

# Monte Carlo simulations of the adsorption of a single polymer chain on rough surfaces

W. Gottstein, S. Kreitmeier\*, M. Wittkop and D. Göritz

*Universität Regensburg, Institut für Experimentelle und Angewandte Physik, D-93040 Regensburg, Germany*

and F. Gotsis

*Universität München, Scheinerstr. 8, D-81679 München, Germany*

*(Received 29 January 1996; revised 1 May 1996)*

The adsorption of a single chain on structured surfaces is investigated using the bond-fluctuation model. The different surfaces were a flat, a stick-like, a pyramidal surface and a surface with square holes. The adsorption starts at about the same temperature for all surface structures, therefore denoted as the adsorption temperature. The rate for further adsorption with decreasing temperature is enhanced for the structured surfaces. The desorption of once adsorbed chains starts markedly below the adsorption temperature. Despite the structure of the surfaces the adsorbed chains show clearly two-dimensional properties for the lowest temperatures. The exception is the surface with square holes. Surprisingly, the chains on this surface keep their three-dimensional properties even when adsorbed onto the surface. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: adsorption; structured surfaces; computer simulation)

## INTRODUCTION

The phenomenon of the adsorption of polymers on surfaces plays an important role in many industrial processes. Adsorbed polymers are widely used as stabilizers or flocculating agents for colloidal dispersions. Another application with tremendous importance for the world-wide car industry is the reinforcement of rubber networks by addition of carbon black filler particles. In biological systems this phenomenon also is of wide occurrence. The adsorption of polymer molecules on cell membranes and organelles, soils and colloidal aggregates are some examples.

Due to its importance much effort has been spent toward this subject in the past. By experimental methods it was possible to measure the thickness<sup>1–3</sup>, the mean bound fraction of polymer segments<sup>4,5</sup> and the polymer volume fraction profile normal to the surface<sup>6,7</sup> of an adsorbed layer. For a theoretical description various methods of theoretical polymer physics have been used, such as mean field theories<sup>8,9</sup>, exact enumeration studies<sup>10–20</sup>, scaling theories<sup>21–23</sup> and renormalization group methods<sup>24–28</sup>. With the development of computers continuously increasing in speed and capacity more and more computer simulations were done, mostly applying the Monte Carlo (MC) method (refs 29–34 and others).

Most of these studies were restricted to the simple case of a completely flat surface. Though in reality a surface always shows some roughness, there exist only a few studies on irregular surfaces. The effect of local curvature had been investigated in refs 35–37. Baumgärtner and

Muthukumar applied the MC-method to ideal chains on the simple cubic lattice to study the influence of amplitude, wavelength and structure of periodic surfaces on the adsorption characteristics<sup>30</sup>. Another study by Douglas deals with the adsorption on fractal surfaces<sup>38,39</sup>.

In this paper we present the results of dynamic MC-simulations based on the 3-dimensional bond-fluctuation model. Our intention was to study the influence of the geometric properties of the surface on the adsorption behaviour. We investigated four surfaces with different structures, one of them the planar surface as reference. To eliminate concentration effects, only one single chain was set into the simulation box at the same time (very dilute case). The attractive interaction of the chains with the surface was modelled by a Van-der-Waals potential, while intramolecular forces between chain segments were neglected (good solvent condition).

## SIMULATION METHOD

The bond-fluctuation model was developed by Carmesin and Kremer<sup>40</sup>. It is a coarse-grained lattice model of high efficiency. On a simple cubic lattice cubes of eight positions represent the monomers. These monomers are connected by a set of possible bond vectors (108 in three dimensions) which ensure self-avoiding and cut-avoiding. The diffusion dynamics is simulated by randomly chosen jumps of monomers in different spatial directions. For further details on the bond-fluctuation-model we refer to the original papers<sup>40–44</sup>. No further interactions within the chain were included. The interaction of the chain with the surface was modelled through the following

\* To whom correspondence should be addressed

- 15 Torrie, G. M., Middlemiss, K. M., Bly, S. H. P. and Whittington, S. G. *J. Chem. Phys.* 1976, **65**, 1876
- 16 Ma, L., Middlemiss, K. M., Torrie, G. M. and Whittington, S. G. *J. Chem. Soc. Faraday Trans. II* 1978, **74**, 721
- 17 Guttman, A. J., Middlemiss, K. M., Torrie, G. M. and Whittington, S. G. *J. Chem. Phys.* 1978, **69**, 5375
- 18 Hammersley, J. M., Torrie, G. M. and Whittington, S. G. *J. Phys. A: Math. Gen.* 1982, **15**, 539
- 19 Ishinabe, T. *J. Chem. Phys.* 1982, **76**, 5589; 1984, **80**, 1318
- 20 Croxton, C. A. *J. Phys. A: Math. Gen.* 1983, **16**, 4343
- 21 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University, Ithaca, 1979; *J. Phys. (Paris)* 1976, **37**, 1445; 1977, **38**, 426; *Macromolecules* 1982, **14**, 1637; 1982, **15**, 492; *J. Phys. Lett. (Paris)* 1983, **44**, 241
- 22 Daoud, M. and Jannink, G. *J. Phys. (Paris)* 1976, **37**, 973
- 23 Daoud, M. and de Gennes, P. G. *J. Phys. (Paris)* 1977, **38**, 85
- 24 Eisenriegler, E., Kremer, K. and Binder, K. *J. Chem. Phys.* 1982, **77**, 6296
- 25 Eisenriegler, E. *J. Chem. Phys.* 1983, **79**, 1052; 1984, **81**, 4666; 1985, **82**, 1032
- 26 Kremer, K. *J. Phys. A: Math. Gen.* 1983, **16**, 4333
- 27 Kosmas, M. K. *Macromol. Chem. Rapid Commun.* 1981, **2**, 563; *J. Phys. A: Math. Gen.* 1985, **16**, 539
- 28 Douglas, J. F., Nemirovsky, A. M. and Freed, K. F. *Macromolecules* 1985, **19**, 2041
- 29 Meirowitch, H. and Livne, S. *J. Chem. Phys.* 1988, **88**, 4507
- 30 Baumgärtner, A. and Muthukumar, M. *J. Chem. Phys.* 1991, **94**, 4062
- 31 Cosgrove, T., Prestige, C. A., King, S. M. and Vincent, B. *Langmuir* 1992, **8**, 2206
- 32 Schaffer, J. S. *Macromolecules* 1994, **27**, 2987
- 33 Hegger, R. and Grassberger, P. *J. Phys. A: Math. Gen.* 1994, **27**, 4069
- 34 Lai, P.-Y. *Phys. Rev. E* 1994, **49**, 5420
- 35 Pincus, P., Sandroff, C. J. and Witten, T. A. *J. Phys. (Paris)* 1984, **45**, 725
- 36 Hone, D., Ji, H. and Pincus, P. *Macromolecules* 1987, **20**, 2543
- 37 Ball, R. C., Blunt, M. and Barford, W. *J. Phys. A: Math. Gen.* 1989, **22**, 2587
- 38 Douglas, J. F. *Macromolecules* 1989, **22**, 3707
- 39 Miljkovic, V., Milosevic, S. and Zivic, I. *Phys. Rev. E* 1995, **52**, 6314
- 40 Carmesin, I. and Kremer, K. *Macromolecules* 1988, **21**, 2819
- 41 Carmesin, I. and Kremer, K. *J. Phys. (Paris)* 1990, **51**, 915
- 42 Rodriguez, A. L., Wittmann, H.-P. and Binder, K. *Macromolecules* 1990, **23**, 4327
- 43 Deutsch, H.-P. and Binder, K. *J. Chem. Phys.* 1991, **94**, 2294
- 44 Wittman, H.-P., Kremer, K. and Binder, K. *J. Chem. Phys.* 1992, **96**, 6291
- 45 Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. and Teller, E. *J. Chem. Phys.* 1953, **21**, 1087
- 46 Wittkop, M., Kreitmeier, S. and Göritz, D. *J. Chem. Phys.* 1996, **104**, 3373
- 47 Vilgis, T. A. and Heinrich, G. *Macromolecules* 1994, **27**, 7846
- 48 Wittkop, M., Sommer, J.-U., Kreitmeier, S. and Göritz, D. *Phys. Rev. E* 1994, **49**, 5472
- 49 Nienhuis, B. *Phys. Rev. Lett.* 1982, **49**, 1062
- 50 Le Guillou, J. C. and Zimm-Justin, J. *Phys. Rev. Lett.* 1977, **38**, 95