Conformational properties of polymers near a fractal surface

Viktoria Blavatska[a], Wolfhard Janke[b]

[a]*Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[b]*Institut für Theoretische Physik and Centre for Theoretical Sciences (NTZ), Universität Leipzig, Postfach 100 920, 04009 Leipzig, Germany*

Abstract

The conformational properties of flexible polymer macromolecules grafted to an attractive partially penetrable surface with fractal dimension $d_s^{p_c} = 91/49$ are studied. Employing computer simulations based on the pruned-enriched Rosenbluth chain-growth method, estimates for the surface crossover exponent and adsorption transition temperature are found. Our results quantitatively reveal the slowing down of the adsorption process caused by the fractal self-similar structure of the underlying substrate.

Keywords: polymer, adsorption, percolation cluster, chain-growth algorithm, surface crossover exponent

1. Introduction

The study of polymers near disordered surfaces is of great importance, since most naturally occurring substrates are rough and energetically (or structurally) inhomogeneous. Surface heterogeneity has a crucial effect on polymer adsorption phenomena [1, 2, 3, 4, 5]. Since most chemical substrates are proved to be of fractal nature [6], studying the influence of a non-trivial surface geometry on polymer adsorption is of particular interest. It is established [7] that the adsorption process is enhanced (diminished) when the fractal dimension of the substrate is larger (smaller) than that of a plain Euclidean surface. A number of studies has been dedicated to polymer adsorption on a family of finitely ramified fractals [8, 9, 10]. Also of great importance is the study of polymers in the vicinity of fluctuating surfaces, such as membranes [11].

Energetical inhomogeneity arises due to the presence of various chemical compounds in the substrate, interacting with the monomers of the polymer chain in a different manner. In the language of lattice models, such surfaces can be modeled as a two-dimensional regular lattice with different types of randomly distributed sites, e.g., one type with attractive interactions with the monomers and the other one being neutral (treated as defects or impurities). In this concern, it is worthwhile to study the situation when the concentration of attractive sites on the surface is exactly at the percolation threshold and a spanning percolation cluster of attractive sites appears [12]. A percolation cluster is a fractal object with fractal dimension $d_s^{p_c} = 91/49 \simeq 1.89$ [13]. The neutral sites of the surface (which do not belong to the percolation cluster) could be considered as penetrable for the polymer chain, so the polymer is adsorbed on an attractive fractal with fractal dimension $d_s^{p_c}$. This can thus model the process of polymer adsorption on an attractive, partially penetrable membrane, which could be of interest in biophysical applications.

In the present paper, we report a careful computer simulation study of polymer adsorption on a fractal substrate formed by a percolation cluster on a two-dimensional square lattice.

2. Methods

We start with a regular two-dimensional lattice of edge lengths up to $L_{max} = 400$, each site of which is assigned to be occupied with percolation probability p_c and empty otherwise. To extract the percolation cluster of occupied sites, which spans around the lattice, an algorithm based on the site-labeling method of Hoshen and Kopelman [14] has been applied.

The polymer chain is modeled as a self-avoiding walk (SAW). To study the conformational properties of SAWs, grafted to the substrate formed by a percolation cluster, we apply the pruned-enriched Rosenbluth method (PERM) [15]. The starting point of a SAW is fixed on a random site which belongs to the percolation cluster. Note, that this starting site is always chosen within a small region around the center of a given percolation cluster to allow the adsorbed polymer chain configurations to be completely located on the cluster. We treat this disordered surface as the $z = 0$ plane of a regular three-dimensional cubic lattice. The chain grows step by step, i.e., the nth monomer is placed at a randomly chosen neighbor site of the last placed $(n - 1)$th monomer ($n \leq N$), taking into account that the chain cannot "penetrate" through the occupied sites of the surface (belonging to the percolation cluster), but only through the empty sites. The growth is stopped, if the total length of the chain, N, is reached (we consider SAWs of length up to $N = 150$). The adsorption energy E_n of a growing chain at the nth step is given by $E_n = N_s(n) \varepsilon$, where ε is the attractive energy between monomers and the percolation cluster sites and $N_s(n)$ is the number of contacts of the polymer chain with attractive sites.

A weight W_n is given to each sample configuration at the nth step, which in our case is given by

$$W_n = \prod_{l=2}^{n} m_l e^{-\frac{E_l - E_{l-1}}{k_B T}}.$$ (1)

Here, m_l is the number of free lattice sites to place the lth monomer and k_B is the Boltzmann constant. In what follows, we will assume units in which $\varepsilon = -1, k_B = 1$. Pruning and enrichment are performed by choosing thresholds $W_n^<$ and $W_n^>$ depending on the current estimate of the partition sum [15].

Note that in the problem under consideration, a double averaging has to be performed: the first $\langle ... \rangle$ over all configurations of the polymer chain grafted to a single percolation cluster; the second average $\overline{\langle ... \rangle}$ is carried out over different realizations of disorder, i.e., over different constructed percolation clusters. We constructed $M = 1000$ clusters.

3. Results

The adsorption transition is in general viewed as a second-order phase transition [16] with the averaged fraction of monomers on the surface $\langle N_s \rangle / N$ serving as order parameter. It tends to zero in the high-temperature (bulk) regime for $T > T_A$ and becomes macroscopic close to the adsorption transition temperature [16]:

$$\langle N_s \rangle / N \sim \begin{cases} \frac{1}{N}, & T > T_A, \\ N^{\phi_s - 1}, & T = T_A, \\ \text{const}, & T < T_A, \end{cases}$$ (2)

where ϕ_s is the universal surface crossover exponent. In the adsorbed phase for $T < T_A$, the fraction $\langle N_s \rangle / N$ is independent of N. For a homogeneous surface these parameters are known [17] to be $\phi_s(d = 3) = 0.484 \pm 0.002$ and $T_A(d = 3) = 3.5006 \pm 0.0009$.

Our analysis of the temperature behavior of the order parameter $\overline{\langle N_s \rangle} / N$ for chain length $N = 150$ is shown in Fig. 1. The number of contacts with attractive sites of the surface increases monotonically as the temperature is lowered and becomes macroscopic within a short temperature interval close to the adsorption transition. At each temperature, the number of adsorbed monomers on the homogeneous surface is larger than that on the percolation cluster due to stronger attraction to the surface. Note that due to the complicated fractal structure of a percolation cluster, it requires a very long observation time for a polymer to find a configuration in the ground state with lowest adsorption energy (corresponding to $\overline{\langle N_s \rangle} / N = 1$).
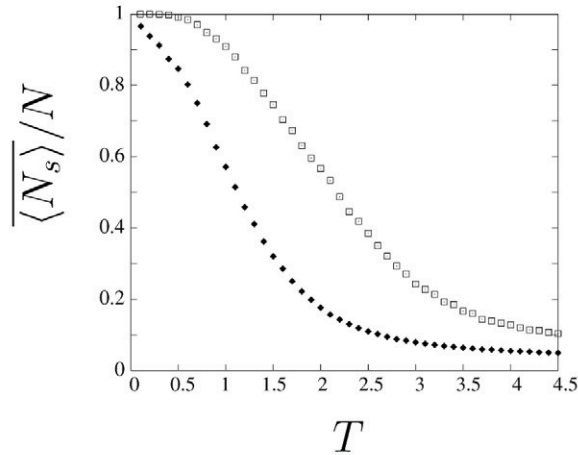
Figure 1: Averaged fraction of monomers of the chain adsorbed on a homogeneously attractive surface (squares) and an attractive percolation cluster (filled diamonds) for $N = 150$ as a function of temperature.

The characteristics of the adsorption transition can be obtained by examining the fluctuations of the adsorption energy near the transition point. The specific heat per monomer is given by

$$C = \frac{1}{NT^2}\left(\overline{\langle N_s^2 \rangle} - \overline{\langle N_s \rangle^2}\right). \tag{3}$$

In the vicinity of the adsorption transition point, the specific heat obeys a scaling form: $C \sim N^{2\phi_s-1}H(|T-T_A|N^{\phi_s})$ [16]. The peak structure of C as a function of temperature indicates transitions or crossovers between physically different states. In the problem under consideration, this corresponds to the transition between bulk and adsorbed regimes. Figure 2 shows the typical specific-heat behavior of SAWs grafted to a homogeneous surface and percolation clusters, respectively. Assuming that the value of the specific heat at its maximum $C_{\max}(N)$ (the height of the specific-heat curve) for each chain length N is already close enough to the asymptotic critical region, we can estimate the crossover exponent ϕ_s by fitting to the form

$$C_{\max}(N) \sim N^{2\phi_s-1}. \tag{4}$$

We obtain $\phi_s = 0.509 \pm 0.009$ and $\phi_s^{p_c} = 0.425 \pm 0.009$.

For finite chain length N, the temperature defined by the position of the specific-heat maximum $T_{\max}(N)$ is well below the transition temperature T_A of an infinitely long polymer macromolecule. This finite-size deviation obeys the scaling behavior

$$T_{\max}(N) - T_A \sim N^{-\phi_s}. \tag{5}$$

We received the estimate for the critical temperature of adsorption onto a homogeneous surface $T_A = 3.47 \pm 0.02$, and for the case of a percolation cluster the result of fitting gives $T_A^{p_c} = 2.64 \pm 0.02$.

Finite-size scaling master plots of the order parameter ($\langle N_s \rangle/N^{\phi_s}$ vs. $|T - T_A|N^{\phi_s}$) validate these estimates [18]. Furthermore, additional scaling analyses of the orthogonal and parallel components of the gyration radius are in good agreement with the exactly known two-dimensional correlation length exponent $\nu_2 = 0.742 \pm 0.006 \approx 3/4$ for a homogeneous surface and yield $\nu_2^{p_c} = 0.772 \pm 0.006$ for the fractal percolation surface [18], in good agreement with our previous estimate for SAWs confined *onto* a two-dimensional percolation cluster [19].

4. Conclusions

We have studied the adsorption of flexible polymer macromolecules on an attractive percolation cluster, formed on a regular two-dimensional square lattice at critical concentration p_c of occupied sites. The conformational properties
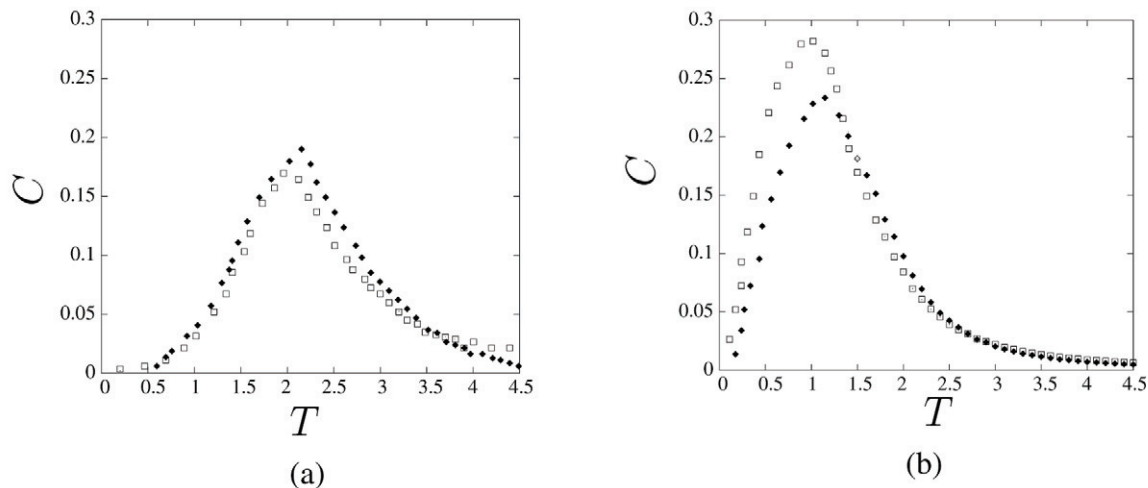
Figure 2: Specific heat per monomer as a function of temperature for a polymer chain near (a) a homogeneously attractive surface and (b) an attractive percolation cluster as a function of temperature. Squares: $N = 40$, filled diamonds: $N = 100$.

of polymer chains in three dimensions grafted with one end to the percolation cluster are studied with the pruned-enriched Rosenbluth method (PERM). Examining the peak structure of the heat capacity, we find an estimate for the surface crossover exponent, governing the scaling of the adsorption energy in the vicinity of the transition point, $\phi_s^{p_c} = 0.425 \pm 0.009$, and for the adsorption transition temperature we obtain $T_A^{p_c} = 2.64 \pm 0.02$. As expected, the adsorption is diminished, when the fractal dimension of the surface is smaller than that of the plain Euclidean surface due to the smaller number of contacts of monomers with attractive sites.

References

[1] M. Kawaguchi and T. Arai, Macromolecules 24 (1991) 889.
[2] G. Huber and T.A. Vilgis, Eur. Phys. J. B 3 (1998) 217.
[3] K. Sumithra and A. Baumgaertner, J. Chem. Phys. 109 (1998) 1540.
[4] M.S. Moghaddam and S.G. Whittington, J. Phys. A 35 (2002) 33; M.S. Moghaddam, J. Phys. A 36 (2003) 939.
[5] J. Zierbarth, Y. Wang, A. Polotsky, and M. Luo, Macromolecules 40 (2007) 3498.
[6] D. Avnir, D. Farin, and P. Pfeifer, Nature 308 (1984) 261; J. Chem. Phys. 79 (1983) 3566.
[7] E. Bouchaud and J. Vannimenus, J. Physique (France) 50 (1989) 2931.
[8] S. Elesović-Hadžić, I. Živić, and S. Milošević, J. Phys. A 36 (2003) 1213.
[9] V. Bubanja, M. Kneževic, and J. Vannimenus, J. Stat. Phys. 71 (1993) 7.
[10] S. Kumar, Y. Singh, and D. Dhar, J. Phys. A 26 (1993) 4835.
[11] T. Auth and G. Gompper, Phys. Rev. E 68 (2003) 051801; Phys. Rev. E 72 (2005) 031904; S. Karalus, W. Janke, and M. Bachmann, Phys. Rev. E 84 (2011) 031803.
[12] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).
[13] S. Havlin and D. Ben Abraham, Adv. Phys. 36 (1987) 155.
[14] J. Hoshen and R. Kopelman, Phys. Rev. B 14 (1976) 3438.
[15] P. Grassberger, Phys. Rev. E 56 (1997) 3682.
[16] E. Eisenriegler, K. Kremer, and K. Binder, J. Chem. Phys. 77 (1982) 6296.
[17] P. Grassberger, J. Phys. A 38 (2005) 323.

[18] V. Blavatska and W. Janke, J. Chem. Phys. 136 (2012) 104907.
[19] V. Blavatska and W. Janke, Europhys. Lett. 82 (2008) 66006; Phys. Rev. Lett. 101 (2008) 125701; J. Phys. A 42 (2009) 015001.