

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

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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.

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## 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

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truncated Lennard–Jones potential

$$V(r) = \frac{\epsilon}{2} \left\{ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right\} \quad (1)$$

with  $\epsilon$  the energy unit.  $r_0$  was chosen to be  $1.1a$ ,  $a$  being the grid unit. The energy for each monomer due to this potential was obtained by a summation over all interactions of the eight positions of the monomer cube with the surface within the range of three grid units. For this purpose the surface layer was extended below the actual surface thus modelling a bulk material. As the Lennard–Jones potential with the above parameters is almost zero beyond a distance of three grid units, the introduced cut-off at three grid units represents no restriction. Figure 1 displays the interaction scheme. Using the Metropolis criterion<sup>45</sup> these energies determined whether the jumps of the monomers were accepted.

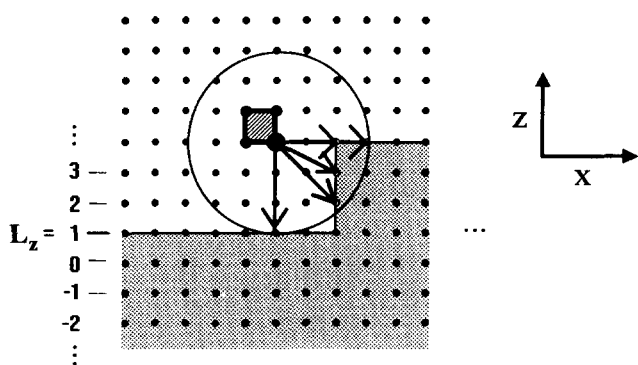


Figure 1 Sketch of the interaction of a monomer with the surface. All energy contributions within the circle were evaluated and added for the surface energy

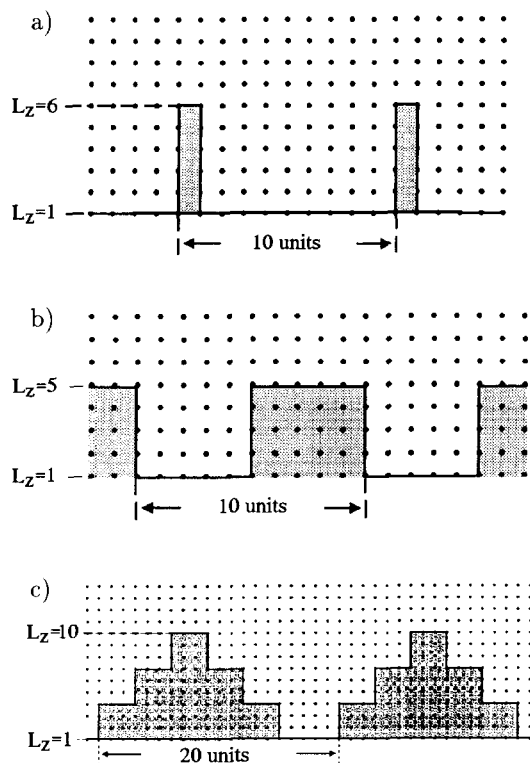


Figure 2 Side view of the different surface structures: (a) stick-like, (b) square holes, (c) pyramidal. The dots represent the underlying simulation lattice with grid unit  $a$ .  $L_z$  denotes the vertical distance

The chain was put into a box with periodic boundary conditions in  $x$ - and  $y$ -direction. In  $z$ -direction the dimension of the box was chosen to be large enough to ensure an unperturbed coil in the box for infinite temperature. At position  $l_z = 1$  the surface was built. Four different types were realized: a pyramidal one, a stick-like one, a surface with square holes and for comparison a flat one. The individual dimensions were taken to fit the periodic boundaries. The details can be found in Figure 2 which shows a side view of the structured surfaces (for a further impression cf. Figure 8). The used chain lengths  $N$  were 20, 35, 50, 80 and 120.

Each simulation was performed in the following manner: an unperturbed chain was created in the simulation box being kept away from the actual surface by a temporary repulsive wall at height  $l_z = h + 3$ ,  $h$  being the maximal height of the surface structure. The additional distance of three layers ensured that the chain started without interaction with the actual surface when the repulsive wall was removed. After a relaxation of about 500 000 MCS\* to obtain equilibrium for the chain the temporary wall was removed. After a temperature dependent relaxation time (of magnitude  $10^6$  MCS), the steady state for adsorption and desorption was reached. During an additional  $10^6$  MCS various observables were calculated at every 500 MCS. For each temperature a total of about 100 independent runs were performed. All quantities were thus averaged both in time and over the independent runs.

## RESULTS AND DISCUSSION

The following discussion is mostly related to chains with chain length  $N = 50$ . The chain lengths not mentioned behave in the same manner because the simulation is in the excluded volume limit for chains with  $N \gtrsim 20$ <sup>46</sup>.

### Energy changes

The gain of energy (in units of  $\epsilon$ ) due to the absorption is displayed in Figure 3 vs the inverse temperature  $\beta\epsilon$ . At infinite temperature the chain is free and no potential energy is stored. At the inverse temperature  $\beta\epsilon \approx 0.14$  the adsorption starts significantly and the energy increases. We denote this inverse temperature therefore as the adsorption temperature  $(\beta\epsilon)_{ad}$ . Due to the different structures of the surfaces the maximum of the achievable energy is drastically changed. The long edges and angles in the pyramidal and square hole surface lead to a clearly higher energy gain per average contact. This can be seen for the highest  $\beta\epsilon$ . It is interesting that the adsorption starts at around the same temperature. This indicates that the surface structure is unimportant for the first contacts of the chain with the surface.

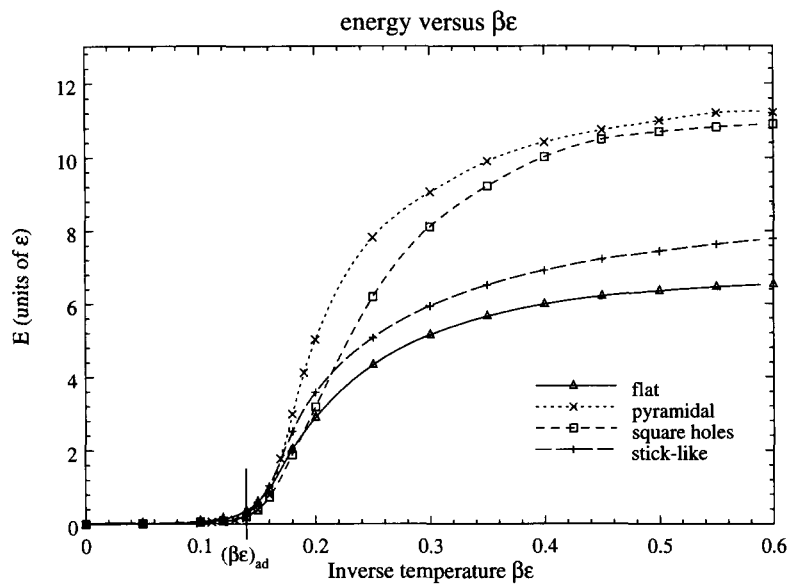
### Adsorption

The fraction of the adsorbed monomers  $P_{ad}$

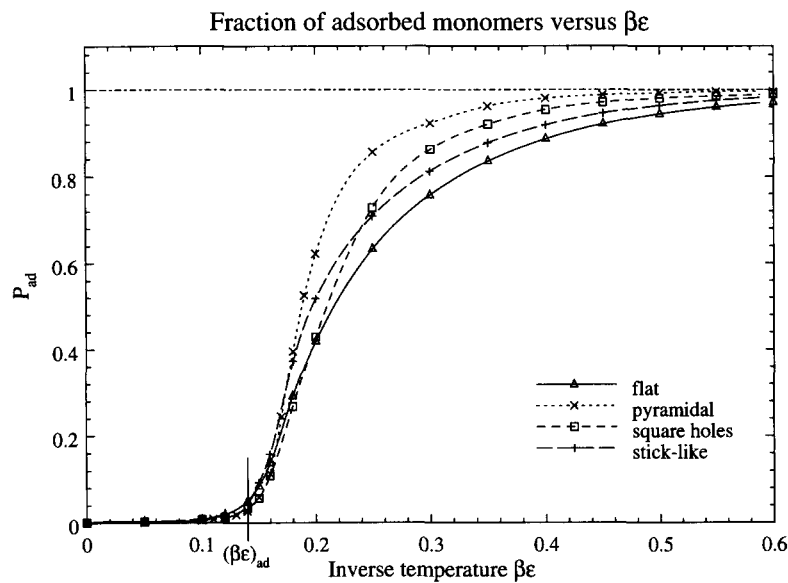
$$P_{ad} = \frac{\text{number of monomers in contact with surface}}{\text{total number of monomers of the chain}} \quad (2)$$

vs the inverse temperature is shown in Figure 4. Despite the fact that the adsorption starts at the same temperature the additional adsorption in further cooling is

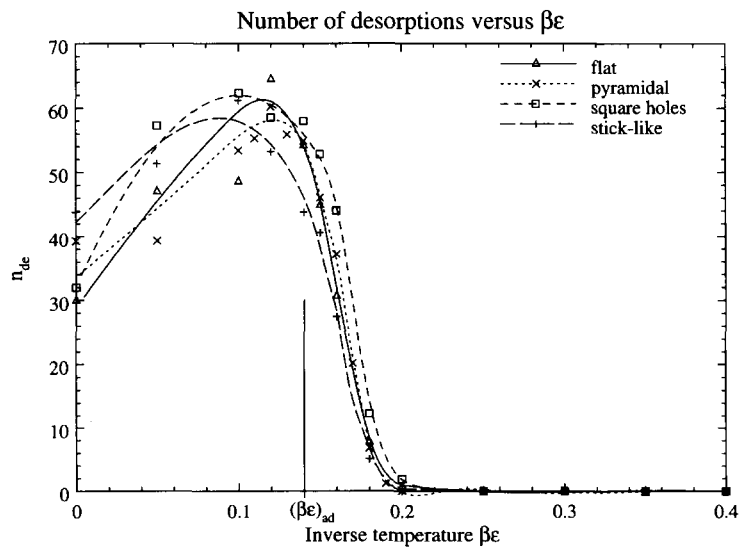
\* One Monte-Carlo-Step (MCS) is one attempted move per monomer



**Figure 3** The gained energy in units of  $\epsilon$  vs the inverse temperature is displayed for the different surface structures.  $(\beta\epsilon)_{ad}$  denotes the adsorption temperature



**Figure 4** The adsorption of monomers onto the different surfaces is plotted vs the inverse temperature.  $(\beta\epsilon)_{ad}$  denotes the adsorption temperature



**Figure 5** The number of desorptions as defined in the text is plotted vs the inverse temperature for the different surfaces. The plotted lines are guides to the eye and should represent the supposed behaviour within the fluctuating data points

significantly accelerated for the structured surfaces. The reason should be a combination of a larger possibility for contacts onto the structures, extending from the bottom into the space of the chain, and the higher energy gain. Douglas<sup>28</sup> and Vilgis<sup>47</sup> proposed a better and faster adsorption on structured surfaces. This should be due to the fact that the entropy loss is diminished. The polymer chain fits easier into the surface roughness without transforming into a two-dimensional state. This might be an additional reason for the pyramidal surface. The adsorption for the square holes starts like the plane surface, but surpasses the stick-like surface at lower temperatures. In the beginning it seems to be much easier for the chain to find a contact with the sticks as to fall into one of the holes. The passing should be due to the higher energy gain during adsorption when the square holes start to get filled.

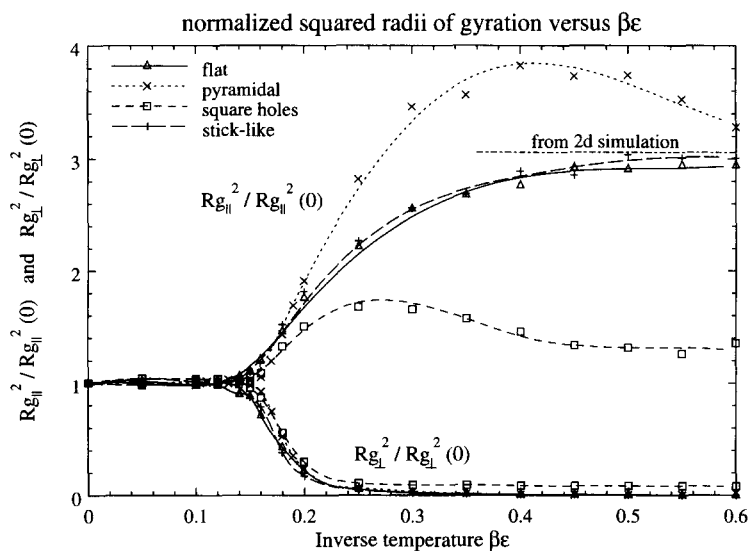
*Desorption*

The number of desorptions  $n_{de}$  is defined in the

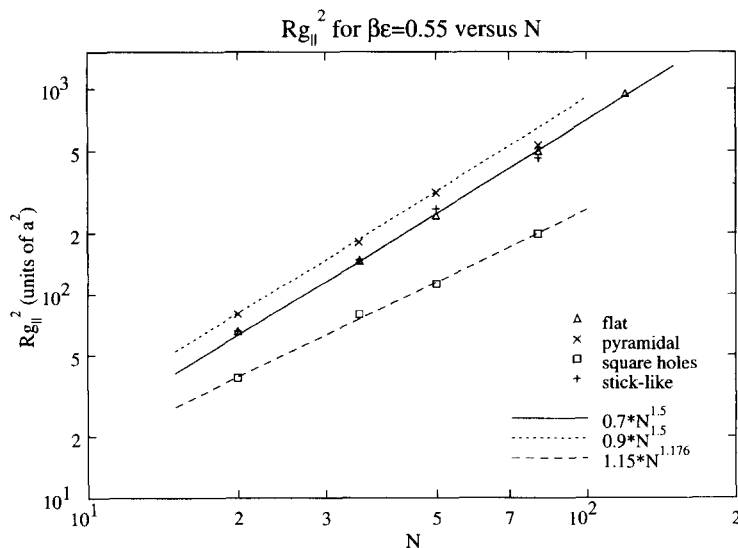
following manner: it is the number of chains which have no contact to the surface in the current time step but had at least one monomer in contact with the surface in the preceding time step. A plot of  $n_{de}$  vs inverse temperature (Figure 5) shows a clear maximum at or slightly above the adsorption temperature [ $(\beta\epsilon)_{ad} \approx 0.14$ ]. Thus the main desorption takes place at the same temperature as the adsorption. However the first desorption processes start at a considerably lower temperature ( $\beta\epsilon \approx 0.2$ ), somewhat depending on the surface structure. The plane surface shows the most pronounced maximum of desorptions. The tighter bound monomers especially on the pyramidal surface decelerate the desorption tendency only by a small amount. Hence within the statistical fluctuations the behaviour of the number of desorptions depends only slightly on the surface structure.

*Radius of gyration*

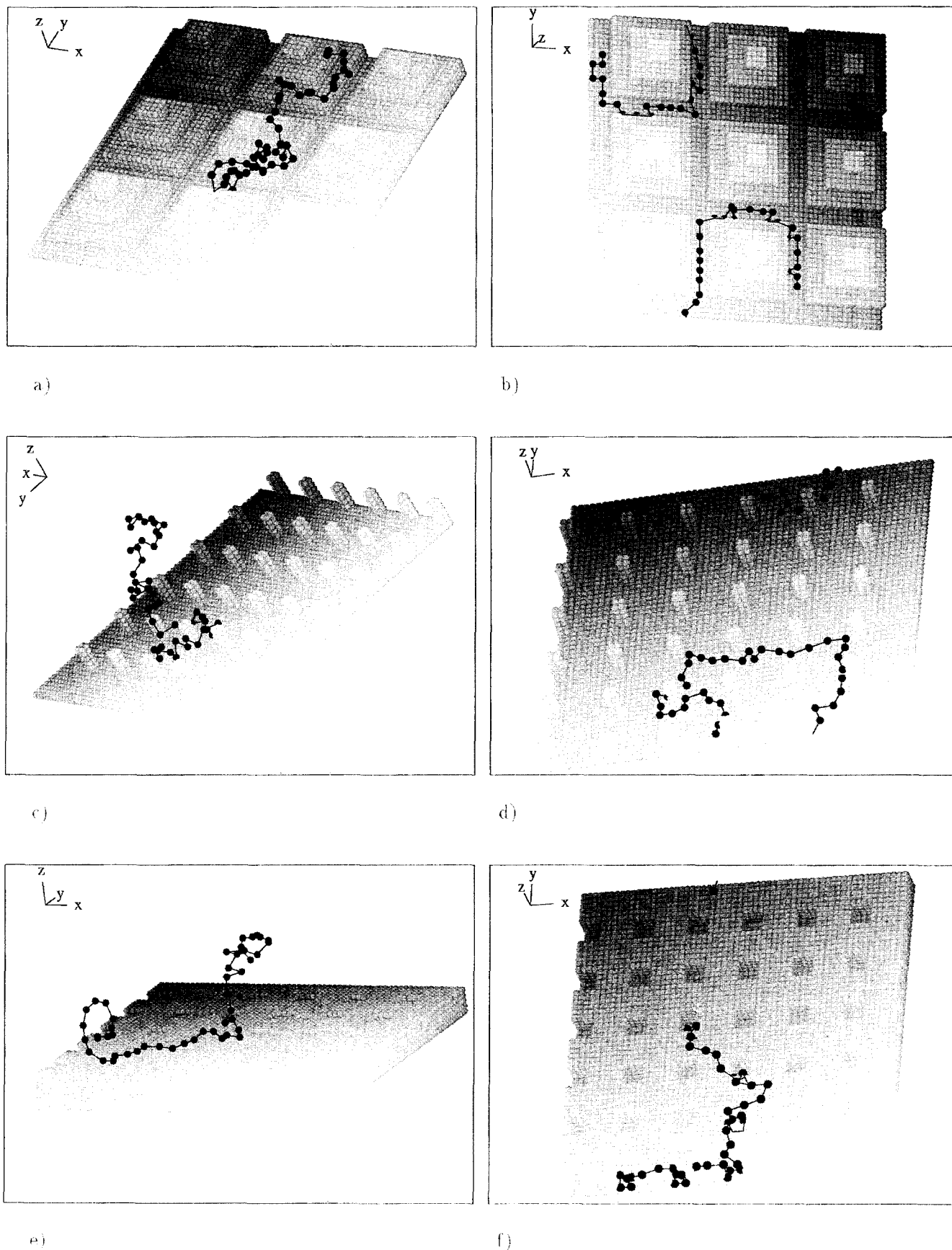
The changes in the mean square radius of gyration perpendicular  $R_{g\perp}^2$  and parallel  $R_{g\parallel}^2$  to the surface can be



**Figure 6** The normalized squared radii of gyration parallel and perpendicular to the different surfaces is plotted vs the inverse temperature for the different surfaces. As comparison the value for a two-dimensional simulation<sup>46,48</sup> is included



**Figure 7** For the different surfaces the scaling dependencies of the adsorbed chain is tested through a plot of  $R_{g\parallel}^2$  vs the chain length  $N$  for  $\beta\epsilon = 0.55$



**Figure 8** Conformational plots for the different surfaces: (a) pyramidal,  $\beta\epsilon = 0.15$ ; (b) pyramidal,  $\beta\epsilon = 0.55$ ; (c) stick-like,  $\beta\epsilon = 0.15$ ; (d) stick-like,  $\beta\epsilon = 0.55$ ; (e) square holes,  $\beta\epsilon = 0.15$ ; (f) square holes,  $\beta\epsilon = 0.55$

seen in Figure 6.  $R_{g\perp}^2$  and  $R_{g\parallel}^2$  are defined as

$$R_{g\perp}^2 = \frac{1}{N} \sum_{i=0}^N (z_i - z_{cm})^2 \quad (3)$$

$$R_{g\parallel}^2 = \frac{1}{N} \sum_{i=0}^N [(x_i - x_{cm})^2 + (y_i - y_{cm})^2] \quad (4)$$

with  $(x_i, y_i, z_i)$  being the coordinates of the  $i$ th monomer and  $(x_{cm}, y_{cm}, z_{cm})$  the centre of mass of the chain. Included in Figure 6 is a horizontal line denoting the mean square radius of gyration of a two-dimensional chain. The value is taken from refs 46 and 48 and corrected for the different vector sets, normally used in the bond-fluctuation model for two and three dimensions. For low temperatures the chain on the plane surface tends to a self-avoiding two-dimensional walk. The potential energy does not restrict the movements parallel to the surface. More surprisingly the stick-like surface behaves completely like the plane surface. The high parallel radius of gyration for the pyramid surface is due to the surface texture leading to the tendency to surround the bottom parts of the pyramids. For the surface with the square hole no drastic increase in  $R_{g\parallel}^2$  takes place and  $R_{g\perp}^2$  does not go to zero. The filled holes keep the chain from getting spread out flat on the surface. The small maximum at moderate temperatures below the adsorption temperature is a hint that the penetration of the chain into the holes is hindered. For a short temperature range the chain tends to a two dimensional behaviour like in the flat case. Only at lower temperatures a significant filling of the holes takes place, reducing the extension of the chain on the surface.

In Figure 7 the squared radius of gyration parallel to the surface  $R_{g\parallel}^2$  is plotted vs the chain length  $N$  for the adsorbed state ( $\beta\epsilon = 0.55$ ).  $R_{g\parallel}^2$  should be proportional to  $N^{2\nu}$  with  $\nu = 3/4$  in the two-dimensional case and  $\nu = 0.588$  in the three-dimensional case<sup>49,50</sup>. We fitted functions with these dependencies through the data points for the different surface structures. As expected the flat surface is showing a clear two dimensional behaviour in the adsorbed state. The same holds for the stick-like structure. More surprisingly the pyramidal structure also delivers two-dimensional features. Despite the fact that the chain surrounds the bottom parts of the pyramids there seems to be enough space for coiling. In our case the pyramids seem only to produce a larger effective Kuhn segment consisting of more than one of the mean segments in the bond-fluctuation model, leading to the larger radius of gyration. In contrast to the other surfaces the data points for the square holes are well fitted by the three dimensional dependency. Although the holes are of finite size the pure existence of the holes seems to keep the chain from spreading out as a two-dimensional coil.

All the above statements can nicely be seen in the plots of selected conformations for different temperatures, given in Figure 8. In the temperature range of the adsorption  $(\beta\epsilon)_{ad}$  parts of the chains are already sticking to the floor, contacts with the sticks can be seen. The square holes are almost empty. The chain on the pyramidal surface is living across the pyramids. When lowering the temperature drastically the square holes get filled and the chain moves towards the valleys in between the pyramids. This is in accordance with

predictions of Ball *et al.*<sup>37</sup> that chains are attracted to corners for pairwise Van-der-Waals interactions at low temperatures.

## SUMMARY AND CONCLUSION

In this paper we investigated the adsorption of single chains on a flat surface, a stick-like one, a surface with pyramids and one with square holes. The computer simulations showed that the adsorption starts at the same temperature for all surfaces thus proposing that the specific surface texture is not of importance for first contacts. The desorption of once adsorbed chains is already significantly non-zero at lower temperatures as the adsorption temperature, although the maximum of the desorption is in the vicinity of the adsorption temperature. The faster adsorption on the pyramidal and the stick-like surface after the initiation should be due to a larger energy gain and an easier way to get into contact with these structured surfaces. The surface with square holes first lacks behind, but finally surpasses the simpler ones. The adsorbed chains show a clear two dimensional behaviour with one exception. In the case of the square holes the chain properties remain three dimensional even in the adsorbed state. The pyramids spread the chain somewhat to larger radii of gyration but do not prohibit a two dimensional state.

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