Study of adsorption effect on orientational and relaxation properties of finite polymer chains near the solid surface

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Abstract. To study dynamic properties of a polymer coating, we consider a polymer chain with finite length. We take into account a chain bending rigidity and assume that the chain is located near an adsorbing flat surface of a solid. One part of the chain is fixed on the surface, and the second one remains free. It is supposed that the cause of chain stretching is the internal effective mean (molecular) field formed as a result of intermolecular interactions with free ends of other chains. Kinetic equations based on the Kubo method are obtained to calculate the relaxation time of the segments. The dependences of the long-range orientational order parameter and relaxation time on the adsorption parameter, the mean field coefficient and chain bending rigidity parameters are calculated. It is shown that a first-order phase transition occurs at the critical point, which is associated with a drastic change in the degree of the chain elongation. We discovered the "critical deceleration" effect, which consists in a sharp increase in the relaxation time near the critical point during the formation of surface polymer layers on the surface of a solid.

1. Introduction
Investigation of the rigidity effect of polymer chains on the polymer surface structure under conditions of limited geometry is an important problem [1, 2]. Currently, there is a number of theory approaches which can adequately describe the behavior of a single flexible polymer chain near a solid surface. However, models of rigid-chain molecules give contradictory results [3, 4] even at the qualitative level. In the work [5], it is shown that the formation of fibrils due to large intermolecular interactions usually occurs during the process of peeling of the polymer coating from the substrate (Fig. 1). In this work, we study a polymer molecule near a solid surface by modifying the model [6] to take into account both the chain bending rigidity and intermolecular interactions.

2. Model
We use a model that is a discrete analog of the chain model with persistent length, i.e. the chains have a bending rigidity. The model is represented as a sequence of $N$ axially symmetric kinetic units with length $l_{\text{unit}}$ which orientations are continually distributed. The chain part consisting of $N_1$ kinetic units is detached, and the other part ($N_2$ kinetic units) is adsorbed on a flat surface (Fig. 2).

It is assumed that the cause of chain stretching is the effect of intermolecular interactions. To describe the effects of the intermolecular orientational interactions, a mean
The thermodynamic bending rigidity of polymer chains is characterized by the energy constant $K$. The constant is calculated by the correspondence of the mean-square and contour length $s$ of a “real” chain, the statistical Kuhn segment of which has length $A$, and the same statistical parameters of the model chain. When $l_{\text{unit}} < A$, the following relation is valid [8]:

$$K = k_B T / 2 \ln \left[ (\nu_0 + 1) / (\nu_0 - 1) \right].$$  \hspace{1cm} (1)

Here $\nu_0 = A / l_{\text{unit}}$ is the number of kinetic units in the statistical Kuhn segment, $T$ is the absolute temperature, and $k_B$ is the Boltzmann constant.

The potential energy of the detached part of the polymer chain is represented as

$$U_1 = -K \sum_n \left( \vec{u}_n^{\text{unit}} , \vec{u}_{n+1}^{\text{unit}} \right) - \sum_n \left( \vec{u}_n^{\text{unit}} , \mu \vec{V} \right)$$  \hspace{1cm} (2)

where $\vec{u}_n^{\text{unit}} = (u_{n,1}, u_{n,2}, u_{n,3})$ is the unit vector in the direction of the n-th kinetic unit in the detached part (Fig. 2), the value

$$\mu = \frac{1}{N_{\lambda}} \sum_n |\vec{u}_n^{\text{unit}}|$$  \hspace{1cm} (3)

is the long-range orientational order parameter which characterizes an average orientation of chain segments. The vector $\vec{V}$ is directed towards the greatest orientation of the kinetic chain units. It is assumed that there is no mean molecular field on the free surface of the polymer coating. Therefore, its value depends on the location of the kinetic unit within the chain:

$$V = V_0 \left[ 1 - \exp \left( - \frac{n}{\lambda} \right) \right],$$  \hspace{1cm} (4)

where $n$ is the number of the kinetic units, which is counted from the free chain end, $\lambda$ is a coefficient depending on the type of free surface.

**Figure 1.** The image of a contact layer between polymer and steel, obtained by means of the scanning electronic microscope [5] (molecular) field $\vec{V}$ is introduced [7]. The thermodynamic bending rigidity of polymer chains is characterized by the energy constant $K$. The constant is calculated by the correspondence of the mean-square and contour lengths of a “real” chain, the statistical Kuhn segment of which has length $A$, and the same statistical parameters of the model chain. When $l_{\text{unit}} < A$, the following relation is valid [8]:

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The potential energy of the adsorbed chain part is determined by the following formula:

\[ U_2 = -\Psi N_2, \]

where the parameter \( \Psi \) characterizes the value of the chain adhesion to the flat surface.

We introduce the following notations for the dimensionless parameters of the mean field (\( q \)), the adhesion (\( \chi \)), and the rigidity (\( r \)):

\[ q = \frac{V_0}{k_B T}, \quad \chi = \frac{\Psi}{k_B T}, \quad r = \frac{K}{k_B T}. \]

3. Algorithm for calculating the orientational ordering of the polymer chain

The value of the long-range orientational order parameter was calculated by the following algorithm:

**Step 0.** We set the initial orientation of the kinetic units located in the detached state. In the ordered state, \( u_{1,n} = u_{2,n} = 0, u_{3,n} = 1, \mu = 1 \). In the disordered state, the orientation of the vector \( \mathbf{u}_n \) was assumed to be uniformly distributed over the sphere. In this case, the value of the long-range orientational order parameter is \( \mu = 0 \).

**Step 1.** The procedure for calculating the order parameter \( \mu \) was performed using the standard Metropolis algorithm.

**Step 2.** Step 1 was repeated until the value of \( \mu \) in the formula (2) becomes equal to the value of \( \mu \) obtained by the Metropolis algorithm and calculated by the formula (3).

**Step 3.** Steps 0-2 were performed for all values of \( N_1 \leq N \). At the given parameters, the length of the detached chain part \( N^* \) was determined by the Boltzmann distribution:

\[ N^* = \frac{\sum_{N_1=0}^{N} N_1 \exp \left( -\frac{U_1(N_1) + U_2(N_2)}{k_B T} \right)}{\sum_{N_1=0}^{N} \exp \left( -\frac{U_1(N_1) + U_2(N_2)}{k_B T} \right)}. \]

The parameter of the long-range orientational order was considered as the value of \( \mu \), calculated when \( N_1 = N^* \).

To obtain the equilibrium value, we chose such the number of Monte-Carlo steps at which results of the simulation for initial conditions in completely ordered and completely disordered states coincide. To eliminate the influence of fluctuations, the computer experiment was repeated 30 times, and the average value of \( \mu \) was calculated.

4. Results of computer simulation of orientational ordering

Fig. 3 shows the calculated dependences of the long-range orientational order parameter \( \mu \) of the polymer system on the mean field parameter \( q \) in the absence of a surface. At a certain value of the parameter \( q_c \), a smooth transition occurs from a disordered state to an ordered one. There is no jump in the order parameter at the transition point. As the chain rigidity increases, the critical point shifts to the left.

Fig. 4 shows the dependences of the long-range orientational order parameter \( \mu \) on the mean field parameter \( q \) at different values of the polymer chain length, the rigidity coefficient \( \lambda \) and the adhesion. At low values of the mean molecular field parameter \( q \), large fluctuations of the order parameter appear. This result can be explained by the fact that in this case, a quite small part of the
Chain is detached (in our calculations $N_1 = 10$), therefore, it does obey no statistics. The orientations of kinetic units near the surface have topological restrictions. At computer simulation, it was taken into account by introducing boundary conditions ($U_{N_1} > 1$), and, therefore, the order parameter is not equal to zero.

The presence of spatial restrictions in the form of the free surface and the surface of a solid (Figs. 4c and 4d) leads to the formation of a jump in the $\mu(q)$ dependence, which is a sign of a first-order transition. With an increase in the chain length (Fig. 4a), the magnitude of the jump increases, and the transition point shifts to the left.

We found, that the order parameter increases with increasing the chain rigidity (Fig. 4b), and the critical point shifts to the left. In addition, the length of the adsorbed chain part decreases with increasing the chain rigidity. This behaviour contradicts the results obtained for a single chain [1]. The contradiction is attributed to the cooperative effect called by de Gennes "together we stand – divided
we fall"[9]. Moreover, this proves the dominant role of intermolecular interactions in the formation of orientationally ordered phase.

5. Calculation of the relaxation time
In this work, the relaxation time was calculated on the base of the Kubo method [10]. This method leads to the equation

$$\frac{\tau}{\tau_0} = \int_{1-\frac{\mu_0}{\epsilon}}^{1} \frac{d\mu}{\mu - \mu_0},$$

(8)

where $\mu_0$ is the equilibrium value of the order parameter, $\tau_0$ is the proportionality coefficient. When performing calculations, we switch to the variable $q$ and use the equation

$$\frac{\tau}{\tau_0} = \int_{q_0}^{\infty} \frac{d\mu}{dq} dq,$$

(9)

where $q_0$ is the value of the mean-field parameter at which the long-range orientational order is equal to the value $\mu_0 + \frac{1-\mu_0}{e}$.

Fig. 5 shows the dependences of the relaxation time of the considered polymer system on the mean field parameter.

**Figure 5** The relaxation time $\tau / \tau_0$ vs. the renormalized mean molecular field parameter $q / q_c$ at different values of the polymer chain length $N$ (a), the rigidity $r$ (b), the coefficient $\lambda$ (c) and the adhesion $\chi$ (d).
As it can be seen from Fig. 5, the relaxation time increases with increasing the chain length \( N \) and with decreasing the rigidity \( r \) and the adhesion coefficient \( \chi \). It can be concluded that the relaxation time of infinite chains at the transition point becomes infinite.

6. Conclusion
When the mean molecular field changes (for example, upon a deformation), a phase transition from the adsorbed state to the detached orientationally ordered one can occur. Under conditions of spatial constraints, the relaxation time decreases, the transition point shifts, and a jump in the long-range orientational order parameter appears, which does not exist in the absence of an adsorbing surface. In rigid-chain polymer systems, the phase transition occurs at lower values of the mean field parameter and the adhesion coefficient.

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