Zbornik radova 49. Konferencije za ETRAN, Budva, 5-10. juna 2005, tom IV
Proc. 49th ETRAN Conference, Budva, June 5-10, 2005, Vol. IV

RANDOM SEQUENTIAL ADSORPTION: RANDOM WALKS ON A SQUARE LATTICE

Ljuba Budinski-Petković, Uranija Kozmidis-Luburić, Nebojša M. Ralević, Selena Grujić,
Faculty of Engineering, Trg D. Obradovića 6, 21 000 Novi Sad, Serbia and Montenegro

Abstract – *Random Sequential Adsorption of nonreversal random walks on a square lattice is studied by Monte Carlo simulations. At the late stage of deposition, the approach to the jamming coverage is exponential for all the lengths of random walks. The jamming coverages are estimated and they have larger values for shorter random walks.*

1. INTRODUCTION

Studying the kinetics of random sequential adsorption (RSA) has attracted a considerable interest in recent years because of its enormous number of applications in the adsorption processes involving a variety of species from a point-like particle to protein-like complex structures in physical, chemical and biological systems. The control of the self-assembly of organic layers forming stable and smooth films is essential for many technological applications. The growing morphology depends on the strength of the binding onto the surface, the interaction between the adsorbed particles and the mobility of the adsorbed particles on the surface.

Generally, adsorption processes may be divided into two categories: (1) annealed adsorption where the species are mobile before they settle onto the surface – a cooperative sequential adsorption; (2) quenched adsorption where the adsorption occurs without subsequent diffusion or desorption. We consider the latter category known as random sequential adsorption.

In RSA deposition models, particles of a finite size are deposited randomly, sequentially and irreversibly onto a substrate. Since the diffusion of adsorbed particles is not allowed, once an object is placed it affects the geometry of all later placements. The dominant effect in RSA is the blocking of the available surface area by the already deposited particles and the limiting ("jamming") coverage is less than in close packing. The quantity of interest is the final coverage $\theta(\infty)$ and the time evolution of the coverage $\theta(t)$, which is the fraction of substrate area occupied by the adsorbed particles. For a review of RSA models, see [1].

Theoretical studies of RSA include some analytical results (for one-dimensional systems) [2-4] and Monte Carlo simulations [5-10]. Analytic progress in solving one-dimensional problems has been possible thanks to the property that the placing of an object on a line divides the line into two independent systems which can be treated separately. This is obviously not he case for two-dimensional lattices where other theoretical approaches were introduced and the computer simulations remain one of the primary tools for investigating these problems.

Depending on the system of interest, RSA models can differ in substrate dimensionality and the substrate can be continuum or discrete. For lattice RSA models, approach to the jamming coverage is asymptotically exponential [8,9]:

$$\theta(t) = \theta(\infty) - A\, e^{-t/\sigma} \qquad (1)$$

where A and σ are parameters which depend on the shape and orientational freedom of depositing objects.

RSA can be used as a model for the processes where events occur essentially irreversibly on the time scales of interest, such as irreversible adsorption of proteins from solution to phospholipid bilayers [11], and spatial patterns in ecological systems [12]. The growth of the grafted polymer layers is also an RSA process [13].

2. DEFINITION OF THE MODEL AND THE SIMULATION METHOD

When making random walks one can impose various conditions depending on the physical situation. If the succesive steps are completely independent we have the Gaussian (non self-avoiding) random walk. A more realistic model for conformational properties of polymers is obtained if we set some restrictions, for example that the walk may pass only once through any lattice site, and we obtain a self-avoiding random walk [14]. In this work, a polymer chain is modeled by a nonreversal random walk (NRRW) that is not allowed to immediately fold back.

The Monte Carlo simulations are performed on the square lattice of size L = 150. Periodic boundary conditions are used in both directions. The finite – size effects, which are generally weak, can be neglected for object dimensions < $L/8$.

The chains are dropped onto the square lattice, one at a time sequentially. At each deposition attempt a lattice site is selected at random. We fix the beginning of the walk at this site and try to deposit the chain. If a chain overlaps with previously deposited chains, the attempt is rejected. Once the chain is deposited on the lattice, it sticks on the surface permanently. The time is counted by the number of attempts to select a lattice site and scaled by the total number of lattice sites. The data are averaged over 100 independent runs for each number of steps N making the random walks.

3. RESULTS AND DISCUSSION

Because of the large number of conformational states of polymer chains, the deposition becomes very slow in the late stage. After long enough time adsorption events become extremely rare and we can assume that the jamming coverage is reached. In order to obtain the values of the jamming coverage, simulations are performed in which each run through the system contains 10^4 attempts per lattice site.

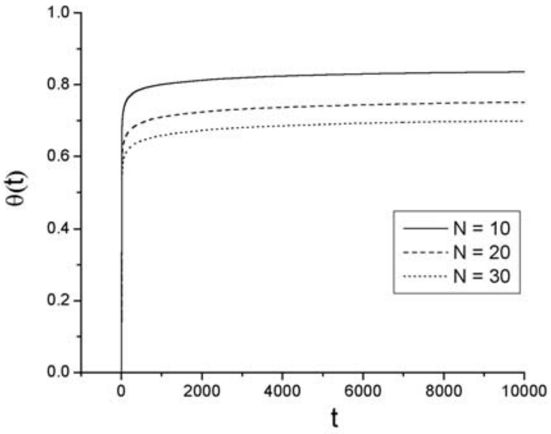

Figure 1. *Evolution of the coverage for N*=10, 20 *and* 30.

The results are obtained for nonreversal random walks made by N = 10, 20 and 30 steps. Variation of the coverage $\theta(t)$ with time is presented in Figure 1. The characteristic behavior can be divided into three time regimes: (1) the short time regime, (2) the intermediate regime, and (3) the very late stage regime. The coverage at very short time is proportional to t, since nearly all deposition attempts are successful. In the very late stage the dynamics is controlled by filling independently the last pores.

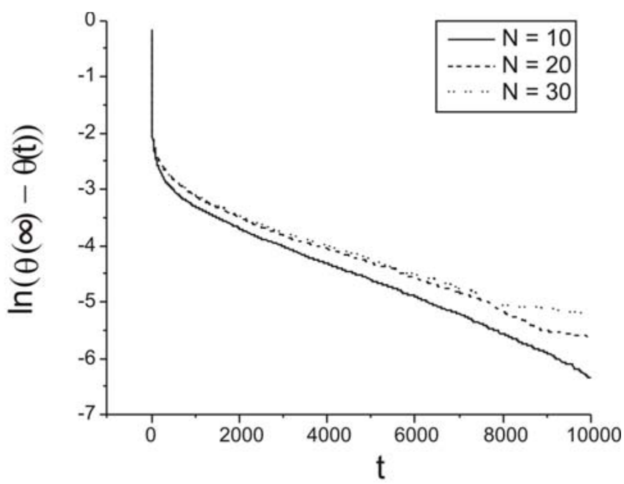

Figure 2. *Dependence of* $\ln(\theta(\infty)-\theta(t))$ *on t for N* =10, 20 *and* 30.

The plots of $\ln(\theta(\infty)-\theta(t))$ are shown in Figure 2 and we can see that these plots are straight lines for the late stages of deposition. This suggests that the approach to the jamming limit is exponential of the form (1). Furthermore, the lines are parallel with one another that means that the length of the walks does not affect the rapidity of the approach to the jamming coverage. The value of the relaxation time σ is determined from the slopes of the lines and for all the lengths of the random walks we have $\sigma \approx 4170$. The large value of σ corresponds to the very slow increase of the coverage in the late stage of deposition. The jamming coverages are also estimated and their values are given in Table 1. We can see that $\theta(\infty)$ decreases with the length of the random walks.

Table 1. *Values of the jamming coverages* $\theta(\infty)$ *for nonreversal random walks made by N=10, 20 and 30 steps.*

N	$\theta(\infty)$
10	0.8401
20	0.7549
30	0.7018

ACKNOWLEDGEMENT

This work was supported by the Serbian Ministry of Science and Technology under the project "Dynamical and Thermodynamical Properties of Strongly Correlated Systems with Complex Structures" (No 1895) and the project "Mathematical Models of Nonlinearity, Uncertainty and Decision" (No 1866).

REFERENCES

[1] J.W. Evans, "Random and cooperative sequential adsorption," *Review of Modern Physics*, vol. 65, pp. 1281-1329, October 1993.

[2] M.C. Bartlet and V. Privman, "Kinetics of irreversible multilayer adsorption," *J. Chem. Phys*, vol. 93, pp. 6820-6823, November 1990.

[3] P.L. Krapivsky, "Kinetics of Random Sequential Parking on a Line," *Journal of Statistical Physics*, vol. 69, pp. 135-150, March 1992.

[4] S. Caser and H. J. Hilhorst, "Exact bounds from a new series-expansion method for random sequential adsorption," *J. Phys. A: Math. Gen.*, vol. 27, pp. 7969-7979, July 1994.

[5] R.S. Sinkovits and R.B. Pandey, "Computer Simulation of Random Sequential Adsorption of Two Interacting Species on a Lattice," *Journal of Statistical Physics*, vol. 74, pp. 457-463, August 1993.

[6] Jian-Sheng Wang and R.B. Pandey, "Kinetics of Jamming Coverage in a Random Sequential Adsorption of Polymer Chains," *Physical Review Letters*, vol. 77, pp. 1773-1776, August 1996.

[7] M.D. Khandkar, A.V. Limaye and S.B. Ogale, "Shape effects in random sequential adsorption of zero-area angled objects on continuum substrate," *Physical Review Letters*, vol. 84, pp. 570-573, January 2000.

[8] Lj. Budinski-Petković and U. Kozmidis-Luburić, "Irreversible deposition of directed self avoiding random walks on a square lattice," *Physica A*, vol. 262, pp. 388-395, June 1998.

[9] Lj. Budinski-Petković and U. Kozmidis-Luburić, "Jamming configurations for irreversible deposition on a square lattice," *Physica A*, vol. 236, pp. 211-219, May 1996.

[10] Lj. Budinski-Petković and U. Kozmidis-Luburić, "Random sequential adsorption on a triangular lattice,"

Physical Review E, vol. 56, pp. 6904-6908, November 2001.

[11] J.J. Ramsden, G.I. Bachmanova and A.I. Archakov, "Kinetic evidence for protein clustering at a surface," *Physical Review E*, vol. 50, pp. 5072-5076, December 1994.

[12] M. Hasegawa and M. Tanemura, in *Recent Development in Statistical Interference and Data Analysis*, edited by K. Matusita, North Holland, Amsterdam, 1980.

[13] A. Karim, V.V. Tsukruk, J.F.Douglas, S.K. Satija, L.J.Fetters, D.H. Reneker, M.D. Foster, *J. Phys. II France 5*, p.p. 1441, 1995.

[14] V. Privman, N.M. Švrakić, "Directed Models of Polymers, Interfaces and Clusters: Scaling and Finite-size Properties," *Lecture Notes in Physics*, vol. 338, Springer, Berlin, 1990.

Sadržaj: Ireverzibilna depozicija slučajnih šetnji kod kojih nije dozvoljeno vraćanje u prethodnu tačku proučavana je pomoću Monte Carlo simulacija na kvadratnoj rešetki. U kasnoj etapi depozicije prilaz granici zagušenja je eksponencijalan za sve dužine slučajnih šetnji, pri čemu vreme relaksacije σ ne zavisi od dužine slučajnih šetnji. Procenjene su vrednosti granica zagušenja i one su veće za kraće slučajne šetnje.

IREVERZIBILNA DEPOZICIJA: SLUČAJNE ŠETNJE NA KVADRATNOJ REŠETKI

Ljuba Budinski-Petković, Uranija Kozmidis-Luburić, Nebojša M. Ralević, Selena Grujić,