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Investigation of polymer surface morphology in the absence of defects

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The study of the surface morphology of the polymer system was carried out using a dynamic model analogous to a discretized persistent-length model with chains having bending stiffness. Analysis of free energy of the polymer system revealed that the intermolecular distance at the air/polymer interface is increased relative to the distance in the bulk of the polymer, which causes the formation of wrinkles on its surface. We find out that the ratio of the wrinkle height to its width is determined by the structure of the polymer (namely its mean-field characteristics, chain bending stiffness, parameters in the Lennard-Jones potential) and the formation temperature.

Keywords: polymer films, structured polymer coatings, wrinkled interfaces, mean-field theory.

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1. Introduction

The unique characteristics of wrinkled interfaces of polymer films play an important role in the creation of flexible electronics, as supports with controlled wettability, for biological applications, etc. [1]. The complexity of the theoretical study of such surface structures is caused by small differences in parameters, such as film thickness, introduction of additives, formation temperature, etc. There are several mechanisms for the formation of folds in polymer: the presence of various types of defects [2], thermal and mechanical effects [3]. The formation of hierarchical folds is also possible when there is a simultaneous change in several parameters in the polymer system [3]. The purpose of this paper is to study the formation of folds resulting from differences in the interchain distance on the surface and in the bulk of the film.

2. Model

The polymer chain is represented as a sequence of axially symmetric kinetic units l_{unit} long with a continuum distribution of their orientations (Figure 1). The thermodynamic bending stiffness of polymer chains contributes to the potential energy of the kinetic unit

$$u_n^{\text{bend}} = -K^{\text{bend}} \cos \Phi_n, \tag{1}$$

where K^{bend} — energy constant of bending stiffness, Φ_n — angle between neighboring n and $n+1$ kinetic units of one polymer chain [4]. The interaction energy of two kinetic units located in different chains l_{unit} long and with diameter d is determined by the formula [4]:

$$u_{n,m}^{\text{inter}} = -K_{n,m}^{\text{inter}} \cos \Psi_{n,m}, \tag{2}$$

where the constant $K_{n,m}^{\text{inter}}$ was estimated in the paper [5] from the Onsager relation [6]:

$$K_{n,m}^{\text{inter}} \sim \left(\frac{l_{\text{unit}}}{r_{n,m}}\right)^3 \frac{d}{r_{n,m} - d}, \tag{3}$$

where $r_{n,m}$ — the distance between the corresponding kinetic units located in different polymer chains (Figure. 1), b — the value of the interchain distance.

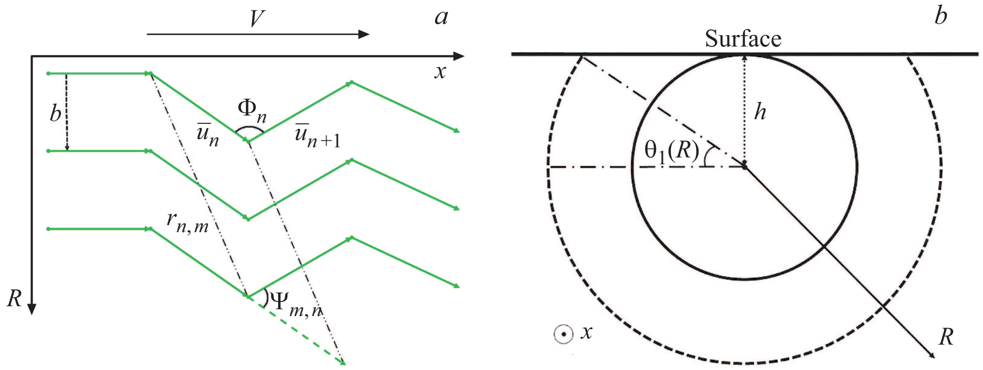

Figure 1. Model of a polymer system. The image is shown in two projections. The axis x is located parallel (a) and perpendicular (b) to the plane of the Figureure θ.

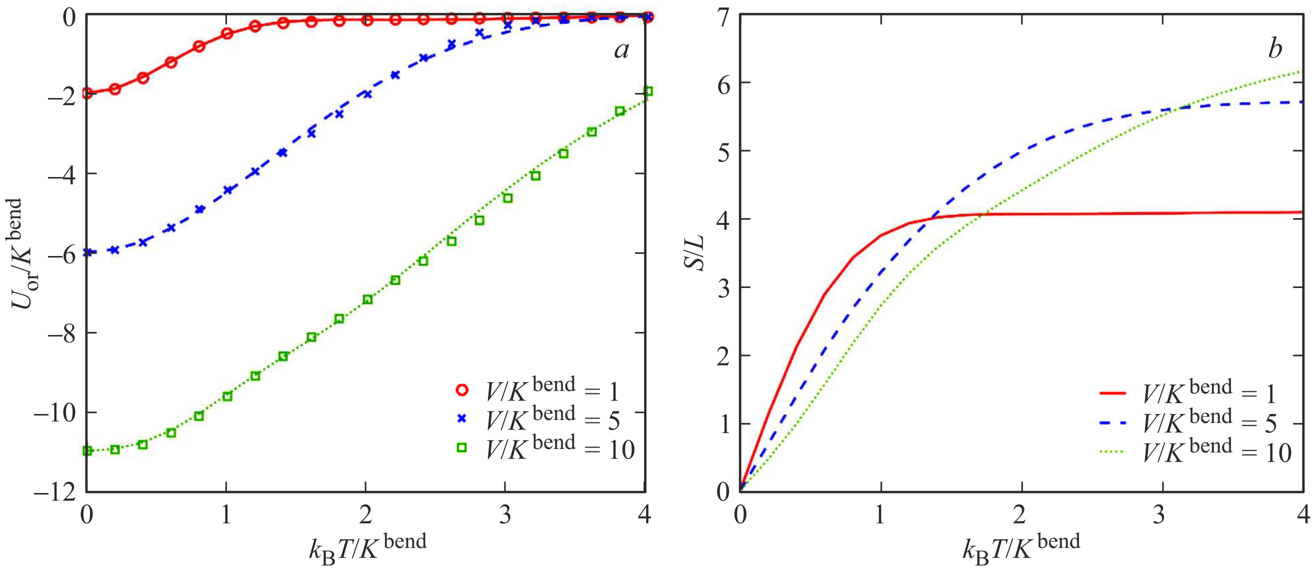

Figure 2. Temperature dependences of the average values of the energy of orientational interactions a — $U_{\mathrm{or}}(T)$ and b — entropy at different values of the mean molecular field V.

For a simplified description of the effects of intermolecular orientation interactions, mean (molecular) field V is introduced [7]. The interaction of one kinetic unit with kinetic units from other chains at the value intermolecular field V is determined by the formula

$$u_n^{\mathrm{inter}} = -(\mathbf{u}_n^{\mathrm{unit}} \mu \mathbf{V}), \tag{4}$$

where $\mathbf{u}_n^{\mathrm{unit}} = (u_{n,1}, u_{n,2}, u_{n,3})$ — unit vector in the direction of n-th kinetic unit, quantity

$$\mu = \frac{1}{N} \left| \sum_n \mathbf{u}_n^{\mathrm{unit}} \right| \tag{5}$$

characterizes the average orientation of chain segments and is a parameter of long-range orientation order. Vector $\mathbf{V}$ is directed towards the greatest orientation of the kinetic units of the chain. N — chain length.

The magnitude of the mean field V can be estimated by integrating over the volume of the film v at the value of the intermolecular distance $b \gg d$ (calculations were performed in cylindrical coordinate system):

$$V \sim \begin{cases} 2\pi \int\limits_b^\infty \int\limits_{-\infty}^\infty \frac{1}{r^4} R dR dx, \text{ if } h \gg b; \\ 2\pi \int\limits_b^h \int\limits_{-\infty}^\infty \frac{1}{r^4} R dR dx + \pi \int\limits_h^\infty \int\limits_{-\infty}^\infty \frac{1}{r^4} R dR dx \\ \quad +2 \int\limits_h^\infty \int\limits_{-\infty}^\infty \int\limits_0^{\theta(R)} \frac{1}{r^4} R dR dx d\theta, \ \text{ if } h \geq b; \\ \pi \int\limits_b^\infty \int\limits_{-\infty}^\infty \frac{1}{r^4} R dR dx, \ \text{ if } h = 0. \end{cases} \tag{6}$$

As a result

$$V \sim \begin{cases} \frac{2\pi^2}{b}, & \text{if } h \gg b; \\ \frac{2\pi^2}{b} - \frac{2\pi}{h}, & \text{if } h \geq b; \\ \frac{\pi^2}{b}, & \text{if } h = 0. \end{cases} \tag{7}$$

3. Modelling method

The energy of orientation interactions U_{or} consists of two terms — the average values of bending stiffness and the energy of the kinetic unit in the mean molecular field

$$U_{\mathrm{or}} = \langle u_n^{\mathrm{bend}} \rangle + \langle u_n^{\mathrm{inter}} \rangle \tag{8}$$

Calculations were made using the Metropolis algorithm. Entropy was calculated using the Clausius formula

$$S = \int_0^T \frac{dU_{\mathrm{or}}}{T}$$

$$(b - \mathrm{const}). \tag{9}$$

Since the integral (9) is improper, the dependences $U_{\mathrm{or}}(T)$ were approximated in the form of a series (the first three terms of the series were taken into account in the calculations):

$$U_{\mathrm{or}} = \alpha_0 \exp(-\beta_0 T^2) + \alpha_1 T^2 \exp(-\beta_1 T^2)$$

$$+ \alpha_2 T^2 \exp(-\beta_2 T^2) + \ldots \tag{10}$$

Figure 2 shows the temperature dependences of the average values of the energy of orientation interactions $U_{\mathrm{or}}(T)$ and the entropy of one kinetic unit at different values of the mean molecular field V.

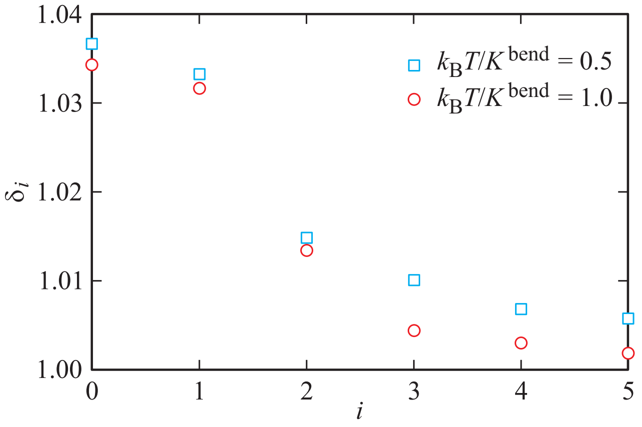

Figure 3. Parameter δ vs. layer number i.

4. Simulation results

Free energy was calculated in a standard way using the formula

$$F = U_{\text{or}} + U_{\text{LD}} - TS, \tag{11}$$

where U_{LD} — Lennard-Jones potential energy. The dependence of free energy on the average interchain distance b has a minimum at a certain point. A decrease in the mean field in the near-surface layers leads to a shift in the point of minimum free energy, which causes increase in the average interchain distance near the surface. In this case, it is convenient to introduce the parameter $\delta_i = \frac{b_i}{b_V}$, which corresponds to the ratio of the interchain distance in i-th layer (b_i) of the polymer coating to the interchain distance inside the film b_V. As can be seen from Figure. 3, the interchain distance near the surface is greater than the interchain distance inside the volume, which leads to the formation of folds.

The geometry of wrinkles can be assessed if they are represented in the form of a sinusoid with a half-cycle λ and amplitude a. The relationship between the parameters of wrinkles and the change in the interchain distance when approaching the surface was obtained:

$$\delta_0 = \frac{2}{\pi}(1 + z^2\pi^2)E\left(\frac{z^2\pi^2}{1 + z^2\pi^2}\right), \tag{12}$$

where E — complete elliptic integral of the second kind, $z = a/\lambda$. Calculations showed that the value z increases with temperature decreasing. It was previously shown that the value λ decreases with temperature increasing, therefore the size of small wrinkles decreases [2].

5. Conclusion

Usually the reason for the formation of rather large folds on the surface of the polymer is defects, the presence of substrate, etc. But besides them, there are also small wrinkles on the surface of the polymer film, which arise due to different values of the interchain distance inside the volume and near the surface. A hierarchical structure of wrinkles is also possible, where one fold overlaps another.

Conflict of interest

The authors declare that they have no conflict of interest.

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