Simulation Studies for Random Sequential Adsorption in Narrow Slit: Two-Dimensional Parking Model

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A parking configuration for cars or hard-rods of equal length on an infinite line, popularly known as the random car parking problem, is the classical one-dimensional version of random sequential adsorption (RSA) process. The statistical properties of parking configurations obtained by the random parking problem were first studied by A. Renyi.[1] When the largest gap between two successive rods is less than the length of a rod, the parking is full or jamming. During the RSA process, particles are deposited at random positions, one at each time step, with the restriction that overlapping with pre-deposited particles is forbidden.

An important nontrivial property of the RSA model is that this irreversible process reaches the jamming limit at large time, and, as a non-Markovian chain sequence, the saturated jamming state depends on the initial configuration. In contrast, the equilibrium fluids exhibit the Markovian stochastic properties, in which the final state has no memory effect from the initial state. The main features observed in the one-dimensional car parking problem persist in various systems of higher-order dimensions. The fundamental and application of the RSA process on this subject has been the central topic of reviews[2] and books.[3] The qualitative and quantitative relevance of higher dimensional RSA has been demonstrated in various research areas including proteins, colloidal particles, polymer chains, granular materials, etc.[4] Very recently, by employing both numerical and theoretical methods, Torquato and his coworkers[5] have made the systematic investigation for the RSA packing in Euclidean space over six hyper-dimensional systems.

Except for the one-dimensional case, there is no exact analytic solution to the RSA problem because the complicated form of the probability density involved in two or more dimensional systems imposes the non-trivial generalization of the theoretical formalism in statistical thermodynamics. When the system dimensionality of the substrate becomes higher, one can often obtain the detailed structures and kinetics of the RSA model using the computer simulation method. As an extremely useful diagnostic approach, simulation results can provide essentially exact data for precisely defined model systems.[6]

Computer simulations used in this way are referred to as machine experiments. For instance, it was from the simulation result for the two-dimensional hard-disc system that Feder[7] first observed the characteristic power law of RSA kinetics at long time,

$$\theta(\infty) - \theta(t) \propto t^{-\frac{1}{d_f}}, \tag{1}$$

where the scaling exponent d_f depends on the geometry of the objects. It is worth noting that d_f indicates the number of degree of freedom for a given object, and, in the case of isotropic particles in the continuum media, d_f -values are equal to the dimensionality d of the system, *i.e.*, d = 1, 2, and 3 for hard-rod, hard-disc, and hard-sphere systems, respectively.

Computational Method

In the present work we have employed the computationally efficient method to generate RSA configurations of hard-discs of diameter σ in the 2-d narrow slit of height L_x and length L_z. In our simulations the length is reduced in units of particle diameter σ, and, the system characteristic size λ (= σ/L_x) is given as the ratio of particle size σ to that of the slit width L_x. The conventional periodic boundary condition is applied to the fundamental box in the axial z-direction to approximate an infinite system in the thermodynamic limit. Particles are placed randomly and sequentially inside the simulation area until the saturation jamming limit is achieved. In order to speed up computations in our RSA simulations, there were two stages involved to determine the time-dependent available space.

The first stage is the same as the standard RSA simulation of hard-core systems described elsewhere.[2,5] We begin with an empty rectangular slit at time $t = 0$, and the trial deposition is drawn from a uniform probability distribution over the entire surface area. To avoid checking for non-overlaps with all other particles in the simulation box, we have employed the linked cell method with the cell length of σ, which significantly reduced the execution time to check the local neighborhood of the attempted particle displacement. This simple RSA method has a severe shortcoming and very time-consuming when the jamming configuration is about to be reached. In the near jamming stage, most of the accessible area is blocked and only tiny disconnected regions are available for further deposition. Not surprisingly, obtaining truly saturated RSA configurations becomes increasingly difficult as the space dimension increases.

To overcome such difficulties, in the second stage, we have employed the event-driven algorithm[8] by dividing the simulation slit along the *z*-direction between successive particle positions. For the narrow slit systems of $\lambda > 2/(2+\sqrt{3})$ ($\approx$ 0.5359), which is given in this work, any particle insertion between two existing particles does not affected the accessible area involved by other particles. This situation makes it possible keeping the track of the time-dependent accessible area, which is the space exterior to the exclusion circles of radius σ centered at two nearest hard-discs along the *z*-direction. If the interior space between two particles is partly accessible, we reduce the size of the accessible area using the known geometries, and, then reevaluate the availability of depositions into this smaller area.

To our knowledge, apart from the case of the 1-*d* car parking problem, this 2-*d* narrow slit packing is another possible case, in which the accessible insertion area in the RSA model can be evaluated algebraically from the known particle geometries. This two-stage procedure enables us to obtain the RSA configurations fast and efficiently, particularly when the system approaches closely to the particle jamming limit. Although computations are more complex in larger slit systems, this geometry-based event-driven method for nearly or completely saturated jamming conditions can be extended to the 3-*d* slit or cylindrical systems using the effective sampling algorithm to determine the accessible area numerically.

In the first stage of the standard RSA algorithm, each trial deposition increases the time t by $1/A$, where A (= $L_x \times L_z$) is the total area of the fundamental slit. The time scale in this first stage is just set by the number of trial runs, whether or not successful in the particle deposition, and the discrete loop index i is simply related to the time scale of runs as

$$t = \frac{1}{A} i . \tag{2}$$

In the event-driven algorithm, where only the potentially successful depositions are tried, the time increment for each trial on the available squares is represented as a random variable,

$$t = \frac{1}{A}\left(\frac{\ln(\xi)}{\ln\left(1 - \frac{A_{acc}}{A}\right)} + 1 \right), \tag{3}$$

where ξ is a uniformly distributed random number between 0 and 1, and A_{acc} is the accessible trial area for the particle deposition. The time expressions in Eqs. (2) and (3) become equivalent each other based on the stochastic probability theories in the discrete lattice model, *e.g.*, the Ising model. With the known value of A_{acc} in Eq. (3), it is possible to generate the RSA configurations much faster than the standard way as in Eq. (2), particularly in the case of approaching to the saturated jamming.

The above event-driven procedure with optimization techniques, *e.g.*, the optimized numerical approaches to find the intersection points between two circles, appears to be very effective to evaluate the accessible area for possible depositions in our model system. We have used the same value of axial length L_z = 20,000 for every λ-value investigated in our simulation studies. All simulation runs have carried out for 1,000 independent configurations, and each configuration, depending on the λ-values, consists of approximately 15,000 to 18,000 hard-discs in the final jamming situation.

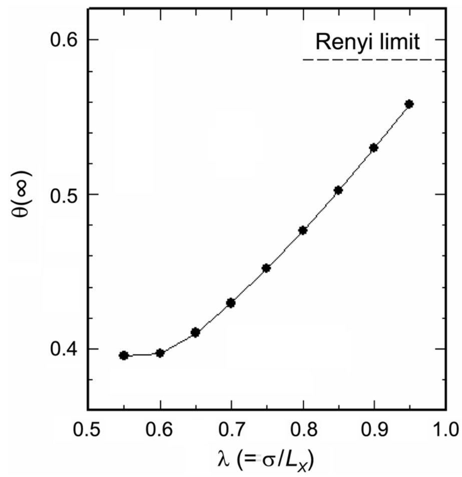

Figure 1. The jamming coverage $\theta(\infty)$ as a function of λ.

Results and Discussion

In Figure 1, simulation results are displayed for the saturated jamming coverage (= $(\pi\sigma^2/4)\, N_s/A$), which is the fraction of the covered area by the N_s number of saturated hard-discs deposited to the total area. For higher λ-values the RSA packing is getting closer to hard-rod one. In the RSA hard-rod model, the exact theoretical predictions including the jamming coverage and the gap-size distribution function, and the density fluctuation can be evaluated in the framework of statistical thermodynamics. The 1-*d* jamming coverage is exactly evaluated to be about 0.7476, which is known as the Renyi constant,[1] and, for our 2-*d* RSA hard-disc systems, this value will be about 0.5869. As can be seen in this figure, the Renyi limit may be closely recovered by the linear interpolation between λ = 0.9 and λ = 0.95.

Although not displayed in Figure 1, the statistical errors, which were measured from the standard deviation of independent configurations in a given λ-value, are smaller than the symbol size itself, ranging over 0.18% to 0.20%. Statistically, larger relative deviations were found to be the case of smaller particle systems, *i.e.*, higher λ-values in our simulation. In our RSA model, however, the standard deviation of λ = 0.55 is larger than that of λ = 0.6, even though the number of jamming particles is larger in the case of λ = 0.55. This discrepancy indicates that particle geometries in the transition from the 1-*d* to the 2-*d* region become topologically more complex. This situation may explain, at least qualitatively, the non-linear behavior of the

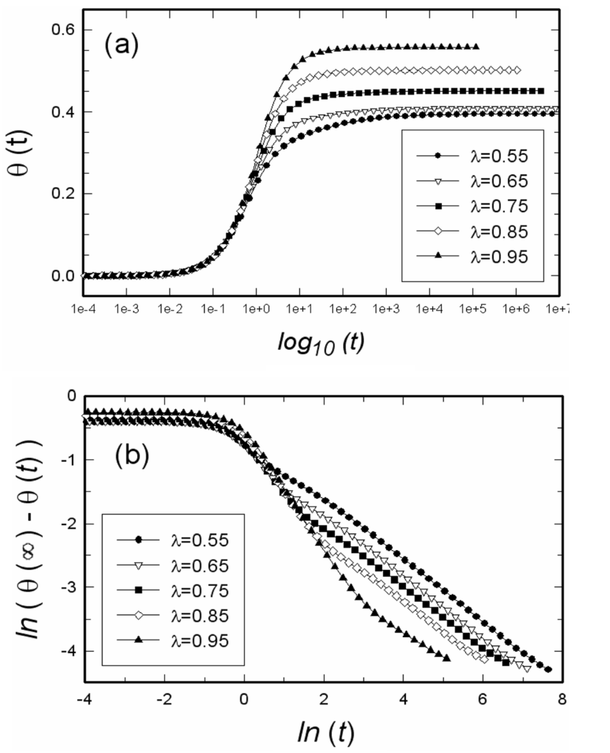

Figure 2. (a) the semilogarithmic plot for $\theta(t)$ versus $\log_{10}(t)$, and (b) the log-log plot for $ln\ (\theta(\infty) - \theta(t))$ versus $ln\ (t)$.

jamming coverage near $0.55 < \lambda < 0.6$. As we increase λ-values, the slope or the approaching ratio to the 1-*d* RSA packing is gradually increasing, *but not linearly*, and, eventually, it reaches to the Renyi limit which is represented as the dashed-line in this figure.

In Figure 2(a) we have displayed the semi-logarithmic plots of the coverage $\theta(t)$ for a few selected runs to illustrate the manner in which resulting coverage curves are changed with increasing time. In the initial time regime, simulation results show the rapid increase in the coverage values, suggesting that most particles get occupied in the initial RSA packing process. In the intermediate regime, after very steep increasing in the logarithmic time scale, there is slowing down in the rate of the coverage increasing followed by the asymptotic regime where the coverage reaches near constant value. The RSA packing exhibits several interesting features which are not presented in equilibrium systems. At larger time *t*, as shown in this figure, there exists the saturated jamming state of the highest possible coverage or the maximum particle density in the RSA model, which is smaller than the corresponding equilibrium system, *e.g.*, $\theta_{\mathrm{RSA}}(\infty) \approx 0.75, 0.55, 0.38$, and $\theta_{\mathrm{EQ}}(\infty) \approx 1.0, 0.91, 0.74$ for $d = 1, 2, 3$, respectively.

The power law exponent d_f can be determined from the slope or its time derivative. As mentioned previously in Eq. (1), the jamming density approaches via the power law in the RSA model. From the slope of the log-log plot in Figure 2(b), we can measure the number of degree of freedom for the RSA packing. Except for the case of $\lambda = 0.95$, the reasonable agreement with the 2-*d* RSA packing ($d_f \approx 2$) is observed. One of the most interesting features observed in this figure is the slope change for very narrow slit system of $\lambda = 0.95$. It is observed that $d_f \approx 1$ in the range of $0 < ln\ (t) < 3$, and $d_f \approx 2.5$ in $ln\ (t) > 3$. Near the saturated jamming limit, almost all accessible areas are occupied by particles, and, the shape and distribution of very few remaining accessible areas will make an important role in further RSA processes. From the averaged gap-size and the corresponding distribution function, we observed larger gap-size as well as more uniformly distributed gap-size function for $\lambda = 0.95$, and we also detected very 1-*d* like pair distribution function in the axial *z*-direction. Those observations support that, in the jamming limit or very close to it, the remaining accessible area disappears less rapidly in the lateral direction, and, under complete jamming conditions, this leads to higher degree of freedom in the lateral region for $\lambda = 0.95$.

In summary, our new algorithm to simulate the RSA packing in the 2-dimensional narrow slit is found to be accurate and fast execution time to generate completely saturated jamming configurations for the systems of $0.5 < \lambda < 1$. We are currently in the progress for applying this new algorithm to investigate the RSA structural properties of both 2-*d* and 3-*d* slit model systems to compare with microcanonical equilibrium systems.[9] Such simulation results, in conjunction with various theoretical and experimental predictions at the atomic or molecular level, will provide both qualitative and quantitative characterizations of the irreversible adsorption process when the adsorption rate is limited by the geometric blockage from previously adsorbed molecules confined within such slit porous media.

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