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Stiff polymer adsorption. Onset to pattern recognition

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Abstract

We present the results of extensive off-lattice Monte-Carlo simulations of a stiff polymer chain adsorbing onto a sticky periodic stripe-like pattern of variable width. We have analyzed, in terms of the chain length and rigidity, the adsorption and the pattern recognition process as a function of the stripe width. We have seen that this process is twofold: (i) the chain adsorbs rather isotropically onto the surface at a characteristic temperature T_c and (ii) a further reduction in the temperature is needed for the chain to reorganize and adjust to the specific pattern. Such polymer reorganization has been studied through the evaluation of the chain *degree of stretching and asphericity*. We have found an optimal stripe width that maximizes the stretching. We have introduced a criteria to estimate the characteristic temperature at which the pattern recognition takes place $T_r < T_c$ and we have studied its dependence with the chain and surface relevant parameters.

Keywords: Polymer adsorption; Pattern recognition

1. Introduction

Polymers physically adsorbed onto solid surfaces has found a wide range of applications, such as protective coatings of electronic devices, lubricants, stabilization of colloidal suspensions, adhesion and, more recently, for biological and medical purposes. Particularly, the generation of surfaces that are able to withstand protein adsorption is a major challenge in the design of blood-contacting materials for medical implants and bioaffinity sensors. Some copolymers (PLL-g-PEG) are found to spontaneously adsorb from aqueous solutions onto metal oxide surfaces (TiO_2), reducing the adsorption of blood serum and individual proteins, such as fibrinogen, that are known to play a major role in the coagulation process and thrombosis [1–3].

It is also of great interest the study of the polymer adsorption onto heterogeneous surfaces that are characterized by a fluctuating polymer–surface interaction [4]. Real biomolecules carry a pattern encoded in their sequence distribution, and a properly chosen functionalized surface may be able to recognize this information and adsorb it strongly [5]. In this sense, a major effort is concentrated in adsorption of flexible polyelectrolytes onto heterogeneously charged surfaces [6–8].

Random heteropolymers are known to be the simplest physical models for proteins or DNA and, like many biological macromolecules, are rigid to a certain extend due to electronic delocalization and steric effects. Since the free rotations about the chain backbone are restricted, the chain statistics cannot be described accurately by conventional models for flexible polymer chains, and only few recent developments have been done in the area of semiflexible polymers at surfaces [9–11].

The purpose of the present paper is to investigate the role of the polymer structure in the adsorption process onto a patterned surface consisting in stripes of variable width. Such structure has been found particularly relevant to the DNA adsorption on charged membranes [12].

By measuring the fraction of monomers adsorbed onto the surface, the degree of stretching and the asphericity, as a function of the system temperature, we have analyzed the adsorption characteristics in terms of the chain length and

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rigidity. We have found that a higher degree of stiffness and an increasing chain length enhances the surface pattern recognition. Our results also indicate that the adsorption transition foregoes the surface recognition and that chains, in the adsorbed state, find an optimal stripe width that maximizes their stretching.

2. Numerical model

We have simulated the adsorption of a semiflexible polymer chain onto a planar surface using off-lattice Monte-Carlo methods. We have considered a polymer chain confined in a unit box with peridic boundary conditions in the *x–y* domain. The length of the cell is chosen to be at least twice the chain length in order to avoid finite size effects. The polymer chain is represented by a *pearl-necklace model* [13] containing N beads of diameter σ. The bond length is defined to be $1{,}1\sigma$; thus, the polymer length is $L=1{,}1\sigma N$. The surface is composed of heterogeneities in the form of stripes oriented along the y-axis with a characteristic width ω. The polymer has an attractive interaction with alternate stripes and a neutral one with the others. A schematic view of the system is presented in Fig. 1. We must note that for $\omega << 1{,}1\sigma$ the polymer will not feel the heterogeneities of the surface and will not be relevant for pattern recognition.

The stiffness of the polymer chain is introduced through the bending potential U_B given by [14]:

$$U_B = \sum_{\theta} \kappa (1+\cos\theta)^2, \tag{1}$$

where θ is the bond angle between any three consecutive sites and κ is the bending constant. Although in real polymer chains the flexibility is limited mainly by imposed restrictions in the torsion angles, the above expression is of general use in coarse-grained polymer models where a monomer does not represent a single carbon group but a collection them. The stiffness parameter κ is directly related to the chain persistence length [11], that can be experimentally measured by scattering techniques [15].

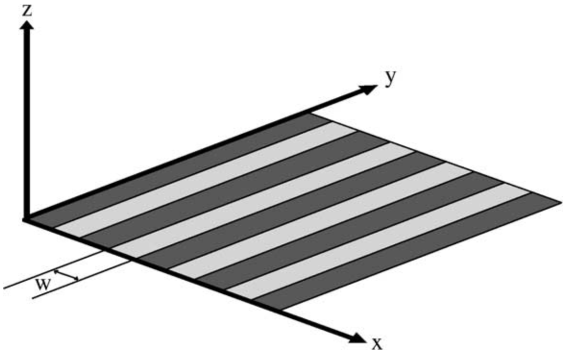

Fig. 1. Schematic representation of a striped surface. Dark stripes have an attractive interaction with the polymer chain whereas clear ones are neutral.

Monomers that are two or more beads apart interact through a steric hard-core potential of the form,

$$U_{\mathrm{steric}} = \sum_{i,j=1}^{N} V(r_{ij}), \tag{2}$$

where V is given by,

$$V(r_{ij}) = \begin{cases} 0, & \text{for } |r_i - r_j| > \sigma \\ \infty, & \text{for } |r_i - r_j| < \sigma \end{cases}. \tag{3}$$

Monomer units have an attractive interaction with the stripes on the surface with adsorption energy $\epsilon<0$. Thus, we define an adsorption potential U_A as,

$$U_A = n_c \epsilon, \tag{4}$$

n_c being the number of i-monomers located onto an attractive stripe and such that their z-coordinate verifies $0<z_i<\sigma$. A hard wall potential is set at the $z=0$ plane; thus, the center of the particles cannot penetrate the surface. The total energy of the system will contain the above contributions and is written as:

$$U = U_A + U_B + U_{\mathrm{steric}}. \tag{5}$$

The initial configuration of the self-avoiding polymer is randomly generated with one monomer attached to the surface $z=0$. Next, the polymer is tried to move by randomly executing a reptating type motion in a forward or reverse direction, or by selecting an individual monomer which position can be rotated, around the axis connecting the previous and following monomer in the chain, an arbitrary angle between 0 and 2π. Chain ends just perform random wiggling motions. Each move is accepted according to the standard Metropolis Monte Carlo algorithm: $\exp(-\Delta U/k_B T) > \eta$, where $0<\eta<1$ is a random number. A link-cell method [16] has been implemented in the algorithm to efficiently check ΔU. For the rest of the paper, we will measure the temperature T in units of $1/k_B$ and hence $T \equiv k_B T$. We have taken $\epsilon = -1 k_B T$. The monomer diameter that defines our unit length is selected to be $\sigma=1$.

At very high temperatures or equivalently at low adsorption energies, the chain has a tendency to diffuse into the bulk. We prevent this by forcing the polymer to have at least one monomer attached to the surface. However, one does not expect any significant change in the statistical properties of the adsorbed chain at low temperatures that are the ones of interest for pattern recognition.

We define one Monte Carlo Step (MCS) as N trials to move the chain. The system has been equilibrated for 10^6 MCS. Subsequently, measurements are taken every 10 MCS. The results have been finally averaged over 10^5 measures.

3. Results and discussion

We have studied the adsorption process of a stiff homopolymer chain onto an attractive striped surface. We

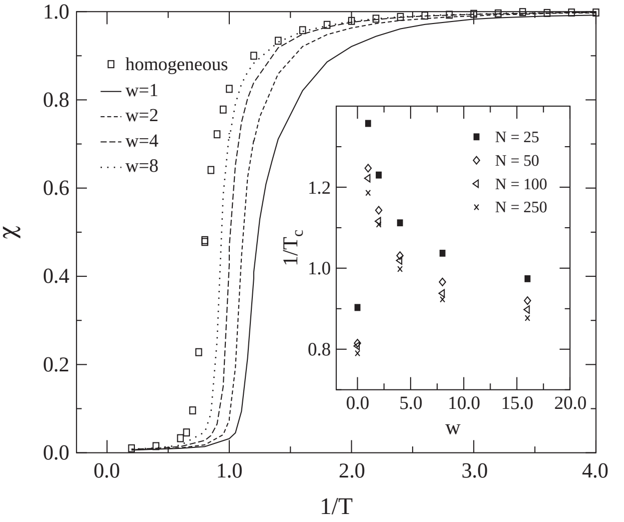

Fig. 2. Fraction of monomers adsorbed onto the surface χ vs. $1/T$ for different values of the stripe width ω. The chain length is set to N=250 and its bending parameter κ=30. Inset: Characteristic adsorbing temperatures as a function of ω for different chain lengths (κ=30).

have investigated the behavior for different chain lengths $N\in[25,250]$ and chain rigidities $\kappa\in[0,30]$ for several values of the stripe width ω. The flexible chain limit corresponds to κ=0.

In previous studies, it has been clearly established that a polymer chain adsorbs strongly onto a planar homogeneous surface at a characteristic temperature that increases with the chain length and stiffness [11]. Thus, we are interested to see how the adsorption process is influenced by structure of an heterogeneous attractive surface that, in our case, is controlled by the stripe width. In Fig. 2, we have plotted the fraction of monomers adsorbed onto the surface $\chi \equiv n_c/N$ vs. the inverse of the temperature $1/T$ for N=250 and κ=30. The results for different widths are compared with those corresponding to an homogeneous attractive surface. We can observe that the transition towards a complete adsorbed state takes place at higher temperatures with increasing the stripe width ω, and that the highest characteristic adsorbing temperature is found for an homogeneous surface. This result can be easily understood since for an homogeneous surface the polymer chain does not need to accommodate to a particular surface pattern once it has been adsorbed. The transition temperatures to the adsorbed state, $T_c(N, \kappa, \omega)$, are determined from the temperature corresponding to the maximum of the specific heat data, that is directly derived from the measure of the fluctuations of the internal energy. The characteristic temperatures T_c as a function of the stripe width ω, for κ=30 and for different chain lengths N, are represented in the inset plot of Fig. 2. We can observe that for a given chain length T_c increases with increasing ω and that at a particular stripe width T_c also increases with N, as expected. Data represented at ω=0 corresponds to an homogeneous attractive surface from which the highest values of T_c are obtained. This characteristic temperature provides a valuable information in order to identify the transition point towards the adsorbed state, however, does not account for pattern recognition yet. One expects that, once the chain is adsorbed onto the surface, then it has to accommodate to the specific pattern, and this process may take place at a lower temperature than T_c.

3.1. Degree of stretching

Since our pattern is composed of stripes oriented along the y-axis, we introduce a parameter that will measure the degree of stretching of the polymer chain, in its adsorbed state, along the y-axis.

The characteristic size of the polymer chain is usually given by its radius of gyration defined as:

$$R_g = \langle R^2 \rangle^{1/2} = \left\langle \left(\vec{r_i} - \langle \vec{r_i} \rangle \right)^2 \right\rangle^{1/2}$$

$\vec{r_i}$ being the postion of the i-monomer. The averaged is performed over all monomer positions. A fully stretched chain of length L=$N\sigma$ has a radius of gyration respect to its center of mass equal to $R = L/\sqrt{12}$; thus, we define the degree of stretching of a polymer chain Q, as the ratio between the y-component of its radius of gyration and the radius of gyration of a fully stretched chain:

$$Q = \frac{\sqrt{12}}{N\sigma} \left\langle R_y^2 \right\rangle^{1/2} \tag{6}$$

The degree of stretching Q as a function of the stripe width ω for different chain lengths is plotted in Fig. 3. The chain rigidity is set to κ=30 and measures are taken at a temperature of $1/T$=4 where the chain is almost completely adsorbed. For the sake of comparison, the results corresponding to an homogeneous attractive surface are included

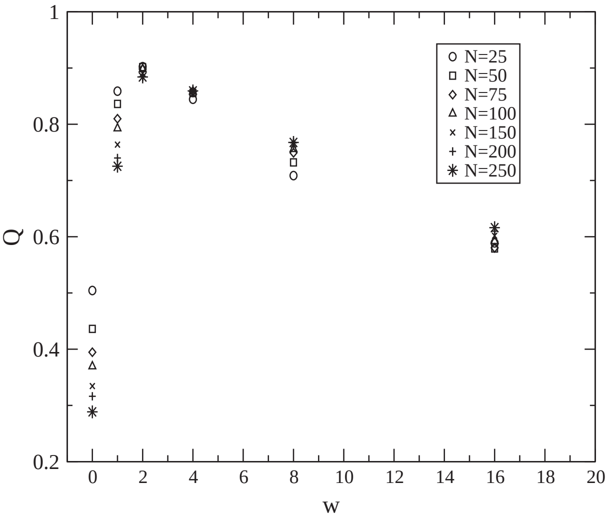

Fig. 3. Measure of the degree of stretching Q vs. the stripe width ω for different chain lengths. The stiffness of the chain is set to κ=30. Q has been evaluated for a completely adsorbed chain $1/T$=4.

in the $\omega=0$ data. Remarkably, we can observe that, independently of the chain length, there is an optimal value for the stripe width ($\omega=2$) that maximizes the stretching Q. The introduction of an attractive striped pattern onto the surface increases notably the degree of stretching, and this stretching is enhanced by the introduction of even small quantities of chain stiffness. The existence of an optimal stripe width is due to a competition between the entropy, that tends to spread the chain over the surface almost isotropically, and the internal energy that accounts for the benging energy and the interaction of the polymer with the surface, that tends to concentrate all the monomers along the major axis of a single stripe. The polymer chain avoids costly jumps between neighbouring stripes by passing over non-adsorbing zones that will rise the internal energy of the system. However, if the stripe width is small enough, the chain can spread over many different stripes without exposing too many monomers to the non-adsorbing regions. A clear snap-shot of this situation is shown in Fig. 4. We have plotted a typical conformation of a flexible polymer chain ($\kappa=0$) of length $N=200$ at $1/T=4$ adsorbed onto a striped surface of width $\omega=1$ (left picture) and $\omega=2$ (center picture). However, by increasing the stiffness of the chain, it will align along the y-axis as it is shown in the right picture of Fig. 4, where a typical conformation of a rigid chain at its optimal stripe width is plotted. From Fig. 3, we can also observe that for narrow stripes ($\omega\leq2$) the higher degree of stretching is obtained for short chains, whereas for increasing ω long chains are the ones that provide the best Q values. This behavior can be easily explained since short chains, even for small values of the bending parameter κ, tend to behave rod-like and can easily adjust to thin stripes; furthermore, jumps among neighbouring attractive stripes will expose a large percentage of monomers to non-adsorbing zones. On the other hand, as ω increases, short chains find more lateral space to try to accommodate more isotropically and, thus, reducing the value of Q.

In Fig. 5, we have plotted the behavior of the degree of stretching as a function of the chain stiffness κ for different values of the stripe width. The chain length is selected to be $N=150$ and the measures are done at $1/T=4$. We can observe that increasing the chain rigidity the degree of stretching increases and, at the same time, the optimal stripe width switches to smaller values. Under these circumstances, the bending energy dominates the entropic contribution.

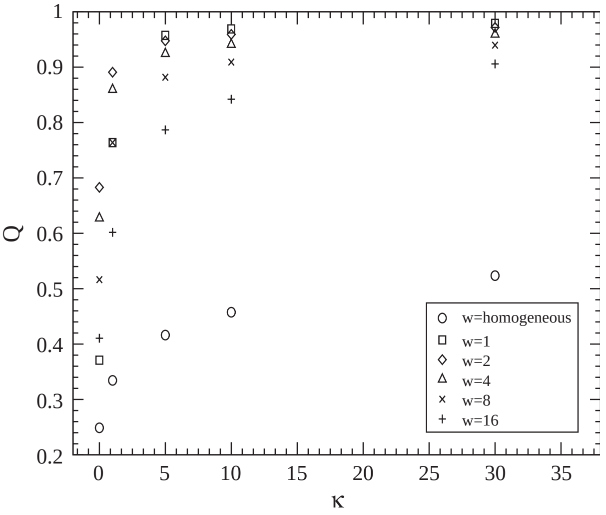

Fig. 5. Degree of stretching Q vs. the chain stiffness κ for different values of the stripe width at $1/T=4$ and $N=150$. For the sake of comparison, we include the results corresponding to an attractive homogeneous surface (○).

The behavior of the y-component of the radius of gyration of the polymer chain $\langle R_y^2\rangle^{1/2}$ with the temperature for different stripe widths is shown in Fig. 6. The chain length is chosen to be $N=100$ and the bending parameter $\kappa=1$. The initial values of $\langle R_y^2\rangle^{1/2}$ (at high temperatures) correspond to a free non-adsorbed polymer chain. By reducing the temperature, the polymer adsorbs onto the surface and $\langle R_y^2\rangle^{1/2}$ grows until it reaches a plateau value that depends on ω. For homogeneous surfaces or wide attractive stripes, this plateau is reached earlier (meaning at higher temperatures) but has a smaller value. The maximum value for an almost completely adsorbed chain ($1/T\to4$) is obtained at the optimal stripe width. While reducing the temperature the maximum degree of stiffness shifts from wider to narrower stripe widths as an indication that the polymer needs a further reduction of the entropic

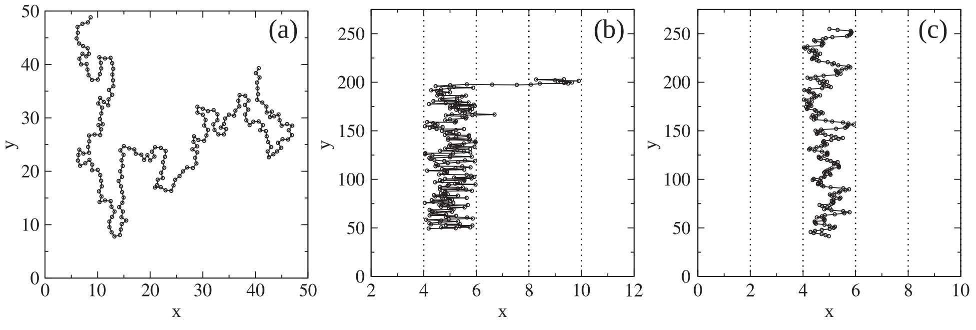

Fig. 4. (a) Snap shot of a typical configuration of a flexible polymer chain adsorbed onto a striped surface with a stripe width $\omega=1$. The chain length is set to $N=200$. (b) Same as before for a stripe width $\omega=2$. (c) Same as (b) for a stiff chain with $\kappa=30$.

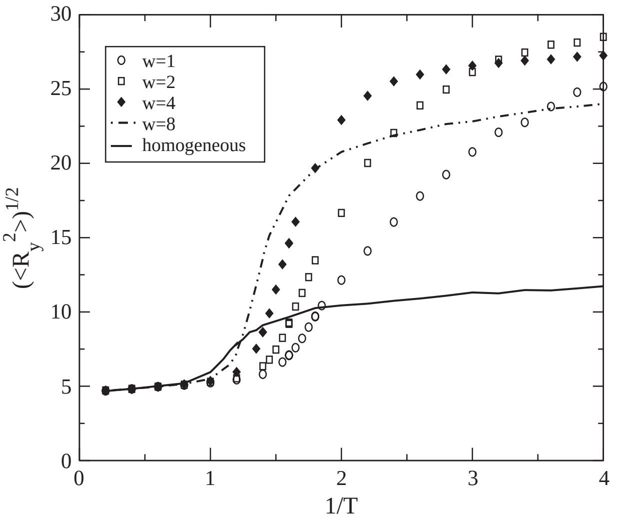

Fig. 6. Variation of the y-component of the radius of gyration $\langle R_y^2 \rangle^{1/2}$ vs. $1/T$ for several stripe widths. N=100 and κ=1.

contribution in order to adjust to thinner attractive stripes. By increasing the chain stiffness, the transition towards the plateau value becomes sharper suggesting the existence of a characteristic temperature T_r at which the surface pattern is recognized by the polymer chain. T_r is expected to be lower than the characteristic adsorbing temperature, T_c, since the polymer chain first adsorbs onto the surface rather isotropically, and a further reduction in the temperature will reduce the number of jumps between neighbouring stripes until the chain aligns along the major axis of a single stripe.

3.2. Asphericity

In order to identify the characteristic temperature at which the recognition takes place T_r we measure the asphericity of the polymer chain defined as:

$$A = \frac{1}{2}\left(\frac{2\langle R_y^2\rangle - \langle R_x^2\rangle - \langle R_z^2\rangle}{\langle R^2\rangle}\right) \tag{7}$$

where R^2=R_x^2+R_y^2+R_z^2. The asphericity ranges from A=0 for a free non-adsorbed chain to A=1 for a fully stretched chain. In the case of a chain adsorbed isotropically onto a planar surface A=1/4. Since the polymer adsorbs onto the surface before it adjusts to the specific pattern we assume $\langle R_z^2\rangle$=0. We define the characteristic recognition temperature, T_r, as the temperature at which the chain adjusts to an specific pattern. Thus, if the stripe width is ω, the polymer chain must adjust to the stripe width and then align along the major axis of the stripe.

Given a chain of length N with a bending parameter κ, it is easy to estimate the expected asphericity value A_{th} of chain adsorbed onto a single stripe. The polymer will form blobs of diameter ω, containing each N_b monomers. The radius of gyration of a blob with radius $r = \omega/2$ is $R_b = r/\sqrt{2}$ that, for an excluded-volume chain, is related to N_b through the Flory expression [17]:

$$R_b = l_p(\kappa)^{1/4} N_b^{3/4}$$

where $l_p(\kappa)$ is the persistence length of a stiff polymer chain. It has been found that l_p=$\gamma\kappa^{1/2}$ [11]. Our best fit to the data gives γ=0.55±0.01. Now, it is possible to know the number of monomers containing each blob:

$$N_b(\omega, \kappa) = \left[\frac{\omega}{2\sqrt{2}}\left(\frac{1}{\gamma\kappa^{1/2}}\right)^{1/4}\right]^{4/3}$$

The total number of blobs is nothing but N/N_b and the polymer will cover an extension along the major axis of the stripe of L_y=$\omega N/N_b$. Then, the radius of gyration along the y-axis follows: $\langle R_y^2\rangle$=$L_y^2/12$ and in its perpendicular direction: $\langle R_x^2\rangle$=$\omega^2/12$.

We have evaluated the asphericity of the polymer chain $A(T)$ and its value has been compared to the expected $A_{th}(N,\kappa,\omega)$. We have defined the temperature at which the pattern recognition takes place when the following criteria is satisfied:

$$T = T_r(N, \kappa, \omega) \ \text{for} \ \frac{A(T)}{A_{th}} \geq 0.99$$

In Fig. 7, we have plotted $1/T_r$ as a function of the stripe width ω for different chain rigidities. The chain length is selected to be N=250. Observe how wider stripes are recognized earlier (at higher temperatures) than narrower ones and that by increasing the stiffness parameter κ, T_r is also raised. The dependence of T_r on the chain length N is shown in Fig. 8. In this case, we have selected κ=30. Observe how T_r increases with increasing the chain length. For the sake of comparison, we have overplotted the

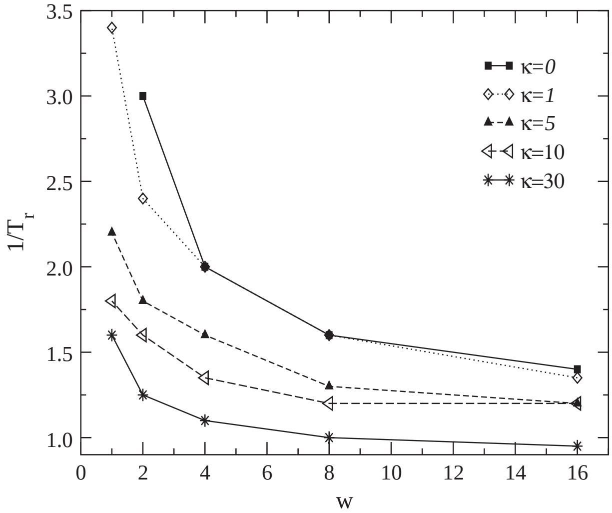

Fig. 7. Characteristic pattern-recognition temperatures T_r vs. the stripe width ω for different values of the chain rigidity. N=250.

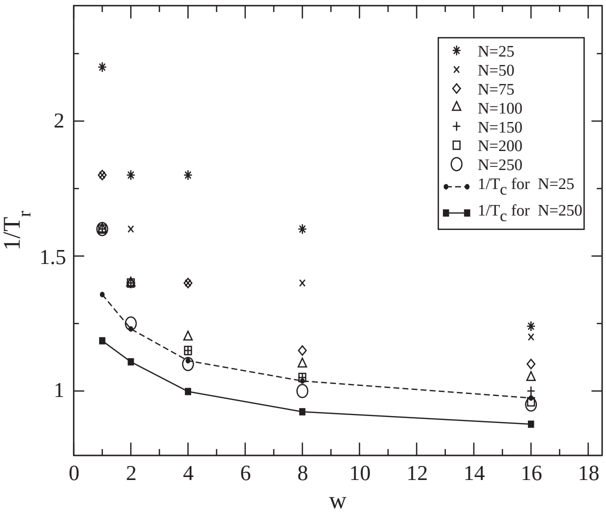

Fig. 8. Characteristic pattern-recognition temperatures T_r vs. the stripe width ω for different chain lengths. The stiffness is set to κ=30. For the sake of comparison, we include the characteristic adsorbing temperatures T_c for N=25 and N=250.

corresponding characteristic adsorbing temperatures T_c for N=25 and N=250. Note that $T_c > T_r$ in all the cases studied supporting the assumption that the polymer first adsorbs onto the surface and then the chain adjusts to the specific pattern.

4. Summary and conclusions

In this paper, we have presented extensive numerical off-lattice Monte-Carlo simulations of a stiff polymer chain adsorbing onto a structured surface consisting in alternated attractive and neutral stripes. We have analyzed, in terms of the chain length and rigidity, the adsorption and the pattern recognition process as a function of the stripe width. We have seen that this process is twofold. During the cooling sequence, the polymer chain first adsorbs onto the surface at a characteristic temperature T_c, and then, a further reduction in the temperature is needed for the chain to reorganize and adjust to the specific pattern. The characteristic adsorbing temperature T_c is found to increase with the stripe width ω.

In order to study the pattern recognition process, we have evaluated the *degree of stretching* Q and the *asphericity* A of the polymer chain. We have found an optimal value of the stripe width that maximizes Q. This optimal width reduces with increasing the chain stiffness. The measure of Q also indicates that short chains accommodate better to narrow stripes at low and moderate chain rigidities; however, this fact does not necessarily implies recognition. We have defined a criteria to estimate the characteristic temperature at which the chain recognizes the pattern T_r. We have verified $T_c > T_r$ in all the cases studied and that T_r increases with the stripe width and the chain length and rigidity.

Despite the simplicity of this model, it might serve to extract useful information on the most relevant chain and surface parameters that are able to enhance the polymer adsorption onto specific patterns. Furthermore, lateral heterogeneities might require the proper selection of lengths scales, including the chain length N and its persistence length l_p, that must be commensurate quantities with the domain size of the pattern. At the same time, heterogeneous surfaces represent a unique means of manipulating the size and the orientation of polymer morphologies over a large range of length scales that are of great interest in bio and nanotechnologies.

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