Adsorption-Desorption Processes on a Triangular Lattice

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Abstract. Reversible random sequential adsorption of binary mixtures of extended objects on a two-dimensional triangular lattice is studied numerically by means of Monte Carlo simulations. The depositing objects are formed by self-avoiding lattice steps. We concentrate here on the influence of the symmetry properties of the shapes on the kinetics of the adsorption-desorption processes in two-component mixtures. We provide a detailed discussion of the significance of collective events for governing the time coverage behavior of component shapes with different rotational symmetries. For the mixtures of equal sized objects, we propose a simple formula for predicting the value of the steady-state coverage fraction of a mixture from the values of the steady-state coverage fractions of pure component shapes.

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INTRODUCTION

Random sequential adsorption (RSA) is a typical model for irreversible deposition of macromolecules and microscopic particles such as polymers, colloids, bacteria, protein or latex particles on solid surfaces. In two dimensions (2D), RSA is a typical model for irreversible and sequential deposition of macromolecules at solid/liquid interfaces. Some examples of the wide range of applicability of this model include adhesion of colloidal particles, as well as adsorption of proteins to solid surfaces, with relaxation times much longer than the formation time of the deposit. See Evans [1] for a comprehensive survey.

There is a number of physical processes that involve both adsorption and desorption of particles. Adsorption-desorption processes are important in the binding of ions to a Langmuir monolayer [2], the interaction of proteins with DNA [3], and in many catalytic reactions. Recently, there has been a renewed interest in the reversible RSA because of its successful application to compaction of granular materials. The results of numerical simulations showed a crucial role of the geometrical character and symmetry properties of the extended objects in the reversible RSA dynamics [4].

Particles in nature, such as colloidal and bioparticles, are not monodisperse. Because their sizes and shapes vary considerably, polydispersity is almost an inevitable property in many experimental situations. The binary mixture is the simplest and the first step toward the understanding of polydisperse systems. In this paper we present the results of Monte Carlo simulations for the reversible RSA of a two-component mixture of extended objects on a triangular lattice.

DEFINITION OF THE MODEL AND THE SIMULATION METHOD

Simulations are performed for objects of various shapes, that are modeled by self-avoiding walks on the two-dimensional triangular lattice. A self-avoiding shape of length ℓ is a sequence of *distinct* vertices $(\omega_0, \ldots, \omega_l)$ such that each vertex is a nearest neighbor of its predecessor, i.e., a walk of length ℓ covers $\ell + 1$ lattice sites.

The process that we have investigated in this paper consists of the random deposition and desorption of extended objects from Table 1 on a triangular lattice of size $L = 120$. Periodic boundary conditions are used along all directions. The reversible RSA process for a binary mixture is as follows. From a large reservoir of shapes we choose one shape at random. We randomly select a lattice site and try to deposit the chosen shape of length ℓ with probability P_+. If the selected site is unoccupied, we fix the beginning of the walk that makes the chosen shape at this site. Then we randomly pick one of the six possible orientations with equal probability, start the corresponding ℓ-step walk in that direction and search whether all successive ℓ sites are unoccupied. If so, we occupy these $\ell + 1$ sites and deposit the object; otherwise, the deposition attempt is rejected. Each adsorption attempt is followed by a desorption one with probability P_-, that starts by choosing a lattice site at random. If the selected site is occupied by an adsorbed object, the object is removed from the lattice. The kinetics of the adsorption-desorption model depends only on the ratio $K = P_+/P_-$. In order to save the computer time it is convenient to take the adsorption probability to be $P_+ = 1$, i.e., to try an adsorption at each Monte Carlo step.

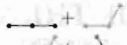
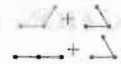
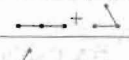
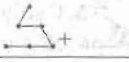
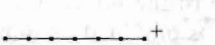
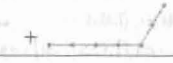
The time t is counted by the number of adsorption attempts and scaled by the total number of lattice sites L^2. The quantity of interest is the fraction of total lattice sites, $\theta^{(x)+(y)}(t)$, covered by the deposited objects (x) and (y) at time t. $\theta^{(x)}(t)$ and $\theta^{(y)}(t)$ denote the coverage fraction of each species adsorbed at time t. The output data are averaged over 100 independent runs for each choice of mixture and each desorption probability P_-.

DENSIFICATION KINETICS

We investigate the role that the mixture composition and the symmetry properties of the shapes play in the deposition process. We will mainly concentrate on the case of binary mixtures, composed of the shapes of equal number of segments.

The time behavior of the coverage fraction for the mixture $(B) + (C)$ in Table 1 is presented in Fig. 1.1 where two relatively low values of $P_- = 0.002$ and 0.001 have been used. The relaxation of the system toward its equilibrium coverage fraction $\theta_\infty^{(x)+(y)}$ is a two-stage process: at very early times of the process, when the coverage fraction is small, the adsorption process is dominant and the coverage grows rapidly in time; for large enough coverages $(\theta^{(x)+(y)}(t) > \theta_{jam}^{(x)+(y)})$ the growth of the coverage fraction requires the rearrangement of the increasing number of particles in order to open a hole large enough for the insertion of an additional particle, and the role of desorption is crucial. This strongly suggests that the collective events are responsible for the evolution of

TABLE 1. Coverage fraction $\theta_{jam}^{(x)+(y)}$ for various binary mixtures. Jamming coverages shown are for $r^{(x)} = r^{(y)} = 1/2$.

$(x)+(y)$	shapes	$n_s^{(x)} + n_s^{(y)}$	$\ell^{(x)} + \ell^{(y)}$	$\theta_{jam}^{(x)+(y)}$
$(B)+(C)$		$2+1$	$2+2$	0.8526
$(C)+(D)$		$1+3$	$2+2$	0.8624
$(B)+(D)$		$2+3$	$2+2$	0.8591
$(F)+(G)$		$3+6$	$5+5$	0.6833
$(I)+(J)$		$2+6$	$6+6$	0.7125
$(J)+(K)$		$6+1$	$6+6$	0.7087

$\theta^{(x)+(y)}(t)$ for $\theta^{(x)+(y)}(t) > \theta_{jam}^{(x)+(y)}$. Because these events involve the multiple particle transitions, they occur on a longer time scale than the simple adsorption/desorption events.

Figure 1.1 shows the time dependence of the coverages $\theta^{(B)}(t)$ and $\theta^{(C)}(t)$ resulting from the reversible RSA of binary mixture of (B) and (C) shapes, for $r^{(B)} = r^{(C)} = 1/2$ and for two values of $P_- = 0.002, 0.001$. For the shape (B) of higher order of symmetry,

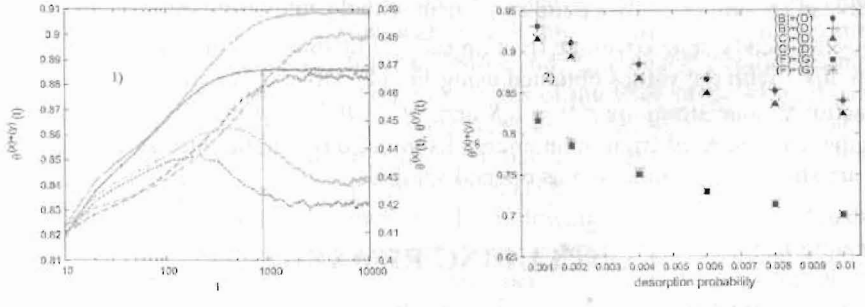


FIGURE 1. Steady-state coverages for the mixtures 1)vs time; 2) vs P_-

$\theta^{(B)}(t)$ is a monotonously increasing function of time and has the same general features as the coverage $\theta^{(B)+(C)}(t)$. On the other hand, for the shape (C) of lower order of symmetry, $\theta^{(C)}(t)$ reaches a broad maximum. One clearly observes that a larger value for the maximum of $\theta^{(C)}(t)$ is reached for the smaller desorption probability P_- and that the maximum of $\theta^{(C)}(t)$ shifts towards larger times as the P_- decreases.

One striking feature of Fig. 1.1 is the fact that the steady-state value $\theta_\infty^{(x)+(y)}$ was reached before the coverages $\theta^{(x)}(t)$ and $\theta^{(y)}(t)$ achieved their asymptotic values $\theta_\infty^{(x)}$ and $\theta_\infty^{(y)}$. The thin vertical line in Fig. 1.1 indicates the beginning of the equilibrium plateau in the time evolution of the coverage fraction $\theta^{(x)+(y)}(t)$. In this regime, the coverage fraction of the mixture fluctuates around its steady-state value $\theta_\infty^{(x)+(y)}$, but the coverage fraction of the shape with the symmetry axis of higher order continues to gro

at the expense of the coverage of the component with the symmetry axis of lower order, that decreases.

COMPOSITION DEPENDENCE OF THE STEADY-STATE COVERAGE FRACTION

Like many other statistical-mechanical problems, exact solutions for the steady-state coverage and for the kinetics of the reversible RSA process in one-component systems exist only in one dimension. Therefore, much of the information about the reversible RSA kinetics of mixtures in higher dimension is provided by numerical simulations or by experiment. We have analyzed the simulation data in order to find a dependence of the steady state coverage fraction of a mixture on the steady-state coverage fractions of pure lattice shapes. We propose the following simple formula for calculating the steady-state coverage fraction $\theta_\infty^{(x)+(y)}$ in the mixture $(x)+(y)$ of equal sized shapes (x) and (y) with fractional concentrations $r^{(x)}$ and $r^{(y)} = 1 - r^{(x)}$ in the infinite reservoir:

$$\frac{1}{\theta_\infty^{(x)+(y)}} = r^{(x)} \frac{1}{\theta_\infty^{(x)}} + r^{(y)} \frac{1}{\theta_\infty^{(y)}}, \tag{1}$$

where $\theta_\infty^{(x)}$ and $\theta_\infty^{(y)}$ are the steady-state coverage fractions of pure lattice shapes.

Formula (1) is supported by a good agreement with the numerical simulations. Fig. 1.2 compares the steady-state coverage fraction $\theta_\infty^{(x)+(y)}$ of some mixtures from Table 1 as a function of P_- with the values obtained using Eq. (1). Objects (x) and (y) are deposited with fractional concentrations $r^{(x)} = 0.8$ and $r^{(y)} = 0.2$, respectively. Closed symbols refer to the data obtained from the numerical simulations, and the results obtained from Eq. (1) are shown for comparison as opened symbols.

CONCLUDING REMARKS

We have performed extensive numerical simulations of the reversible RSA using binary mixtures composed of the shapes of different rotational symmetries on a triangular lattice. The simulations have shown that the coverage kinetics of a mixture strongly depends on the symmetry properties of the component shapes. We have proposed a simple formula (1) that can be used to predict the value of a steady-state coverage fraction of a mixture from the values of the steady-state coverage fractions of pure component shapes.

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