Simulation of deformation in thin polymer films

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Abstract. A model of the polymer system for computer simulation of deformation processes is presented. The model is a synthesis of analytical calculations (polymer chain in a tube) and a computer experiment (simulation of the orientational ordering of polar groups by the Monte Carlo method). Thanks to analytical calculations, this model makes it possible to analyse relatively large systems compared to other models. At the same time, the spent CPU time remains constant. The results of a simulation of stretching (stress-strain curves) a thin polymer film for various values of chain stiffness are given. The obtained curves have a characteristic "yield drop".

1. Introduction
Polymeric coatings on the surface of solids are currently a subject to special requirements. Special attention is paid to the temperature patterns of development and decline of highly elastic deformation. [1]. Unfortunately, well-developed concepts of the crystal plasticity are inapplicable to disordered solids, including polymers. The most adequate model predicting the viscoelastic properties of polymer melts and concentrated solutions is the model of reptations, or a tube model [2]. There are numerous modifications of the basic model of reptations, which use additional factors and corrections (for example, [3] and [4]). Currently, innovative approaches are being actively developed to describe the deformation behavior of solids with spatial disorder [5]. One of the most common methods of computer simulation is the method of molecular dynamics (MMD). The simulation of MMD has significant limitations associated with a small volume of the system under consideration and slow relaxation when an external voltage is applied. In practice, this makes it practically impossible to use MMD for the study of poorly crosslinked grids and to obtain quasi-equilibrium stress-strain dependences. Therefore, the aim of this work is to develop a model that is a synthesis of analytical calculations and computer simulation methods. This model adequately describes the deformation processes and uses less CPU time when performing calculations.

2. Model
Figure 1a shows the chemical structure of polyvinylidene fluoride (PVDF). Polymer chains are located perpendicular to the plane of the figure and have polar groups (marked with p in Fig.1b), which are perpendicular to the backbone of the polymer chain. Based on the chemical structure, a model of a multi-chain polymer system has been developed. It is considered that the macromolecule is surrounded by other chains. As in the model of reptations, in this model it is assumed that, due to topological limitations, the chain does not extend beyond the limits of the tubular cylindrical region (Fig. 2). The diameter D of the tube is equal to the interchain distance and depends on the chemical structure of the

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polymer, the temperature, and the magnitude of the deformation. The value of interchain distance is usually about 10 Å. The diameter of the tube D we determined from the condition of a minimum of free energy.

![Figure 1. Chemical structure of PVDF molecule](image1)

![Figure 2. Orientation of the polymer chain](image2)

The most universal measure of the flexibility of a polymer molecule is the Kuhn segment length \( l \). Its value is determined experimentally by light scattering. For most of the known synthetic polymers, Kuhn segment values are in the range of 15 - 30 Å. That is, the Kuhn segment length and the interchain distance are comparable with each other. But the length of the Kuhn segment depends on the temperature. Therefore, in this paper we characterize the flexibility of a polymer molecule by its bending stiffness \( E \), which we consider a constant.

The stiffness is related to the length of the Kuhn segment by the formula

\[
E = \frac{k_B T}{2} l
\]  

(1)

We consider the area of the polymer molecule, which lies in the plane (Figure 2). A polymer molecule touches the tube wall at the point O and intersects the tube radius at the point A. \( \vec{u}(s) \) is the tangential unit vector along the chain as a function of the contour distance \( s \) from the point O. Then, a correlation function has a form:

\[
\langle \vec{u}(s) \cdot \vec{u}(0) \rangle = \exp\left(\frac{k_B T s}{E} \right)
\]  

(2)

\( \theta_0 \) denotes the average cosine of the angle between the vectors \( u(A) \) and \( u(0) \). The angle value \( \theta_0 \) characterizes the chain elongation. Fig. 3 shows the dependences of \( \theta_0 \) on the ratio of the Kuhn segment length to the tube radius. When \( \theta_0 = 0 \), the macromolecule is completely extended and the dipole can rotate only in a plane perpendicular to the tube axis. The value \( \theta_0 = \pi / 2 \) corresponds to the polymer disorder state. In this case, the macromolecule can arbitrarily fold inside the tube.
It is assumed that the main contribution to the potential energy of the system is made by the interaction energy of the polar groups. On the other hand, the chain topology has the main influence on the system entropy. The free energy of the system is calculated using the formula

\[ F = U_{LD} + U_D - TS \]

\[ U_{LD} = \sum_{n,m} \varepsilon \left( r_{12}^{12} - 2r_{12}^{6} \right) \]

\[ U_D = \frac{1}{4\pi\varepsilon_0} \sum_{n,m} r^2 \left( \vec{p}_n \cdot \vec{p}_m \right) \left( \vec{p}_n \cdot \vec{r} \right) \left( \vec{p}_m \cdot \vec{r} \right) \left( \vec{p}_n \cdot \vec{r} \right) \left( \vec{p}_m \cdot \vec{r} \right) \]

\[ S = -\frac{a}{D^2} + \frac{b}{L} \]

\( n, m \) denotes the pairs of nearest-neighbor dipoles, \( U_{LD} \) - Lennard-Jones potential, \( U_D \) - potential of dipole-dipole interactions, \( S \) - entropy of the system.

Each polar group interacts with eight dipoles located on adjacent chains and two dipoles of the same chain. The orientation of each dipole is characterized by two angles \( \phi \) and \( \theta \) (Fig. 1b). The polar angle \( \phi \) characterizes the dipole orientation in the plane \( \beta \) (Fig. 1b) and can take any value in the interval \([0; 2\pi]\).

The distribution of the angle \( \theta \) (orientation of the plane \( \beta \) relative to the plane XOY) depends on the elongation degree of the chain and its value lies in the interval \([-\theta_0; \theta_0]\). For boundary value \( \theta_0 = 0 \) the lattice model corresponds to the XY model, and for \( \theta_0 = \pi / 2 \) - the Heisenberg model. To calculate the entropy of the system under consideration (the third term in formula 3), the entropy formula for a polymer molecule in a tube is used [5].

**Figure 3.** The location of the polymer chain inside the tube

**Figure 4.** The dependence of the angle \( \theta_0 \) on the diameter of the tube \( D \) for different values of the Kuhn segment
3. Simulation of deformation

The calculations were carried out by the Monte Carlo method. Figures 4 and 5 shows the free energy dependences of the polymer system on the interchain distance for different values of the chain stiffness.

**Figure 5.** The dependence of the free energy of the polymer system on the interchain distance for different values of stiffness

(□ - $E / \sigma_0 = 20$; ○ - $E / \sigma_0 = 200$)

**Figure 6.** The Dependence of the minimum free energy on temperature

To calculate the strain, we decomposed the free energy into a Taylor series near the equilibrium position. The external force $f$ is calculated by the formula

$$f = \left( \frac{\partial F}{\partial L} \right)_{Y,T} \quad (4)$$

The force-strain diagram is presented in fig. 6. with a stiffness value of $E = 200\sigma_0$. Initially (point A1), the system was in an unordered state. Section A1-A2 corresponds to the elastic stretching of the polymer chain.

For further stretching, less force is required, so a characteristic “yield point” appears on the diagram. The simulation data showed that in the A4-A5 section, a negative force is needed for the deformation, which contradicts any experiment. To avoid controversy, we made a horizontal straight line A3-A6, taking into account that the deformation work on this section is equal to zero. On the section A3-A6, a phase transition from a disordered state to an ordered one occurs. At the point A3, $\theta_0$ is approximately $\pi / 2$, and at the point A6 it tends to zero with increasing deformation.

With further deformation, the force on the area A6-A7 increases, because intermolecular distance decreases. For very large deformations, this model cannot be used, since chain breaks are not taken into account.
Figure 7. The dependence of force on relative stretching, $\delta$ - system elongation

4. Conclusion

The presented model allows us to calculate the amount of free energy for various parameters of the polymer system. This is the advantage of this modeling method compared to MMD. In addition, because orderliness is calculated analytically, it becomes possible to use the Monte Carlo method to study the deformation of the system.

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