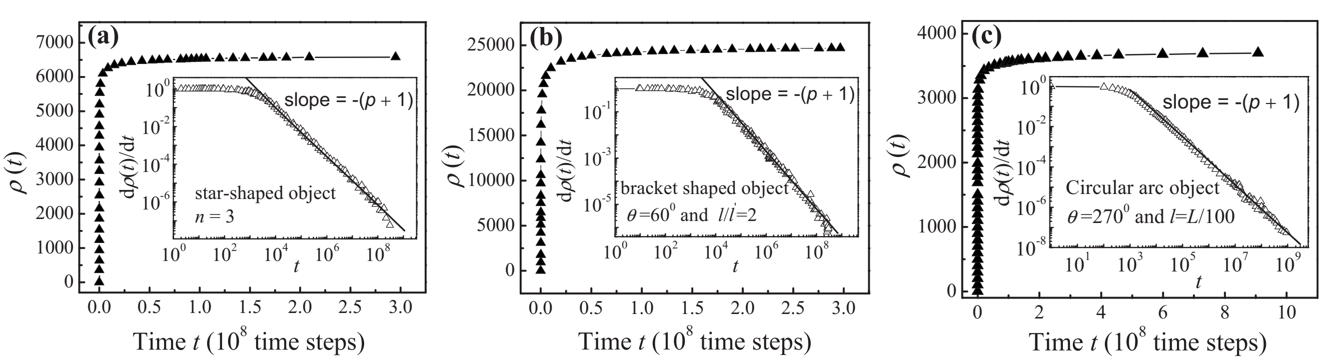

FIG. 2. Plot of number density $\rho(t)$ against time t for (a) 3-star-shaped, (b) bracket-shaped, and (c) circular arc objects on a 2D continuum substrate. The inset in each graph shows the plot of $d\rho/dt$ against time t on a log-log scale with linear fit in the late time regime.

This then leads to a power law $\rho(\infty)-\rho(t)=\int_0^{h_c}dhn(h,t) \sim n(0,t_c)\int_0^{h_c}dhe^{-kAh^2t}\sim t^{-1/2}$, in asymptotic time regime. For elongated objects such as ellipses, these arguments were extended by Talbot *et al.* [4] to explain the observed power law behavior $\rho(\infty)-\rho(t)=t^{-1/3}$. In this case, it has been argued that the rate of disappearance of the targets must be proportional to h^3, since it seems reasonable that the range of available orientations goes to zero as h. Regarding the density of targets, they followed the same assumption that it goes to a constant when h goes to zero.

Later Viot *et al.* [10] studied the RSA of unoriented anisotropic objects on a 2D continuum substrate simulationally and analytically for various shapes (spherocylinders, ellipses, and rectangles) and elongations. Their analytical treatment leads to the equation $\Theta_\varepsilon(\infty)-\Theta_\varepsilon(t)\sim\varepsilon\left(\frac{\int_0^z dxe^{-x^3}}{z^{1/3}}+c\frac{e^{-z}}{z^{1/2}}\right)$, where $z=\varepsilon^2 t$, ε is a parameter of anisotropy and $c>0$. This equation implies $t^{-1/2}$ law for isotropic objects ($\varepsilon\to 0$) and $t^{-1/3}$ for strongly elongated objects. For weakly elongated objects one gets a mixture of $t^{-1/2}$ and $t^{-1/3}$ regimes that leads to an effective exponent intermediately between the bounds 1/3 and 1/2.

As seen in our simulations, the exponents in all the three cases are significantly lower than the lower bound 1/3 and are also seen to be highly sensitive to the shape of the object. The analysis by Viot *et al.* hence cannot be applied here to analyze our results. Nevertheless, all these systems leading to the jammed state in RSA on a continuum substrate follow power law behavior. Also, it is interesting to note that even for objects with zero area, each adsorbed object blocks some area of the substrate for the position of the center of the newly arriving object. With advancement of time, such blocking continues to increase and a critical time t_c is reached when the substrate area consists of isolated targets [for instance, Fig. 3(b) shows one such target area in the case of RSA of 3-star objects]. The feature that the asymptotic regime is characterized by isolated targets due to the presence of exclusion areas around adsorbed objects is thus common to all of these systems. The classical arguments proposed by Pomeau and Swendsen and extended by Talbot *et al.*, hence, can be generalized to accommodate the systems studied in this paper.

Consider one such isolated target. Consider a point (x,y) lying in the area a of this target. The probability that the center of the newly arriving object will be in the small area element $dxdy$ around this position is $dxdy/L^2$. The object having orientation from certain subintervals of the angular interval (0-2π) allows it to satisfy no overlap condition and eliminates the targets upon adsorption. Let $\Omega(x,y)$ be the cumulative spread of these subintervals. Then, the probability that the fallen object in this area element gets adsorbed is $\Omega(x,y)/2\pi$. The probability w (the weight associated with the target) that this target disappears in unit time is hence given by $\iint_{\text{area of the target}}\Omega(x,y)dxdy/2\pi L^2$.

The weight w of the target depends upon its linear size h. As mentioned earlier, in the case of RSA of circular discs, $w(h)$ scales as h^2, while for elliptical objects, Talbot *et al.* argued that $w(h)\sim h^3$. However, with the complicated shape of objects, the shapes of the isolated targets are equally complex. This makes it difficult to know how the range of orientation scales with h. It is hence reasonable to generalize the assumption and to consider $w(h)=Ah^\alpha$, where α is a positive real number.

We also generalize the treatment in another aspect. In both of the previous works on RSA of circular discs and ellipses, the authors [3,4] make the assumption that the density of targets $n(h,t_c)$ goes to a constant $n(0,t_c)$ when h goes to zero. Noting that this assumption is hard to justify and also due to the fact that the targets in our case could be of complex nature, we generalize the assumption and consider that the density of targets $n(h,t_c)$ goes as $h^{-1+\beta}$, where β is a positive number ($\beta=1$ corresponds to classical assumption done by Swendsen and Talbot *et al.*).

The rate of disappearance of any target of linear size h is now given by the product of its weight $w(h)=Ah^\alpha$, the density of targets $n(h,t)$, and the rate of deposition k, i.e.,

$$\frac{dn(h,t)}{dt}=-kAh^\alpha n(h,t).$$

As a consequence, the density of targets $n(h,t)$ decays exponentially in time according to

$$n(h,t)=n(h,t_c)e^{-kAh^\alpha(t-t_c)}.$$

The total number of targets at any instant $t(t>t_c)$ will be $\int_0^{h_{\max}}n(h,t)dh$, where $h_{\max}$ is the maximum of the linear sizes of the targets present at that instant.

Hence, $\rho(\infty)-\rho(t)=\int_0^{h_{\max}}n(h,t_c)e^{-kAh^\alpha(t-t_c)}dh$ and with $n(h,t_c)\sim h^{(-1+\beta)}$, one gets $\rho(\infty)-\rho(t) \sim\int_0^{h_{\max}}h^{(-1+\beta)}e^{-kAh^\alpha(t-t_c)}dh\sim\int_0^\infty h^{(-1+\beta)}e^{-kAh^\alpha(t-t_c)}dh$.

Defining $kAh^\alpha(t-t_c)=g$, one gets $\rho(\infty)-\rho(t)\sim\frac{1}{\alpha}[kA \times(t-t_c)]^{-\beta/\alpha}\int_0^\infty g^{(\beta-\alpha)/\alpha}e^{-g}dg \therefore \rho(\infty)-\rho(t)\sim(t-t_c)^{-\beta/\alpha}\sim(t)^{-p}$, where $p=\beta/\alpha$, in the asymptotic regime.

The power law approach to the jammed state thus gets established also for the zero area objects disallowing the domain formation through this generalized analytical treatment.

The positive real numbers α and β, besides determining the rate of increase of the number density of adsorbed objects, also contain significant information about the nature of the isolated targets. While α tells how the weight of the target scales with its linear size, β gives the size distribution of those targets. In view of this, knowledge of the values of α and β for any given system gives good insight about the nature of the isolated targets for that system. Hence, in order to analyze the same, we employ Monte Carlo simulations and find the weight and size of each of the isolated targets present at a certain time t, beyond t_c, as follows.

In an ongoing RSA simulation run, after a sufficiently long time $t(t>t_c)$, whenever the object gets successfully adsorbed at a certain (x,y) position on the substrate, it is clear that this position is in the area of one of the isolated targets. The area a of this target (and hence the linear size h) and its associated weight w are obtained by carrying out Monte Carlo integrations: We temporarily remove this newly added object and carry out a large number of adsorption trials N [$N=N_pN_o$, where $N_p=10^4$ is the number of trials for positions within the area $2l\times 2l$ around the point (x,y) and $N_o=3600$

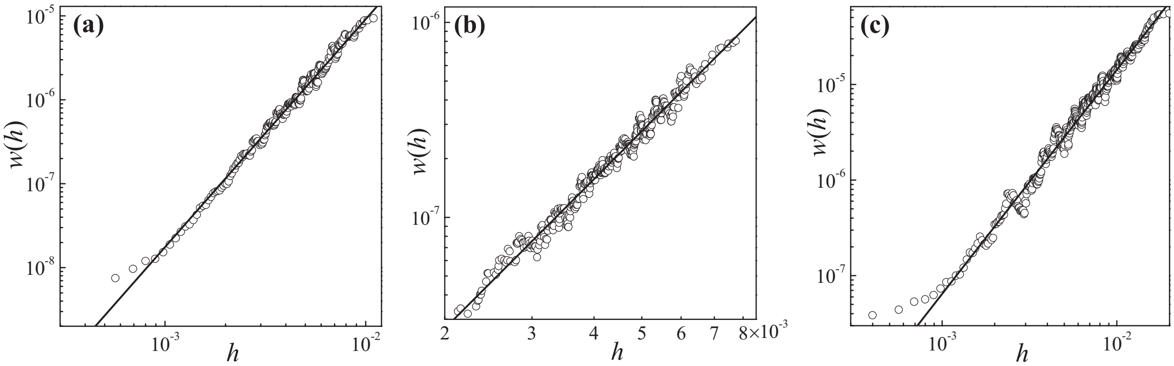

FIG. 4. Plot of target weight $w(h)$ against target size h for (a) 3-star-shaped, (b) bracket-shaped, and (c) circular arc objects, on a log-log scale. The slope of the linear fit gives the value of α in each case.

is the number of orientations for each trial position] with the test object. Let N_{ps} be the total number of trial positions having at least one successful adsorption attempt for some orientation and N_s be the total number of successful trials. The area of the target and its associated weight are given by $a=(N_{ps}/N_p)\times 4(l/L)^2$ and $w=(N_s/N)\times 4(l/L)^2$, respectively. In this fashion we get the information about all the targets.

Figure 4 shows a log-log plot of $w(h)$ versus h for the three types of objects. A good linear fit in all of the cases validates the assumption $w(h)=Ah^{\alpha}$. The average values of α for the star-shaped object, bracket-shaped object, and circular arc object are 2.67±0.05, 2.60±0.07, and 2.32±0.03, respectively.

If one wants to obtain the values of β one must carry out Monte Carlo integrations at the instant t_c, where catching the instant t_c is almost impossible. However, one can obtain the β value from the known value of exponent p and the α value for that system. The β values so obtained are 0.72, 0.34, and 0.44 for the star-shaped object, bracket-shaped object, and circular arc object, respectively.

It can be immediately noticed that the α values for star-shaped and bracket-shaped objects are the same within the error limits. However, the values of the exponent p are significantly different in the two cases. This clearly highlights the crucial role of the β value, i.e., the size distribution of the targets in the RSA dynamics. Due to the assumption that the number density $n(h,t_c)$ goes to a constant $n(0,t_c)$ when h goes to zero, this finding remained unrevealed.

In conclusion, we have studied RSA on a 2D continuum substrate of a new class of zero area objects, which disallow the domain formation and hence lead to a jammed state configuration as for the case of finite area objects. We show that for all such systems the number density $\rho(t)$ at instant t approaches the jamming density $\rho(\infty)$ as a power law $\rho(\infty)-\rho(t)\sim t^{-p}$, as that for RSA of the finite area objects. The exponent p is found to be sensitive to the object specifics. However, interestingly, the feature that the asymptotic regime is characterized by isolated targets due to the presence of exclusion areas around adsorbed objects is common to both finite area objects and the zero area objects that disallow the domain formation. This fact renders the universal behavior of a power law approach in the asymptotic time regime to all of the RSA systems irrespective of the object types therein. Generalization of the analytical treatment applied in the case of finite area objects is also proposed to accommodate zero area objects. This treatment reveals the crucial role of the distribution of the density of targets in the RSA dynamics.

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