Supramolecular textures formed on polymer coating surface of solids: a mean-field study

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Abstract. We developed a mean-field model describing a system of interacting polymer chains in the contact with a spherical granule surface. It is shown that the size of supramolecular structures formed by macromolecules near the granules does not depend on the size of these granules but depends on the temperature and properties of polymer chains. We revealed that the size dependence of supramolecular formations on the mean molecular field changes sharply at the certain critical field value which depends on the temperature.

1. Introduction
In the formation of polymer films from a low concentrated solution, when macromolecules may be stacked relatively freely, various supramolecular structures are formed on the film surface, e.g. ones in the shape of “seaweeds” [1], with a spherical or cylindrical morphology [2], etc. Understanding and controlling the morphology of solid polymer coating surfaces is crucial, as it is closely related with its thermal and mechanical properties [3]. Furthermore, to increase in the strength of the coating [4], a filler is added into the polymer material in the form of polyacryl or polyamide granules, etc. [5]. The filler leads to the appearance of “radial viscous fingers” [6], which are collected in star-shaped clusters scattered over the entire sheet surface (Fig. 1). The average thickness of the “finger” determines additional optical effects caused by

Figure 1. The optical microscopy image of sheet metal surface with a polyester textured coating.
strong light scattering on the roughness of such coatings [7]. For example, these effects lead to noticeable fluctuations in the shadness of polymer coatings of metal sheets, which is the cause of poor-quality products.

Existing models for studying the surface morphology are based on the laws of the elasticity theory [8, 9]. Therefore, they do not allow to study conformational properties of polymer chains from the known surface textures. On the other hand, well-developed models of a individual polymer molecules or ordered chain formations (“brushes”, etc.) near a spherical particle [10–12] are not appropriate for evaluation of the surface morphology. The aim of this work is to build a model of polymer chains near a spherical surface, the conformation of which allows to evaluate its morphology.

2. Model

To calculate the potential energy of macromolecule, a dynamic persistent length model is used, where the chains have a bending rigidity. The persistent chain model was proposed by Hearst and Harris [13] and was used later in various modifications [14]. The model chain is represented as a sequence of axially symmetric kinetic units with the length $\ell_{\text{unit}}$. The size of the kinetic unit may exceed the size of the link $\ell_{\text{link}}$. The ratio $\ell_{\text{unit}}/\ell_{\text{link}}$ determines the number of polymer chain segments located in one kinetic unit. The unit vector in the direction of the $k$-th kinetic unit is defined as $\vec{u}_k = (u_{k,1}, u_{k,2}, u_{k,3})$.

In this work, for the simplified description of intermolecular orientational interactions, the mean (molecular) field $V$ is introduced. This approach was originally developed in the Maier-Saupe theory [15–17].

The potential energy of the kinetic chain unit (if it does not lie on the granule surface) consists of two components corresponding to orientational interactions and the Lennard-Jones potential, correspondingly. The potential energy of orientational interactions for one kinetic unit is equal to

$$w_k^{\text{unit}} = \mu V u_{k,3} \ell_{\text{unit}},$$

where $V$ is the constant that characterized interaction between kinetic units and the molecular field created by other chains in an ordered state. The value $\mu$ is defined by the following formula

$$\mu = \frac{1}{N} \sum_{i=1}^{N} u_{i,3},$$

where $N$ is the number of kinetic units in the chain. The parameter $\mu$ characterizes the average orientation of the kinetic units [18] to the direction of the mean field. This parameter is defined as a long-range parameter. The energy of the kinetic unit is calculated from the condition corresponding to the minimum value of the Lennard-Jones potential energy, when the intermolecular distance is equal to $b_0$. The Lennard-Jones interaction potential for two segments in adjacent polymer chains on the square lattice is determined by the formula

$$w_{LD} = \varepsilon \left( \frac{b_0^{12}}{b^{12}} - \frac{2b_0^6}{b^6} \right),$$

where $\varepsilon$ is the depth of Lennard-Jones potential well, $b$ is interchain distance, $b_0$ is distance by that Lennard-Jones potential has a minimum. This potential describes interactions between segments of different chains. We used the nearest neighbors approximation (for square lattice), therefore, the Lennard-Jones potential energy of one kinetic unit at $b = b_0$:

$$w_0 = -4 \frac{\varepsilon \ell_{\text{unit}}}{\ell_{\text{link}}},$$
In the proposed model, it is assumed that polymer chains are adsorbed on a spherical surface of radius $R$ (Fig. 2), forming supramolecular structures in the form “viscous fingers”. The size of such structure is limited by the solid angle $\Phi$. The position of a individual polymer chain inside the finger is characterized by the angle $\theta$ ($\theta < \Phi$). One ends of the chains are adsorbed on the granule surface, the opposite ends are stretched due to the orienting action of the mean field. Therefore, each chain can be divided into three sections $AB$, $BC$ and $CD$ with lengths $\ell_1$, $\ell_2$ and $\ell_3$, respectively. The potential energy of the chain in each of the sections is calculated by different procedures.

**Section $AB$.** The energy of orientational interactions

$$w_1 = -\mu_1^2 V_1 \ell_1,$$

where $\mu_1$ and $V_1$ are respectively the long-range orientation order and the mean field parameters in the section $AB$. The intermolecular distance in this section is equal to $b_0$ and, therefore, it is not necessary to consider the Lennard-Jones potential since it’s equal to $w_0$, which is the energy reference point.

**Section $BC$.** The distance between chains $b(y)$ along the $y$ axis in $BC$ varies linearly from $b_g$ to $b_0$. It is assumed that the mean field is created due to dipolar interactions between chains, so the energy of orientational interactions is calculated by the formula

$$w_{2or}(\theta) = - \int_0^{\ell_2(\theta)} \mu_2(y) \frac{V_0 b_0}{b(y)} dy,$$

where $\mu_2(y)$ is the long-range orientational order parameter in the layer. The dependence $\ell_2(\theta)$ in the integral (6) is defined by the formula

$$\ell_2(\theta) = R \sqrt{(g \theta - \sin(\theta))^2 + (1 - \cos(\theta))^2},$$

where $g = b/b_0$, $R$ is the granule radius (see Fig. 2). The fact that section $BC$ can be represented as a straight line is an approximation, but its correctness is confirmed by the results of scanning probe microscopy (Fig. 3).

![Figure 2. The model of the polymer system near the granule.](image-url)
Figure 3. The scan microscopy picture of the "finger" near the granule

The Lennard-Jones potential in this section should be taken into account in the form

$$w_{2LD}(\theta) = \frac{4\varepsilon}{\ell_{\text{link}}} \int_0^{\ell_2(\theta)} \left( \frac{b_0^{12}}{b^{12}(y)} - \frac{2b_0^6}{b^6(y)} \right) dy - \frac{w_0}{\ell_{\text{unit}}} \ell_2(\theta).$$  \hspace{1cm} (8)

Section CD. Here, the energy is calculated by the formula

$$w_3 = -\psi \ell_3,$$  \hspace{1cm} (9)

where the parameter $\psi$ characterizes the strength of adsorption [19].

The ratio between the lengths $\ell_1$ and $\ell_3$ is determined from the Boltzmann distribution:

$$\ell_1 = \frac{\int_0^{L-\ell_2} zF(z)dz}{\int_0^{L-\ell_2} F(z)dz},$$  \hspace{1cm} (10)

where $L$ is the contour chain length, $F(z) = \exp \left( \frac{\mu_1 V z + \psi (L - z - \ell_2)}{k_BT} \right)$. The total energy of one chain is equal to

$$w(\theta) = w_1(\theta) + w_{2\sigma r}(\theta) + w_{2LD}(\theta) + w_3(\theta).$$  \hspace{1cm} (11)

The values of the long-range orientational order parameters $\mu_1$ and $\mu_2$ in Eqs. (5), (6) were calculated by means of the Monte-Carlo method by the simple iteration method using the following algorithm:

1) initially, the value $\mu = 1$;
2) then, the equilibrium configuration of system was determined by the Monte-Carlo technique (the Metropolis algorithm [20]);
3) the new value $\mu$ was calculated and then, we return to step 2 while the quantity $\mu$ is not changed.

The energy of polymer chains located inside the "finger" is equal to

$$W(\Phi) = 2\pi R^2 n \int_0^\Phi w(\theta) \sin(\theta) d\theta,$$  \hspace{1cm} (12)

where $n$ is the concentration of macromolecules (number of chains adsorbed per unit area of the granule). The solid angle $\Phi$ is shown in Fig. 2.

3. Results of simulations

The dependence of the potential energy of the chain on the angle $\Phi$ is shown in Fig. 4. At a certain angle $\Phi_0$, the energy has a minimum. Therefore, the thickness of the "finger" $d$ can be determined by the formula

$$d = 2R\Phi_0 \frac{b_0}{b_g}.$$  \hspace{1cm} (13)
Figure 4. The renormalized energy $W/n\varepsilon$ of the polymer chain system vs. the angle $\Phi$ at different values of the normalized temperature $k_BT/\varepsilon = 100(\bigcirc)$ and $200(*)$. The dimensionless mean field parameter $V_0\ell_{\text{link}}/\varepsilon = 100$.

Figure 5. The angle $\Phi_0$ vs. the inverse radius of the granule $R$ for different values of the mean field parameter $V_0\ell_{\text{link}}/\varepsilon = 100(\bigcirc); 200(*) ; 300(\bigtriangleup); 400(\square)$. The normalized temperature $k_BT/\varepsilon = 100$; $b_g/b_0 = 0.5$.

Figure 6. The angle $\Phi_0$ vs. the dimensionless mean molecular field parameter $V_0$ at different normalized temperatures $k_BT/\varepsilon = 100 (\bigcirc)$ and $150 (*)$; $b_g/b_0 = 0.5$; $L/R = 2$.

Calculations show that the thickness of the “finger” does not depend on the size of the granule. This fact is confirmed by the dependences shown in Fig. 5, since the function $\Phi_0 (L/R)$ is linear. This conclusion is confirmed by the optical microscope method. The granules in the paint material have different sizes. At the same time, the sizes of the “fingers” located on the coating surface are the same within the microscope error. Therefore, for the simulation the surface morphology of a textured polymer coating of solids, the granule size can be chosen arbitrarily. Unfortunately, we cannot simulate in case when $d > 2R$, because the granule is located inside the “finger” and the model requires a modification.

The dependence of the angle $\Phi_0$ on the mean field parameter at different temperatures is shown in Fig. 6. As one can see from the figure, this angle increases with increase in the mean field and decrease in the temperature. The dependences sharply change the slope at certain values of temperature and mean field. However, this feature requires additional research.

4. Conclusion

The model has been developed for studying the morphology of chains adsorbed on the surface of spherical granules. It is shown that the size of supramolecular textures of the type “viscous fingers” formed by polymer chains around spherical granules, does not depend on the size of the granules. This size is determined only by the temperature and properties of the polymer.
We revealed that the dependence of the “fingers” size on the mean molecular field is sharply changed at a certain value of this field, the magnitude of which depends on the temperature.

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