Computer Simulation of Phase Transitions, Orientational Order and Mobility in Low-and Highmolecular Ferroelectric Nano-Systems

T. Petrova, O. Maksimova, A. Maksimov, A. Nastuljavichus, O. Baruzdina, A. Baidganov

Cherepovets State University, Lunacharskii Pr., 5, Cherepovets, 162600, Russia, *to_87@bk.ru*

ABSTRACT

Polarization and mobility of charged particles in polymer ferroelectrics in an internal or external ordering fields has been investigated using the dynamic Monte Carlo method. The simulation showed that in the absence of the external electric field, a decrease to zero of the order parameter, heat capacity and susceptibility peaks occur at the same critical temperature T_c, that suggests the existence a second order phase transition. The switching on an external electric field leads to an increase of the critical temperature T_c and its smearing. At a certain frequency of the external field there are resonance and a maximum of the area of hysteresis curve, being its location weakly depends on the temperature and the constants of interactions.

Keywords: polymer ferroelectrics, phase transitions, order parameter, heat capacity, mobility, Monte Carlo method

1 INTRODUCTION

In recent years, mono- and multilayer low-and high-molecular ferroelectric surface structures (films, layers etc.) attract the most scientific and practical interest owing to different applications in modern nanotechnologies [1, 2]. A change of direction of the spontaneous polarization requires a reorientation of chains in the lattice and can occur at relatively small force effects, which is of great practical importance for the display technology [3].

A crystallization of anti- and ferroelectric polymers can be realized in different their structural modifications. For example, the crystallization from a melt of poly-vinylidene-fluoride [PVDF] usually proceeds in the α-phase with the monoclinic lattice with antiparallel packing of dipolar moments of chain links (in the anti-ferroelectric state), and copolymer vinylidene-fluoride with tetra-flour-ethylene [PVDF (VDF-TrFE)] in a crystalline state has the parallel packing of the chains (in the ferroelectric one) [4].

The study of such structures has of interest because of their unique physical-chemical characteristics, such as thermo-mechanical and dielectric properties, important e.g. for its using as protective PVDF and other polymer coatings for sheet steel [1]. The peak temperature of the metal (PTM) is one of the most important indicators to ensure the required parameters of painting coating (gloss, strength etc.). The solution of the problem concerning of an adsorption of macromolecules on surfaces creates a base for development of the adhesion theory of polymers [2].

The results of the research, obtained by the NMR, polarized luminescence, EPR and other methods, show that an ordering and mobility of fragments of polymer chains can be sensitive indicators of the structural configuration of these systems [5]. A theory describing a behavior of macromolecules with different mechanisms of flexibility in ordered polymer systems of infinitely large or finite size (layers, domains etc.) with a developed segmental mobility should correctly take into account intermolecular interactions, particularly, of orientation type. For studying this problem, e.g. the Gotlib-Maksimov's models of such systems [6] were used, in which, on the one hand, the individual polymer chains with the given bending rigidity are chosen, and on the other hand, local interchain interaction is taken into account.

2 MODEL

In these models, a system of polymer chains is considered as a three-dimensional cubic lattice, which contains N, M and L nodes. A position of node is characterized by the set of three numbers i, j and k. Every node is related with a dipole (rigid chain kinetic unit); its orientation is determined by the spherical angles (Fig.1).
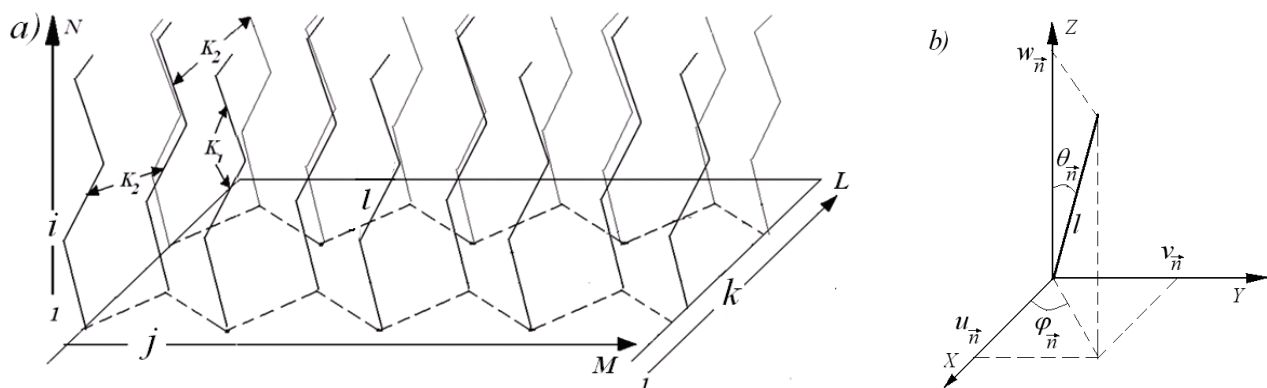

Figure 1: *a* - the model of multichain polymer system, *b* - orientation of chain unit in the spherical coordinate system.

The potential energy of interaction of dipole type for the chain systems in the lattice has the form:

$$V = -\sum_{i,j,k} K_1 \cos(\Phi_{i,j,k,i+1,j,k}) -$$
$$-\sum_{i,j,k} K_2 \cos(\Phi_{i,j,k,i,j+1,k}) -$$
$$-\sum_{i,j,k} K_2 \cos(\Phi_{i,j,k,i,j,k+1}) - pE \sum_{i,j,k} \cos(\phi_{i,j,k}) \quad (1)$$

where $\Phi_{i,j,k,i',j',k'}$ is the spatial angle between the dipoles located in the nodes i, j, k and i', j', k' of the lattice, p is the module of the dipole moment of kinetic chain unit, E is the strength of external electric field, $\varphi_{i,j,k}$ is the angle between the vectors $\vec{p}$ and $\vec{E}$.

The energetic constant K_1 along the longitudinal curved direction X of the lattice describes intrafchain orientation interactions; its value is related to the bending rigidity of the chain, which determines the persistence length of the isolated chain. The constant K_2 characterizes orientation interactions between neighboring units of different chains in the transverse curved directions Y and Z of the lattice. The value of the constant K_2 is also determined by a specific chemical structure of the interacting polymer chains; it can be estimated, for example, from the multipole expansion of the interaction energy of two identical dipoles p in neighboring chains [7]:

$$K_2 = \frac{1}{4\pi\varepsilon_0} \frac{p^2}{r^3}, \quad (2)$$

where r is the mean distance between neighboring chains, ε_0 - dielectric constant.

The proposed model can be used, for example, to simulate physical properties of PVDF, which consists of carbon chains with the distance ~ 2.6 Å between side groups CH_2–CF_2 (Fig. 2). Links of the macromolecule of PVDF have the dipole moment p equal to 2.1 D, and directed perpendicular to backbone of the chain. This moment is related with the electronegative fluorine and electropositive hydrogen in these groups [4].
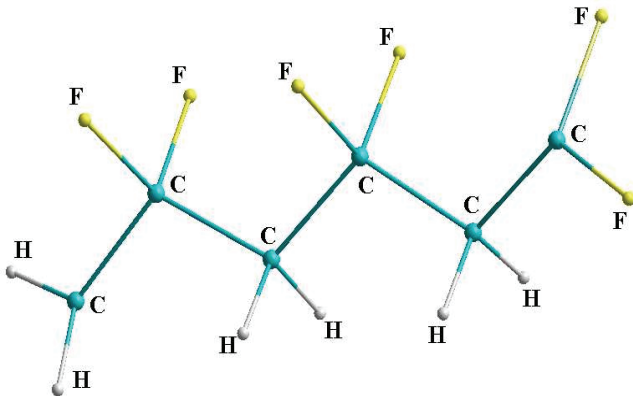

Figure 2: Structure of polyvinylidenefluoride macromolecule $[CH_2CF_2]_n$.

The computer simulation of the process of polarization and mobility of charged particles in the polymer ferroelectrics has been carried out using the dynamic Monte Carlo method. The following tasks will be solved:

1) to calculate a configuration of dipoles in the lattice depending on the temperature, internal structure (constants of intra-and intermolecular interactions in the potential (1)), the external electromagnetic field;
2) to obtain dependences of heat-capacity, susceptibility and conductivity on internal/external characteristics;
3) to study the mobility of charged particles in the lattice;
4) to study a surface energy of polymer coatings for metals at different temperature regimes of its drying.

3 RESULTS OF SIMULATION WITHOUT EXTERNAL FIELD

To prove an existence of a phase transition, the temperature behavior of the mean cosine of the angle of a chain link respectively to the axis of preferred direction (the long-range orientation order parameter) μ (Fig. 3), the heat capacity C (Fig.4) and the dielectric susceptibility χ (Fig.5) have been analyzed. The simulation showed that in the absence of the external field, a decrease to zero of the order parameter, peaks of heat capacity and susceptibility occur at the same critical value of the parameter $z_c = k_B T_c / K_1$ (Fig. 3-5), that suggests the existence a second order phase transition. The value of critical temperature T_c depends on the constant of interchain interactions and decreases with the decrease of the parameter of anisotropy $\varepsilon = K_2 / K_1$.
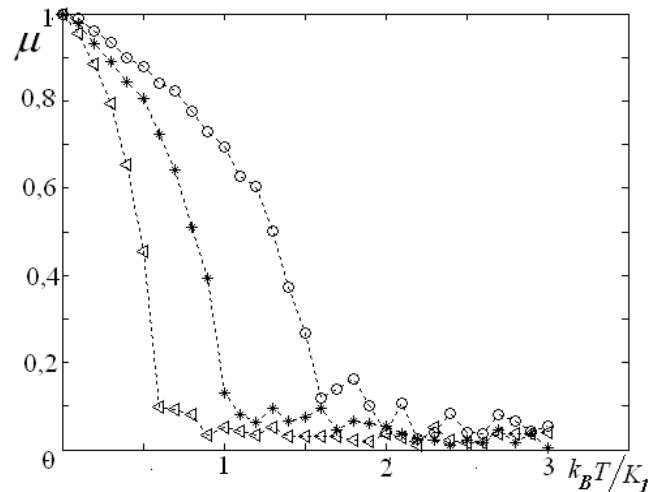

Figure 3: The long-range orientation order parameter vs. the reduced temperature $z_c = k_B T_c / K_1$. The parameter of anisotropy $\varepsilon = 1(o), 0.5 (*), 0.2(\Delta)$.

The heat capacity of the system was calculated as:

$$C = \frac{1}{k_B T^2} \left[\langle e \rangle^2 - \langle e^2 \rangle \right]; \quad (3)$$

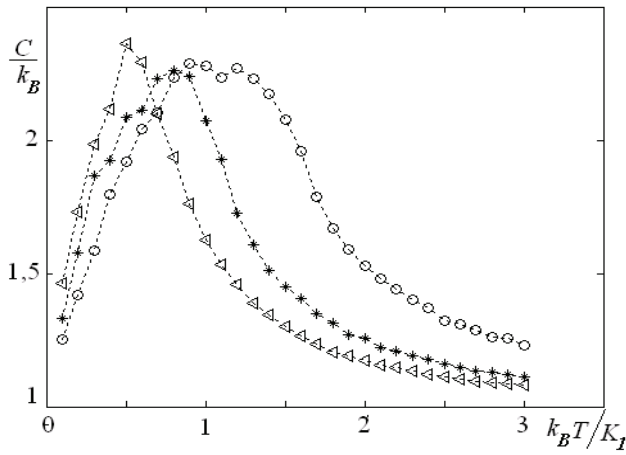where e is the energy of a single link of the polymer chain.

Figure 4: The heat capacity vs. on the ratio k_BT/K_1. The parameter of anisotropy $\varepsilon = 1(o), 0.5(*), 0.2(\Delta)$.

The susceptibility of the system was calculated as:

$$\chi = \frac{1}{k_BT}\left[\langle P\rangle^2 - \langle P^2\rangle\right],\qquad(4)$$

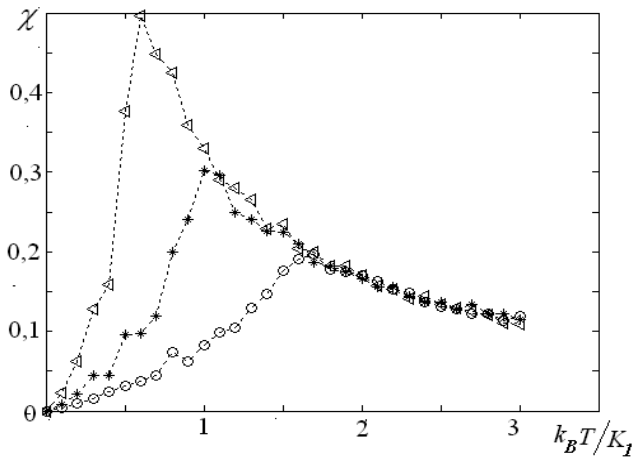where P is the module of polarization vector of the system.

Figure 5: The dielectric susceptibility vs. the ratio k_BT/K_1. The parameter of anisotropy: $\varepsilon = 1(o), 0.5(*), 0.2(\Delta)$.

4 EFFECT OF EXTERNAL ELECTRIC FIELD

The switching on an external electric field leads to an increase of the critical temperature T_c and its smearing. The dependences of susceptibility of the ferroelectric polymer in an external electric field on the temperature are shown in the Fig. 5. Calculations have been made without taking into account the relaxation time (i.e., it was thought that the heating of the sample was carried out rather slowly).

To take into account the relaxation time in an alternating electric field, an averaging along the Markov's chain in the Monte Carlo method is considered as a dynamical interpretation, that is, the number of successive configurations k is related with a some time scale.
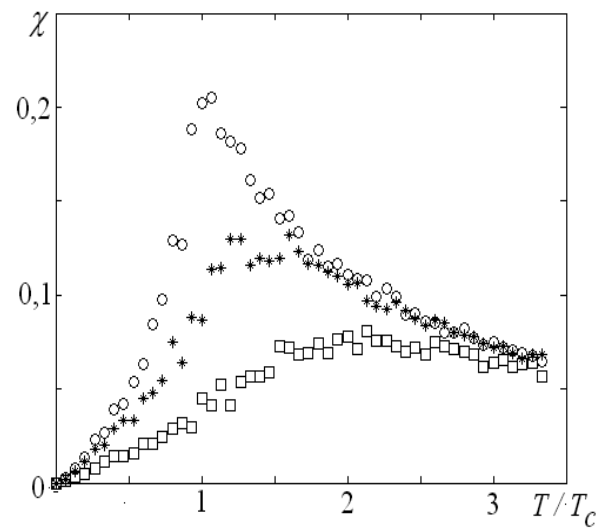

Figure 6: The susceptibility vs. the reduced temperature T/T_c The ratio $pE/K_1 = 0$ (o), 0.5 (*), $2(\square)$.

The dependences of areas of the hysteresis curves ($\mu(pE/K_1)$ for ferro- and antiferroelectrics on the frequency of the field at different values of the ratio are shown in Fig. 7. Therefore at a certain frequency of the external field there are resonance and a maximum of the area of hysteresis curve, being its location weakly depends on the temperature and the constants of interactions. The height of peak increases with decrease of temperature and increase in energy of interactions between molecules.
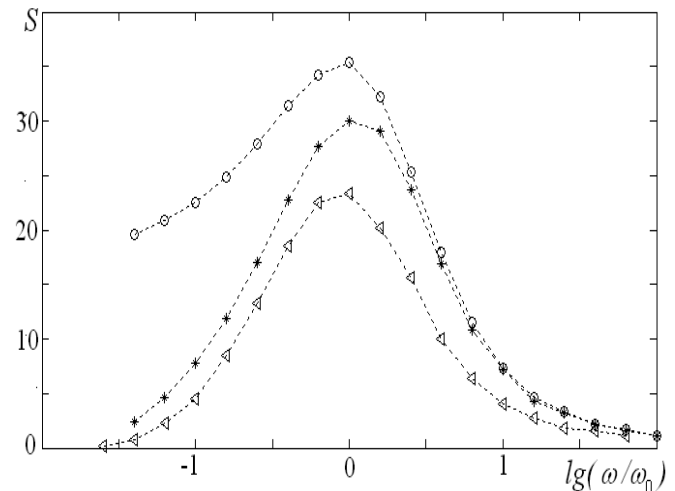

Figure 7: The areas of the hysteresis curves $\mu(pE/K_1)$ vs. the logarithm of frequency of the external field at different values of the ratio $k_BT/K_1 = 0.2(o), 2(*), 5(\Delta)$.

Calculation of conductivity of ferroelectrics was realized also by the Monte Carlo method. The dependence of the number of electrons n which have reached to the given border of the lattice on the ratio k_BT/K_1 is shown in Fig. 8. Since the value n is proportional to the conductivity, then from this dependence it is possible to study a temperature behavior of the conductivity of a ferroelectric.
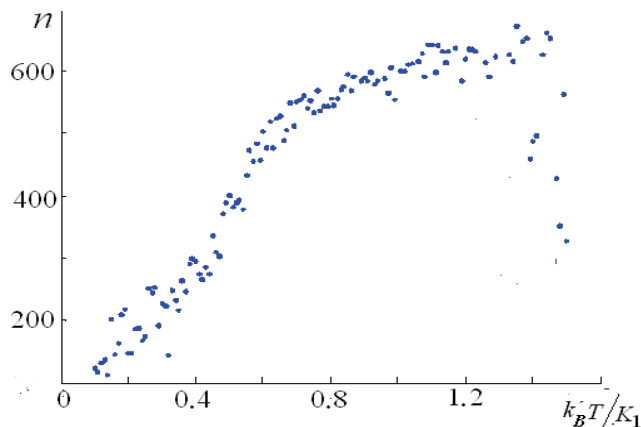
Figure 8: The number of the electrons n which have reached to the left border of the lattice vs. the ratio $k_B T/K_1$.

5 INVESTIGATION OF SURFACE EFFECTS

Adhesion of polymers for solid surfaces is one of the major factors determining properties of any polymer composite materials [1, 2]. The organic thin-film coatings of metal posses a protective ability, durability, elasticity, and anti-friction properties. These coatings are ideally suited to simplify the requirements for technological processes and further develop of the concepts of anticorrosion protection, e.g. for car industry.

Energy of a surface tension was calculated as excess of energy of surface layer on interface boundary of phases (comparatively to the energy in a body), caused by the distinction of intermolecular interactions in the both phases. The calculated dependences of energy of a surface tension on the temperature are shown in Fig. 9.
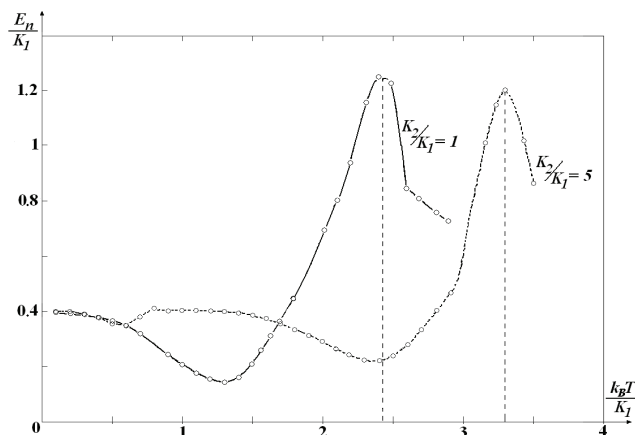

Figure 9: The energy of a surface tension E_n on the reduced temperature $k_B T/K_1$ at the values of the ratio $K_2/K_1 = 1,5$.

It's seen, that at some temperature (a peak temperature of the metal), there is a maximum value of the surface tension energy, at which adhesion of the polymer coating is best. If the constant of interchain interaction K_2 increases, the maximum of the surface energy is shifted to higher temperatures.

6 CONCLUSIONS

For a study of polymer systems in the vicinity of the phase transition the Landau's classical mean- field theory is unsuitable, because of properties of system are very sensitive to external influences, and fluctuations of ordering in the system are considerably manifested. The simulation showed that in the absence of the external field, a decrease to zero of the order parameter, the heat capacity and susceptibility peaks occur at the critical temperature T_c, that suggests the existence of a second order phase transition.

The switching on an external electric field leads to an increase of the critical temperature T_c and its smearing. At a certain frequency of the external field there are resonance and a maximum of the area of hysteresis curve, being its location weakly depends on the temperature and the constants of interactions. The height of peak increases with decrease of temperature and increase in energy of interactions between molecules.

Results of the simulation in an alternating electric field are in an agreement with the Drude-Lorentz's classical theory which is based on the assumption that dipolar moments of molecules under the influence of external electric field execute damping oscillations with inherent cyclic frequency.

REFERENCES

[1] I.C. Sanchez, and L.E. Fitzpatrick, "Physics of Polymer Surfaces and Interfaces", Boston: Butterworth-Heinemann, 1992.

[2] A. Karim, and S. Kumar, "Polymer Surfaces, Interfaces and Thin Films," Singapore: World Scientific, 2000.

[3] H. Fujikake, H.Sato, T.Murashige. "Polymer-stabilized ferroelectric liquid crystal for flexible displays". Displays. V.25(1), P. 3–8. 2004.

[4] H.M. Tong and L.T. Nguyen, (Eds.), "*New Characterization Techniques for Thin Polymer Films*", New York: John Wiley, 1990.

[5] V.V. Kochervinskii. "Features of structural transformations in ferroelectric polymers based on PVDF in the fields of high intensity," Polymer Science, V.50(7), 1407-1440. 2008.

[6] A.V.Maksimov, Yu.Ya. Gotlib, O.G.Maksimova, and S.S. Shevchenko, "Nano-Scaled Intrachain Ordering and Dynamics in Two-Dimensional Polymer Domains", Macromolecular Symposia, V.175(1), P. 309-320, 2001.

[7] A.V. Maksimov, and O.G. Maksimova, "Orientation Order in Two-Dimensional Polymer Systems as Described in Terms of Vax-Larkin Model," Polymer Science, Ser. A, V.45(9), P.859-866, 2003.