ADSORPTION-DESORPTION PROCESSES ON DISCRETE SUBSTRATES – OPTIMIZATION OF MONOLAYER GROWTH

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Abstract
Kinetics of the deposition process of dimers on a 1D lattice in the presence of desorption is studied by Monte Carlo method. The growth of the coverage $\theta(t)$ above the jamming limit to its steady-state value $\theta_\infty$ is analyzed when desorption probability $P_{\text{des}}$ decreases both stepwise and linearly (continuously) over a certain time domain. We report a numerical evidence that the process of vibratory compaction of granular materials can be optimized by using a time dependent intensity of external excitations.

Introduction
In RSA processes particles are randomly, sequentially, and irreversibly deposited onto a substrate. The dominant effect in RSA is the blocking of the available substrate area since the particles are not allowed to overlap. The system is jammed in a nonequilibrium disordered state for which the limiting (jamming) coverage $\theta_{\text{jam}}$ is less than the corresponding density of the closest packing. The possibility of desorption makes the process reversible and the system ultimately reaches an equilibrium state when the rate of desorption events becomes comparable to the rate of adsorption events. The density of particles in the steady state depends only on the desorption or adsorption rate ratio [1,2].

Within the framework of the adsorption-desorption model it was shown in [3] that the increase of packing fraction can be accelerated by changing the desorption rate during the adsorption-desorption process. The aim of this work is to investigate how do various temporal dependencies of the desorption rate hasten or slow down the deposition process.

Simulation method
The Monte Carlo simulations of adsorption-desorption processes are performed on a one-dimensional lattice of size $L = 10^5$ with a periodic boundary condition. The adsorbing objects are dimers covering two sites. The time $t$ is counted by the number of adsorption attempts and scaled by the total number of lattice sites $L$. The data are averaged over 100 independent runs.

At each Monte Carlo step adsorption is attempted with probability $P_a$ and desorption with probability $P_{\text{des}}$. In the case of adsorption-desorption processes the kinetics is governed by the ratio of desorption to adsorption probability $P_{\text{des}}/P_a$ [1,4,5]. Since we are interested in the ratio $P_{\text{des}}/P_a$, in order to save computer time, it is convenient to take the adsorption probability to be $P_a = 1$. For each of these processes a lattice site is selected at random. In the case of adsorption, we try to place the dimer with the beginning at the selected site, i.e., we search whether adjacent site in a randomly chosen direction is unoccupied. If so, we place the dimer. Otherwise, we reject the deposition trial. When the attempted process is desorption, and if the selected site is occupied by a dimer, the object is removed from the lattice.
Results and discussion
Simulations of the adsorption-desorption processes of dimers were performed for a wide range of desorption probabilities $P_{\text{des}} = 0.001 – 0.050$. In Fig. 1 the coverage is plotted as a function of time for different values of $P_{\text{des}}$. Notice that the curves for different values of $P_{\text{des}}$ always cross. This means that, for the reversible RSA model, the coverage is not always monotonic in $P_{\text{des}}$. In Fig. 1, for example, the system with $P_{\text{des}} = 0.030$ has a higher coverage than the system with $P_{\text{des}} = 0.010$ for $15 \leq t \leq 500$; above $t \approx 500$ coverage is higher for the lower value of desorption probability, $P_{\text{des}} = 0.010$. As already discussed in the context of the parking lot model [3], the existence of a minimum in the insertion probability (the fraction of the substrate that is available for the insertion of a new particle) is a sufficient condition for this phenomenon. It follows that for a given finite time, the densification can be made more efficient by changing the desorption probability $P_{\text{des}}$ during the deposition process.

Figure 1. Temporal behavior of the coverage $\theta(t)$ for various desorption probabilities $P_{\text{des}}$. Red (solid) lines correspond to values $P_{\text{des}} = 0.010 + n \cdot 0.005$, $n = 0, 1, 2, \ldots, 8$. Blue (dashed) lines correspond to values $P_{\text{des}} = 0.0010 + n \cdot 0.0005$, $n = 0, 1, 2, \ldots, 17$. The equilibrium coverage $\theta_{\text{eq}}$ is found to decrease with the desorption probability $P_{\text{des}}$. The horizontal line represents the jamming coverage for dimers, $\theta_{\text{jam}} = 0.8766$.

The possibility to hasten the dynamics of reversible RSA is studied by decreasing the desorption probability from $P_{\text{des}}^{(I)} = 0.050$ to $P_{\text{des}}^{(F)} = 0.010$ in a stepwise manner. Starting from an empty lattice, the system evolves at fixed desorption probability $P_{\text{des}}^{(I)} = 0.050$ up to the coverage $\theta^{(I)}$ above the jamming coverage $\theta_{\text{jam}}$. Then, the desorption probability is abruptly lowered at fixed time intervals $t_c$. Those time intervals follow each other directly without any gap. We always use an instantaneous drop of $P_{\text{des}} = 0.005$ for a change of the desorption probability $P_{\text{des}}$, so that the final probability of $P_{\text{des}}^{(F)} = 0.010$ is reached after eight abrupt changes of $P_{\text{des}}$. The final desorption probability $P_{\text{des}}^{(F)}$ does not change further in time. In Fig. 2, we demonstrate that the deposition process can be made much more efficient by decreasing the desorption probability $P_{\text{des}}$ in time. Several horizontal arrows are inserted in Fig. 2 and
placed at certain values of the coverage $\theta$ in the range $[0.890, 0.955]$. These arrows show how much more time is needed for a system to reach a given coverage $\theta$ in the case when the desorption probability has the constant value $P_{\text{des}}^{\text{min}}(\theta)$ in time.

Figure 2. Temporal behavior of the coverage $\theta(t)$ when the desorption probability $P_{\text{des}}$ decreases from $P_{\text{des}}^{(1)} = 0.050$ to $P_{\text{des}}^{(F)} = 0.010$ in a stepwise manner. The desorption probability is abruptly lowered by $\Delta P_{\text{des}} = 0.005$ at fixed time intervals $\Delta t_c = 10, 25, 50, 75, 100$, as indicated in the legend. Arrows show how much more time is needed for a system to reach the given coverage $\theta$ in the case when desorption probability has the constant value $P_{\text{des}}^{\text{min}}(\theta)$ in time (e.g., see Fig. 1). The horizontal line represents the jamming coverage for dimers, $\theta_{\text{jam}} = 0.8766$.

It is important to consider the case when the desorption probability varies continuously over a certain time domain. Here we show that the linear decay in the desorption probability as a function of time may be used to hasten the deposition process. The system first evolves at a fixed desorption probability $P_{\text{des}}^{(1)}$, up to the intersection point of relaxation curves at time $t_1$. Then, the desorption probability starts to decrease linearly with time according to $P_{\text{des}}(t) = K \cdot (t - t_1) + P_{\text{des}}^{(1)}$, where $t_1 < t < t_2$. The final probability of $P_{\text{des}}^{(2)}$, is reached during the time interval $\Delta t = t_2 - t_1$, so that the negative slope coefficient $K = -(P_{\text{des}}^{(1)} - P_{\text{des}}^{(2)}) / (t_2 - t_1) = -\Delta P_{\text{des}} / \Delta t$ depends on the time interval $\Delta t$.

In Fig. 3 the temporal dependence of coverage $\theta(t)$ is displayed for the fixed probabilities $P_{\text{des}}^{(1)} = 0.050$ and $P_{\text{des}}^{(2)} = 0.010$, and for different time intervals $\Delta t = 0, 10, 20, 40, 100, 200, 500, 10^3, 2 \times 10^3, 5 \times 10^3, 10^4, 2 \times 10^4$. Several horizontal arrows are placed at certain values of coverage $\theta$ in order to show that much more time is needed for a system to reach a given coverage $\theta$ in the case when the desorption probability has a constant value $P_{\text{des}}^{\text{min}}(\theta)$ in time.
We have investigated numerically the kinetics of the deposition process of dimers on a 1D lattice in the presence of desorption. A systematic approach is made by examining deposition with various time dependencies of the desorption probability $P_{\text{des}}$. We focused on the time evolution of the coverage $\theta(t)$ in the whole postjamming time range $\theta(t) > \theta_{\text{jam}}$. We have shown that the time needed for a system to reach a given coverage $\theta$ may be less if $P_{\text{des}}$ decreases in time. We have considered the behavior of the system when the desorption probability $P_{\text{des}}$ decreases both stepwise and linearly (continuously) over a certain time domain. Furthermore, the initial and final desorption probability do not have arbitrary values. If $P_{\text{des}}$ is large enough, the system will not reach the jamming. In other words, there is an upper limit $P_{\text{des}}^{(B)}$ of the desorption probability, above which the steady-state coverage will be lower than the jamming limit. For our 1D system we use $P_{\text{des}}^{(B)} \approx 0.10$. The greatest impact on the deposition rate is obtained if the initial value of the desorption probability $P_{\text{des}}^{(I)}$ corresponds to the limiting value $P_{\text{des}}^{(B)}$. The final value of the desorption probability $P_{\text{des}}^{(F)}$ determines the maximal value of the coverage $\theta_{\infty}(P_{\text{des}}^{(F)})$ that can be achieved.

Since the time needed for a system to reach a given coverage $\theta$ can be significantly reduced if $P_{\text{des}}$ decreases in time, we propose the application of an analog procedure to optimize the compaction process in weakly vibrated granular materials. Granular materials are complex systems exhibiting rich macroscopic phenomenology and showing many characteristic glassy behaviors. One of the striking features of granular materials are the memory effects observed by measuring the short-time response to an instantaneous change in tapping acceleration [6].
The short-term memory effects observed in granular materials are reflected in the fact that the future evolution of the packing fraction $\theta$ after time $t_0$ depends not only on the $\theta(t_0)$, but also on the previous tapping history. Response properties of granular media and the observation of short-term memory effects indicate that the change in tapping acceleration can affect the dynamics and efficiency of the compaction process.

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**References**