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*conformational entropy, polymer chain, rough surface*

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# THE CONFORMATIONAL ENTROPY OF (112) SAW CHAIN GRAFTED TO A ROUGH SURFACE

Conformation of a polymer chain terminally attached to a rough surface has been studied. The method of calculation of the conformational entropy based on the analysis of the segment density distribution in the perturbed coil has been proposed. The results have been confronted with those of a simulation made with the (112) SAW chain on a cubic lattice.

## 1. INTRODUCTION

Naturally occurring surfaces are usually microscopically rough and/or energetically inhomogeneous. The heterogeneity leads to an enhancement of adsorption of different species, including polymers, under quite general conditions. Upon increasing the surface irregularity, the number of polymer-surface interactions is strongly enhanced relative to those on the idealized planar surface, as a consequence of a higher probability of polymer-surface intersection with increasing roughness (see Fig. 1) and reduced conformational entropy of the polymer chain adsorbed on the surface Since the method of calculation of the entropy of the chain near the surface derived within the renormalization group theory [1] is restricted only to extremely large chains and flat surfaces, the question of the effect of the surface topology on the conformational entropy of the chain is of significant interest [2]. The objective of this study is to determine the entropy decrease caused by the terminal attachment of the polymer chain to the surface represented by the uncorrelated Gaussian surface (uGs), the Brownian surface (Bs) and the fractional Brownian surface (fBs)[3].

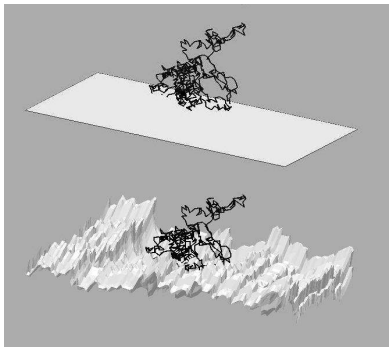

Fig. 1. Schematic representation of the polymer chain terminally attached to flat and rough surfaces.

## 2. THEORY

The entropy of the terminal attachment of the chain to the flat surface is a function of the number of possible conformations of the free ($\Omega_{free}$) and attached chain ($\Omega_{att}$):

$$\frac{\Delta S}{k_B} = \ln\left(\frac{\Omega_{gr}}{\Omega_{free}}\right) = \ln\left(1 - \frac{\Delta\Omega}{\Omega_{free}}\right) \approx -\frac{\Delta\Omega}{\Omega_{free}} \tag{1}$$

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where $\Delta\Omega$ is the number of conformations eliminated by the surface. The latter equality is a consequence of the relatively small value of $\Delta\Omega$ as compared with $\Omega_{free}$. The distance between the surface attached segment and the coil center is [4]:

$$Z = 6^{-1/4} bN^{\nu} \tag{2}$$

The radial segment density distribution in the coil formed by the unperturbed chain reads [4]:

$$\rho(x,y,z) = \frac{(r/b)^{1/\nu}}{B\sqrt{\pi N}b^2} \exp\left(-\frac{9}{N}\left(\frac{r}{b}\right)^{1/\nu}\right) \tag{3}$$

where $b$ is the segment length, $r=(x^2+y^2+z^2)^{1/2}$, $x$, $y$, $z$ are the Cartesian coordinates and $B$ – the normalization constant. The $\nu$ coefficient is the universal scaling exponent equal to 1/2 for the ideal and 3/5 (or 0.588) for SAW chains [5].

The segment density distribution (3) of a chain terminally attached to the flat surface is cut-off by the plane $z=Z$. The integral of the segment density distribution at $z=Z$ (see Fig. 2a) is a measure of the number of points of intersection between the Z plane and all conformations of an unperturbed polymer coil:

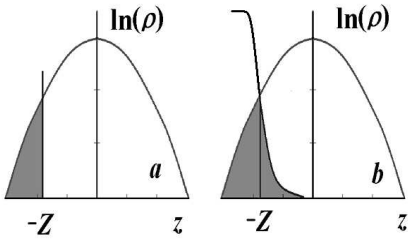


Fig. 2. Schematic geometrical interpretation of the integral $H$: a) flat surface, b) a surface represented by error function (uGs)

$$H = \int_{-L}^{L}\int_{-L}^{L} \rho(x,y,Z)\,dx\,dy \tag{4}$$

where $L=Nb/2$. For $\nu=1/2$ the integral (4) is approximately equal to

$$H = \frac{1}{45}\sqrt{\pi}N^{3/2} + \frac{1}{5}\frac{\sqrt{\pi}}{b^2}Z^2N^{1/2} \approx \frac{1}{45}\sqrt{\pi}N^{3/2} \tag{5}$$

The numerical calculation of (4) shows that $H$ scales with $N$ as

$$H = CN^{U} \tag{6}$$

with $U=3/2$ and 17/10 for $\nu=1/2$ and 3/5, respectively. The $H$ integral is not a simple linear function of the number of conformations crossing the plane (equal to $\Delta\Omega$) since some chains cross the plane more than once. In order to find a correlation between the number of eliminated conformations and the integral $H$ we studied the $H=f(\Delta\Omega)$ function using the MC simulation method (see 2.2), finding that

$$\frac{\Delta S}{k_B} = \frac{\Delta\Omega}{\Omega_{free}} = -\frac{1}{3}H^{1/3} \tag{7}$$

Finally, taking into account Eq. 6, for $\nu=1/2$ the simple scaling law can be written as:

$$\frac{\Delta S}{k_B} = -C'N^{1/2} \tag{8}$$

If the polymer chain is attached to the rough surface, the area of the surface which cuts-off the distribution (3) is larger than that of the flat surface by a factor $L^{D-2}$, where $L$ is the perimeter of a chosen fragment of the surface and $D$ is the fractal dimension of the surface. We postulate that Eqs (7) and (8) can be generalized by power laws with the exponent $W$ related to the fractal dimension of the surface in the following way

$$\frac{\Delta S}{k_B} = -C'N^{W(D)} \tag{9}$$

## 3. SIMULATION

### 3.1. THE SURFACE GENERATION

Two methods were used to simulate rough surfaces: i) the method producing the uGs with independently calculated elevations of each point with the normal distribution of elevation and ii) the „random midpoint displacement with successive random addition" (RMD) method [3] to simulate fractal surfaces. The latter method consists of generation of a surface with a unit grid, whose corners are displaced randomly at the normal to the grid. Each displacement is generated by Gaussian random number of a given standard deviation $\sigma$. The construction of the surface proceeds in recursively reducing the mesh size and the standard deviation of elevations by factors of 2 and $2^{3-D}$, respectively The method produces Bs (at $D$=2.5, self-similar surface) and fBs (at $D\neq2.5$, self-affine surface). The results obtained are the averages of $10^4$ simulation data sets

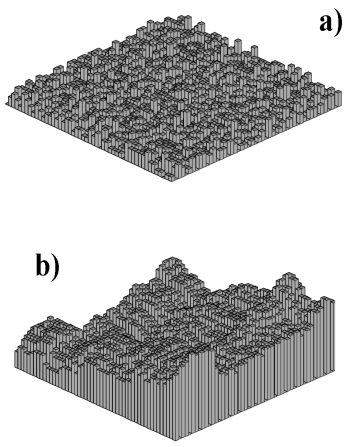


Fig. 3. Examples of surfaces: a) uGs ($\sigma$=1.0), b) Bs ($\sigma$=2.0)

### 3.2. THE POLYMER CHAIN GENERATION

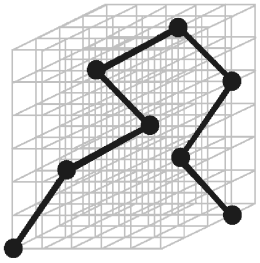

Fig. 4. Schematic representation of a fragment of (112) SAW chain

. The modified SAW technique [6] was used to simulate the chain conformation. The modification consists in the method of generation of position of each succeeding segment. The new position is calculated as a sum of coordinates of the penultimate segment and the permutation of the shift coordinate set ($\pm a,\pm a,\pm 2a$) (so-called (112) SAW) where $a$ is the lattice constant. Each step was selected from the lattice sites that do not violate the SAW restriction. The technique applied partially suppressed the attrition problem [7]. No configurational bias correction was performed. Periodic boundaries of the simulation box were applied. The linear dimensions of the unperturbed (112) SAW coil scale with the exponent of 0.50. The results are based on $10^4$ simulation data sets. In parallel to the chain generation, the entropy calculations were performed by means of the statistical counting method [8].

## 4. RESULTS

As seen from Fig 5, all $\Delta S$=f($N$) dependencies for chains terminally attached to different rough surfaces can be expressed by the simple power law (Eq. 9).

The Fig. 6 shows the dependence of the exponents $W(D)$ of the power law (Eq. 9) on the "experimental" fractal dimension $D$ defined as

$$D = \ln(A_S)/\ln(L_S) \tag{10}$$

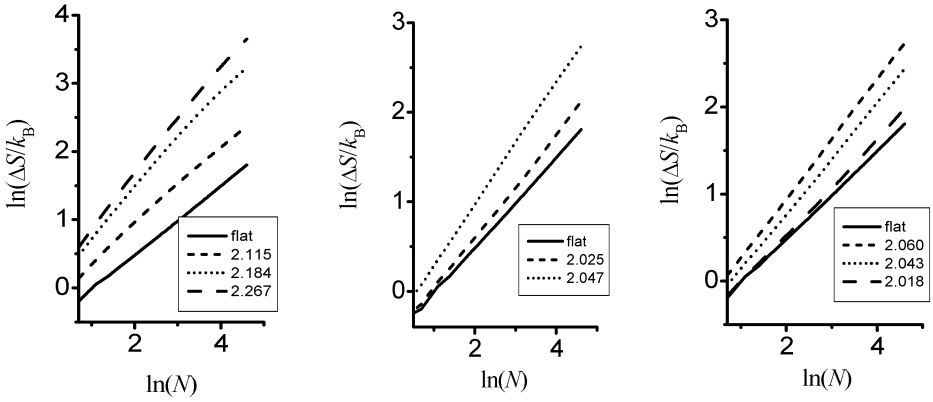


Fig. 5 The adsorption entropy vs. polymer chain length obtained for different surfaces: a) uGs, b) Bs, c) fBs ($\sigma$ values are included in figures).

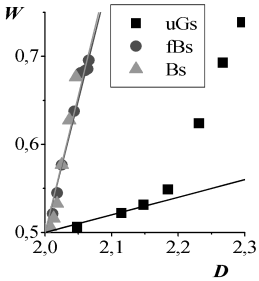


Fig. 6. The $W$ vs. $D$ relationships obtained for different surfaces.

where $A_s$ is the area of the square of the side length equal to $L_s$. As seen the scaling exponents calculated for Bs and fBs are linearly dependent on the fractal dimension of the surface:

$$W = 1/2 + 3(D-2) \tag{11}$$

The power law (9) with the exponent given by Eq. (11) is valid for all self-similar and self-affine surfaces. The $W$ exponent obtained for uncorrelated surface (uGs) is given by a more complex relationship. The initial small slope of the $W$=f($D$) dependence results from the weaker lateral restrictions of the chain conformation at small roughness of uGs as compared with those of Bs and fBs.

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ENTROPIA KONFORMACYJNA ŁAŃCUCHA (112) SAW ZAKOTWICZONEGO NA POWIERZCHNI NIEJEDNORODNEJ GEOMETRYCZNIE

*Praca dotyczy konformacji łańcucha polimeru zakotwiczonego jednym końcem na powierzchni niejednorodnej geometrycznie Zaproponowano metodę obliczania entropii konformacyjnej opartą na analizie rozkładu gęstości segmentów w zaburzonym kłębku. Uzyskane wyniki skonfrontowano z wynikami symulacji łańcucha (112) SAW w sieci regularnej.*