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 θ_∞ is analyzed when desorption probability P_{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 θ_{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_{des}. In the case of adsorption-desorption processes the kinetics is governed by the ratio of desorption to adsorption probability P_{des}/P_a [1,4,5]. Since we are interested in the ratio P_{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_{des} =0.001–0.050. In Fig. 1 the coverage is plotted as a function of time for different values of P_{des}. Notice that the curves for different values of P_{des} always cross. This means that, for the reversible RSA model, the coverage is not always monotonic in P_{des}. In Fig.1, for example, the system with P_{des} =0.030 has a higher coverage than the system with P_{des} =0.010 for $15 \leq \underline{t} \leq 500$; above $t \approx 500$ coverage is higher for the lower value of desorption probability, P_{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_{des} during the deposition process.
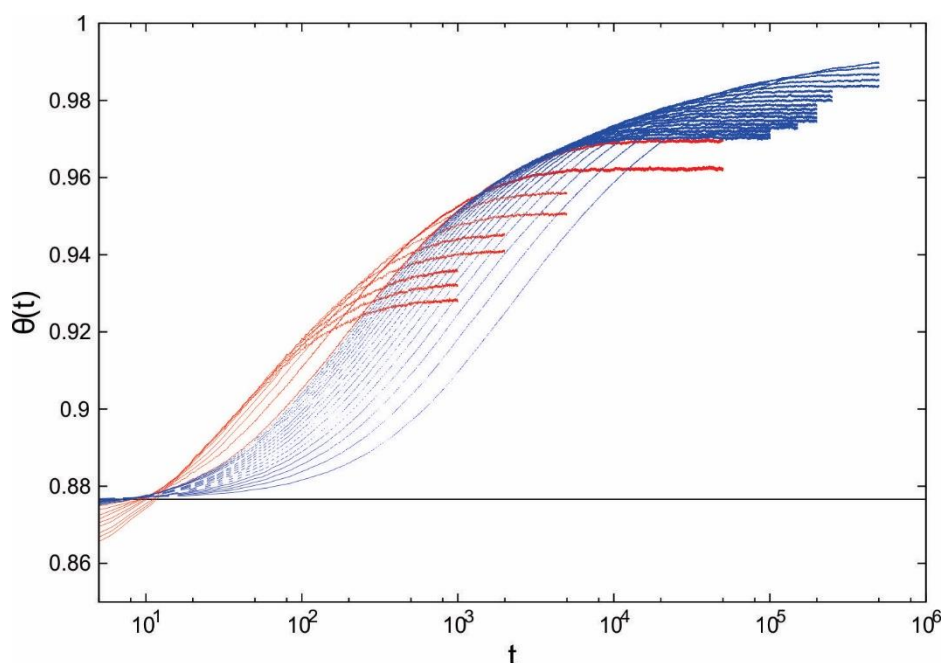

Figure 1. Temporal behavior of the coverage θ(t) for various desorption probabilities P_{des}. Red (solid) lines correspond to values P_{des} = 0.010 + n·0.005, n =0,1,2,...,8. Blue (dashed) lines correspond to values P_{des} = 0.0010 + n·0.0005, n = 0,1,2,...,17. The equilibrium coverage θ_{eq} is found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

The possibility to hasten the dynamics of reversible RSA is studied by decreasing the desorption probability from $P_{des}^{(I)}$ =0.050 to $P_{des}^{(F)}$ =0.010 in a stepwise manner. Starting from an empty lattice, the system evolves at fixed desorption probability $P_{des}^{(I)}$ =0.050 up to the coverage $\theta^{(I)}$ above the jamming coverage θ_{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_{des} =0.005 for a change of the desorption probability P_{des}, so that the final probability of $P_{des}^{(F)}$ =0.010 is reached after eight abrupt changes of P_{des}. The final desorption probability $P_{des}^{(F)}$ 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_{des} in time. Several horizontal arrows are inserted in Fig. 2 and

placed at certain values of the coverage θ in the range [0.890, 0.955]. These arrows show how much more time is needed for a system to reach a given coverage θ in the case when the desorption probability has the constant value $P_{des}^{min}(\theta)$ in time.
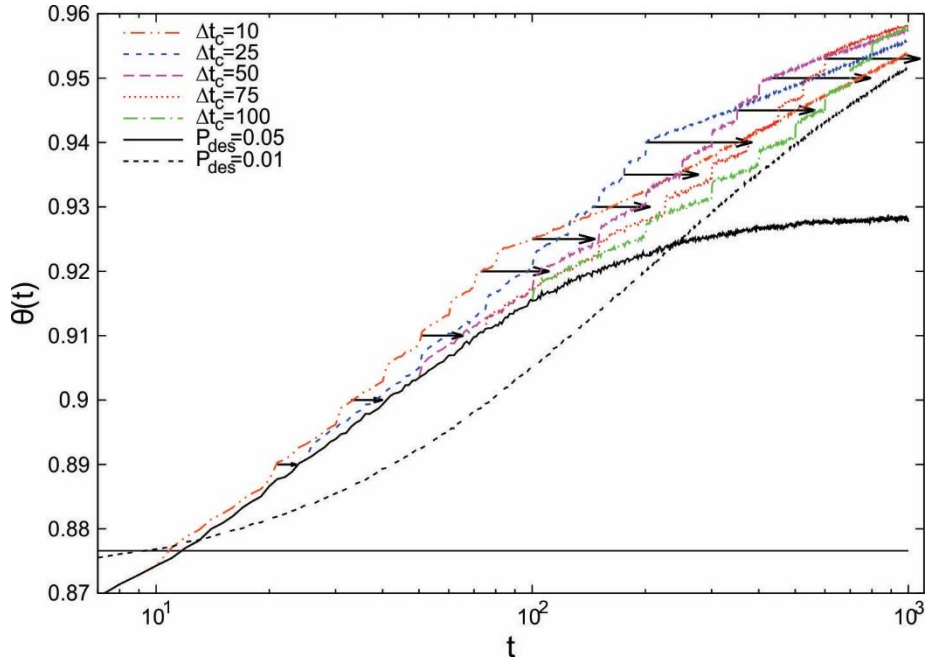

Figure2. Temporal behavior of the coverage $\theta(t)$ when the desorption probability P_{des} decreases from $P_{des}^{(I)} = 0.050$ to $P_{des}^{(F)} = 0.010$ in a stepwise manner. The desorption probability is abruptly lowered by $\Delta P_{des} = 0.005$ at fixed time intervals $\Delta t_c = 10, 25, 50, 75, 100$, as indicated in the legend. Arrows show how much more time is needed for a system to reach the given coverage θ in the case when desorption probability has the constant value $P_{des}^{min}(\theta)$ in time (e.g., see Fig. 1). The horizontal line represents the jamming coverage for dimers, $\theta_{jam} = 0.8766$.

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 $P_{des}^{(1)}$, up to the intersection point of relaxation curves at time t_1. Then, the desorption probability starts to decrease linearly with time according to $P_{des}(t) = K \cdot (t - t_1) + P_{des}^{(1)}$, where $t_1 < t < t_2$. The final probability of $P_{des}^{(2)}$, is reached during the time interval $\Delta t = t_2 - t_1$, so that the negative slope coefficient $K = -(P_{des}^{(1)} - P_{des}^{(2)}) / (t_2 - t_1) = -\Delta P_{des}/\Delta t$ depends on the time interval Δt.

In Fig.3 the temporal dependence of coverage $\theta(t)$ is displayed for the fixed probabilities $P_{des}^{(1)} = 0.050$ and $P_{des}^{(2)} = 0.010$, and for different time intervals $\Delta t = 0, 10, 20, 40, 100, 200, 500, 10^3, 2\times10^3, 5\times10^3, 10^4, 2\times10^4$. Several horizontal arrows are placed at certain values of coverage θ in order to show that much more time is needed for a system to reach a given coverage θ in the case when the desorption probability has a constant value $P_{des}^{min}(\theta)$ in time.
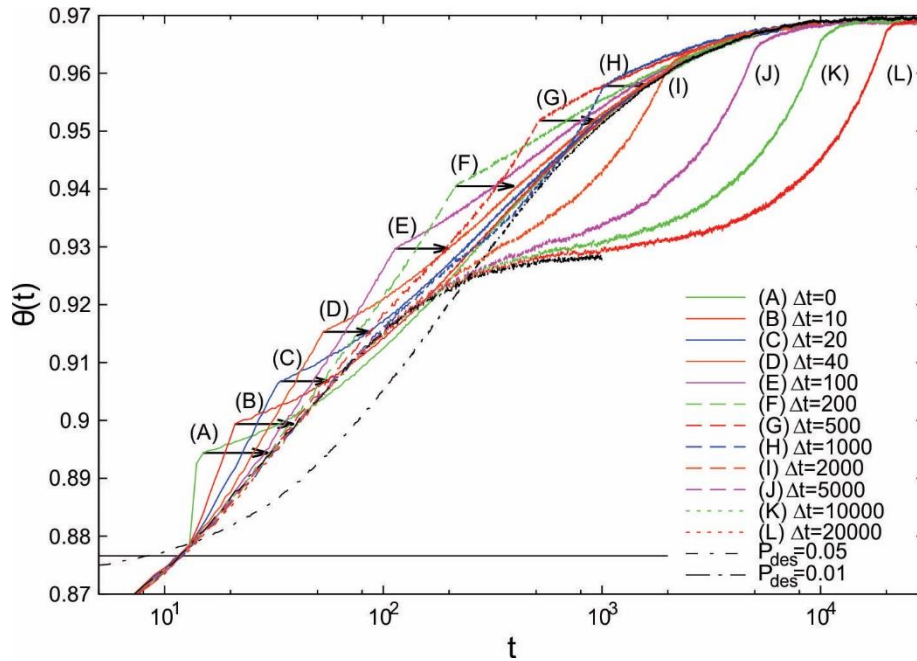
Figure3. Temporal behavior of the coverage $\theta(t)$ when the desorption probability P_{des} decreases linearly with time from $P_{des}^{(1)} = 0.050$ to $P_{des}^{(2)} = 0.010$. The final probability of $P_{des}^{(2)}$ is reached during the time interval Δt. Curves (A)–(L) correspond to various time intervals Δt ranging from 0 to 2×10^4, as indicated in the legend. Arrows show how much more time is needed for a system to reach the given coverage θ in the case when desorption probability has the constant value $P_{des}^{min}(\theta)$ in time(e.g., seeFig.1).The horizontal line represents the jamming coverage for dimers, $\theta_{jam} = 0.8766$.

Conclusion

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_{des}. We focused on the time evolution of the coverage $\theta(t)$ in the whole postjamming time range $\theta(t) > \theta_{jam}$.

We have shown that the time needed for a system to reach a given coverage θ may be less if P_{des} decreases in time. We have considered the behavior of the system when the desorption probability P_{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_{des} is large enough, the system will not reach the jamming. In other words, there is an upper limit $P_{des}^{(B)}$ of the desorption probability, above which the steady-state coverage will be lower than the jamming limit. For our 1D system we use $P_{des}^{(B)} \approx 0.10$.The greatest impact on the deposition rate is obtained if the initial value of the desorption probability $P_{des}^{(I)}$ corresponds to the limiting value $P_{des}^{(B)}$. The final value of the desorption probability $P_{des}^{(F)}$ determines the maximal value of the coverage $\theta_\infty(P_{des}^{(F)})$ that can be achieved.

Since the time needed for a system to reach a given coverage θ can be significantly reduced if P_{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 θ 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.

References
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