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Surface pattern effects upon polymer adsorption

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Abstract

By means of generalized-ensemble Monte Carlo simulations, we investigate the influence of pattern recognition effects upon the adsorption behavior of a flexible elastic polymer. For this purpose, we compare the adsorption of the polymer at a uniform, unstructured substrate with the recognition of a hexagonal surface pattern, mimicking a graphene sheet. Canonical statistical analysis methods are used for the identification of the respective structural phases and for the construction of hyperphase diagrams of adsorption.

1. Introduction

The study of polymer chains grafted on solid surfaces has drawn much attention in various fields of research, such as improving the biocompatibility of biomaterials [Wei et al. (2014); Carignano and Szleifer (2000)], stabilization of colloidal dispersions [Russel et al. (1992)], and adhesion enhancement with polymers [Sides et al. (2001)]. Combining layered inorganic matter, e.g. graphene and carbon nanotubes, with polymers has also been explored to achieve improvements in their electrical and mechanical properties, thermal stability, and chemical resistance [Potts et al. (2011); Alexandre and Dubois (2000)]. Thus, understanding the behavior of adsorbed polymers in different environments and surface conditions may potentially lead to the development of improved materials and novel technological applications.

Cooperative polymer behavior can only be investigated systematically by means of computer simulations. However, the complexity of interactions among atoms or monomers typically results in the formation of a rough free-energy landscape, which renders simulations of polymers a challenging problem. The roughness is generally governed by finite-size effects that are difficult to tackle [Bachmann (2014)].

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In this work, we study a coarse-grained model for a polymer that is grafted to the surface of a substrate [Li and Park (2001); Möddel et al. (2011, 2014)]. To investigate the influence of pattern recognition effects on polymer adsorption, two different types of surfaces, a flat homogeneous substrate and a hexagonal surface pattern that mimics a graphene sheet, are studied. Generalized-ensemble Monte Carlo methods such as parallel tempering [Swendsen and Wang (1986); Geyer (1991); Hukushima and Nemoto (1996); Hansmann (1997)] have been introduced to overcome the difficulty of getting trapped in local free-energy minima. Structural and thermodynamic quantities are obtained in extensive parallel tempering simulations to study the effect of temperature and surface attraction upon the formation of structural polymer phases. The canonical statistical analysis of expectation values and their thermal derivatives help identify conformational phases and construct hyperphase diagrams for both scenarios which facilitate comparisons.

2. Model and method

In this study, we used a bead-spring off-lattice polymer model [Schnabel et al. (2009a,b); Seaton et al. (2009); Gross et al. (2013); Bachmann (2014)] for an elastic, flexible homopolymer. The polymer conformations are governed by the energies between non-bonded monomers, bonded monomers, and monomer-surface attraction. The interaction between non-bonded monomers is described by a truncated and shifted Lennard-Jones (LJ) potential,

$$E_{\text{NB}} = \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] + U_{\text{shift}} \right\}, \qquad r_{ij} < r_c, \tag{1}$$

where N is the number of monomers in the polymer chain and r_{ij} is the distance between non-bonded monomers i and j; σ is the van der Waals distance and ε is the monomer-monomer interaction strength. The potential minimum is located at $r_0 = 2^{1/6}$. The constant, $U_{\text{shift}} = 4\varepsilon[(\sigma/r_c)^{12} - (\sigma/r_c)^6]$, makes the potential vanish at the cutoff radius $r_c = 2.5\sigma$; for distances $r_{ij} \geq r_c$ it is set to zero. In this work, we simulated a 13mer ($N = 13$) with $r_0 = 1$, and $\varepsilon = 1$. The interaction between bonded monomers is given by the finitely extensible nonlinear elastic (FENE) potential and the shifted Lennard-Jones (LJ) potential,

$$E_{\text{B}} = -\frac{1}{2}KR^2 \sum_{i=1}^{N-1} \ln\left[1 - \left(\frac{r_{ii+1} - r_0}{R} \right)^2 \right] + \eta \sum_{i=1}^{N-1} \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r_{ii+1}} \right)^{12} - \left(\frac{\sigma}{r_{ii+1}} \right)^6 \right] + U_{\text{shift}} \right\}, \tag{2}$$

where we set $K = 98/5$, $R = 3/7$, and $\eta = 0.1$.

Two types of substrate, one representing a continuous body with flat homogeneous surface and the other a single hexagonal surface layer, are studied. In both cases, the surface is located parallel to the xy-plane at $z = 0$. The first monomer is grafted on the surface. For the flat continuous surface, the bulk of the substrate is homogeneous and the potential is calculated by integrating the Lennard-Jones potential between a monomer and an element of the substrate over the negative z half plane:

$$E_{\text{S}} = \varepsilon_S \sum_{i=1}^{N} \left[\frac{2}{15} \left(\frac{1}{z_i} \right)^9 - \left(\frac{1}{z_i} \right)^3 \right], \tag{3}$$

where ε_S is the strength of surface attraction and z_i is the distance of the ith monomer from the surface. In the hexagonal surface case, the interaction between monomers and surface atoms is described by the shifted LJ potential, which is the same as Eq. (1), multiplied by the surface attraction ε_S. To accelerate the calculations of the surface interaction, translational and rotational symmetries of the lattice are exploited. The surface adsorption properties of the polymer were examined in both cases for various values of $\varepsilon_S \in [0.2, 3.0]$.

Thermodynamic and structural properties of our polymer model were obtained by employing parallel tempering (replica exchange) Monte Carlo, i.e., parallel Metropolis sampling at multiple temperatures, $T_1 < T_2 < ... < T_M$, and allowing for exchanges of configurations with neighboring replicas. The polymer configurations are updated using single-monomer displacement moves. In each Monte Carlo update, we selected a non-grafted monomer and shifted it by a random distance in the interval $[-\Delta r, \Delta r]$ in each direction inside a cubic box. The probability of accepting a trial move at T_i ($i = 1, 2, ..., M$) is

$$P(E_1 \rightarrow E_2) = \min\left(1, \exp\left[(E_1 - E_2)/k_{\text{B}}T_i\right]\right), \tag{4}$$

where E_1 and E_2 are the total energies of the system before and after performing a trial move in the ith temperature thread. The maximum displacement Δr is adjusted during the equilibration period in order to improve the acceptance rate at each temperature, but it is kept constant during the simulation. At a given Monte Carlo step, we exchange the current conformations between neighboring replicas with probability

$$P\left(E_i, T_i \to E_j, T_j\right) = \min\left(1, \exp\left[\left(E_i - E_j\right)\left(1/k_{\text{B}}T_i - 1/k_{\text{B}}T_j\right)\right]\right), \tag{5}$$

where E_i is the total energy and T_i is the temperature of the replica i. We used in our simulations $M = 40$ to 79 replicas within the temperature range $T \in [0.05, 3.00]$.

To describe conformational phases, we analyzed expectation values of several quantities and their thermal derivatives, which can be expressed by means of the fluctuation formula,

$$\frac{\text{d}}{\text{d}T}\langle O \rangle = \frac{\langle O \cdot E \rangle - \langle O \rangle \langle E \rangle}{k_{\text{B}}T^2}. \tag{6}$$

Of particular interest is the specific heat

$$C_V(T) = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_{\text{B}}T^2} \tag{7}$$

and thermodynamic averages of structural quantities like the radius of gyration tensor components parallel and perpendicular to the surface,

$$
\begin{aligned}
R_{g\parallel} &= \left(\frac{1}{N}\sum_i^N\left[(x_i - x_{cm})^2 + (y_i - y_{cm})^2\right]\right)^{1/2}, \\
R_{g\perp} &= \left(\frac{1}{N}\sum_i^N (z_i - z_{cm})^2\right)^{1/2},
\end{aligned}
\tag{8}
$$

where $x_{cm} = \sum_{i=1}^N x_i/N$ is the center-of-mass of the polymer in x-direction. We also introduce the number of surface contacts n_s (spatial component $z < 0.3$) as an additional quantity that aids in distinguishing adsorbed phases and locating the adsorption transition. The positions of peaks and "shoulders" of these quantities are used to identify conformational transitions and to construct hyperphase diagrams.

3. Result and discussion

3.1. Flat continuous surface

The structural adsorption behavior of the grafted 13mer on a flat continuous surface is summarized in the T-ε_S hyperphase diagram as shown in Fig. 1. The letter code of the dominant structural phases is adopted from Möddel et al. (2011) and the bands represent the transition regions between phases. At high temperature, the polymer tends to stretch out, exhibiting a desorbed extended (DE) conformation. In the regime of high surface attraction ($\varepsilon_S > 1$), reducing the temperature makes it more favorable for the chain to adsorb on the surface (AE). The adsorption transition is signaled by the fluctuations, $\text{d}\langle R_{g\perp}\rangle/\text{d}T$ and $\text{d}\langle n_S\rangle/\text{d}T$, and shifts to lower temperatures if the surface attraction is reduced. Decreasing temperature causes the adsorbed extended chain to collapse and to form a globular structure (AG).

Unlike the work of Möddel et al. (2011), no peak indicating the wetting transition can be found in the low surface attraction regime ($\varepsilon_S < 1$). This is due to the small system size which only allows for a small number of surface contacts. At very low temperatures below the freezing transition, three types of compact structures (AC1, AC2, and AC3) are observed, depending on the surface attraction strength. For $\varepsilon_S \leq 1.25$, the adsorbed compact polymer structure resembles an icosahedron attached to the surface. For stronger surface attraction, the number of layers of the polymer conformation parallel to the substrate gets smaller, and it is single-layered for $\varepsilon_S \geq 2.75$.
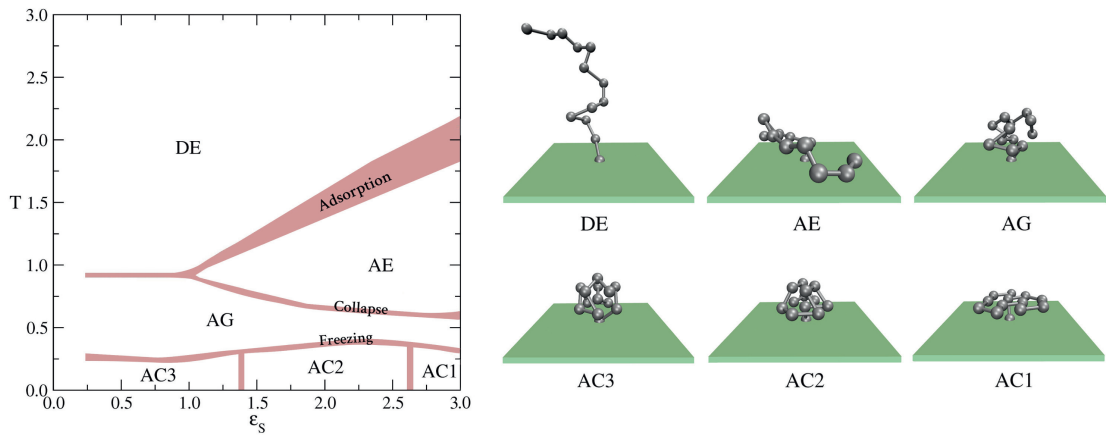
Fig. 1. Hyperphase diagram parametrized by adsorption strength ε_S and temperature T of the grafted 13mer on a flat continuous surface. The structural phases are divided into desorbed expand (DE), adsorbed expand (AE), adsorbed globule (AG), adsorbed compact with single layer (AC1), adsorbed compact with double layer (AC2), and adsorbed compact with triple layer (AC3).
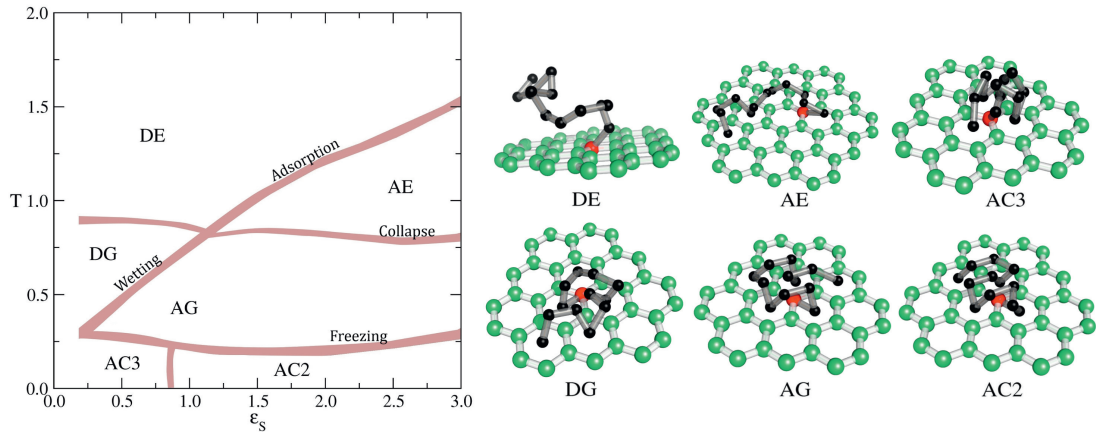

Fig. 2. Hyperphase diagram parametrized by adsorption strength ε_S and temperature T of the grafted 13mer on a hexagonal surface. The structural phases are divided into desorbed expand (DE), desorbed globule (DG), adsorbed expand (AE), adsorbed globule (AG), adsorbed compact with double layer (AC2), and adsorbed compact with triple layer (AC3).

3.2. Hexagonal surface

At high temperatures, $T > 1$, grafting on a hexagonal surface leads to similar polymer behavior. The expanded phases, desorbed (DE) and adsorbed (AE), are directly comparable with the case of a flat continuous surface (see Fig. 2). However, for temperatures $T < 1$, the hexagonal surface pattern affects the structure formation of the polymer. Energetically attractive positions for monomers are located in the centers of hexagonal rings. At low adsorption strengths, $\varepsilon_S < 1.5$, the intramolecular polymer interactions circumvent the structure from reaching these delocalized favorable sites in the surface plane, retaining desorbed globule (DG) rather than adsorbed globule (AG) structures. At low temperatures and larger adsorption strengths, surface energies dominate and enhance pattern recognition of the surface. In the studied case, where lattice constant and equilibrium bond length r_0 coincide, the occupation of low-energy sites by successive polymer beads is suppressed by the finite character of the FENE bonds. Hence, the structure is forced to extend in the z-direction, which explains the absence of an AC1 phase.

4. Conclusion

In this work, we have shown that the conformational hyperphase diagrams of a grafted flexible elastic bead-spring polymer model resembles the structural phase diagram of the bead-stick polymer [Möddel et al. (2011)] for two different substrates. However, significant differences in the adsorbed compact phases for polymer adsorption at the patterned substrate [Möddel et al. (2014)] are encountered depending on surface properties. Hexagonal substrates allow for different adsorbed phases, preventing single-layer film-like structures, which form a dominant phase in the homogeneous case. Moreover, the wetting transition can hardly be detected for the non-patterned homogeneous surfaces within the investigated properties. More specific order parameters and larger system sizes are expected to lead to more detailed insights into the adsorption behavior of polymers on surfaces in future studies.

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